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Chemical Deposition of $La_{0.7}Ca_{0.3}MnO_{3\pm\delta}$ Films on Ceramic Substrates

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In this paper, it is reported the growth of $La_{0.7}Ca_{0.3}MnO_{3\pm\delta}$ films using a chemical solution deposition method (CSD) by the spin-coating technique. Such solution was prepared through a route based on modified polymeric precursor method. Spin-coating deposition on different ceramic substrates was performed and analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The magnetic response of the prepared specimens was studied using a SQUID magnetometer. The obtained results indicated uniform deposition on $SrTiO_3$ and $LaAlO_3$ substrates with similar characteristics. Furthermore, significant differences were detected in the Mn^{3+}/Mn^{4+} valence ratio and a corresponding diverse magnetic response was observed. The sample prepared on $SrTiO_3$ and $LaAlO_3$ presented a critical temperature around 270 K as expected.

Keywords: *chemical solution deposition, Pechini method, spin-coating, magnetic material*

1. Introduction

Thin films based on manganites receive considerable investments and efforts, due to the fact that this material has potential usage in magnetic devices[1]. Besides, properties such as the magnetoresistance effect, as well as a variety of fundamental physical properties have been systematically studied[1,2]. Phenomena such as ferromagnetism, antiferromagnetism, ferrimagnetism and paramagnetism, can be found in manganite oxides systems containing metallic elements and a rare-earth element. Thus, it is expected to understand the structural and magnetic properties of these compounds in both films and in bulk.[3,4]. Amongst several methods used for the growth of oxide thin films, it is pointed the methods based on techniques such as Magnetron Sputtering, Laser Molecular Beam Epitaxy and Pulsed Laser Deposition[5,6,7]. In the case of the synthesis of $La_{0.7}Ce_{0.3}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ films, both are commonly grown on $SrTiO_3$ substrates through laser deposition techniques[8,9].

Considering $LaMnO_3$ compounds at low temperatures, the presence of Mn^{3+} provides the insulating behavior and with the antiferromagnetic coupling. The replacement of transition metals at the manganese sites generates valence fluctuation, allowing the coexistence of cations Mn^{3+} and Mn^{4+}[8]. In such cases, the magnetic responses in zero-field-cooling (ZFC) and field-cooling (FC) curves show ferromagnetic response and Curie temperature (Tc) of about 260 K[9]. It is also found reports on film synthesis of $La_{1-x}Ca_xMnO_{3\pm\delta}$ grown on several ceramic substrates, studying mismatch between the substrate and the film and electrical resistivity[10], as well as their electrical transport and magnetic responses[11]. Other studies describe the synthesis of $La_{0.67}Ce_{0.33}MnO_3$ film deposited at identical conditions on substrates of $SrTiO_3$, $LaAlO_3$, MgO, $NdGaO_3$ and Si, through DC-sputtering technique[12]. Furthermore, by the use of targets synthesized through the solid state reaction route, films with thickness of 200 nm, epitaxially oriented toward (001), showed that the magnetic properties are dependent on the used substrate[12].

Compared to physical deposition techniques, the one based on chemical solution deposition (CSD) represents an effective alternative, considering that this one allows the achievement of good quality samples with relatively lower costs[13]. In these cases, the obtained solution can be deposited on the substrate through the deposition techniques such as spin-coating, dip-coating and spray-coating, ending with thermal treatments that support the phase formation on the substrate.

Considering the chemical deposition technique, recent works aim to understand the structural and optical properties in $La_{0.7}Ca_{0.3}MnO_3$ films, deposited on substrates of $LaAlO_3$, via chemical vapor deposition from the vapors of metalloorganic compounds (MODVD) technique[14]. Generally, the properties of films prepared by chemical methods and questions such as epitaxy, post-annealing treatment, as well as the final quality of the samples have been studied in recent years[1,15,16,17]. It is also necessary to comment that film formation and its properties can present differences according to the method for the deposition and the substrate used[15,18].

