Journal of Alloys and Compounds 667 (2016) 225–228

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Magnetic and Raman spectroscopic study of laser ablated 100 (nm) thin film of $La_{0.85}Te_{0.15}MnO_3$ deposited on $LaAlO_3$

Irshad Bhat [a], Shahid Husain [b, *], Tariq Ahmad War [c]

[a] Department of Applied Physics, College of Engineering, Zakura Campus, University of Kashmir, Hazratbal, Srinagar, 190006 J&K, India
[b] Department of Physics, Aligarh Muslim University, Aligarh, 202002 U.P, India
[c] Department of Physics, H.K.M Degree College, Bandipora, 193502 J&K, India

ARTICLE INFO

Article history:
Received 21 September 2015
Received in revised form
17 January 2016
Accepted 21 January 2016
Available online 22 January 2016

Keywords:
Thin film
PLD
Paramagnetic to ferromagnetic transition
Raman Spectroscopy

ABSTRACT

We report the magnetic and Raman spectroscopic study of 100 nm thin film of electron doped manganite system $La_{0.85}Te_{0.15}MnO_3$ grown on (001) $LaAlO_3$ single crystal substrate by pulsed laser deposition. The magnetization results show Paramagnetic to Ferromagnetic (PM–FM) phase transition. The film is assumed to be of orthorhombic in nature. A correlation of Raman modes with magnetic ordering has been observed. A softening of the 610 cm^{-1} (B_{2g}) stretching mode is observed near and above the magnetic ordering temperature. The behaviour has been ascribed to magnetic interactions due to spin–phonon coupling terms.

1. Introduction

The colossal magneto resistance (CMR) effect and associated exotic physical properties exhibited in various electron doped pervoskite manganites have been the subject of extensive research. In this class of manganites, the electrons are the majority charge carriers. Such materials exhibit a significant value of CMR that is associated with the mixed-valence state of Mn^{3+}-Mn^{2+} [1]. These electron doped manganites can be utilized to fabricate functional devices based on the *p–n* junctions of the pervoskite manganese oxides [2]. These p–n junctions are fabricated using electron (*n*-type) and hole-doped (*p*-type) manganites. This property of colossal magneto-resistance (CMR) has made these manganites promising candidate to be used as magnetic field sensors, elements in magnetic random access memories and spintronic devices [1–4].

The crystal structure of the undoped parent compound $LaMnO_3$ depends on the synthesis conditions [5,6]. At least two well-determined phases exist at room temperature: the orthorhombically distorted ~ space group (*Pnma*) and the rhombohedrally distorted ~ space group $R\bar{3}c$, both are paramagnetic insulators. The rhombohedral phase is of special interest as it is typical for some $R_{1-x}A_xMnO_3$ (R = rare earth, A = divalent or tetravalent cation) materials exhibiting CMR. It is plausible to expect the phonon spectra of this phase to be sensitive to some specific features associated with the CMR. Such as the variations of Jahn-Teller distortions with the Mn^{4+}/Mn^{3+} (in case of hole doping) and Mn^{3+}/Mn^{2+} (in case of electron doping) ratio as well as with the temperature near T_c. The phonon spectra will also be sensitive to the degree of rhombohedral distortions.

There is always a possibility of a lattice polaron formation resulting from the strong Jahn-teller character of the Mn^{3+}/Mn^{2+} ions. The polaron formation is responsible for the larger change in electron kinetic energy at T ~ T_c, as well as other anomalous physical properties of these materials [7–10]. Such polarons are expected to be present when $\tau_h . > \omega_\alpha^{-1}$, where τ_h is the electron transfer time and ω_α is the frequency of an optical-mode lattice vibration associated with a dynamic Jahn-Teller distortion [11]. Therefore, lattice vibrations possibly play an important role in the conduction mechanism of this class of materials.

At present there is a scanty data on the Raman spectra of rhombohedral $LaMnO_3$ and related compounds and the assignment of the observed spectral structures is still ambiguous. The main difficulties arise because of the very low Raman intensities, which has given rise to speculations that some of the broad bands in the experimental spectra may correspond to second order Raman processes [12]. The importance of the phonons is often invoked and

* Corresponding author.
E-mail address: s.husain@lycos.com (S. Husain).

http://dx.doi.org/10.1016/j.jallcom.2016.01.149
0925-8388/

proved by the drastic observed isotope effects [13], but the Raman spectra of doped compounds are still not deeply understood. Raman phonons have been studied in orthorhombic $LaMnO_3$ single crystals [14,15], and, in Sr doped [15–17] and Ba doped compounds [18], as well as in Ca doped pellets [16,19] and thin films [20]. Several of these studies report the effect of the oxygen content and the rhombohedral structure on the Raman features. The low temperature Raman spectra of a pure compound show a softening of the stretching mode below the magnetic transition [21].

In this study, we have investigated the magnetic and Raman spectroscopic properties of $La_{0.85}Te_{0.15}MnO_3$ thin film grown on $LaAlO_3$ (001) single crystal substrate by pulsed laser deposition. In the present work the correlation between the phonon modes and the magnetic ordering is clearly evidenced.

2. Experimental

The standard solid state reaction method was employed to prepare the (target) bulk polycrystalline sample of $La_{0.85}Te_{0.15}MnO_3$ [22,23].

