



# Preparation and characterization of epitaxial $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_z$ thin films grown by pulse laser deposition

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## Abstract

The amorphous citrate process was used to synthesize powder of conducting and ferromagnetic oxide  $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_z$  ( $z = 3$ ) and thin films of it were prepared by pulse laser deposition (PLD). The epitaxial nature of the films had been established by X-ray diffraction (XRD), and Rutherford backscattering spectrum (RBS). After anneal at  $800^\circ\text{C}$  in  $\text{O}_2$  atmosphere, the thin films exhibit metallic and magnetic properties. Ferromagnetic resonant spectra reveal that there are nonuniform regions of distinct magnetization in-plane of the films, which are related to the random distribution of lanthanum in the film, as confirmed by the RBS spectrum. The magnetization measured by a vibrating sample magnetometer is different from that obtained from the ferromagnetic resonance spectrum.

**Keywords:** Epitaxial  $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_z$ ; Pulse laser deposition

## 1. Introduction

The strontium-substituted lanthanum manganese oxide,  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ , is a well-known ferromagnetic oxide material with high electrical conductivity [1,2]. It has potential applications as resistors and high-temperature electrodes in the electrical industry. Recently, it has attracted much attention stimulated by the discovery of giant magnetoresistance (GMR) effect in  $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_z$  [3],  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_z$  [4], and  $\text{Nd}_{0.65}\text{Sr}_{0.35}\text{MnO}_z$  [5]. Also, previous studies on

such materials show that, sandwiched in between two  $\text{YBa}_2\text{Cu}_3\text{O}_7$  thin films, the magnetic properties of  $\text{La}_x\text{Sr}_{1-x}\text{MnO}_z$  layer have effect on the supercurrent passing through the magnetic barrier, and the supercurrent could be detected at the thickness of  $\text{La}_x\text{Sr}_{1-x}\text{MnO}_z$  up to  $500 \text{ \AA}$ . This phenomenon is called the proximity effect [6]. These researches reveal that the transport properties of this complicated oxide are electron spin related, as in the cuprate superconductor [7]. Although the discoveries are continued to be reported, the detailed knowledge about the basic metallic and magnetic properties of the films is absent and a complete understanding of the origin of these phenomena is still not available. In this paper, we describe the preparation of epitaxial

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$\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_2$  (LSMO) thin films and the characterization of their electrical and magnetic properties using a vibrating sample magnetometer and ferromagnetic resonance.

## 2. Experimental

### 2.1. Preparation

#### 2.1.1. Synthesis of LSMO

A nominal composition of  $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_2$  (LSMO) was prepared by a citrate complex method. The process included mixing ‘‘analar’’ grade citric acid and the metal nitrates,  $\text{Mn}(\text{NO}_3)_2\text{-H}_2\text{O}$ ,  $\text{La}(\text{NO}_3)_3\text{-H}_2\text{O}$ , and  $\text{Sr}(\text{NO}_3)_2$ , in the required proportion, each dissolved in 10 ml de-ionized water. Then, the water was vaporized gradually at a temperature of 200°C to form the amorphous citrate precursor. Fired from 400 to 800°C, the conditions to fabricate the pure perovskite phase of LSMO powder were examined. The powder was pressed into a pellet and then sintered at 1200°C to prepare the target for the laser ablation.

#### 2.1.2. Laser ablation

The LSMO thin films were fabricated on (001)  $\text{SrTiO}_3$  single-crystalline substrates in 300 mTorr  $\text{O}_2$  atmosphere by pulse laser deposition (PLD), using an equipment described in detail previously [8]. A KrF excimer laser operating at a wavelength of 248 nm, a pulse duration of 20 ns, and a pulse energy of 300 mJ were used to ablate materials from the target. The laser repeat rate was 3 Hz and the beam area on the target was  $1.5 \times 1.5 \text{ mm}^2$ , resulting in a power density of 10 mJ/cm<sup>2</sup>. The temperature of the substrate was 700°C. The as-grown films were annealed at 800°C for 4 h in oxygen atmosphere.