In this paper, it was studied the synthesis viability of $La_{0.7}Ca_{0.3}MnO_{3\pm\delta}$ (LCMO) thin films deposited on ceramic substrates of $SrTiO_3$ (STO), $LaAlO_3$ (LAO) and MgO, via CSD. For chemical synthesis, it was used Pechini method[18], conducted with oxides and carbonates, less complex to the traditional synthesis Sol-Gel realized from precursors such as alkoxides and acetates[1]. The deposition was accomplished by spin-coating technique and determined the formation of the desired phase, the morphology, the states of electronic configuration and magnetic responses from the synthesized samples. The comparation of the properties from synthesized films with results found in the literature allowed evaluating the quality of the final samples.

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2. Experimental Details

Based on a modified polymeric precursor method to perform chemical synthesis of complex oxides[19], solutions were prepared using high purity (Aldrich) La_2O_3, $CaCO_3$ and $MnCO_3$ as precursors. These compounds were dissolved in stoichiometric ratio into deionized water by adding HNO_3 and mixed with citric acid at a metal/citric acid proportion of 1/3. After 30 minutes, ethyleneglycol was also added at a temperature of 60 °C, at a carboxylic acid/ethylene glycol molar ratio of 60/40. Under constant stirring, NH_4OH was added until the solution's pH was 7. Ethylenediaminetetraacetic acid (EDTA) was then added to the solution as a complexant agent at proportion EDTA/acid citric of 1/4. The temperature was increased to 90 °C in order to evaporate the water excess and form a gel with a viscosity of up to 15 cp.

Three different types of (100) ceramic substrates STO, LAO and MgO were used in this study. Previous to deposition, substrates were cleaned ultrasonically in acetone at 80 °C for 10 minutes and then washed with deionized water. The obtained gel was then deposited on the different substrates by spin-coating at 1500 rpm for 60 seconds, optimized values for viscosity were deposited. In this process two drops were deposited over the stationary substrate. This process was repeated four times for each sample, and between each deposition, the films were pyrolized on a hot plate at 300 °C. Heat-treatment followed at 500 °C/2 hours + 900 °C/4 hours and post-annealing at 500 °C for 30 minutes under O_2. All heat-treatment was performed in step ratio of 5 °C/min.

After deposition, crystallographic phases were analyzed by X-ray diffraction in a Rigaku DMAX 2100/PC diffractometer. Chemical elements, quantitative analysis and microstructure were determined using a scanning electron microscope, associated to an electron dispersive energy spectrometer (SEM/EDS) FEG/ Philips with a resolution of 2 nm. For surface analysis and manganese valence state analyses, X-ray photoelectron (XPS) spectra were taken using a VG ESCA 3000 system and using MgKα radiation with overall energy resolution of approximately 0.8 eV. The energy scale was calibrated using the Fermi level and C1s peak at 284.5 eV. The spectra were normalized to maximum intensity after a constant background subtraction. Magnetic measurements were performed using a Quantum Design SQUID Magnetometer.

3. Results and Discussion

The use of modified polymeric precursors methods with the addition of EDTA on the synthesis, showed effective in obtaining the solution to be deposited on the substrate. EDTA is generally used, since it can connect itself to the most of metallic elements, in addition to increasing the stability of some components through the complexation of the species, depending on the pH used[20,21]. There were no signs of precipitation in the solutions.

In Figures 1 to 3 the diffractograms of LCMO film are presented, deposited on the STO, LAO and MgO substrates, respectively. It is possible to observe the diffraction peaks of the substrates and the deposited polycrystalline phase. The diffraction peaks of the film are quite evident in the positions realized on the STO and LAO substrates. Therefore, for the case of MgO substrate, its intensity is relatively low. A good match of the layer deposited directly on the substrate requires that factors such as the proximity of lattice parameters of film and substrates are considered. In the case of perovskite-type substrates such as STO and LAO, this difference is around 1%, and in the case of MgO substrate, this difference increases to about 7%[1]. One can relate the result described above to the best or the worst adaptation of the film to the substrate, since the samples were synthesized in the same way, following the same procedures. The influence of the difference

