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# Electrical and Optical Properties of $La_{0.7}Ca_{0.3}MnO_3$ Polycrystalline and Thin Film

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The $La_{0.7}Ca_{0.3}MnO_3$ thin film shows a metal-insulator transition at temperature around 150 K, about 100 K lower than that of the polycrystalline sample. It is found that the activation barrier in the thin film is lower than that in the bulk sample. The FIR reflectance of the thin film exhibits a new mode which is not present in the bulk sample. We propose that the new mode is the corresponding surface bending mode.

## 1. Introduction

The properties of $R_{1-x}A_xMnO_3$ and related rare earth manganate perovskites have attracted much attention in recent years mainly due to discovery of their colossal magnetoresistance [1-5]. Apart from CMR, these materials have also revealed many interesting phenomena in fundamental physics and show a metal-insulator (MI) transition near ferromagnetic (FM) ordering temperature, $T_c$. Below the Néel temperature $T_N$, it is an A-type antiferromagnetic (AF) insulator. Staggered orbital ordering was observed in the ferromagnetic planes [6], which can be driven by either the intra-atomic Coulomb interaction in the orbitals [7] or the cooperative Jahn-Teller (JT) splitting of the degenerate $e_g$ orbital [8,9]. Just below $T_c$, its temperature dependent resistivity $\rho(T)$ shows a metal like behaviour. Furthermore it is found that physical properties of CMR materials vary significantly under different growth conditions and in different sample geometries. MI transition temperatures $T_{MI}$ in bulk samples and that in thin films are quite different and $T_{MI}$ also varies in thin films grown under different conditions. The $La_{0.7}Ca_{0.3}MnO_3$ thin films grown on the on $SrTiO_3$ substrate have different $T_{MI}$ under different conditions. The film deposited by PLD shows a $T_{MI}$ about 190 K under zero magnetic field [10]. For the films deposited by DC-sputtering method, the $\rho(T)$ curves in zero field show that the $T_{MI}$ depends strongly with the annealing treatment. $T_{MI}$ is at about 130 K without annealing treatment and $T_{MI}$ increased up to 247 K after annealing treatment [11]. It has been demonstrated [12-14] that $T_{MI}$ and CMR properties of manganite film on the perovskite type substrate such as $SrTiO_3$, $LaAlO_3$ and $NdGaO_3$ etc. are influenced by strains arising from subtle lattice mismatch between the film and the substrate.

In this paper we present an experimental study on the lattice vibrational properties and MI transition in thin films grown by pulsed laser deposition method. The results are then compared to that of the bulk sample. We used far infrared reflection spectroscopy to determine the vibrational modes in the bulk and in thin film structures. The temperature dependent resistivity has been measured in bulk and thin film samples to compare the MI transition in these two systems. A new vibrational mode shows up the reflectance of thin films. We attribute this to the surface mode. Our transport measurements revealed that the MI-transition temperature in the thin film about 100 K lower than that in the bulk sample. The value of the resistivity is about two orders of magnitude larger than that of the bulk.

## 2. Experiments

A polycrystalline target of $La_{0.7}Ca_{0.3}MnO_3$ was prepared through the solid-state reaction process in air. A stoichiometric mixture was first grounded and sintered at a temperature of 1000 $^oC$ for 70 hours then quenched out of the furnace at 450 °C. The powder was grounded again and then pressed to a shape of 25 mm diameter and of thickness about 3mm. The sample is then sintered in furnace with higher temperature. The rate of temperature increase was 290 $^oC$/hr. A temperature of 1450 $^oC$ was reached, and the sample was maintained at this temperature for 6 hours. The temperature was decreased to 1200 °C at a rate of 50 °C/hr and then at 120 °C/h to the end.

