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Lanthanum Cobaltites Obtained by Sol-gel Method at Different Calcination Temperatures

Juan M. Oviedo C[1*], Luis C. Sánchez P[2], Miguel J. Espitia R[3],

[1,2]GAMASCO Group, Universidad de Córdoba, Montería, Colombia.
*E-mail: jmoviedo@correo.unicordoba.edu.co**
*(*Corresponding autor: luiscarlos@correo.unicordoba.edu.co)*

[3]GEFEM Group, Universidad Distrital "Francisco José de Caldas", Bogotá, Colombia.
E-mail: mespitiar@udistrital.edu.co

Abstract

Lanthanum cobaltites were synthesized in acid medium by using the sol-gel method, considering calcination temperatures of 700 and 900 °C. The obtained compounds were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Changes in structural and morphological properties are reported.

Keywords: Cobaltites, Sol-gel method, X-ray diffraction, SEM.

INTRODUCTIÓN

The study of materials with Perovskite structure and general formula ABO_3 [1] has recently become important, due to its several properties such as: electrical, mechanical [2] optical [3], magnetic [4], catalytical properties, etc [5]. Among these perovskites highlights the cobaltites of lanthanum with interesting electrical catalytic, thermoelectric, properties, among others, which depend on their constituent elements and the synthesis method used. Different works have been reported on the study of properties of these compounds. Structural, electrical, thermo-electric power and magnetic properties of $LaCoO_3$ was investigated by Benedict et al [6]. Gonjal et al, studied magnetic, dielectric and charge transport properties of $LaCoO_3$ synthesized by two different techniques: microwave assisted and conventionally heated ceramic synthesis [7]. Young Jung et al, investigated photocatalytic activity for the decomposition of methyl orange on the $LaCoO_3$ perovskite type oxides prepared at different conditions using microwave process [8]. Jun-Chao Ding et al, estimated CO gas sensing properties of the $LaCoO_3$ thick films finding excellent CO sensing properties in the temperatures range of 200 to 600 °C [9]. While, R. Newton et al, evaluating the selective CO oxidation reaction of $LaCoO_3$ [10]. D. Meziani et al, studied Hydrogen evolution under visible light over $LaCoO_3$ prepared by chemical route [11]. Yang et al, studied the effect of redox properties of $LaCoO_3$ perovskite catalyst on production of lactic acid from cellulosic biomass, obtaining that the $LaCoO_3$ perovskite can effectively catalytic conversion of cellulosic biomass to lactic acid in hydrothermal media [12]. Perovskite-type oxide $LaCoO_3$ as a cathode catalyst for use in a direct borohydride fuel cell (DBFC) was studied by Y. Liu et al [13]. The experimental results demonstrated that the $LaCoO_3$-catalysed cathode shows good electrocatalytic activity for oxygen reduction in alkaline solutions ions. Dacquin et al, investigated catalytic activity of $LaCoO_3$ obtained by different methods in the decomposition of N_2O [14].

Different synthesis methods have been developed to obtain cobaltites. One of the most widely used methods is the solid state reaction method, based on powder milling and thermal treatment for extended periods of time. Another method to obtain cobaltites is the sol-gel method, which allows the preparation of high quality and homogeneity products using low calcination temperatures. In this work, lanthanum cobaltites were synthesized by sol-gel method considering calcination temperatures of 700 and 900 °C. Structural and morphological properties of the compounds were conducted.

