

## Solid Oxide Fuel Cells: Strontium-Doped Lanthanum Manganite Obtained by the Citrate Technique

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**Abstract:** Nowadays, the  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  (LSM) is one of the most common cathodic materials used in the solid oxide fuel cells (SOFCs). The dopant strontium increases the electronic conductivity of the material, besides presenting an excellent electrochemical performance, relatively good chemical and thermal stability and compatibility with solid electrolyte of  $\text{ZrO}_2/\text{Y}_2\text{O}_3$  (YSZ). In this work, a contribution to the study of synthesis of LSM is presented with strontium concentration of 50 mol % by the citrate technique. The powders have been characterized for various techniques, as gas absorption and adsorption, X-ray fluorescence spectroscopy, laser scattering granulometry, gas helium pycnometry, scanning electron microscopy (SEM), X-ray diffractometry (XRD) and calculations of theoretical density and particle average diameter. The ceramics have been characterized by SEM and XRD. The adequate characteristics of LSM have been evaluated aiming at the use in the preparation of suspensions for thin films cathodic of SOFCs.

### Introduction

The strontium-doped lanthanum manganite ( $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  - LSM) is a ceramic material of great importance, which had mainly to its use as cathode in solid oxide fuel cells (SOFCs), that operate in high temperatures (800 to 1000 °C). The SOFCs possess advantages as high efficiency (kinetic favorable) and the internal reform in the cell. Therefore, being of great importance in the application in stationary units and cogeneration of electricity and heat.

In the last years, the great interest of the researchers in relation to the LSM, is mainly does to its characteristics such as: good chemical and thermal stability, high catalytic activity in the reduction of the oxygen, thermal expansion coefficient similar to the solid electrolyte of yttria stabilized zirconia ( $\text{ZrO}_2/\text{Y}_2\text{O}_3$  - YSZ) and high electric conductivity [1,2,3]. According MINH [1], the strontium is the element preferential chosen as dopant of the cathodic material of the SOFCs for allowing the attainment of bigger electronic conductivity, that is gotten of the increase of formation of cations  $\text{Mn}^{4+}$  and for the substitution of cations  $\text{La}^{3+}$  for  $\text{Sr}^{2+}$ .

In these considerations, in the present work is given to the emphasis in the synthesis of the cathodic material of LSM by the citrate technique (or liquid mixture), Pechini method modified [4].

Of this form, it is intended to collaborate for the advance of the knowledge as for the process of attainment of a ceramic material with characteristics adjusted for use as cathode in SOFCs.

## Materials and Methods

The departure materials used in the synthesis of the LSM had been the following reagents: lanthanum nitrate hexahydrated, with 99.99 % of purity; strontium nitrate, with 99.93 % of purity; manganese nitrate tetrahydrated, with 99.99 % of purity (Aldrich); acid citric e ethylene glycol, P.A. (Merck).

The powders of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  had been synthesized for x equal 50 mol % of strontium ( $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  - LSM 50), gotten by the citrate technique, that consisted initially in the mixture of nitrates of strontium, manganese and lanthanum, in the required ratios with distilled water. Acid citric and ethylene glycol in ratio 60:40 [5] in weight is mixed in becker and kept under agitation and the heating at 60 °C. The individual solutions of each precursor are added to the citric acid solution of more ethylene glycol under agitation and heating to the temperature between 80 and 110 °C. In this stage, the water is evaporated until the attainment of a viscous liquid. The nitrate in  $\text{NO}_2$  ions initially is evaporated, occurring polyesterification, fixing and distributing cations to long of organic chain and, getting itself a resin. The following stage consists of the evaporation of residual nitrate and of transformation of the resin in dust of LSM, calcination of the resinous material to air at 1100 °C for 24 hours for a complete synthesis of the reaction and elimination of residual carbon. The LSM 50 sample was submitted to the disaggregating in atritor mill.

According to BAYTHOUN and SALE [6], superior temperatures at 1000 °C are necessary to remove carbon of the product, therefore in lower temperatures of calcination, it is observed the presence of carbon in the carbonate form or free carbon resultant of the decomposition of the citrate.

The powders gotten after the disaggregating and drying they had been conformed in pellets the cylindrical form with 10 mm of diameter, using presses hydraulic uniaxial and isostatic.

In the stage of processing, the thermal treatments of sintering had been carried through the temperatures of 1300, 1400 and 1500 °C for 4 hours. Such conditions of sintering had been adopted in accordance with the works divulged in literature [7,8,9]. The authors had verified that temperatures of sintering between 1100 and 1500 °C, varying time from 2 to 4 hours, influence the density and the porosity of the sintered material.