The deposition of $La_{0.7}Ca_{0.3}MnO_3$ thin film was carried out on MgO (100) by PLD, using an excimer laser system. The particulars of the deposition system were: fixed laser beam, the target to substrate distance 15mm; the target rotation rate is 10 rotations/min, and the background pressure is $10^{-6}$ torrs. The laser beam hits the target at an incident angle of $45^o$. The MgO substrate was mounted on the sample holder using silver paste and was parallel to the target. The deposition conditions were: the laser repetition rate of 3 Hz, the energy density on the target ~ 3.0Jcm$^{-2}$ and total energy per-pulse ~600mJ.

The crystal structure of both the crystalline target and the thin film were examined by X-ray diffraction. The resistivity of both samples were measured by using the four-probe technique over the temperature range of 50 – 300 K. The surface of the thin film was examined by the atomic force microscopy (AFM). Far-infrared reflectivity was measured at near-normal incidence at the room temperature using a Bomem DA3.26 rapid-scan interferometer equipped with a DTGS detector.

## 3. Results and Discussions

The X-ray spectra of the film and bulk are shown in Fig.1 (a) and (b). The intensities of (121) and (200) are weaker as compared to that of bulk. This indicates the film on MgO substrate is polycrystalline and well textured. This result may arise in the way suggested by Vlalkov [15]: it may be that the high mismatch of the lattice constant between the film and MgO substrate (about 9%) has a more crucial influence on growth than substrate temperature and the chamber pressure.

In order to investigate surface area of the thin film in more detail, we scanned a larger surface by AFM. A 2x2 μm$^2$ was scanned from smooth areas and analysed as a 3D image in Fig. 1 ( c) which shows that grain shapes are roughly circular. Fig. 1 (d) shows the image of the bulk sample obtained by Scanning Electron Microscopy (SEM). The image of sample shows that some grains size are up to 30 μm which is almost 10 times as big as the size of grains of the same compound sintered at a lower temperature.

Fig. 2 (a) shows the temperature dependence of resistivity of the $La_{0.7}Ca_{0.3}MnO_3$ thin film (upper) and target (lower). The target exhibits the mental-insulator transition temperature at 255 K. The resistivity of $La_{0.7}Ca_{0.3}MnO_3$ thin film grown on MgO substrate shows several interesting features. (1) The transition temperature is around 150 K, about 100 K lower than that of the target. The reasons that the insulating phase in the thin films can persist at a much lower temperature are (i) the increased localization in samples of reduced dimensionality as expected from the theory of weak localization, and (ii) possible diffusion of MgO into the thin film region which caused additional carrier scattering. (2) Overall the resistivity of the thin film is about two orders of magnitude larger than that of the bulk sample. The metallic region in both systems can be well represented by a power-law form, except for the bulk sample near $T_{MI}$ where a rapid increase is observed. The insulating region is rather interesting. The carrier transport in the insulating region is of activation type, i.e. resistivity is given as $\rho(T) = \rho_0 \exp\left(\frac{E_a}{kT}\right)$. Here $E_a$ is the activation energy which is determined by the polaronic binding

potential. We found that $E_a/k \sim 500K$ for the thin film as compared to $E_a/k \sim 800K$ in the target. The quantity $\rho_0$ represents the resistivity at high temperature. It is found that $\rho_0$ is around 0.15 Ωcm for the thin film and $10^{-4}$ Ωcm for the bulk sample. A much larger value of $\rho_0$ for the thin film structure is consistent with the grain sizes of the bulk and thin film samples shown in Fig.1c and Fig.1d. In general the value of resistivity increases as the grain size decreases. On the other hand a smaller value of $E_a$ in the thin film structure can be understood from the point of view of reduced polaronic potential barrier in reduced dimensionality.

