Superlattices and Microstructures 87 (2015) 42–46

Contents lists available at ScienceDirect

Superlattices and Microstructures

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

X-ray magnetic circular dichroism on $La_{2/3}Ca_{1/3}Mn_{0.97}Fe_{0.03}O_3$ thin films

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ARTICLE INFO

Article history:
Received 8 March 2015
Received in revised form 1 July 2015
Accepted 3 July 2015
Available online 3 July 2015

Keywords:
X-ray magnetic circular dichroism
Magnetic thin films
Magnetic interactions
Complex oxides

ABSTRACT

The element-selective technique of X-ray magnetic circular dichroism (XMCD) has been used to study the magnetic properties of $La_{2/3}Ca_{1/3}Mn_{0.97}Fe_{0.03}O_3$ (LCMFO) thin films. XMCD measurements below the ferromagnetic ordering temperature at the Mn and Fe $L_{2,3}$ absorption edges allow the determination of the contributions and relative orientations of the Mn and Fe magnetic moments. A reduction in the Mn $L_{2,3}$ XMCD signal of the LCMFO sample compared to that for the parent $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) system reveals important modifications in the electronic and magnetic properties with the presence of Fe. The Fe $L_{2,3}$ X-ray absorption (XAS) for the LCMFO film is characteristic of Fe^{3+}, and the comparison with multiplet calculations shows that the Fe dopants occupy octahedral sites in the crystal, which is consistent with Fe^{3+} substituting Mn^{3+} in LCMO. The magnetic moments of Mn and Fe are found to align antiparallel, which suggests the presence of Mn–O–Fe superexchange coupling. This result is consistent with macroscopic magnetometry measurements on the LCMFO system, which show a decrease in saturation magnetization of LCMO with Fe doping.

1. Introduction

Complex oxides, particularly those based on manganite oxides, have been the focus of intense studies in the last decades due to their rich phenomena, such as metal–insulator transitions and magneto-transport properties [1,2]. Perovskite type compounds, such as $La_{1-x}Ca_xMnO_3$ (LCMO) manganites, exhibit different magneto-electronic properties (paramagnetic (PM), ferromagnetic (FM) or antiferromagnetic (AFM) order), depending on the concentration, x. These magnetic phenomena have been studied taking into account the competition between orbital degrees of freedom, charge ordering and spin interaction, where the indirect coupling between Mn ions, play a fundamental role. Their FM order is caused by double exchange (DE) via Mn^{3+}–O^{2-}–Mn^{4+}, whereby FM interactions between localized spins are mediated by the hopping of itinerant spins.

Manganites have shown high sensitivity to small changes in their structural parameters, and several studies have been focused on the Mn ion's environment, where the transport and magnetic properties are determined by the electronic transfer [1,2]. An important issue addressed in these compounds has been the study of magnetic properties in transition metal

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http://dx.doi.org/10.1016/j.spmi.2015.07.009
0749-6036/

(TM)-doped LCMO, by substituting Mn sites with metallic atoms. Even though there have been reports related with Fe-doped $La_{2/3}Ca_{1/3}Mn_{1-y}Fe_yO_3$ (LCMFO) [3], open questions regarding the spin configuration for Fe and Mn and the correlation between magnetic interaction and structural changes remain.

In order to increase the understanding of the magnetic properties of these doped systems, we have performed X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements on the LCMFO films. The element selective techniques of XAS and XMCD provide unique information about the electronic and magnetic state of the Mn and Fe atoms of these LCMFO systems [4], which allow us to gain a deeper insight into the magnetic interaction between these magnetic atoms in doped manganites.

2. Material and methods

LCMO and LCMFO samples were grown by dc magnetron sputtering on (100)-$SrTiO_3$ (STO) and (100)-$LaAlO_3$ (LAO) single-crystal substrates by dc magnetron sputtering under identical deposition conditions. Targets used for deposition were prepared from bulk stoichiometric ferromagnetic, pure LCMO, and doped LCMFO (with 3 at.% Fe concentration enriched with ^{57}Fe at 96.05%). During the deposition process the substrate temperature was kept at 850 °C, under a high purity oxygen pressure of 500 m Torr, a substrate-to-target distance of 40 mm and 35 W deposition power. The film thickness was determined by atomic force microscopy (AFM) and scanning electron microscopy (SEM) images, using a Nanosurfs SPM and a JEOL JSM 6490LV microscope, respectively. The LCMO and LCMFO films employed in this study are 260 and 200 nm thick, respectively.