## Results and Discussion

The powders of LSM 50 they had been characterized by the following techniques: gas absorption for infrared, X-ray fluorescence spectrometry (XRF), laser scattering granulometry, gas adsorption (BET), gas helium picnometry, and calculations of theoretical density and particle average diameter, whose values are presented in Table 1; scanning electron microscopy (SEM) and X-ray diffractometry (XRD) in Figure 1.

The LSM 50 powders observed in scanning electron microscope they are presented in the form of agglomerates and the particle sizes are inferior at 1  $\mu\text{m}$ . The type of morphology observed in the sample is similar to gotten in the work of the GAUDON et al. [10] for the process sol-gel.

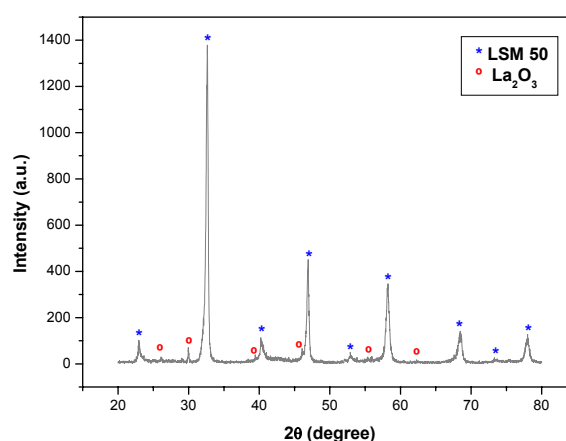
The X-ray diffractogram referring to composition LSM 50 shows the formation of the tetragonal crystalline structure with lattice parameters  $a = b = 5.4883 \pm 0.0070 \text{ \AA}$  and  $c = 7.7393 \pm 0.0002 \text{ \AA}$ . These results show that the concentration of dopant Sr, influences in the transition of the crystalline structures due to substitution of sites of  $\text{La}^{3+}$  for the  $\text{Sr}^{2+}$ . According to ROMARK et al. [11], this transformation of crystalline structure occurred for the  $\text{La}_{0.4}\text{Sr}_{0.6}\text{MnO}_3$  sample.

Table 1- Results values of characterization technique of LSM 50 powders.

TECHNIQUE	RESULTS
Gas absorption for infrared	$0.0593 \pm 0.0001 \text{ C \%}$
X-ray fluorescence spectrometry	$\text{La}_{0.45}\text{Sr}_{0.55}\text{MnO}_3$
Laser scattering granulometry	$0.88 \text{ \mu m}$
Particle average diameter	$0.30 \text{ \mu m}$
Gas adsorption	$3.32 \pm 0.02 \text{ m}^2/\text{g}$
Theoretical density	$6.08 \text{ g/cm}^3$
Gas helium pycnometry	$6.02 \pm 0.01 \text{ g/cm}^3$



(a)



(b)

Figure 1 - Micrograph obtained by SEM (a) and diffractogram obtained by XRD (b) of LSM 50 powders.

The calculations of lattice parameters had been possible, due to the programs Crystallographica Search Match (CSM) and Celref, and JCPDS information card (N°89-786) existing of these material, that it allowed to find the lattice parameters with its crystalline structure and space group. The identification was of visual and comparative character, to get the crystalline structure and its fine lattice parameter, of the synthesized sample.

For the sample LSM 50, was also identified the presence of a small amount of  $\text{La}_2\text{O}_3$  (JCPDS N°5-602), proceeding from the not total polymerization with ions  $\text{La}^{3+}$ . The result of the crystalline structure is in accordance with the data presented for GAUDON et al. [10], that also they had verified the presence of  $\text{La}_2\text{O}_3$ .

The presence of  $\text{La}^{3+}$  in the form of  $\text{La}_2\text{O}_3$  is influenced by the ionic ray of the crystallite. The ion  $\text{La}^{3+}$  possess the ionic ray of  $1.46 \text{ \AA}$  while that of the ion  $\text{Sr}^{2+}$  is of  $1.54 \text{ \AA}$ ; and this last one for possessing the ray biggest limits the substitution of the  $\text{La}^{3+}$  for the  $\text{Sr}^{2+}$  in the structure type perovskite of  $\text{LaMnO}_3$  [8,12].

