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STUDY ON STRUCTURE, MICROSTRUCTURE AND ELECTRICAL PROPERTIES OF $La_{0.67}Ca_{0.33}MnO_3$ SYSTEM IN BULK AND THIN FILM

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ABSTRACT

Manganite compound of $La_{0.67}Ca_{0.33}MnO_3$ polycrystalline in bulk and thin film have been prepared by solid state reaction and pulsed laser ablation deposition method (PLAD), respectively. Rietveld's refinement showed both samples in single phase of orthorhombic structure with space group of Pbnm. Bulk and thin film showed much different microstructure, where bulk have relatively much more larger crystalline size (~1-2 μm) as compare to thin film (~40-60 nm) samples. Bulk sample showed typical insulator-to-metal transition (T_p) at 218 K when H=0T and shift to 224 K in H=1T. However, thin film sample shows almost insulating over the entire range of temperature and no T_p is observed at the entire measurement range. In this work, we observed that microstructure formation change when convert from bulk to film and drastically charge it electrical resistance.

Keywords: polycrystalline; perovskite manganite; thin film; magnetoresistance

INTRODUCTION

The perovskite manganites $La_{0.67}A_{0.33}MnO_3$ (A=Ba, Sr, Ca) have been attracted much attention due to their magnetic and electrical transport properties. When La^{3+} is doped with a divalent ion, portions of Mn^{3+} ion are converted to Mn^{4+} ions. These will create a mobility of e_g electrons between pairs of Mn^{3+} and Mn^{4+} ions through oxygen and double exchange (DE) mechanism is responsible for the ferromagnetic and metallic properties [1]. With the applied magnetic field, the resistivity largely decreases and hence leading the colossal magnetoresistance (CMR) phenomena, meanwhile the metal-insulator transition (T_p) will shifts to higher temperatures. However, numerous experimental results showed that Jahn–Teller (JT) distortions [2] might also influence the structural and magnetic properties of these materials. It is well know that, grain size has the direct consequence on the electrical and magnetic properties of the system. The better the grain connectivity, the less will be the electron scattering between the grains, and hence smoother movement of electrons. From the previous study [3], bulk and polycrystalline thin film showed different magnetic and electrical properties due to the strain and lattice mismatch among the film and substrates. In view of this, we are reporting the structural, microstructure and electrical properties of $La_{0.67}Ca_{0.33}MnO_3$ system in bulk and thin film form.

EXPERIMENTAL DETAILS

Polycrystalline of $La_{0.67}Ca_{0..33}MnO_3$ (LCMO) pellet was prepared by conventional solid-state reaction method. High purity (>99.5%) precursors La_2O_3, $CaCO_3$ and $MnCO_3$ powder were mixed in stoichoimetric proportions. This powder was ground in mortar and pre-sinter at 900 ^{o}C for 12 hours. The calcined powder was ground, sieve and presses into pellets of 13 mm in diameter, and then sintered in air at 1300 ^{o}C for 24 hours. These polycrystalline pellets were used as targets to deposit film using Nd-YAG pulsed laser ablation system. The fused silica glass substrates was mounted on the heater (400 ^{o}C) and placed parallel to the target at a distance of 4 cm. High purity of oxygen was introduced into the chamber and held constant during the deposition process. After deposited for 2 hour, the samples were slowly cooled to room temperature in oxygen environment. This sample was annealed in the furnace at 700 ^{o}C for 4 hours. The structures of samples were characterized by X-ray diffraction (XRD, Philips PW 3040/60 Xpert Pro) in the 2θ range 20°-80° using Cu Kα radiation at room temperature. The XRD data were analyzed using Rietveld refinement technique to confirm the phase formation as well as to obtain the structural parameters. The morphology of bulk and thin film were investigated with the scanning electron microscope (LEO1455 VP-SEM) and Supra 55 Field-emission scanning electron microscope (FE-SEM), respectively. The electrical resistance of all samples was measured with liquid nitrogen cryostat embedded in Lake Shore 7604 Hall measurement system with and without magnetic field in the temperature range from 80 K to 300 K.

