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Structure and magnetotransport properties in plasma-sprayed $La_{0.78}Sr_{0.22}MnO_3$ thick film

M.T.D. Orlando[a,]*, A.G. Cunha[a], J.C.C. Freitas[a], C.G.P. Orlando[a], S. Bud'ko[b,1], B. Giordanengo[b], I.M. Sato[c], L.G. Martinez[c], E.M. Baggio-Saitovitch[b]

[a] *Centro de Ciencias Exatas, Departamento de Física, Universidade Federal do Espírito Santo, Av Fernando Ferrari S/N, Vitória, ES 29060-900, Brazil*
[b] *Centro Brasileiro de Pesquisas Físicas, Rua Dr. Xavier Sigaud 150, Rio de Janeiro 22290-180, Brazil*
[c] *Instituto de Pesquisas Energéticas e Nucleares, Travessa R 400, USP, São Paulo 05508-900, Brazil*

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Abstract

Thick films of $La_{0.78}Sr_{0.22}MnO_3$ were produced by the plasma-spray technique onto stainless-steel substrate at 930°C. These films were obtained without the use of bond-layer, buffer-layer and annealing after deposition. The compound was deposited by a plasma-spray torch using nitrogen as the working gas. The films with thickness varying from 20 to 60 μm have good adherence and are composed of large splats with high degree of interconnection and small number of defects, as revealed by scanning electron microscopy. X-ray diffractometry analysis of the as-deposited film revealed that it had the same crystal structure as the original bulk. Measurements of electrical resistivity versus temperature for the film revealed a magnetic transition temperature near 340 K, with a ferromagnetic/metallic behavior below this temperature. The magnetoresistance of $La_{0.78}Sr_{0.22}MnO_3$ films exhibited similar magnetic field dependence as compared to the bulk sample, which indicates that the plasma-spray technique can be successfully employed for the deposition of thick films of manganites on large-area substrates while maintaining the main bulk properties. © 2002 Published by Elsevier Science B.V.

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1. Introduction

The perovskite-type manganites $RE_{1-x}AE_xM$-MnO_3 (RE = rare earth or Y, AE = alkaline earth) have been extensively studied in recent years due to their intriguing electrical and magnetic properties. These materials present a remarkably large negative magnetoresistance (commonly referred to as colossal magnetoresistance (CMR)) near the Curie temperature T_C, which places them as promising candidates for applications in magnetic recording devices (for a recent review on CMR in manganites see Refs. [1,2]). The $La_{1-x}Sr_xMnO_3$ compounds exhibit a ferromagnetic metallic (FM) state for x in the range from 0.16 up to about 0.5. T_C increases steeply with x up to the value

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*Corresponding author. Fax: + 55-27-33352823.
E-mail address: orlando@cce.ufes.br (M.T.D. Orlando).

[1] Current address. Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, IA 50011, USA.

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0.3; then it goes through a maximum near 360 K and decreases thereafter up to the ferromagnetic–antiferromagnetic boundary just below $x = 0.5$ [1,3].

The studies on the electric and magnetic properties of the $La_{1-x}Sr_xMnO_3$ compounds have focused on both bulk samples and thin films [3–6]. A detailed study on the magnetic and transport properties of the highest T_C sample $La_{0.67}(Sr, Ca)_{0.33}MnO_3$ in the form of polycrystalline pellets, single crystals, and annealed thick films produced by MOCVD has been reported by Snyder et al. [7]. There are several possible methods, under normal atmospheric conditions, which can be employed for the preparation of manganite thick films on large ceramic or metal surfaces, such as: rapid quenching, spray pyrolysis, screen-printing, and atmospheric plasma spraying. The plasma-spray technique has a deposition rate three orders of magnitude larger than the sputtering technique and therefore it is a convenient way to produce large coverings on suitable substrates [8–11]. Usually, after the deposition, the ceramic films have to be annealed under flowing oxygen for several hours and then slowly cooled down to room temperature in order to recover the chemical structure.