The pulsed laser deposition (PLD) (Lamda physic, Germany model complex, 201, $\lambda = 248$ nm) of the $La_{0.85}Te_{0.15}MnO_3$ (LTMO) film was carried out using an excimer laser charged with KrF (wavelength of 248 nm and repetition rate of 10 Hz). The thickness of the film is measured with the help of an XP1 telystep profilometer. Magnetization measurement was carried out using 7-T MPMS SQUID-VSM. Temperature dependent Raman spectra were recorded in backscattering geometry using a 10 mW Ar (488 nm) laser source coupled with a Labram-HR800 micro-Raman spectrometer equipped with a 50 × objective, appropriate notch filter and a Peltier cooled charge-coupled device detector. LAO was selected as a substrate since its low intensity and simply structured Raman signal allows to extract the phonon spectrum of $LaMnO_3$ even for thin films.

3. Results and discussions

3.1. Magnetisation

The characteristic magnetic behaviour of the $La_{0.85}Te_{0.15}MnO_3$ thin film has been shown in Fig. 1. The magnetization as a function of temperature is measured in zero-field cooled (ZFC) and field cooled (FC) conditions with an applied field of 0.1 T. A ferromagnetic-paramagnetic phase transition is observed at T_c~205 K which presents a small hysteresis between the FC and ZFC measurements in an applied field of 0.1 T. Similar behaviour has been reported earlier in LTMO bulk and in thin film forms [24,25]. We have also plotted the hysteresis loop at 10 K as shown in the inset of Fig. 1 which confirms the presence of a weak ferromagnetic component in the low temperature phase.

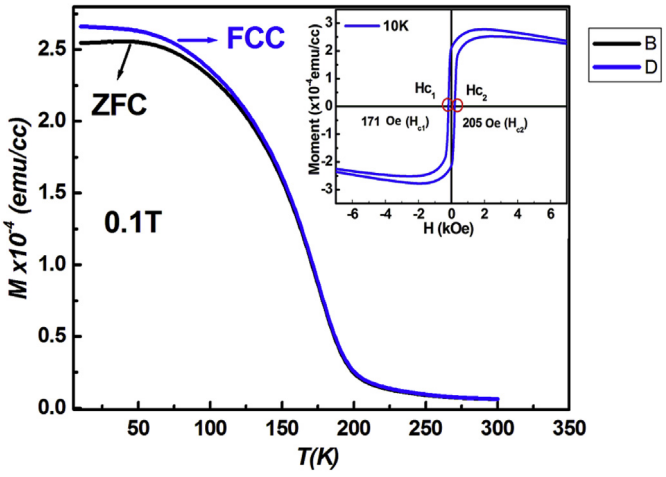

Fig. 1. Temperature dependence of magnetization (FC and ZFC) of $La_{0.85}Te_{0.15}MnO_3$ thin film measured in an external field of H = 0.1 T. Inset shows the hysteresis loop at 10 K.

3.2. Raman spectroscopy

Raman scattering is a versatile technique for detecting the incorporation of dopants and the resulted defects and lattice disorders in the host lattice. Temperature dependence of Raman spectra for LTMO/LAO thin film is shown in Fig. 2a. One observes that rhombohedral manganites and slightly orthorhombic distorted manganites have similar Raman spectra. Such spectra is typical of all manganites, almost independent of the averaged crystallographic long range symmetry (orthorhombic [26–28] or rhombohedral [14,29,30]), the degree of doping (undoped [26,28–30] or doped [26,27,29]), or of the ion at the A site. The unit cell of the host lattice $LaMnO_3$ with an orthorhombic Pnma space group give rise to 24 Raman active modes [31,32]:

$$\Gamma^{\mathrm{Raman-ortho}} = 7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$$

while as the rhombohedral structure can be described with respect to the ideal cubic structure by considering a rotation of MnO_6 octahedra about the [*111*] pseudo cubic diagonal, leading to the $\overline{aaa}$ tilt system. The rhombohedral distortion gives rise to five Raman-active modes [12,32].

$$\Gamma^{\mathrm{Raman-rhomb}} = A_{1g} + 4E_g$$

The bulk samples of LTMO show rhombohedral crystal symmetry using the $R\,\overline{3}\,c$ space group that assumes six equal distances of the Mn–O bonds of MnO_6 octahedra [22] but, in strained thin film the in-plane lattice parameters are compressed to match the substrate, yielding a pseudo cubic or tetragonal unit cell [23]. By looking at the Raman spectra of LTMO film it can be assumed that the film is of orthorhombic in nature, with pnma space group [14]. As often, the $LaMnO_3$ thin films show orthorhombic structure at lower temperatures. Since the film is (in-situ) annealed at 750 °C in excess of oxygen, we expect a less oxygen non-stoichiometry as reported earlier [33].

Anomalous changes in all the phonon frequencies and line widths are observed in the LTMO thin film at lower temperatures. The factors affecting the phonon frequencies and the line-width are anharmonicity, electron–phonon interaction, and electron spin-lattice coupling.

The most pronounced peaks displayed for the entire temperature range are at 221, 276, 334, 433, 490, 607 and 670 cm^{-1} (Fig. 2a). The modes at 221, 276 and 334 cm^{-1} are associated with A_{1g} symmetry [34] (rotation of the oxygen octahedral around the hexagonal $[001]_h$ direction) and modes at 433, 490 and 607 cm^{-1} correspond to B_{2g} symmetry [35]. The 465 cm^{-1} and 670 cm^{-1} band may be due to Jahn-Teller excitations occurring at lower temperatures ($T < T_c$), and disappears at higher temperatures [36]. At lower temperatures, the spectra show pronounced modifications, especially in the temperature range 220–180 K, At lower temperatures additional peaks emerge at 433, 476, 607 and 670 cm^{-1}, which cannot be distinguished clearly at higher temperature (above 220 K). However, due to the high intense peak of LAO substrate observed at around 488 cm^{-1}, it was not possible to analyse the phonon frequencies and the corresponding line width for 490 cm^{-1}