

# Structural, magnetic and magneto-electric properties of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ thin films prepared by pulsed laser deposition

S. Calderón V<sup>a,c,\*</sup>, L. Escobar-Alarcón<sup>b</sup>, Enrique Camps<sup>b</sup>, S. Muhl<sup>c</sup>, M. Rivera<sup>c</sup>,  
I. Bentacourt<sup>c</sup>, J. Olaya<sup>a</sup>, A. Mariño<sup>a</sup>

<sup>a</sup>Universidad Nacional de Colombia, Bogotá, Colombia

<sup>b</sup>Instituto Nacional de Investigaciones Nucleares (ININ), México D.F., Mexico

<sup>c</sup>Universidad Nacional Autónoma de México, México D.F., Mexico

Available online 14 March 2008

## Abstract

Precursor powders of lanthanum strontium manganate ( $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ) were synthesized by solid state reaction with  $x = 0.1, 0.33$  and  $0.6$ . These materials were annealed at temperatures between  $900$  and  $1300^\circ\text{C}$  to produce a crystalline powder which was then compressed to form  $1\text{ cm}$  diameter targets for the pulsed laser deposition (PLD). Thin films were deposited from these targets at room temperature by PLD in an  $80/20\text{ Ar/O}_2$  atmosphere at  $7.5 \times 10^{-2}\text{ Torr}$ . The thin films were annealed at  $900^\circ\text{C}$  in air. The structural characterization of both the bulk material and the thin films was studied by X-ray diffraction which indicated that they were polycrystalline but for the films the degree of crystallinity was strongly influenced by the final annealing temperature. The composition and morphology were analyzed using SEM and EDS. The thin film samples exhibit a semiconductor behavior and high magnetoresistance ( $0.7\text{--}42\%$ ) at room temperature with a magnetic field of  $1.7\text{ T}$ .

© 2008 Elsevier Ltd. All rights reserved.

**Keywords:** Resistivity; Manganites; PLD; Magnetoresistance; Magnetic property

Over the last few years much attention has been focused on perovskite manganites of the general formula  $\text{A}_{1-x}\text{B}_x\text{MnO}_3$ , where A is La, Nd, Pr or another rare earth cation and B is Ca, Sr, Ba or another divalent cation [1]. In these materials the competition between drastically different phases induces stable states where the carriers are not homogeneously distributed [2]. Moreover, the interrelation between the crystalline structure and the physical properties is one of great importance [3]. The compound  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  solves a problem for practical applications, because by replacing the rare earth La with Sr the Curie temperature becomes higher than room temperature and this implies that the CMR effect is apparent at room temperature [4].

The films were grown on silicon and amorphous quartz substrate at room temperature by pulsed laser deposition

(PLD) using an Nd:YAG laser at  $1064\text{ nm}$  with a fluence of  $8.5\text{ J/cm}^2$  in an  $80/20\text{ Ar/O}_2$  atmosphere at  $7.5 \times 10^{-2}\text{ Torr}$ . After deposition the films were annealed in air at  $900^\circ\text{C}$  for  $1\text{ h}$ . The  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  (LSMO)  $x = 0.15$  (LSMO15),  $0.33$  (LSMO33) and  $0.4$  (LSMO40) targets were prepared by solid state reaction and annealing at temperatures between  $900$  and  $1300^\circ\text{C}$ . The resulting powders were then compressed at  $6\text{ ton/cm}^2$  to form  $1\text{ cm}$  diameter discs. X-ray diffraction (XRD) measurements were performed using a Siemens D-5000 and a D8 Bruker diffractometers with Cu-K $\alpha$  radiation ( $\lambda = 1.5406\text{ \AA}$ ). The composition and morphology were analyzed using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Magnetic measurements were performed using vibrating sample magnetometer. A traditional four-point method was adopted to measure the magnetoresistance at room temperature with a magnetic field of  $1.7\text{ T}$ .

Fig. 1 presents the XRD pattern for LSMO33 and shows that both the bulk material and the thin films were polycrystalline, without significant differences in the

\*Corresponding author at: Universidad Nacional de Colombia, Bogotá, Colombia.