RESULTS AND DISCUSSION

Figure 1(a) showed the XRD patterns for the bulk and thin film measured at room temperature. It is found that bulk sample shows highly crystalline character as compare with the thin film sample. The decrease in the FWHM value or another word the increases in the sharpness of XRD peaks for bulk sample clearly indicates the increases in the crystallinity [4]. The crystallographic data obtained from the XRD pattern were refined by the Rietveld's in pseudo-Voigt mode profile fitting method and the full profile fitting to the room-temperature XRD spectrum for bulk sample is shown in Figure 1(b). Both samples are in single phase with an orthorhombic perovskite crystalline structure without any detectable other phase. The extra peaks (mark with "*") for thin film spectrum is refer as the peak from the sample holder during measurement. Further, using the refined patterns the unit cell parameters, average bond angle and average bond length for all samples were computed and given in Table 1. The lattice parameter b, c and unit cell volume, V, for bulk sample are bigger as compare with thin film sample. However, the bond angle Mn-O-Mn and bond length $d_{Mn\text{-}O}$ for both samples are slightly different or unchanged.

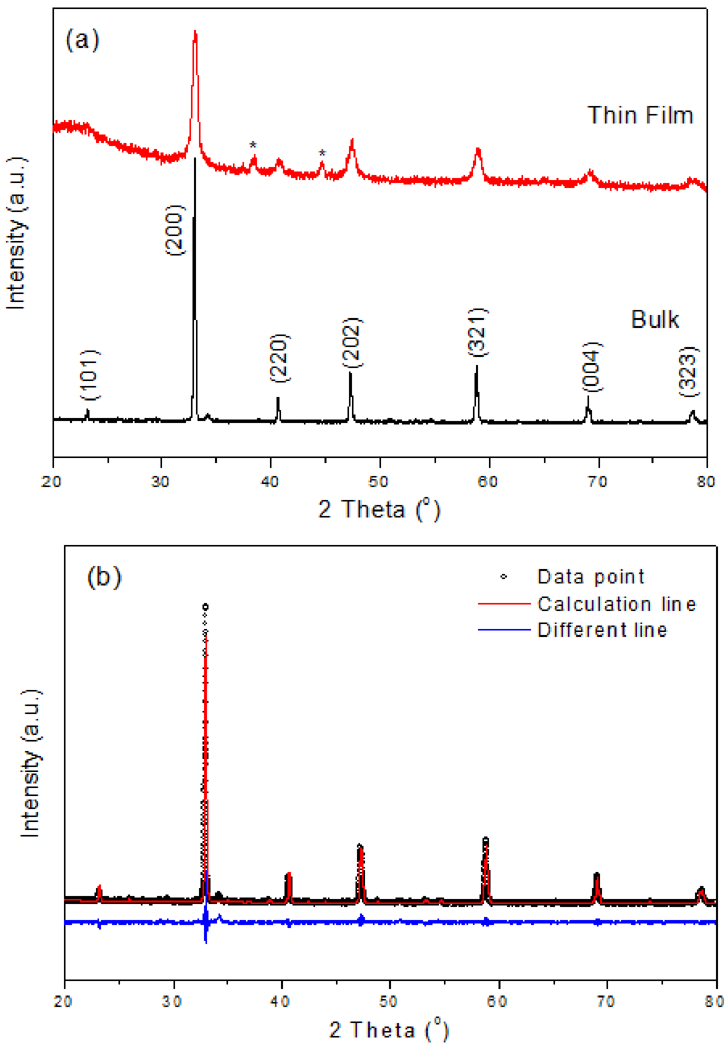

Figure 1: (a) X-Ray diffraction patterns of the $La_{0.67}Ca_{0.33}MnO_3$ in bulk and thin film on fused silica glass substrates and (*) marked as the peak from measurement sample holder and (b) Full profile fitting of XRD spectrum for bulk sample

The microstructures of bulk and thin film have been study with SEM and FE-SEM, respectively, as show in Figure 2. The surface microstructures of thin film (100,000x) are very different than the bulk (5,000x). Thin film has relatively much smaller average grain size as compare to bulk. This observation is consistent with the XRD result where the peaks for thin film are broader as compare with bulk sample. The difference of the microstructure is very important for manganites system where reported work [5-6] stated that grain boundaries and interfaces play a key role for the magneto-transport and electrical properties. Thin films have an average grain size of 40-60 nm with high porosity. However, for bulk sample, the grains were partially connected to each other with average grain size of 1-2 μm.