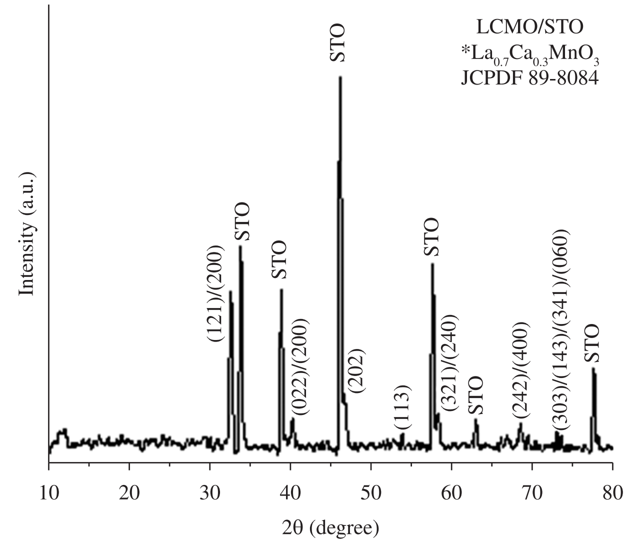

Figure 1. X-ray diffraction of $La_{0.7}Ca_{0.3}MnO_{3\pm\delta}$ deposited on $SrTiO_3$ substrate.

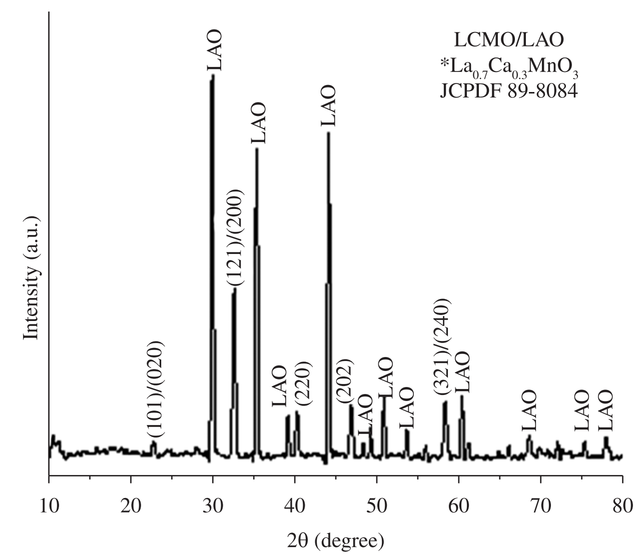

Figure 2. X-ray diffraction of $La_{0.7}Ca_{0.3}MnO_{3\pm\delta}$ deposited on $LaAlO_3$ substrate.

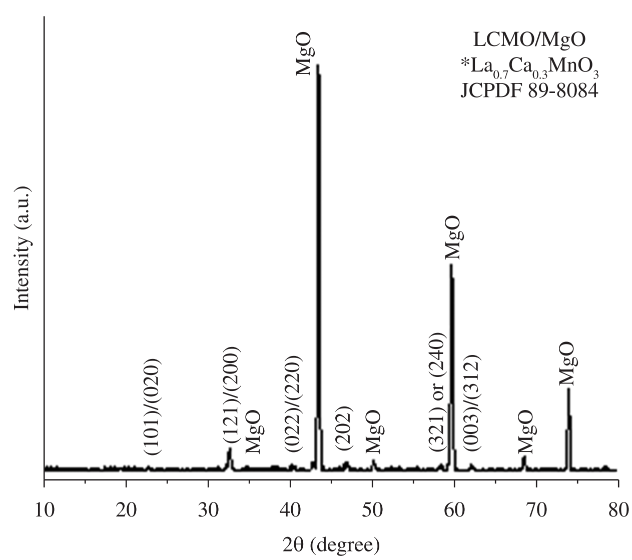

Figure 3. X-ray diffraction of $La_{0.7}Ca_{0.3}MnO_{3\pm\delta}$ deposited on MgO substrate.

among the lattice parameters of film and substrate, as well as its influence on physical properties of LCMO films have been studied[22] and they are critical for the samples based on chemical methods[12,23].

