Superlattices and Microstructures 92 (2016) 181–189

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

Comparative study of the Raman vibrational modes in pure and Fe-doped $La_{2/3}Ca_{1/3}MnO_3$ thin films

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ARTICLE INFO

Article history:
Received 8 March 2015
Received in revised form 3 February 2016
Accepted 15 February 2016
Available online 18 February 2016

Keywords:
Magnetic oxides
Raman spectroscopy
Phonons
Thin film

ABSTRACT

A comparative study of Raman spectra at room temperature of $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) and $La_{2/3}Ca_{1/3}Mn_{0.97}Fe_{0.03}O_3$ (LCMFO) thin films, grown on monocrystalline substrates $LaAlO_3$, is presented. The films were grown with thickness between 30 and 130 nm under identical deposition conditions by DC magnetron sputtering system at high O_2 pressure. In order to observe changes in the vibration modes of the lattice due to the substitution of Mn by Fe ions, we compared the different values of wave numbers obtained from the fittings of each Raman spectrum. The results show that the characteristic—and most intense-peak at ~486 cm^{-1} corresponds to the substrate. In the LCMO thick films, Raman modes are very weak and mix up with the substrate one, whereas in LCMFO, these modes were found in three intervals around 220–250 cm^{-1} (υ_1), 450–520 cm^{-1} (υ_2) and 610–720 cm^{-1} (υ_3). A mode at ~717 cm^{-1} is associated to structural disorder due to Fe doping effect. In both LCMO and LCMFO films, the conduction mechanism are related with electron localization and the electronic transition is mediated by phonons. According to the T* values from resistivity data fit (Variable Range Model -VRH), it is observed once more that the Fe doping relaxes the strain effects.

1. Introduction

$La_{1-x}A_xMnO_3$ (A = Sr, Ca, Ba, etc) perovskites offer a diversity of physical properties, depending on the doping concentration and A-site ionic radius. Among this family of manganite, $La_{1-x}Ca_xMnO_3$ (LCMO) has been extensively studied because they exhibit a metal–insulator transition (T_{MI}) accompanied by the so-called colossal magnetoresistance (CMR) effects [1]. These magnetic oxides have a rich and complex physics related to the significance of electron-lattice and electron–electron interactions in them. Their structural, magnetic and transport properties are intrinsically related. Many of these properties are explained by the double exchange (DE) mechanism, via the interaction between $Mn^{3+} - Mn^{4+}$ ion pairs [2,3]. Any deviation of the $Mn^{3+} - O - Mn^{4+}$ bond angle or bond length affects the DE interaction. Although, the DE model has given an appropriate qualitative description of the ferromagnetic (FM) metallic behavior, some experiments have shown that this model alone is insufficient to explain other physical properties in these compounds, including CMR. These issues can be experimentally proven via doping on the Mn site (which is essential to the double exchange) with other trivalent elements or transition metals. Numerous investigations have shown that a partial replacement of the Mn^{3+} ions in LCMO with other transition

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http://dx.doi.org/10.1016/j.spmi.2016.02.020
0749-6036/

metals, e.g. Cr, Fe, Cu, Al, reduce both the FM exchange and metallic conduction [4–12]. Particularly, most of these studies have been based on Fe-doped manganite polycrystalline samples.

The replacement of Mn^{3+} by Fe^{3+} poses a subject of great interest due to their compatible ionic sizes and their different magnetic moments. Several papers have been published using various methods such as neutron scattering diffraction, Raman spectroscopy, Mössbauer spectroscopy, magnetometry and resistivity, among others, but the local structural distortion of $Mn(Fe)O_6$ octahedra and the Jahn-Teller effect (JT) have not yet investigated deeply [9–12]. Thus, Raman scattering can be a useful tool to get information regarding phonon modes, electron states, lattice distortion, spin excitations, etc.; associated to the Fe effects. Most lattice vibration modes in various manganite compounds have been identified from Raman measurements. The phonons involved in the JT mechanism correspond to the tilting and stretching modes, so it is important to identify these particular oscillations [13,16]. Moreover, up to our knowledge only a few studies in polycrystalline thin films have been performed to probe the structural and magnetotransport effects induced after substitution of Fe in the Mn sites [17,18].