In the present paper we describe the use of the plasma-spray technique for the preparation of thick films of $La_{0.78}Sr_{0.22}MnO_3$. Magnetic and transport properties of the produced films are discussed and compared to the bulk precursor. Several aspects may change the properties of the thick films produced by plasma-spray, such as working gas, substrate temperature, substrate preparation, and others. In the present experimental procedure, N_2 working gas was used in a similar way as described previously for the YBaCuO superconductor [12], which led to thick films with good adherence, reduction of the microcracks formation during the quenching and preservation of the magnetic and transport properties of bulk samples.

2. Experimental details

Bulk samples of $La_{0.78}Sr_{0.22}MnO_3$ were produced by standard solid-state reaction of La_2O_3 (99.9995%), $SrCO_3$ (99.996%) and MnO_2 (99.9997%). The mixed powder was pressed into pellets ($2.0 \times 6.0 \times 2.5\,mm^3$) and heated at 400°C/h up to 1350°C, held at this temperature for 12 h and then cooled at 400°C/h down to room temperature. The pellets were then crushed into powder and the procedure was subsequently repeated three other times. In these re-treatments the pellets were held at 1350°C for 24 h under oxygen flow.

$La_{0.78}Sr_{0.22}MnO_3$ pellets were finally ground in a mortar to produce a fine powder, which was sieved down to 250 mesh granulometry. The plasma-spray deposition was carried out in open atmosphere. The plasma was formed by ionizing N_2 gas with an electric DC arc of 190 A and a 37 kW arc power level. The powder was dragged by argon flow to the outlet of the plasma jet. Inside the plasma jet, it was heated up to the plastic state, accelerated and projected onto stainless-steel (304) substrates. The substrates used were mounted in the form of small platelets positioned in front of the plasma torch (mosaic technique [12]). Before coating, the substrates were first sand blasted for best adherence. They were then heated near 930°C with the plasma jet, and the $La_{0.78}Sr_{0.22}MnO_3$ powder was plasma sprayed for 2–3 s onto the substrates. About 20 substrate platelets were used in each coating procedure. Several thick film samples were prepared, with average thickness between 20 and 60 μm. In some cases the deposited films were cooled under an O_2 stream immediately after the shut-off of the plasma; nonetheless, the best results were obtained for samples prepared without this last step.

The thick films, the precursor powder, and the substrate were characterized by X-ray diffraction (XRD) in a Rigaku D-2000 equipment, using Cu-$K_{\alpha 1}$ radiation. To ensure the good quality of the samples, the XRD analysis was performed on samples collected after each heat treatment step. The morphology of grains in the deposited films was investigated by scanning electron microscopy (SEM), using secondary and back-scattering electrons. X-ray energy-dispersive spectrometry (EDS) was performed in order to evaluate the local chemical composition of the samples (powder and deposited film).

Pellets and thick films were also characterized by magnetic and transport measurements. AC electrical resistivity was measured by using a four-probe standard method ($f = 16\,\text{Hz}$, $I_{\text{rms}} = 10\,\text{mA}$) with an EG&G Lock-In 5210 amplifier. Magnetization was measured in a Quantum Design MPMS-5 SQUID magnetometer, in 100 Oe or 10 kOe applied magnetic field. All these measurements were performed between 4.2 and 350 K. Magnetoresistance measurements were conducted with a Linear Research LR-700 AC bridge, at 4.2 K and in magnetic fields up to 8 T.

3. Results and discussions

The XRD patterns of the $La_{0.78}Sr_{0.22}MnO_3$ powder and thick film are shown in Fig. 1. The patterns are well explained with the assumption of a nearly cubic perovskite structure, with a lattice parameter $a = 3.88(1)$Å for both the film and the powder (Fig. 1a and 1b, respectively). This value is in accordance with previous results obtained for lanthanum manganites of similar composition [5,7]. A small splitting of the peaks near $2\theta = 32.9$, 40.6, 58.3, 68.8, and 77.9° shows that in fact the structure is not perfectly cubic; a monoclinic cell has been reported in other manganites, like $La_{0.80}Sr_{0.20}MnO_3$ [13] and $La_{0.825}Sr_{0.175}Mn_{1-x}Cu_xO_3$ [14], which explains the splitting observed in the XRD spectra of Fig. 1.