EXPERIMENTAL METHOD

Materials synthesis was prepared from nitrates considering an appropiate citrate/nitrate ratio. 0.423 M solutions of lanthanum nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$) and cobalt nitrate nonahydrate ($Co(NO_3)_2 \cdot 6H_2O$) were prepared. Suitable volumes of solutions were added slowly with constant stirring in a solution of citric acid 0.133 M. The solution was maintained at 70 °C for two hours with stirring and reflux. The resulting solution was evaporated to remove the solvent and allow the spontaneous combustion of the final complex. The obtained solids were crushed, sieved and calcined at 700 and 900 °C with heating rate 5 °C/min. X-ray diffraction (XRD) patterns were obtained with a Panalytical X.Pert PRO MPD equipment with CuKα1 radiation (λ=1.5418 Å) and the Scanning Electron Microscopy (SEM) was carried out with a JEOL/EO JSM-6490-LV equipment. Rietveld refinement of XRD patterns was realized using Fullprof-Suite program, and crystallite sizes was estimated using X Powder program.

RESULTS AND DISCUSSIONS

Structural properties

The XRD patterns adjusted by Rietveld refinement of $LaCoO_3$ at calcination temperatures of 700 and 900 °C, are shown in Figure 1. The phase identification was carried out using HighScore X'pert 2.1 program, taking into account the data base PDF2-2004. The identified phase for the samples corresponds to hexagonal perovskite structure and $R\bar{3}c$ (#

167) space group, without the presence of impurity phases. The parameters obtained from refinement are listed in Table 1. Crystallite sizes, estimated by Scherrer equation and Williamson-Hall graphs, considering: (G) Gaussian, (L) Lorentzian and (PV) Pseudo Voigt line profile, are listed in Table 2. The crystallite size estimation from Scherrer for our samples, was carried out considering the peak (024) localized at 47.6 degrees as shown in Figure 2.

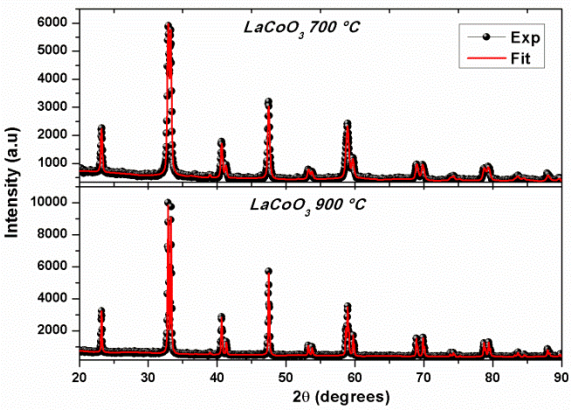
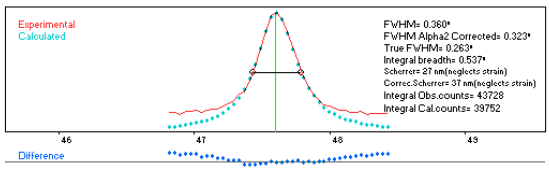
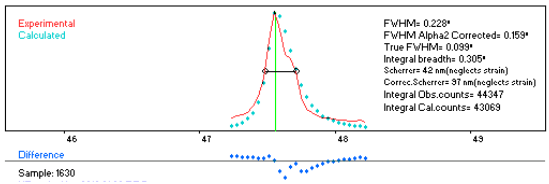


Figure 1. XRD pattern of $LaCoO_3$ at calcination temperatures of 700 and 900 °C.



(a)



(b)

Figure 2. Crystallite sizes of $LaCoO_3$ calcined at (a) 700 °C and (b) 900 °C, estimated by Scherrer equation.

Table 1: Obtained parameters from Rietveld refinement of the XRD patterns.

Temperature (° C)	Structural parameters			
	***a*(Å)**	***b*(Å)**	***c*(Å)**	**V(Å^3)**
700	5.4444	5.4444	13.1200	336.7922
900	5.4456	5.4456	13.1007	336.4476

Table 2: Crystallite sizes, estimated by Scherrer equation and Williamson-Hall graphs.

Temperature (° C)	Crystallite sizes (nm)			
	Williamson -Hall Plots			Scherrer
	G	L	PV	
700	22.36 ±5.83	28.61 ±8.88	28.40 ±8.79	27
900	45.32 ±8.90	49.46 ±8.63	49.34 ±8.62	42

Lattice parameters are not affected appreciably with the calcination temperature while the crystallite size increases with calcination temperature, associated with increased crystallinity of the samples as shown in Tables 1 and 2.