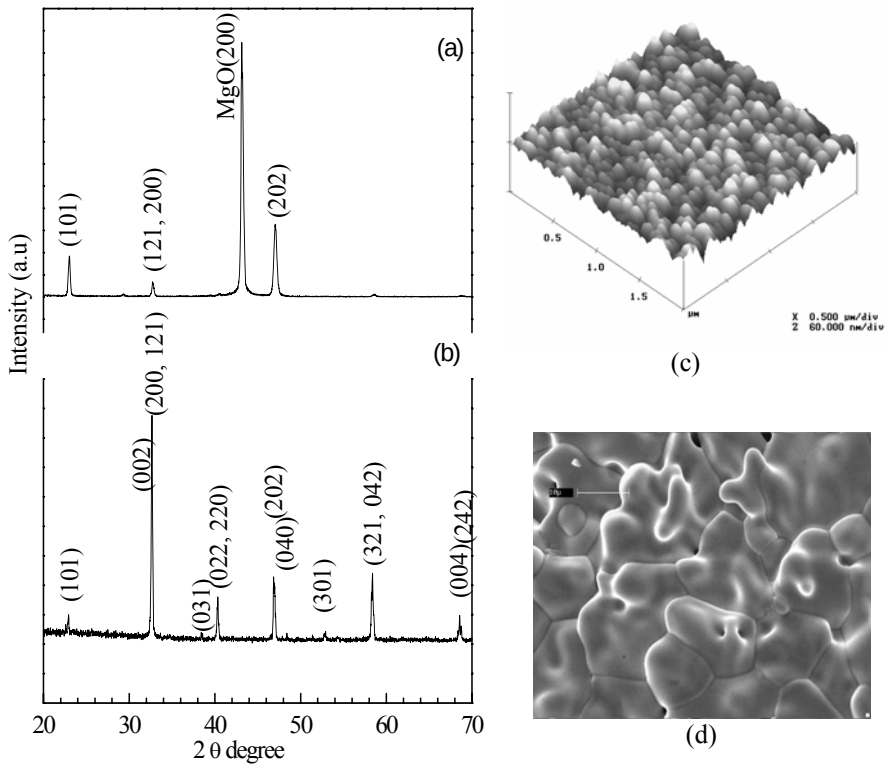


Fig. 1. (a) and (b) are X-ray patterns of thin film on MgO substrate and crystalline sample respectively. (c) The surface of the thin film investigated by AFM and (d) the grain size of crystalline sample examinated by SEM.

FIR reflection measurement was performed in both the thin film and the target. Fig.2(b) shows the reflection spectra of the $La_{0.7}Ca_{0.3}MnO_3$ target and thin film. Three modes were observed in the reflectance of target. The three modes energies are 'external' ~ 172cm$^{-1}$,'bending' ~ 343 cm$^{-1}$ and 'stretching' ~ 580 cm$^{-1}$. The reflectance of the thin film is qualitatively different. (*i*) The three modes are still present at 168 cm$^{-1}$, 330 cm$^{-1}$, 602 cm$^{-1}$, respectively for 'external', 'bending' and 'stretching' modes. The spectral weights of these modes are rather different as compared to that of the bulk target sample. There is a reduction in the reflection in the external and stretching modes, but the reflection is enhanced in the bending mode. (*ii*) The reflectance of the thin film exhibits some new modes, which are not present in the target. The most noticeable one is at 405cm$^{-1}$. Both external and bending modes of thin film have lower energies than the corresponding modes of the target, but the energy of the stretching mode of the thin film is higher as compared to that of the bulk. We propose that the new mode is the corresponding surface stretching mode, which has similar origin of the bulk mode but under additional surface confinement.