The produced thick films (thickness varying from 20 to 60 μm) had good aspect and substrate adherence. The SEM image of a typical deposited film is shown in Fig. 2, where one can see the existence of large splats with well-defined boundaries, along with small aggregates. Some micro-cracks, which are generated during the fast cooling of the film [8], can be detected inside the main splats when observing the film with back-scattering radiation (not shown). However, the concentration of micro-cracks is low and the splats show a high degree of interconnection. EDS analysis showed a nearly homogeneous composition of the deposited film, in agreement with the nominal stoichiometry ($La_{0.78}Sr_{0.22}MnO_3$). Based on SEM, EDS and XRD results one can thus conclude that the plasma-spray deposition process did not cause any appreciable change in the structure and chemical composition of the manganite. Moreover, one can expect the magnetic properties of the thick deposited films to be similar to those of bulk samples.

The presence of large splats in plasma-spray deposited films has been reported for many ceramic materials [8,10,11]. The formation of this micro-structure has been described by Bewlay and Cantor [9] in a deposition regime they

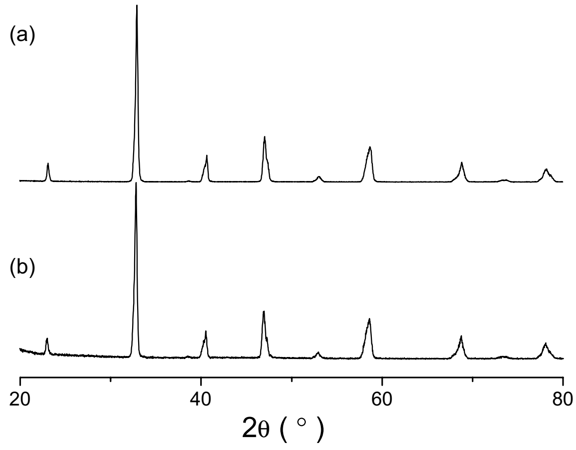

Fig. 1. XRD spectra of (a) $La_{0.78}Sr_{0.22}MnO_3$ thick film (as prepared); (b) powder $La_{0.78}Sr_{0.22}MnO_3$.

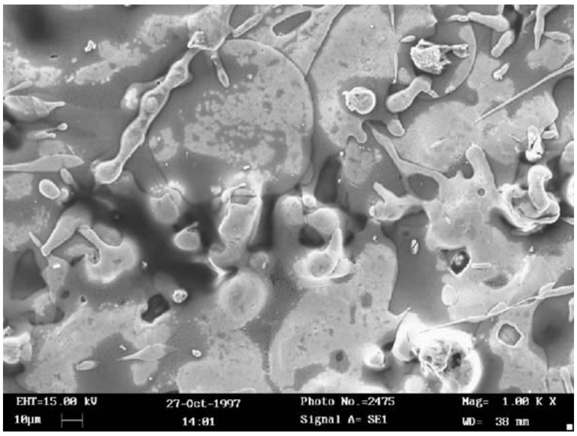

Fig. 2. SEM image of the deposited $La_{0.78}Sr_{0.22}MnO_3$ thick film.

denominated ‘A’. In such a regime, the droplets are liquid or partially liquid at the point of spray deposition and the rate of heat supply accompanying them is less than the rate at which heat can be extracted from the spray deposit they generate. Consequently, the liquid droplets spread upon deposition, forming a splat. Because heat is extracted from them relatively quickly, each splat solidifies before the arrival of subsequent droplets, giving rise to a spray deposit made of an agglomeration of splats. There are boundaries between the solidified splats and there is a large amount of porosity in the spray deposit. The temperature of the substrate employed during the deposition (930°C) is far below the melting temperature of the manganite (above 1200°C), which explains the formation of splats in the deposited films. This is in contrast to what occurs in plasma-sprayed YBaCuO films, where the high temperature of the substrate prevents the solidification of the individual droplets, giving rise to a “liquid pool” on the deposition surface [12].

