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Strain effects on $La_{0.5}Ca_{0.5}MnO_3$ thin films

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Abstract

Thin films of $La_{0.5}Ca_{0.5}MnO_3$ (LCMO) deposited on $SrTiO_3$ (STO) with orientations (1 0 0) and (1 1 1) and on (0 0 1) $SrLaGaO_4$ (SLGO) substrates have been studied by Raman spectroscopy. Three different thicknesses for each substrate were studied at room temperature. The energy and the width of the A_g tilting mode have shown thickness and substrate dependence, implying an effect of the lattice mismatch on the tilting angle. Low temperature measurements (80 K) have been carried out at different scattering polarizations for the thicker films (290 nm). The spectra of LCMO/STO(1 0 0) films are strongly affected by the paramagnetic to ferromagnetic (FM) or charge ordered (CO) antiferromagnetic (AF) transitions. The Jahn–Teller (JT) modes gain intensity close to the transition temperature, where a considerable softening of the tilting mode has been also observed. New bands appear below Neel temperature (T_N) for LCMO/STO(1 0 0), while this transition cannot be observed on the other films. A possible explanation is the phase coexistence which is discovered at the FM to CO/AF region (210–150 K) for LCM/STO(1 0 0) films. However, a strain effect seems to destroy the FM phase on contrary to the bulk. The JT modes do not appear (partially hidden by the spectrum of the substrate) in the spectra of LCMO/STO(1 1 1) films, which show a metallic-like spectrum, consistent with the resistivity measurements. The JT distortion appears decreased in LCMO/SLGO(0 0 1) films and the transition temperatures are affected from the strains.

Keywords: Colossal magnetoresistance; Manganites; Raman scattering; Strains; Thin films

1. Introduction

Considerable theoretical and experimental research has been carried out on rare-earth manganites with the general formula $R_{1-x}A_xMnO_3$ (R: a trivalent rare-earth ion; A: a divalent alkaline-earth ion) [1] due to their colossal magnetoresistance (CMR) effect [2]. Apart from their possible applications (magnetic switches and memories) manganites have been deeply investigated due to the complex physics, which governs their properties. At first, the double exchange (DE) model has been proposed to understand the physics of manganites [3]. A more quantitative agreement between theory and experiment has been obtained by assuming a Jahn–Teller (JT) induced charge-localization competing with DE [4]. It has been shown for bulk samples, that a slight variation of the Mn–O bond length or the Mn–O–Mn angle modifies the physical properties of the material [5].

$La_{1-x}Ca_xMnO_3$ has a very rich phase diagram of ground states with competing order parameters [6]. The parent compound is $LaMnO_3$, which belongs to the family of rotationally distorted perovskites [7] and is an antiferromagnetic (AFM) insulator. The bulk compound at the phase boundary with $x = 0.5$ is a paramagnetic (PM) insulator and undergoes first a ferromagnetic (FM) transition and a simultaneous AFM and charge ordering (CO) transition at low temperature [8]. In thin films, which are required for the technological applications, there are structural changes, which lead to changes in physical properties, due to the strains from the substrate [9].

An extensive amount of Raman data exists for the LCMO series and an assignment for most of the phonons has been proposed [10,11]. In addition, there are studies for $La_{0.5}Ca_{0.5}MnO_3$ bulk compound [8,10,12] but to the best of our knowledge little work has been done on films [13,14].

In the present work, we present a systematic study of the Raman active phonons of LCMO thin films. In order to study the growth related effect of strain and orientation, LCMO films with three different thicknesses were deposited on (1 0 0), (1 1 1) oriented planar $SrTiO_3$ (STO) and (0 0 1) $SrLaGaO_4$(SLGO) single crystal substrates, respectively. The expected strain in each film is different related to the lattice mismatch and the film thickness.

2. Experimental

The LCMO films were deposited by pulsed laser deposition (PLD) technique with three thicknesses (290, 220, 145 nm). The

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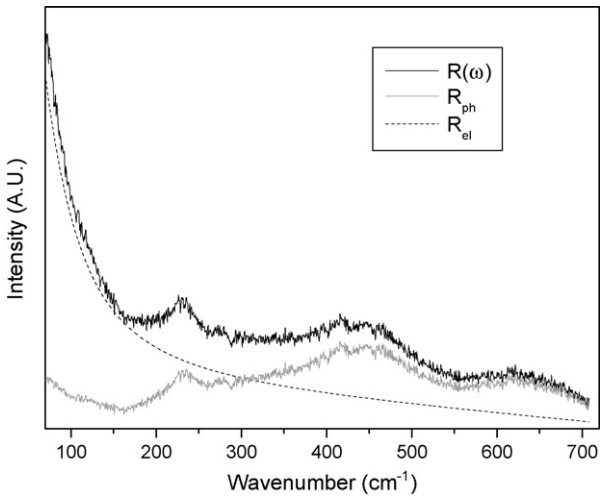

Fig. 1. Typical Raman spectra of LCMO/STO(1 0 0) films at RT as collected (black spectrum), thermally corrected spectrum (R_{ph}, gray scale spectrum) and the diffusive contribution (R_{el}, dashed line).

structural properties of the as grown films were studied by using X-ray diffraction (XRD) technique. It can be concluded that these films are single phase and have orthorhombic crystal structure. For films on (1 0 0) STO and (0 0 1) SLGO, the (0 2 0) planes of the LCMO films are identified to be parallel to the substrate surface (*b*-axis oriented). However, films on (1 1 1) STO are oriented along the (0 2 2) direction. A more analytical discussion about the preparation and characterization (XRD, magnetization, resistivity) methods is presented elsewhere (Figs. 1–3, respectively) [15]. Epitaxial strains of the films according to the lattice parameters of bulk LCMO are calculated in two different in-plane directions by the formula $(a_{bulk} - a_s) \times 100/a_s$.