Structural characterization by X-ray diffraction (XRD) has revealed the high crystalline quality of these samples. They show that both LCMO and LCMFO films have a perovskite-like single phase (Fig. 1(a)), without any detectable impurity or secondary phase. XRD patterns (Fig. 1(b)) show three reflection lines, with the strongest peaks corresponding to those of the LAO substrate. The additional two peaks were indexed according to an orthorhombic structure in the *Pbnm* space group, with (020) and (040) Miller indexes, associated to the LCMO phase. The lattice parameters were extracted by Gaussian and Lorentzian fits of these peaks (see inset in Fig. 1(b)). Results for the LCMO films show that these peaks are centered at 23.0° and 47.06°, and correspond to lattice parameters $a = 5.4572(3)$ Å, $b = 5.4571(6)$ Å and $c = 7.7176(7)$ Å. These results are in agreement with data reported for similar manganites systems [3]. For the LCMFO films, the peaks are equivalent to those of the LCMO, located at 23.06° and 47.08°, corresponding to lattice parameters $a = 5.4550(3)$ Å, $b = 5.4551(2)$ Å and $c = 7.7145(8)$ Å. Therefore, no substantial changes in the lattice parameters are found for the doped LCMFO films compared to those of the LCMO parent compound.

The macroscopic magnetic properties of the samples were studied by magnetization measurements performed with the vibrating-sample magnetometer (VSM) option from a Quantum Design Physical Properties Measurement System (PPMS). Both magnetization as a function of the applied field, $M(H)$, and as a function of temperature, $M(T)$, were measured, with the magnetic field applied parallel to the film plane. The $M(T)$ curves were measured after zero-field cooling (ZFC) and field cooling (FC) the samples. All magnetization measurements showed a FM–PM transition typical of these compounds (Fig. 1(c)). A broadening around the magnetic ordering temperature T_C is observed, showing that the transition extends over a wide temperature region. T_C for LCMO and LCMFO samples was estimated by fits of the $M(T)$ curves using a Gaussian model [5], in the critical region around the transition. T_C is reduced in the Fe doped sample, as compared to the undoped LCMO, from 231 ± 1 K to 178 ± 1 K, respectively. The saturation magnetization M_S of the LCMO film decreases by about 17% with the Fe doping (Fig. 1(c)).

XAS and XMCD spectra at the Mn $L_{2,3}$ edges were measured at beamline 6.3.1 of the Advanced Light Source, and those at the Fe $L_{2,3}$ edges at ID32 beamline of the ESRF. A bending magnet and a VLS-PGM monochromator with fixed exit slit and refocusing mirror were used in the former case, and an APPLE-II undulator and a plane grating monochromator were used in the latter. The degree of polarization at the Mn and Fe $L_{2,3}$ edges was ∼100% and the total electron yield (TEY) detection

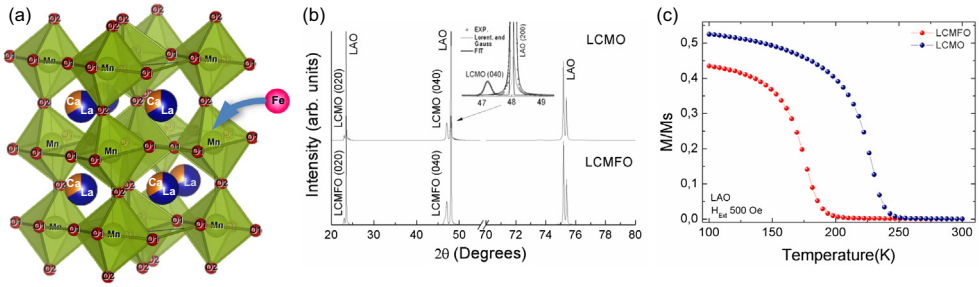

Fig. 1. (a) Illustration of the perovskite-like LCMO crystal parent compound. Fe dopants substitute Mn atoms in the LCMFO crystal. (b) XRD pattern for the LCMO and LCMFO films grown on LAO. Inset show the fit with Lorentzian and Gaussian functions. The most intense peaks correspond to the LAO substrate. No substantial changes between the LCMO and LCMFO patterns are evident. (c) $M(T)$ curves for the LCMFO and LCMO films grown on LAO. The normalized magnetization and Curie temperature are reduced with Fe doping.