The pellets of the sample of LSM 50 powders had been sintered at 1300, 1400 and 1500 °C for 4 hours. These ceramics of LSM 50 had been characterized by the hydrostatic method, calculations of porosities, scanning electron microscopy (SEM) and X-ray diffractometry (XRD).

The results gotten for the densities by the hydrostatic method had been observed that to the measure that the sintering temperature increases, it has an increase in the hydrostatic densities (HD) for sample LSM 50 (Table 2).

The values of porosity of sample LSM 50 had been calculated through the relation between the HD and the theoretical density (TD), presented in Table 2. It was verified that the porosity values determined for sample LSM 50 are in accordance with literature [13] that it is 30 % approximately.

Table 2 - Values of hydrostatic density and porosities calculated.

SAMPLE	TD (g/cm <sup>3</sup> )	HD (g/cm <sup>3</sup> )			POROSITY (%)		
		1300 °C	1400 °C	1500 °C	1300 °C	1400 °C	1500 °C
LSM 50	6.08	3.52	3.62	4.64	42.11	40.46	23.68

The LSM 50 sintered pellets had been fractured and observed in a scanning electron microscope. In Figure 2 the micrographs of the fracture surfaces of the sintered pellets are presented 1300, 1400 and 1500 °C for 4 hours, observing themselves it presence of open pores with bigger frequency, whose fracture occurs predominantly for intergranular mechanism.

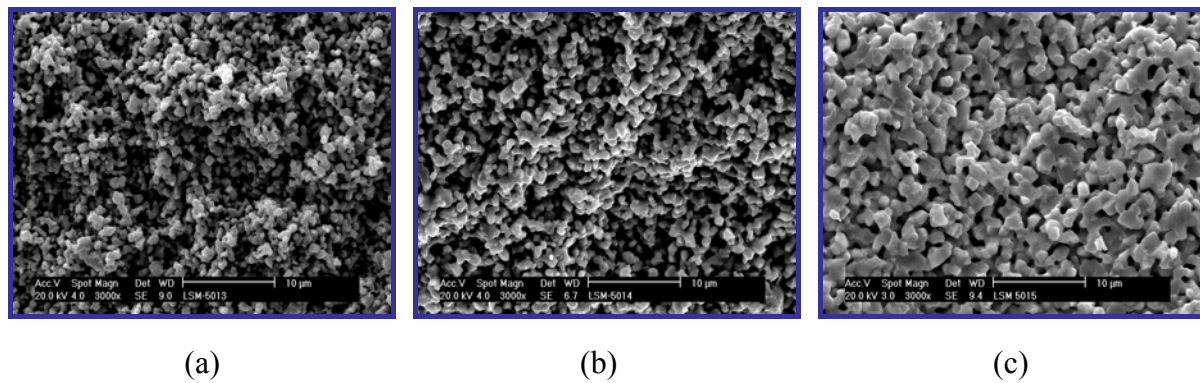


Figure 2 - Micrographs of the fracture surfaces the LSM 50 sintered samples at 1300 (a), 1400 (b) e 1500 °C (c) for 4 hours.

The X-ray diffractograms of LSM 50 samples with thermal treatment at 1300, 1400 and 1500 °C are presented in Figure 3. These ceramic samples had been called as LSM 5013 (LSM 50 at 1300 °C), LSM 5014 (LSM 50 at 1400 °C) and LSM 5015 (LSM 50 at 1500 °C). For all these samples, had verified the formations of the intrinsic crystalline structures as also the presence of secondary phase mentioned previously for the sample in the form of powders. The LSM 50 samples had presented tetragonal crystalline structure.

In Table 3, the lattice parameters of the crystalline structure calculated of the sintered samples are presented the different temperatures of sintering.

For the calculations of lattice parameters had been used the programs CSM and Celref, together with JCPDS information card. Samples LSM 5013, LSM 5014 and LSM 5015 had used the information card N°89-786 again, in the definition of its crystalline structures and lattice parameters.

The results joined show that it does not have transformation of crystalline structures of powders synthesized in relation the sintered samples, indicating that exist stabilization to a sintering temperature of up to 1500 °C.