E-mail address: SCALDERONVE@UNAL.EDU.CO (S. Calderón V).

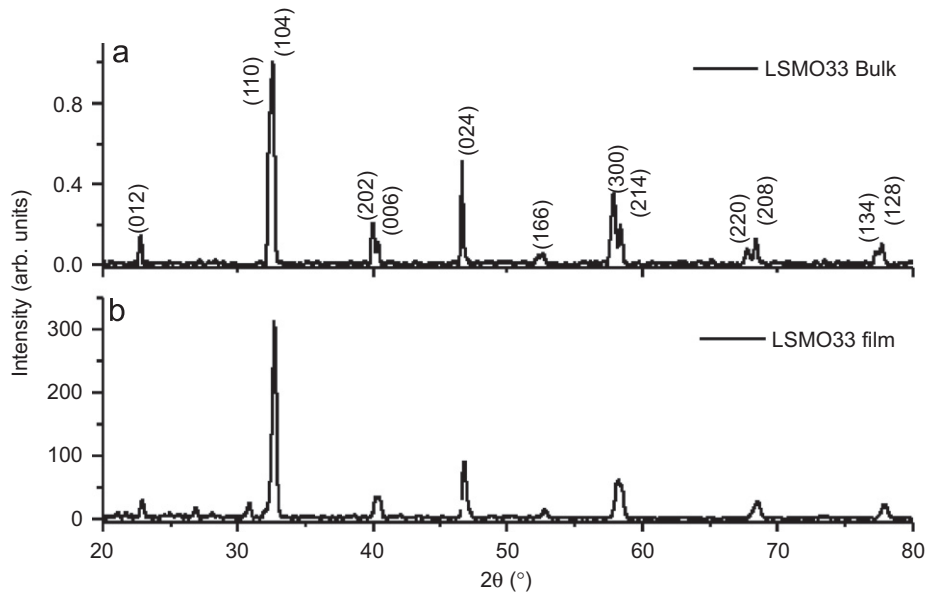


Fig. 1. X-ray diffraction pattern of LSMO33: (a) the polycrystalline powder, (b) a film on an Si substrate.

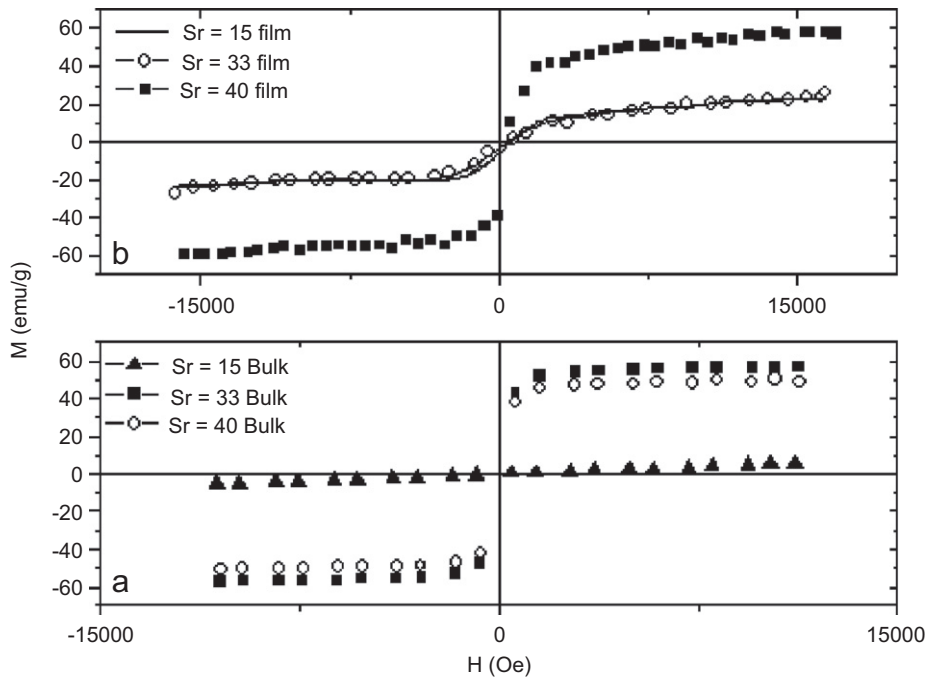


Fig. 2. Magnetic hysteresis curves at 300 K: (a) bulk, (b) thin films.