Considering the three most intense diffraction peaks, the medium crystallite size calculated via Debye-Scherrer equation[24] for LCMO/STO and LCMO/LAO was estimated at about 20 nm.

The microstructural characterization of LCMO/STO and LCMO/MgO samples can be observed in Figures 4 and 5, respectively. In both images, it can be noted the typical polycrystalline structure, in agreement with microstructures reported in the literature[15,17]. The atomic percentages obtained for LCMO/STO and LCMO/LAO samples showed values very close to the desired stoichiometry. Therefore, in the case of LCMO/MgO sample, the atomic percentages values for La, Ca and Mn elements showed much lower. Another important observed characteristic is the porosity. Being in the presented micrographs, it is a characteristic of films from Sol-Gel routes. The porosity arises due to the removal process of organic compounds, prior to the formation of the desired phase[15]. For the case of EDTA use, it is expected an increase in the porosity, since this propitiates a greater carbon chain, compared to the use of citric acid.

The XPS analysis for the determination of oxidation states of manganese can be observed in Figures 6 and 7. The spectra in binding energy region of Mn2p for LCMO/STO and LCMO/MgO samples are present respectively. The values of the ratio Mn^{3+}/Mn^{4+} for lanthanum manganite films are highly dependent on the synthesis process, and they are still subjects of study[25,26]. The presence of oxidation states Mn^{3+} e Mn^{4+} is expected for LCMO phase, although Mn^{2+} state is also reported after thermal treatments in spatial conditions[26]. The deconvolution results performed in the binding energy spectra of Mn2p are showed in Table 1. It can be noted that for LCMO/MgO sample there is a smaller contribution of Mn^{4+}, whereas for LCMO/STO and LCMO/LAO samples the ratio Mn^{3+}/Mn^{4+} are similar. As any other oxides, lanthanum manganese perovskites are oxygen deficient materials, thus fluctuating valence in these materials is directly related to oxygen stoichiometry. Considering the XPS results, it can be stated that the charge balancing of the deposited samples on STO and LAO substrates are close, and that the oxygen stoichiometry has an estimated value between 2.91 e 3. Moreover, for LCMO/STO and LCMO/LAO samples, the values of atomic percentages are shown in agreement with the results obtained from microstructural analysis. It