Usually, plasma-sprayed films are produced with two other films between the substrate and thick film, named bond-layer and buffer-layer. The bond-layer is used to improve the adherence between film and substrate; the buffer-layer is placed between bond-layer and thick film when the film must be annealed at temperatures above 900°C, in order to avoid contamination of the deposited film by substrate and bond-layer material [10]. In the procedure used in this work, the substrate is oxidized by atmospheric oxygen when it is being heated near 900°C by the plasma jet, generating a thin film of iron oxide. This film acts as a buffer-layer between the substrate and the manganite film. After the plasma-spray deposition, an oxygen jet cools the film and substrate rapidly. In this way the possibility of contamination by substrate material is minimized.

The magnetization curve recorded for the powdered $La_{0.78}Sr_{0.22}MnO_3$ (not shown) indicates a ferromagnetic transition with $T_C \sim 380\,K$, a value that is in accordance with previous results obtained for samples with similar composition [7]. The AC resistivity versus temperature plot (Fig. 3a) of the as-prepared film displays the occurrence of a broad maximum around 340 K, as is typical in materials with a metal–insulator transition [1,2,7]. Below this temperature, the behavior is metallic, which is associated with the ferromagnetic double-exchange mechanism typically found in manganites with similar Mn^{+3}/Mn^{+4} ratio [1,3]. Fig. 3b shows a comparative plot of the AC resistivity for the pellet and the thick film. It can be seen that there is a shift in the maximum position, with the metal–insulator transition for the film occurring nearly 40 K below the corresponding temperature for the pellet. The behavior is similar for both samples in a temperature range below T_C, which confirms the bulk characteristic of the film. However, as can be seen

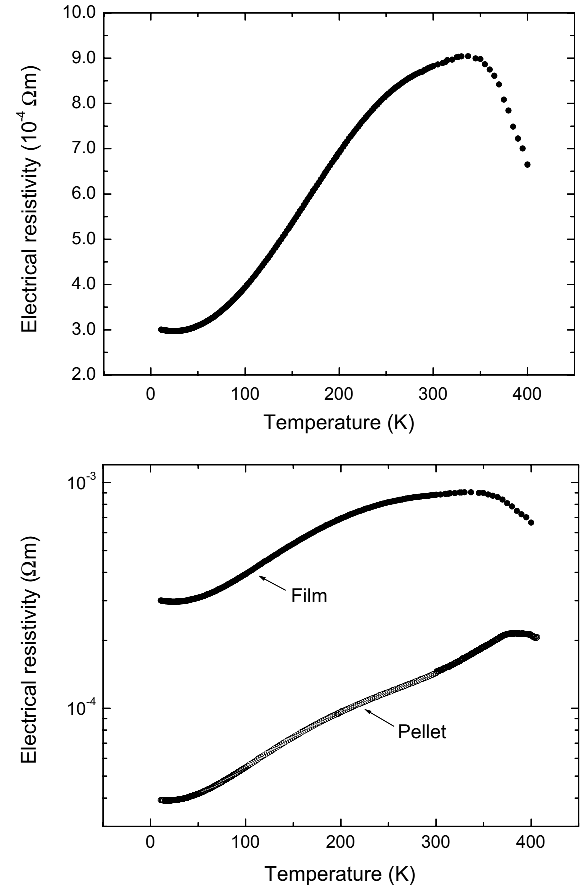

Fig. 3. (a) AC electrical resistivity versus temperature plot for the $La_{0.78}Sr_{0.22}MnO_3$ thick film. (b) Comparative AC electrical resistivity versus temperature plot for $La_{0.78}Sr_{0.22}MnO_3$ pellet and deposited film.

in the plot, the resistivity value is increased by a factor of 10 in the thick film, which can be justified by the existence of micro-cracks inside the splats in the plasma-sprayed films.