XRD patterns. The SEM studies showed that the morphology of the films is very different to the bulk material. This difference is very important because some results suggest that the grain boundaries and interfaces play a key role in the intergrain magnetoresistance [5] of manganites. Additionally, we found a decreasing relation between the particle size of the bulk material and the % Sr, and that the films were covered with spherical droplets of  $\sim 0.8$   $\mu\text{m}$ .

The coercive field for the films at room temperature was twice that of the bulk material and the saturation magnetization was stable up to an applied field of 1.2 T for  $x = 0.33$ , but changed with the % Sr due to the variation in the ferromagnetic coupling between La and Mn (Fig. 2). The LSMO15 sample was paramagnetic as bulk material (Fig. 2a) and ferromagnetic in thin film form (Fig. 2b), whereas the other compositions did not show substantial changes. This can be attributed to the fact that

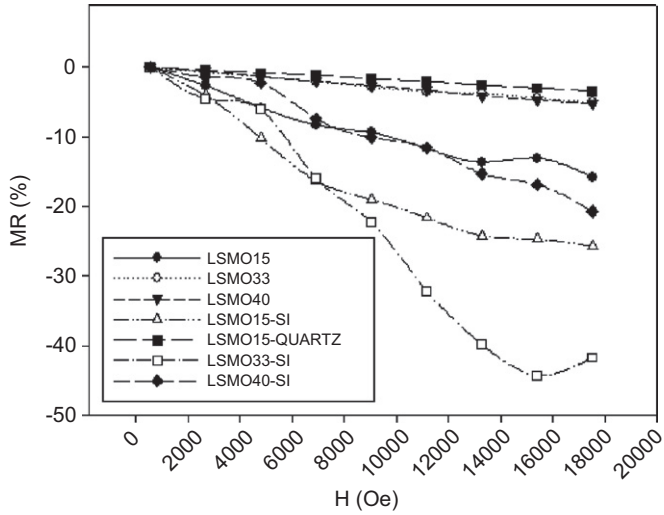


Fig. 3. Magnetoresistance of the LSMO at 300 K. The external magnetic field  $H$  is parallel to the applied current  $I$ .

the concentration  $x = 0.15$  is very close to the PI-FM transition limit and according to Korolyov [6] the F to AF transformation in these systems is of a percolation type,

that is the system separates into F and AF phases within a range of  $x$  values.

All the thin film samples were semiconductors. The maximum MR ratio at room temperature for the films grown on Si was 42.3%. For the bulk materials this maximum decreased as the Sr ratio  $x$  increased. Fig. 3 shows that the films grown on amorphous quartz had a minimum MR ratio, lower than the material in bulk.

In conclusion,  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  was successfully synthesized by solid state reaction and grown on Si and amorphous quartz substrates. Some characteristics, such as the low coercivity and the colossal magnetoresistance of LSMO at room temperature were the same for bulk and thin film material but the film properties were probably also affected by strain-induced phenomena.

## References

- [1] R.J. Bella, et al., *Solid State Ionics* 131 (2000) 211–220.
- [2] E. Dagotto, *Nanoscale Phase Separation and Colossal Magnetoresistance*, first ed., Springer, Berlin, 2003.
- [3] M. Sirena, et al., *Thin Solid Films* 373 (2000) 102–106.
- [4] S.Y. Yang, et al., *J. Magn. Magn. Mater.* 226–230 (2001) 690–692.
- [5] T. Zhu, et al., *Solid State Commun.* 117 (2001) 471–475.
- [6] A.V. Korolyov, et al., *J. Magn. Magn. Mater.* 213 (2000) 63–74.