### 2.2. Characterization

The samples were characterized by powder X-ray diffraction (XRD) and Rutherford backscattering analysis. The phase purity and lattice parameters were determined by XRD measurements which were performed with a Rigaku diffractometer using  $\text{Cu K}\alpha$  radiation at room temperature and Si as an internal standard. Rutherford backscattering spec-

trum (RBS) was used to establish the epitaxial nature of the LSMO on  $\text{SrTiO}_3$  substrate and measure the thickness of the thin films.

Electrical resistance versus temperature was measured by the standard four-point probe method from 300 to 80 K. A vibrating sample magnetometer was employed for the measurement of magnetization with the applied field being perpendicular to the surface of the film.

Using a conventional spectrometer, we studied the ferromagnetic resonance (FMR) of the film at room temperature. We glued the samples to the end face of a quartz rod and located them at the center of the microwave cavity which operated at 9.78 GHz. The angle between the direction of the applied magnetic field and the surface normal changed from 0° to 90°.

## 3. Results and discussion

### 3.1. Structures

Fig. 1 shows the XRD pattern for the powder fired at 400°C (a) and 800°C (b). The figures indicate that the precursor transformed to a single perovskite-type powder phase of LSMO, even at as low a temperature as 400°C, and the XRD spectrum of LSMO fired at 800°C is almost the same as that fired at 400°C. The obtained LSMO powders were

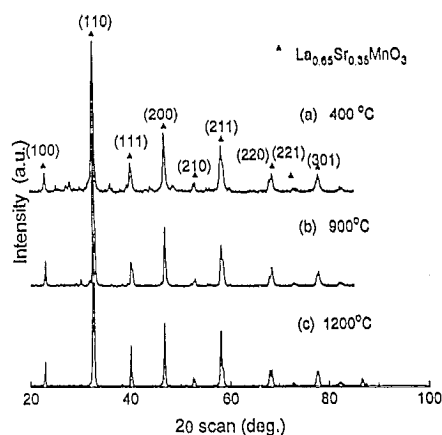


Fig. 1. XRD patterns of the powders processed by the citrate complex method and calcined at 400°C (a), 800°C (b), and sintered at 1200°C (c), showing that the pure perovskite phase of  $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_2$  can be synthesized at 400°C and kept stable up to 1200°C.

determined to be pseudo cubic with a lattice of  $3.85 \pm 0.002 \text{ \AA}$ , which is the same as in the previous report [1]. The results reveal that the method is very suitable for the preparation of LSMO target. The powder was pressed into pellets and sintered at  $1200^\circ\text{C}$  for 4 h. Fig. 1c is a typical XRD measurement of these pellets which shows that the as-prepared LSMO samples correspond to a perovskite-type phase. At  $1200^\circ\text{C}$ , the pellets were sintered with the density of  $6.0 \text{ g/cm}^3$  which serve as suitable targets for laser ablation.

In comparison, conventional solid-state reaction of a mixture of high-grade  $\text{MnO}$ ,  $\text{La}_2\text{O}_3$  and  $\text{SrCO}_3$  oxides was also used. The powders were weighed in stoichiometric proportions and thoroughly mixed together in an agate ball mill for 2 h. The mixed powder was set onto an  $\text{Al}_2\text{O}_3$  boat, put into a tubular furnace, and calcined in air at  $800^\circ\text{C}$  for 12 h. This followed by a regrinding and an identical heat treatment. The resultant black products were obtained with the perovskite phase. The powder was pressed into pellets and then sintered at  $1200^\circ\text{C}$  for 12 h. The fabricated pallets had poor quality (low density) which was attributed to the large size of the powder particles and were not suitable to be used as the targets for laser ablation.

Fig. 2 shows a  $\theta$ - $2\theta$  scan of diffraction of LSMO grown on  $\text{SrTiO}_3$  substrate in which only the (00 $l$ ) of  $\text{SrTiO}_3$  and LSMO are detected. The result shows that the grown thin film is perfectly  $c$ -axis oriented. The measured  $c$ -axis constant was  $3.80 \pm 0.002 \text{ \AA}$ , which is 1.5% smaller than that of the target. This

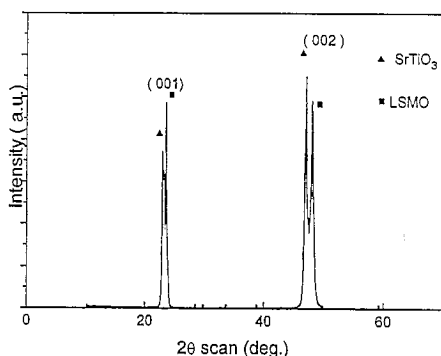


Fig. 2. XRD pattern of a  $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_2$  film deposited by PLD at  $700^\circ\text{C}$  on (001)  $\text{SrTiO}_3$ . The peaks indicated with  $\blacksquare$  are (00 $l$ ) reflections of the  $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_2$  thin films, and the peaks indicated with  $\blacktriangle$  are (00 $l$ ) reflections of  $\text{SrTiO}_3$  substrates.