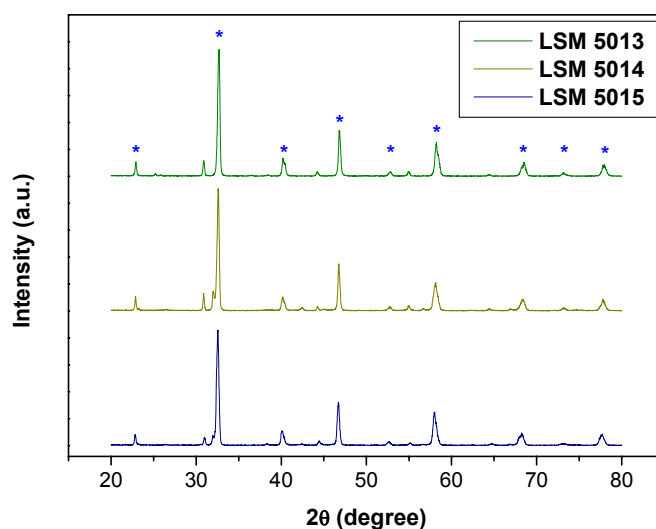


Figure 3 - Diffractograms obtained for XRD of LSM 50 sintered samples the different temperatures.

Table 3 - Lattice parameters calculated of the sintered samples.

SAMPLES	LATTICE PARAMETERS (Å)	
	a = b	c
LSM 5013	5.4764 ± 0.0052	7.7581 ± 0.0003
LSM 5014	5.4909 ± 0.0059	7.7547 ± 0.0003
LSM 5015	5.5037 ± 0.0051	7.7646 ± 0.0005

## Conclusion

The citrate technique used in this work, made possible the synthesis of strontium-doped lanthanum manganite powders with strontium 50 mol % approximately.

The analyses by XRF, had shown that the synthesis was efficient in the attainment of composition LSM 50, with values around calculated stoichiometric and as well as the removal of residual carbon at 1100 °C for 24 hours was satisfactory.

The micrograph of powders gotten by SEM, had shown that the particle sizes are in the form of agglomerates and are inferior at 1 µm. The results gotten in the analysis laser scattering granulometry prove the same results (< 1 µm).

The powders were observed by XRD, having gotten itself it formation of main phase LSM and a small formation of secondary phase of La<sub>2</sub>O<sub>3</sub>. The crystalline structure of LSM 50 powders found was tetragonal.

For the sintered samples, the LSM 50 allowed to get from 20 to 45 % of porosity, that strengthen the data observed in the micrographs of fractured surface. This result is favorable, mainly for the oxidant gas flow in the cathode.

The analyses by XRD, the sintered samples they had shown the presence of the tetragonal crystalline structure, indicating that the crystalline structure of the material in the studied temperatures, does not occur structural transformations in the powders and processed ceramics.

The characteristics of powders and of ceramics gotten for sample LSM 50 are contributions for the study of the cathodic material in the manufacture of the unit cells in the SOFCs.

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## References

- [1] N.Q. Minh, *J. Am. Ceram. Soc.*, 76, 3 (1993), p. 563-588.
- [2] T.F. Fuller, *Electrochem. Soc. Interface*, 6, 3 (1997), p. 26-32.
- [3] O. Yamamoto, *Electrochim. Acta*, 45 (2000), p. 2423-2435.
- [4] M.P. Pechini, US Patent N° 3.330.697 (1967).
- [5] P.A. Lessing, *Ceram. Bull.*, 68, 5 (1989), p. 1002-1007.
- [6] M.S.G. Baythoun, F.R. Sale, *J. Mater. Sci.*, 17 (1982), p. 2757-2769.
- [7] K. Katayama, T. Ishihara, H. Ohta, S. Takeuchi, Y. Esaki, E. Inukai, *J. Ceram. Soc. Jpn.*, 97, 11 (1989), p. 1327-1333.
- [8] A. Hammouche, E. Siebert, A. Hammou, *Mat. Res. Bull.*, 24 (1989), p. 367-380.
- [9] H.B. Park, Y.S. Hong, S.J. Kim, *J. Mat. Sci. Lett.*, 16 (1997), p. 1782-1785.
- [10] M. Gaudon, C. Laberty-Robert, F. Ansart, P. Stevens, A. Rousset, *Solid State Sci.*, 4 (2002), p. 125-133.
- [11] L. Romark, K. Wiik, S. Stolen, T. Grande, *J. Mater. Chem.*, 12 (2002), p. 1058-1067.
- [12] A.M. Duprat, P. Alphonse, C. Sarda, A. Rousset, B. Gillot, *Mater. Chem. Phys.*, 37 (1994), p. 76-81.
- [13] J.M.J. Blomen, M.N. Mugerwa. *Fuel cell systems*. New York: Plenum Press (1993).