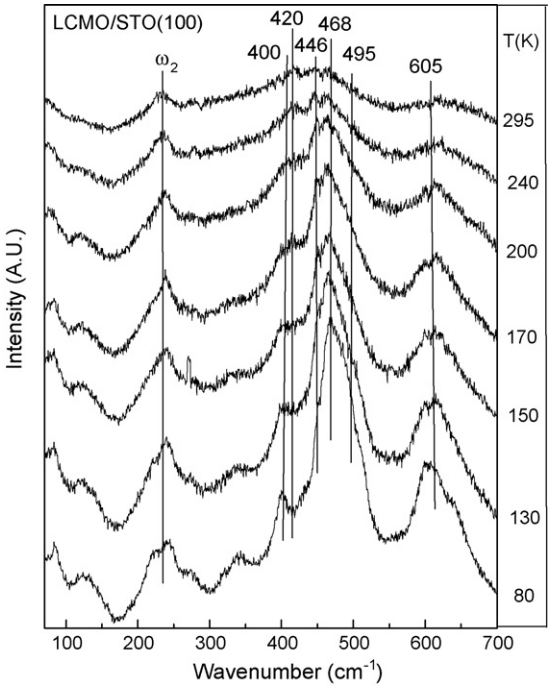

Fig. 2. Low temperature Raman spectra of LCMO/STO(1 0 0) at selected temperatures corrected by the thermal factor.

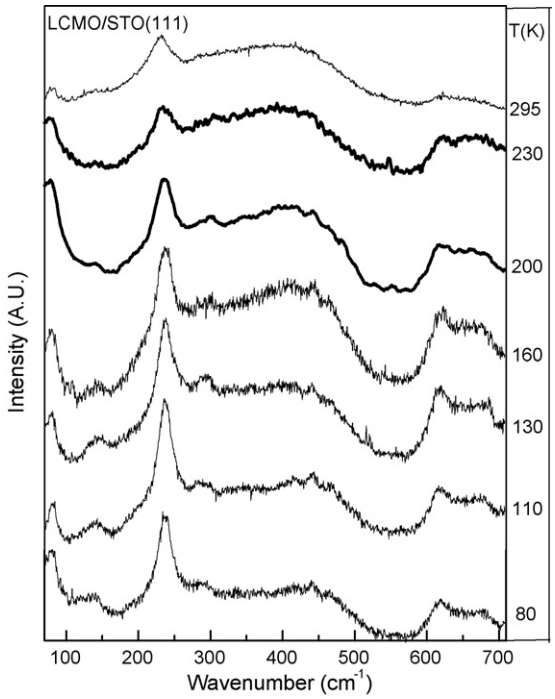

Fig. 3. Low temperature Raman spectra LCMO/STO(1 1 1) at selected temperatures corrected by the thermal factor.

It is found out that epitaxial strains are 1.86% tensile and 1.92% tensile (for two in-plane directions) for the films on (1 0 0) STO and 2.12% tensile and 1.92% tensile for the LCMO films coated on (1 1 1) STO [15].

The Raman spectra were obtained using a T64000 Jobin-Yvon triple spectrometer, equipped with liquid nitrogen cooled charge coupled device (CCD) and a microscope. The 514.5 nm line of an Ar^+ laser was used for excitation and an Oxford cryostat for the low temperature measurements [16].

3. Results and discussion

Fig. 1 presents a typical spectrum of LCMO/STO(1 0 0) film at RT. There are three main contributions to the Raman intensity of the LCMO films; first order (R_{ph}), second order, and electronic scattering (R_{el}). R_{ph} follows the selection rules while the second order represents the density of states (DOS) and exhibits broad bands. R_{el} contributes to the Raman background and intensity. The Raman spectrum $R(\omega)$ can be fitted and analytically expressed by the following equation [17]:

$$R(\omega) = R_{ph} + R_{el}$$

where

$$R_{ph} = [1 + n(\omega)] \sum_{i=1}^{n} \frac{A_i \omega \Gamma_i}{(\omega^2 - \omega_i^2)^2 + \omega^2 \Gamma_i^2}$$

represents the phonon modes with associated phonon frequency ω_i, linewidth Γ_i and amplitude A_i and

$$R_{el} = [1 + n(\omega)] \left[\frac{A\omega/\tau}{\omega^2 + (1/\tau)^2} \right]$$