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Table 1: Lattice parameters of LCMO samples based on Rietveld refinement in the orthorhombic space group Pbnm of XRD patterns measured at room temperature

Sample	Bulk	Thin Film
a(Å)	5.445(1)	5.463(3)
b(Å)	7.688(2)	7.658(3)
c(Å)	5.459(1)	5.422(2)
V (Å)	228.4917	226.850
$d_{Mn-O(1)}$ (Å)	1.955	1.953
$d_{Mn-O(2)}$(Å)	1.949	1.942
Mn-(O1)-Mn (^{o})	160.19 (1)	160.2 (2)
Mn-(O2)-Mn (^{o})	160.85 (1)	160.8 (3)
R_{exp} (%)	10.28769	3.14222
R_p(%)	9.29702	2.89309
R_{wp}(%)	12.17784	3.87509
GOF	1.40121	1.52086

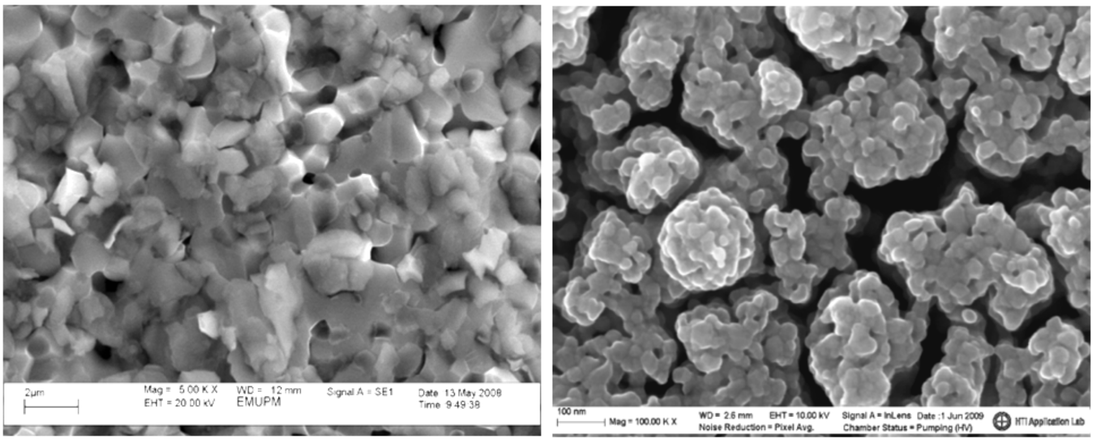

Figure 2: SEM and FE-SEM microstructure of bulk of 5,000x (upper) and thin film of 100,000x (lower) sample

The resistance versus temperature curve in 0T and 1T magnetic field for bulk and thin film sample are shown in Figure 3. The bulk sample display a typical insulator-to-metal transition (T_p) behaviour where resistances increases from room temperature and reach a maximum at T_p and then gradually decreases at lower temperature. T_p is shift to higher value and the resistance decreased when 1T magnetic field is applied [7]. When magnetic field is applied, the localized electron spin (t_{2g}) align parallel with the field, therefore the electron can be easily transfer from Mn^{3+} to Mn^{4+}. Hence, the resistance is reduced with the applied magnetic field [8]. On the other hand, thin film deposited on fused silica substrate shows almost insulating over the entire range of temperature suggested that T_p might be lower than the measurement range. Nevertheless, thin film

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sample show similar behaviour as bulk where resistance drops when 1T magnetic field was applied. The large shifting of T_p between bulk and thin film sample might be due to the high porosity of thin film microstructure that cause the breaking or destroy of Mn-O-Mn bridge. This weakens the electrical transport mechanism (DE) and causes much higher resistance. Beside that, this high resistance value of thin film also might be due to the presence of a disorder interfacial layer between grains boundary in smaller grain size and hence increases the spin scattering effect.