It has to be emphasized that films deposited at lower substrate temperature revealed very low T_C values (about 70 K); the expected T_C values have been recovered after the films have been oxygenated at 600°C for 12 h. The use of a pre-heated substrate appears, thus, to be essential for preserving the structure, magnetic and transport properties of the deposited films, eliminating the need of a posterior annealing, as it is common in thin manganite films [7,15].

The magnetic field dependence of the magnetoresistance of the $La_{0.78}Sr_{0.22}MnO_3$ thick film at 4.2 K shows a behavior similar to the pellet sample (Fig. 4). However, the magnitude of the effect is larger in the pellet than in the film. The magnetoresistance ratio of the deposited film reached the value of –30% under a magnetic field of 8.0 T, whereas for the pellet the corresponding value was around –40%. The different thick film behavior starts at 0.07 T; up to 1 T the fractional values follow the same field dependence as found in the pellet samples. The different values in the 0.07–1 T range can be explained by a small oxygen deficiency in the grain boundary region, which causes a local modification in the Mn^{+3}/Mn^{+4} ratio.

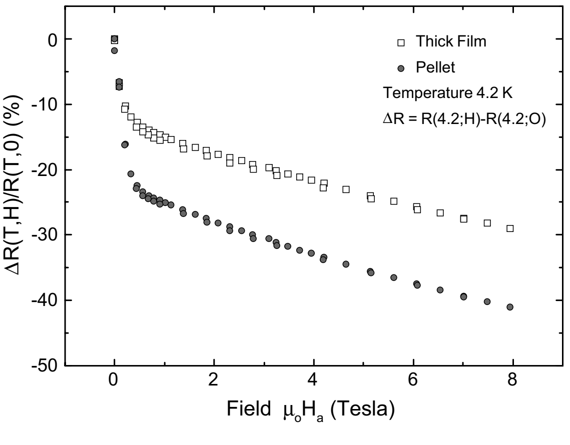

Fig. 4. Magnetic field dependence of the magnetoresistance ($f = 16$ Hz) at 4.2 K for $La_{0.78}Sr_{0.22}MnO_3$ pellet and deposited film.

4. Conclusions

Thick films (20–60 μm) of $La_{0.78}Sr_{0.22}MnO_3$ were deposited onto pre-heated (930°C) stainless-steel substrate by using the plasma-spray technique, without the addition of bond- or buffer-layers. XRD and SEM results showed that the deposition process caused no appreciable change in the chemical composition or in the structure of the film as compared to the bulk sample. The plasma-sprayed films are constituted of large splats, showing high degree of interconnection and small number of micro-cracks. The thick deposited films presented magnetic and transport properties similar to bulk samples. AC electrical resistivity showed a maximum near 340 K and a ferromagnetic/metallic behavior at low temperatures. The resistivity values of the films were higher than those of the pellet samples, as a consequence of the micro-cracks generated inside the splats during the solidification of the deposited films. The magnetoresistance ratio of the deposited film reached a value of –30% at 4.2 K, under a magnetic field of 8.0 T, as compared to –40% for the pellet. Both pellet and film presented similar magnetic field dependence for the magnetoresistance, above 1 T. A different behavior for lower fields can suggest the existence of oxygen-underdoped regions in the film, possibly in the grain boundaries.

The presented results show that the plasma-spray technique can be successfully employed for the deposition of thick films of manganites on large-area substrates. The high melting temperatures of these compounds allow the preservation of their main bulk properties that are of technological interest, particularly the high magnetoresistance. Further work is needed to investigate the modifications in the properties of the deposited films as a consequence of systematic variation of the operational deposition parameters.

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