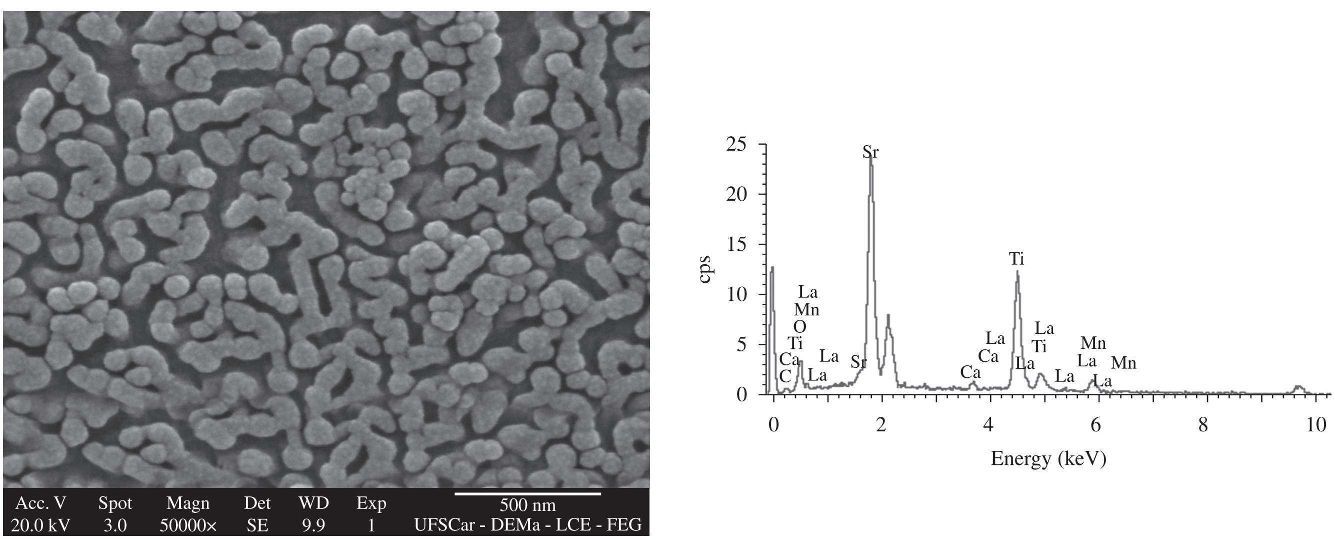

Figure 4. Representative studies of microstructure and chemical composition of LCMO/STO samples by SEM/EDS.

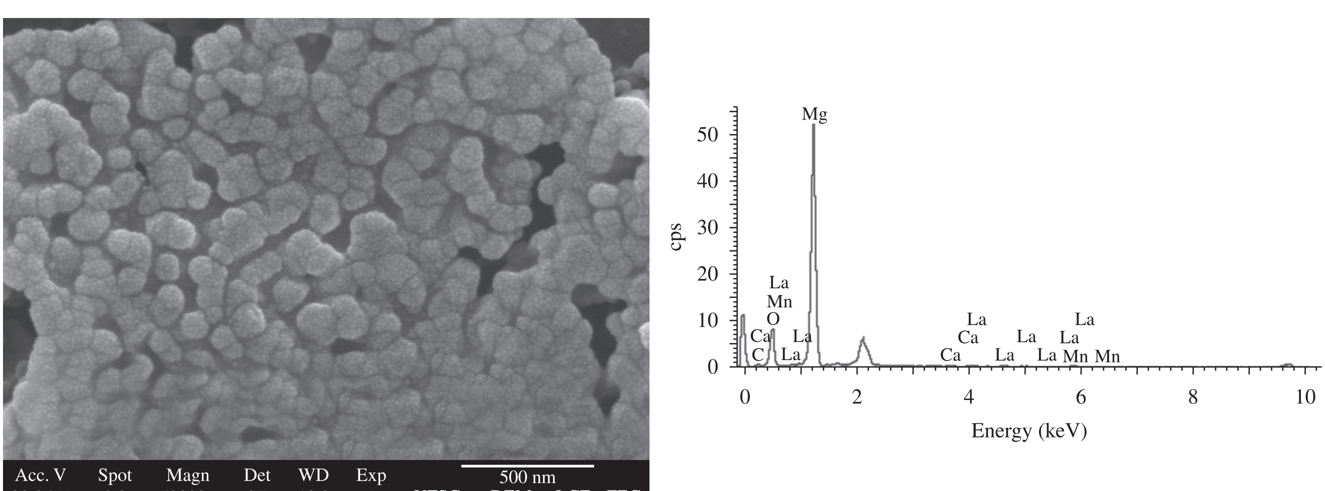

Figure 5. Representative studies of microstructure and chemical composition of LCMO/MgO samples by SEM/EDS.

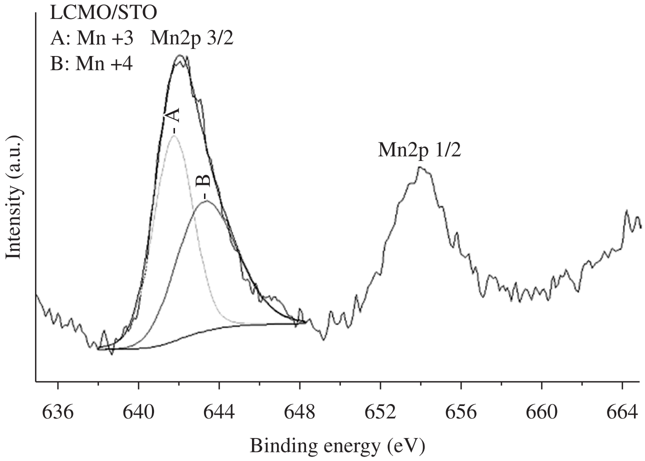

Figure 6. XPS analyses for LCMO/STO sample, Mn2p spectra.