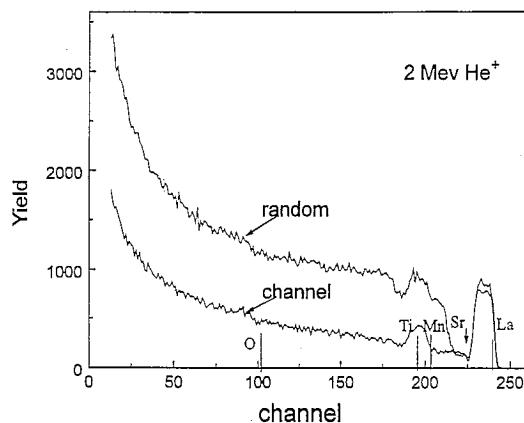


Fig. 3. Rutherford backscattering spectrum showing energy versus intensity for both channeling and random 2 MeV  $\text{He}^+$  ions backscattering from the  $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_2$  film with  $2000 \pm 60 \text{ \AA}$  thickness on a (100) $\text{SrTiO}_3$  substrate.

suggests that the thin film suffers the tensile strain due to the epitaxial growth. As expected, the small lattice misfit between LSMO and  $\text{SrTiO}_3$  (1.2%:  $a_{\text{LSMO}} = 3.85 \text{ \AA}$  and  $a_{\text{SrTiO}_3} = 3.90 \text{ \AA}$  at room temperature) should prompt the epitaxy of LSMO on  $\text{SrTiO}_3$  and the epitaxially induced  $a$ -axis parameter match should in turn result in the LSMO  $c$ -axis parameter reduction. If we assume that the film is elastically isotropic, the Poisson ratio can be calculated to be  $\nu = 1/3$ .

The epitaxial nature of LSMO thin films was confirmed by the RBS, using 2.0 MeV  $^4\text{He}^+$  ions. In Fig. 3, the random and ion channeling spectra are given. The lanthanum, strontium and manganese backscattering signals occurred at their expected surface positions as indicated in the figure. The strontium and titanium backscattering signals originated from the substrate. The RBS spectrum can be used to estimate the thickness of LSMO film as  $2000 \pm 60 \text{ \AA}$  [9], which is consistent with the measurement by a surface profilometer on a delaminated portion of the samples. The minimum backscattering yield in the (001) direction is measured using the manganese signal and amounted to approximate 30%. This suggests that the film exhibits obvious in-plane alignment with the substrate, i.e. the film is epitaxially grown on  $\text{SrTiO}_3$ , but with some misalignment with the substrate. Typically, single crystals or perfectly matched epitaxial thin films exhibit a minimum yield in RBS channeling experiments of 2–3%. Interest-

ingly, both the ion channeling and random spectra have almost the same signal yield as that of lanthanum. This suggests that lanthanum atoms are arranged in the thin film randomly, which may be responsible for the magnetic properties described below.

### 3.2. Properties

The as-grown films were almost insulators, but after being annealed in  $O_2$  atmosphere at  $800^\circ C$  for 4 h, these films show low resistance. This indicates that the oxygen stoichiometry in the film has been changed during the annealing process. According to Jonker [1], the existence of mixed valence states of  $Mn^{4+}$  and  $Mn^{3+}$ , and the valence state exchange between them are responsible for their metallic character. In fact, the annealing process increases the ratio of  $Mn^{4+}$  in the films through the oxygen content.

The electrical resistance dependence on temperature from 300 to 80 K of the annealed thin films showed metallic behavior. The resistance ratio ( $R_{300}/R_{100}$ ) of LSMO was about 5. In the measured temperature range, no anomaly can be seen in the LSMO resistance data.