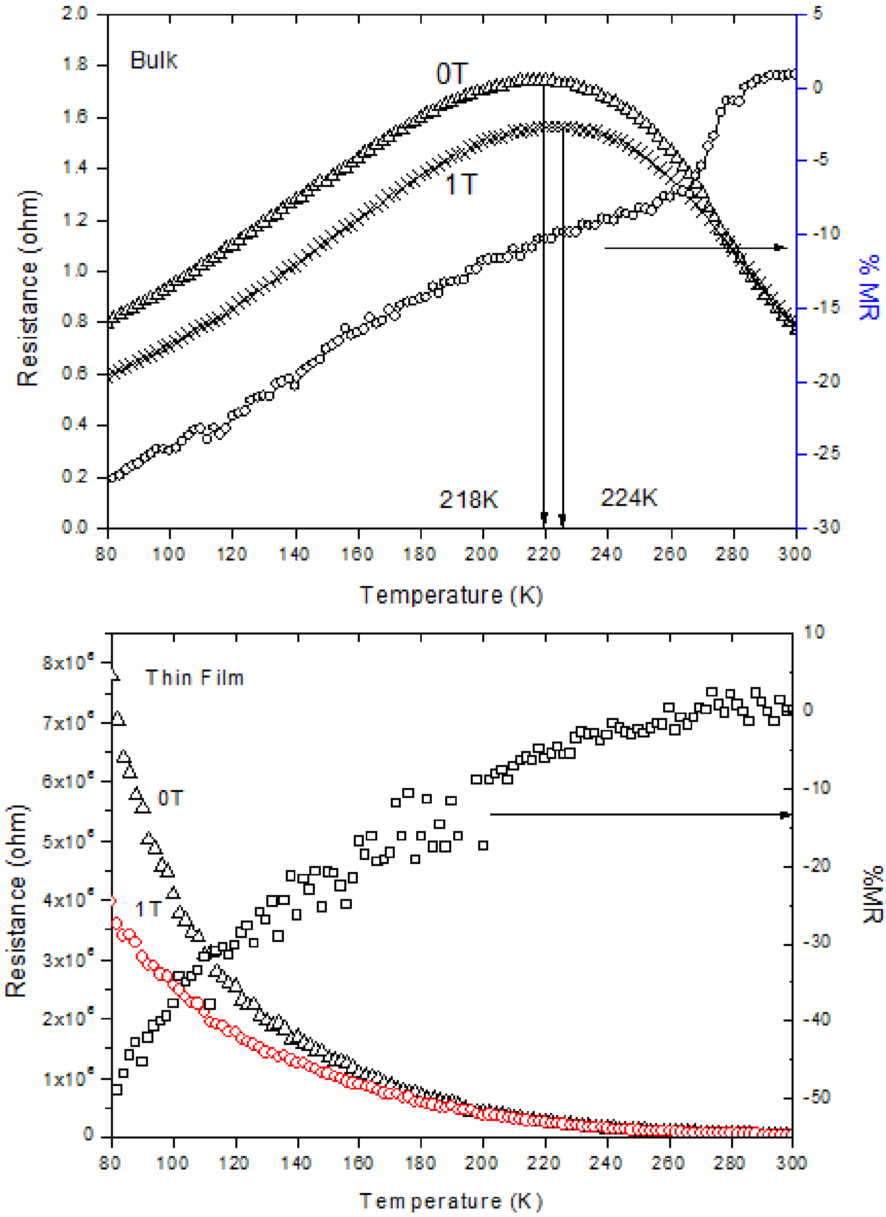

Figure 3: Resistance versus temperature curve for $La_{0.67}Ca_{0.33}MnO_3$ for bulk (upper) and thin film (lower)

The percentage of magnetoresistance calculated as %MR=[(R_H-R_o)/R_o]x100 where R_H and R_o are the resistance at zero and at 1 Tesla magnetic field, respectively. Figure 3 shows the variation of %MR with temperature for bulk and thin film. The -MR value of bulk and thin film increases linearly as the temperature cooled down from room temperature to 80 K. Both sample show typical polycrystalline behaviour where no significant higher changes of MR at T_p or T_c. The highest MR value for bulk is -27% however thin film show almost double of MR value which is -50% as compare to bulk sample at 80 K.

CONCLUSION

As a conclusion, bulk sample of $La_{0.67}Ca_{0.33}MnO_3$ was successful prepared by solid-state reaction and further grown on fused silica substrates using pulsed laser deposition method. Rietveld's refinement showed that thin film remains in pure single phase of orthorhombic structure with Pbnm space group. The microstructure of bulk is partially connected with average grain size of (~1-2 μm) however, thin film showed much smaller grain size (~40-60 nm). Bulk sample showed typical insulator-to-metal transition (T_p) at 218 K when H=0T and shift to 224 K in H=1T. Nevertheless, the T_p for thin film is not seen throughout the measurement range and its resistance is much higher that almost near to insulator.

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