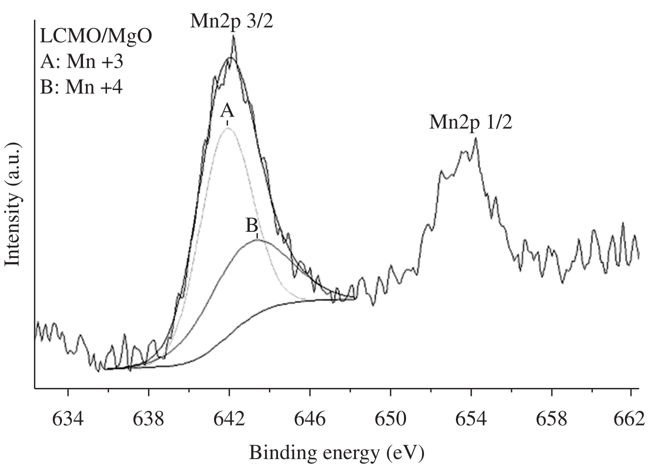

Figure 7. XPS analyses for LCMO/MgO samples, Mn2p spectra.

Table 1. Surface states and relative values of manganese valence for prepared samples.

Sample	Mn +3 (641.3 eV) content (%)	Mn +4 (642.9 eV) content (%)
LCMO/MgO	61.1	38.9
LCMO/STO	53.9	46.1
LCMO/LAO	50.7	49.3

was not considered the presence of Mn^{2+}, since it was not observed a contribution around 641 eV, typical of Mn^{2+} state[25].

In Figure 8 are present the magnetization as a function of curves for films deposited on STO and LAO substrates. Under a field application of 100 Oe, the ZFC curves showed the ferromagnetic response, in which the value of magnetic transition temperature (Tc) for LCMO/STO sample was around 276 K and for LCMO/LAO was around 274 K. These are intermediate values to those reported in the literature[1,17], which indicates that the Tc value moves to higher temperatures with increasing grain[17]. The FC curves showed in the transition temperature the ferromagnetic order considering double exchange interactions due to the presence of manganese in the oxidation states 3+ e 4+. Considering the LCMO/MgO sample, it was observed the paramagnetic response. This behavior can be justified by the non-optimized stoichiometry for this sample[27], a

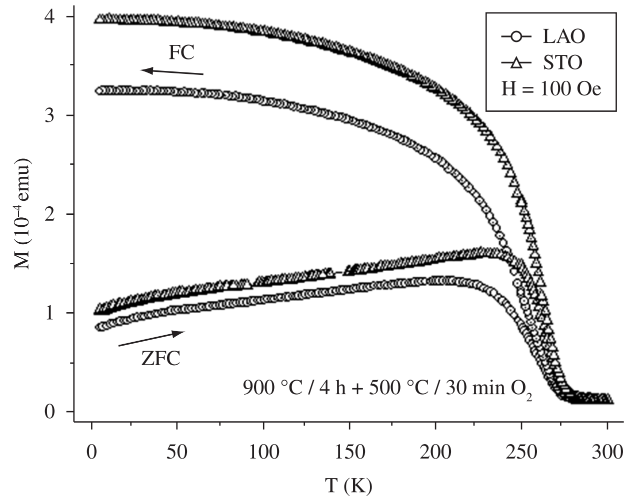

Figure 8. Magnetization as a function of temperature measurements for LCMO/STO and LCMO/LAO samples. ZFC and FC curves for an applied field of 100 Oe.