The transition point of bulk LSMO from ferromagnetics to antiferromagnetics is 360 K. A typical hysteresis loop was obtained with 241.8 Oe of coercivity, 6.9 emu/g of remanence and 26 emu/g of magnetization. The measurement is almost the same as the result reported by Ju et al. [4].

Fig. 4 shows the measured FMR spectra expressed in absorption derivatives of an LSMO film.

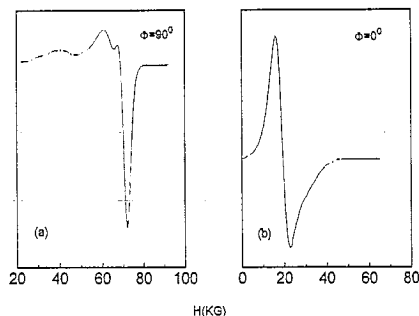


Fig. 4. Room-temperature FMR spectra for  $\phi = 90^\circ$  ( $H$  perpendicular to the surface) and  $\phi = 0^\circ$  ( $H$  parallel to the surface), showing noticeable asymmetry and multiple resonance at  $\phi = 90^\circ$ .

Fig. 4a and 4b correspondent to the situation of  $H$  perpendicular and  $H$  parallel to the film surface, respectively. The signal in Fig. 4a is obviously asymmetric and could be described by multi-Lorentzian lines [10], meanwhile Fig. 4b is symmetric and could be well described by Lorentzian line, indicating that the local magnetic nonuniformity exists in the in-plane of the film. In Fig. 4b, the peak-to-peak width of 500 Oe is among the smallest linewidths observed for LSMO thin films [10], indicating a higher crystalline quality. Using the standard demagnetization equations [11] and supposing the Lande  $g$ -factor equals 2.14, the magnetization can be calculated as about 54 emu/g, which is different from the value measured by VSM. The same situation has taken place in the Ni–Mo magnetic superlattice [11], where an anisotropy field was introduced to modify the magnetization of VSM. The source of the anisotropy field can be attributed to the stress suffered by the thin film due to its epitaxial growth.

The inhomogeneity of the magnetic properties in the  $La_{1-x}Sr_xMnO_2$  thin films was suggested by other authors, based on the observation of the broadened magnetic transition. As pointed out by Jonker,  $La_{1-x}R_xMnO_2$  has ferromagnetic properties due to a strong positive magnetic exchange interaction between  $Mn^{3+}$  and  $Mn^{4+}$  ion pairs. So the observed magnetic inhomogeneity should be attributable to the nonuniform distribution of  $Mn^{3+}$  and  $Mn^{4+}$ . From the RBS spectrum (Fig. 4), Mn and Sr atoms distribute uniformly in the films, meanwhile the lanthanum distribution shows a disorder which in turn induces the disorder of  $Mn^{3+}$  ion distribution. Interestingly, a similar disorder of lanthanum distribution has been observed in  $LaNiO_3$  and  $La_{1-x}Ca_xMnO_2$  thin films grown by PLD. The reason that causes the disorder is still being investigated.

It has been suggested that  $La_{1-x}R_xMnO_2$  has metallic and ferromagnetic properties due to double exchange between  $Mn^{3+}$  and  $Mn^{4+}$  ions as was mentioned earlier. This means that the metallic and ferromagnetic properties originate from the same physical mechanism. So the ferromagnetic nonuniformity should also induce the nonuniform electrical properties in the film. Furthermore, taking into account the giant magnetoresistance effect observed in LSMO [4] with the similar magnetic nonuniformity, we believe that the nature of magnetic order may

play an important role in the mechanism of giant magnetoresistance in the film of such materials.

#### 4. Conclusions

In conclusion, pure perovskite phase  $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_z$  can be synthesized conveniently by the amorphous citrate process. The epitaxial thin films of  $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_z$  have been prepared by pulse laser deposition. The films show magnetic and metallic properties. The films contain nonuniform regions of distinct magnetization which may relate with the disorder of lanthanum in the films. We consider that the nonuniformity may play an important role in the anomalous transport process in such mixed valence manganese films. The values of magnetization measured by vibrating sample magnetometer and ferromagnetic resonance are different, which is attributed to the stress suffered by the epitaxial films.

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