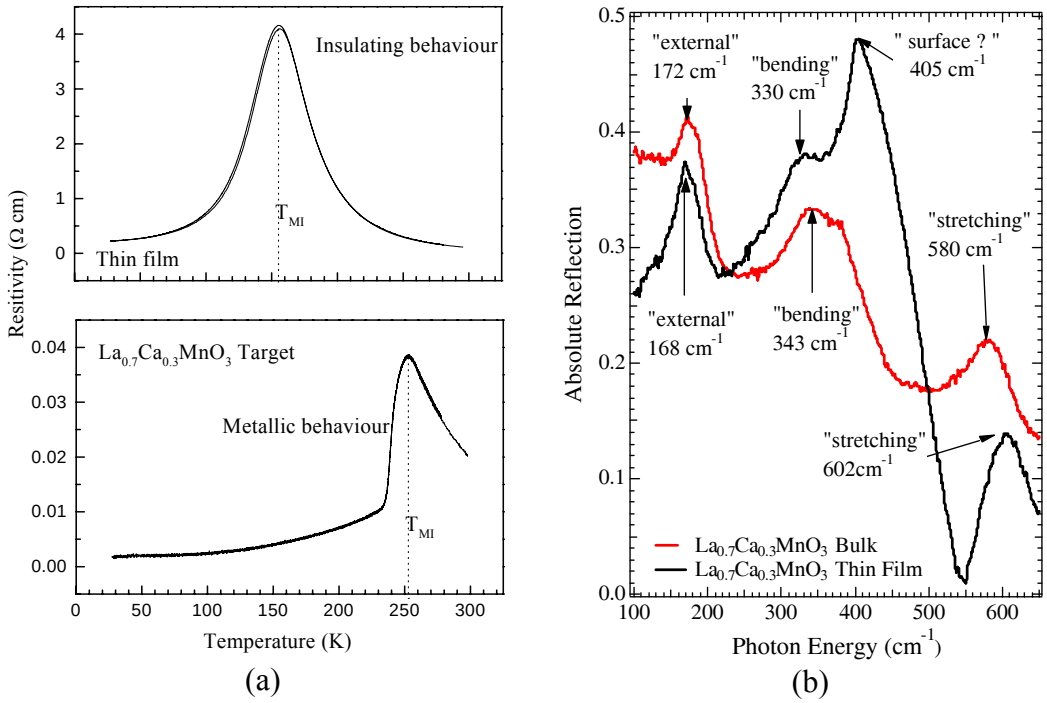


Fig. 2. (a) Temperature dependent resistivity of the thin film (upper panel) and bulk (lower panel), (b) FIR reflection spectra of $La_{0.7}Ca_{0.3}MnO_3$ target and thin film, the thin film a new mode at 450 cm$^{-1}$.

In conclusion, the transport and optical properties of the thin film were investigated. We found that due to the reduction of polaronic potentials in thin films, the activation energy is smaller in the thin film as compared to that of the bulk sample. A new surface mode (at 405 cm$^{-1}$) has been identified in the reflectance.


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## References


[1] R. von Helmolt et al, Phys. Rev. Lett. 71, 2331 (1993).
[2] S. Jin et al, Science 264, 413 (1994).
[3] Y. Tokura, Colossal Magneto-resistive Oxides, Gordon and Breach Science Publish (2000).
[4] F. Ye et al , Phys. Rev. B **75**, 144408 (2007) .
[5] S. Valencia et al , Phys. Rev. B **75**, 184431 (2007)
[6] Y. Murakami et al, Phys. Rev. B **81**, 582 (1998)
[7] R. Maezono, S. Ishihara, and N. Nagaosa, Phys. Rev. B **58**, 11583 (1998);
[8] J. Van den Brink et al, Phys. Rev. B **59**, 6795 (1999)
[9] K. H. Ahn and A. J. Millis, Phys. Rev. B **58**, 3697 (1998)
[10] T. Yotsuya et al, Materials Chem. and Phys. 54, 169 (1998).
[11] A. De Santis et al, journal of MMM, 262,152(2003)
[12] B. Biswas et al, Phys. Rev. B 61 9665 (2000).
[13] F. Tsuia et al, Appl. Phys. Lett. 85 5417 (2000).
[14] H.W. Zandbergen et al, Phys. Rev. b 60 10259(2000).
[15] E. S. Vlakhov et al, J. App. Phys.83, 2152 (1998).