Similar results for structural parameters are reported by R. Newton et al [10] for $LaCoO_3$ synthesized by a modified citrate method with calcination temperature of 600 °C and by K.T.C. Roseno et al [15] for $LaCoO_3$ prepared by the polymerization complex route method with calcination temperature of 650 °C. Crystallites size estimated by R. Newton et al was 23 nm while K.T.C. Roseno et al, reported crystallites size about 25 nm. H. Li et al [16] report crystallites size estimated about 55 nm for $LaCoO_3$ prepared by citric-complexing method with calcination temperature of 700 °C.

On the other hand, D. Meziani et al [11], report lattice constants a=0.5443 nm and c=1.3060 nm for $LaCoO_3$ synthesized by nitrate route with calcination temperature of 950 °C. Crystallites size estimated was about 55 nm. S. Ivanova et al [17], report similar results for structural parameters of $LaCoO_3$ prepared by two methods: thermal decomposition of the La–Co citrate precursors with annealed of powder between 600 and 900 °C and conventional solid state reaction between La_2O_3 and $CoCO_3$ at 800 and 900 °C.

In Figure 3, SEM images of the samples at different magnifications (X1000 and X3000) are shown. For these can be observed, in general different grain sizes (size distribution) with irregular crystallites and different dimensions possibly associated with the synthesis method. The samples exhibit agglomeration of about some micrometers, consisting of crystallites with size of about 28 nm and 49 nm for calcined samples at 700 and 900 °C respectively, as estimated by Williamson-Hall plots (Table 2).

Our results are in agree to by repoted by S. Ivanova et al [17] for $LaCoO_3$ oxides prepared at 800 °C from citrate precursors, D. Meziani et al [11] for $LaCoO_3$ synthesized by nitrate route with calcination temperature of 950 °C and Y. Liu et al [13] by $LaCoO_3$ prepared at 700 and 900 °C by sol–gel method.

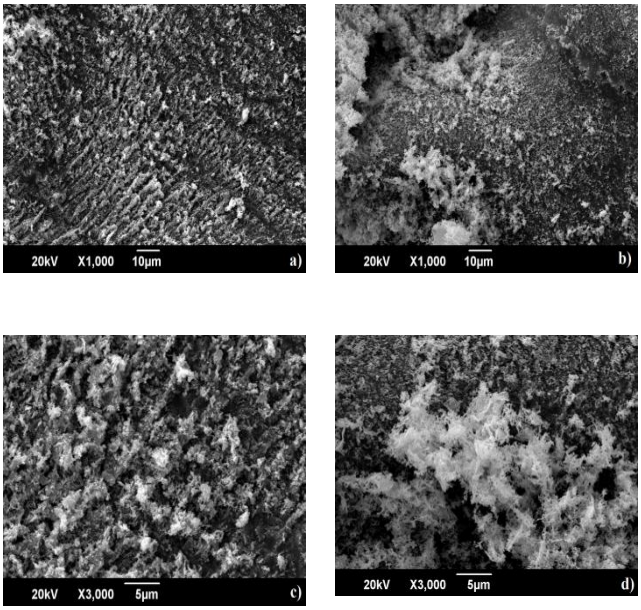


Figure 3. SEM images of $LaCoO_3$ at different magnifications calcined at (a) and (c) 700 °C; (b) and (d) 900 °C.

CONCLUSIONS

Lanthanum cobaltites were obtained without the presence of impurity or secondary phases. Lattice parameters are not influenced of significantly way by calcination temperature of synthesized samples, while crystallinity of the samples increases as the calcination temperature increases. The morphology of samples consists of agglomerations with different grain sizes with irregular shapes, associated with the used synthesis method.

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