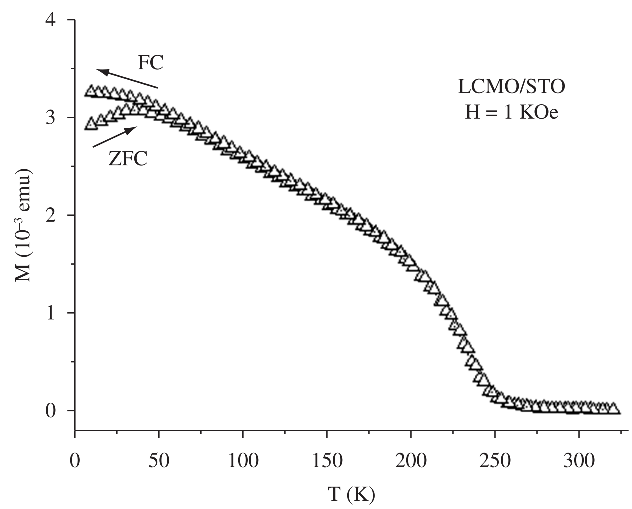

Figure 9. Magnetization as a function of temperature measurements for LCMO/STO sample. ZFC and FC curves for an applied field of 1 KOe.

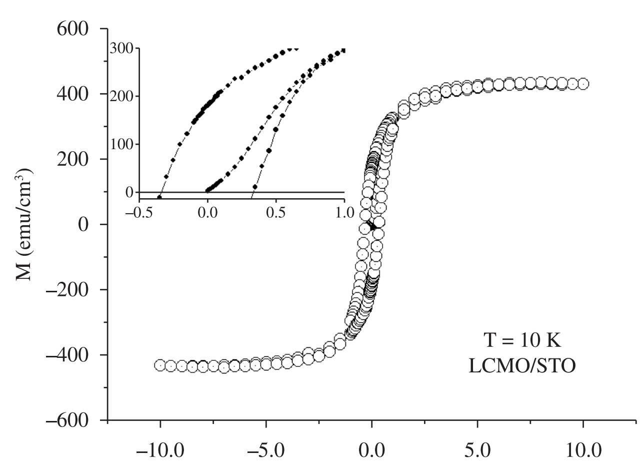

Figure 10. Magnetization vs. applied field for the LCMO/STO sample taken at 10 K. The inset shows details of the magnetic hysteresis.

result evidenced by the low atomic percentages observed in the microstructural analysis. Another important point is the oxygen content, since it has a key role in the magnetic response of films based on oxidase manganites. The values obtained in this study present magnetic critical temperature values close to those observed for in-situ annealed samples prepared by rf-magnetron sputtering[28]. Under a field application of 1 KOe, it is observed for LCMO/STO sample the magnetic order is kept, by reducing the Tc value to 250 K, as shown in Figure 9. The measurement of magnetization (M) by the applied magnetic field (H) for LCMO/STO film can be seen in Figure 10. In 10 K, it was noted in the hysteresis a low value for coercivity, as well as the saturation magnetization in 5 KOe. Both results indicate the existence of surface effects in this sample, consistent with results reported by other groups[29,30].

4. Conclusions

In this work, it was studied the synthesis, structural and magnetic characterization of LCMO films obtained via CSD, grown on substrates of STO, LAO and MgO. The analyses showed a similar formation of the film on the substrates of STO and LAO. For these samples, the results obtained by XRD, XPS and SEM, indicated the film formation with stoichiometry very close to the required ($2.91 < 3 \pm \delta < 3$) and obtained through physical methods of deposition. It was also observed the attainment of porous films, characteristic of films obtained via Sol-Gel methods. For LCMO/STO and LCMO/LAO samples were found similar values for the Mn^{+3}/Mn^{+4} ratio, without the presence of Mn^{2+} oxidation state. The magnetic responses of LCMO/STO and LCMO/LAO samples indicated a critical temperature around 270 K, as expected for high-quality samples. This work indicates that the procedures used in this contribution can be considered suitable for the synthesis of manganite-based films.

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