Previously, we reported the change of the structural and magnetic properties due to the substitution of Mn with Fe in LCMO films grown on $SrTiO_3$ and $LaAlO_3$ substrates [17,18]. In these films, saturation magnetization, Curie temperature, metal-insulator transition, and magnetoresistance vary non-monotonically with increasing Fe concentration. This behavior can be understood in terms of competing influences between the relaxation of epitaxial strain due to increased disorder and the Fe doping, which initially improves the FM order. However, a detailed, a comparative study in doped and undoped LCMO thin films by means of Raman spectroscopy has not emerged. Therefore, in the present work, we have investigated the Raman scattering in LCMO and LCMFO thin films of different thickness grown onto (100)-$LaAlO_3$. Our aim is to study the change of Raman active mode induced by Fe-doping and strain coming from lattice-substrate mismatch. In addition, we have analyzed the conduction mechanism in both LCMO and LCMFO films by electron-electron and electron-magnon scattering model and Mott's variable-range-hopping (VRH) conduction law.

2. Samples and experimental procedure

The films were grown on (100)-$LaAlO_3$ (LAO) single-crystalline substrate under the same conditions by DC-magnetron sputtering system, using the stoichiometric ceramic targets of LCMO and LCMFO. During the deposition, the substrate temperature and high purity oxygen environment were kept at 850 °C and 500 mTorr, respectively. Five LCMO samples with varying thickness (23, 55, 60, 80 and 130 nm) and two LCMFO ones with thicknesses 27 and 80 nm were prepared. The thickness of each film was determined from analysis of grazing incidence X-ray diffraction. The structural properties of as-grown LCMO and LCMFO layers were characterized using X-ray diffraction (XRD). XRD patterns of the films were registered using a two-circle diffractometer (Panalytical X'Pert Pro) with CuKα radiation ($\lambda = 0.15418$ nm) for standard $\theta-2\theta$ scans on symmetric reflections. Magnetic measurements were performed via vibrating-sample magnetometer technique (VSM) with the physical properties measurement system (PPMS, Quantum Design). All data were collected by using a 40-Hz vibration frequency for the detection coil with 2-mm. Magnetization vs. temperature (M vs. T) after zero field cooling (ZFC) was determined under an applied external magnetic field H of 300 Oe. Besides, the electrical resistivity was recorded using DC four-probe method in the transport option of the PPMS system over the temperature range 5 K–300 K. Raman spectra were measured at room temperature in a Horiba Jobin Yvon (Labram HR) Nikon (BX41) microscope, with a CCD detector (Wright 1024 × 256 pixels) and appropriate notch filter. The 632.8 nm He–Ne laser line was used for excitation. The samples were placed on a glass slide and focused with the microscope for optical alignment. The laser beam was focused on the sample with a spot size of approximately 1 μm, using a 100X microscope objective without filter. For all measurements the parameters (aperture (1000 μm) screen (600 μm), power, acquisition time (40 s), etc.) were kept as constants.

3. Results and discussion

In Fig. 1(a), we show the XRD patterns recorded on LCMFO films (27 and 80 nm) grown on LAO. All films are single phase without any detectable impurity or secondary phase. LCMO and LCMFO peaks on different thicknesses were fitted using Gaussian and Lorentzian functions, as seen in the insets (left and right) in Fig. 1(a). The lattice parameters were calculated with the help of the peaks positions found from the fit (Table 1). It is assumed that the structure of the films is identical to the structure reported for the bulk materials, with an orthorhombic unit cell of the space group *Pbnm* [17,18].

Magnetization, $M(T)$, and resistivity, $\rho(T)$, curves as functions of temperature (5–300 K) in both LCMO and LCMFO samples are shown in Fig. 1(b). All films show transitions to the ferromagnetic state (T_C), and metal-insulator (T_{MI}) ones within this temperature range (Table 1). T_C is determined from the peak in the dM/dT versus T plots, whereas the T_{MI} is estimated from $d\rho/dT$ vs T plots in the point where $d\rho/dT \rightarrow 0$ (see inset Fig. 1(b)). We have found that the doping affects the magnetic and transport properties, with a reduction of the transition temperatures (T_C and T_{MI}). Values of T_C and saturation magnetization in the LCMO sample are larger for the Fe-doped sample.

For the LCMO parent compound, DE is the dominant magnetic interaction between Mn ions and, as previously mentioned, it is responsible of the FM character of LCMO. In LCMFO, Fe^{3+} dopants into Mn sublattice, substitute Mn^{3+} ions and reduce DE, leading to a reduction of the magnetization and to an increase of the resistance (Fig. 1(b)), as well as causing a decrease of T_C and T_{MI}. Recent studies performed in LCMO and LCMFO films by XCMD (element-selective X-ray magnetic circular dichroism), have evidenced the existence of antiparallel alignment (antiferromagnetic coupling) of the net magnetic moments of Mn and