Magnetic, structural properties and B-site order of two epitaxial La$_2$CoMnO$_6$ films with perpendicular out-of-plane orientation.

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Abstract. We report on the magnetic and structural properties of two epitaxial La$_2$MnCoO$_6$ thin films grown on (001)-oriented SrTiO$_3$ (STO) substrates, prepared in order to achieve opposite characteristics: one showing perfect Co/Mn cation ordering and a single domain structure; and the second presenting strong B-site disorder. These two films (115 nm) were grown with different orientations. The ordered film with LMCO[110]//STO[001], and the second (disordered) with LMCO[001]//STO[001]. The former consistent with $P2_1/n$ symmetry and the latter with $Pbnm$ structure. Their different ferromagnetic properties are discussed.

1. Introduction

Ferromagnetic insulators are attracting a growing interest due to their interesting properties for different applications. Among them different families of double-perovskites have been recently found to exhibit very attractive dielectric properties [1,2]. Ferromagnetic La$_2$MnCoO$_6$ presents magnetocapacitance effects close to room temperature, making it a good candidate for device applications [2-4]. In La$_2$MnCoO$_6$, giant dielectric response can be induced by magnetism. The initial interest of this material was related to obtaining ferromagnetism at elevated temperatures (T$_c$ close to RT) by ordering Mn and Co. In addition, a large change in the dielectric response has been observed in the vicinity of the ferromagnetic transition temperature. Moreover, the transition can be shifted under magnetic field.

Different studies centered in bulk and thin films of Ln$_2$MnCoO$_6$ (Ln=Lanthanide) have been conducted during last years, exploring their dielectric, magnetic and structural properties [2-8]. It is apparent that the order of Co and Mn species is key for the ferromagnetic state. Co/Mn ordered La$_2$MnCoO$_6$ presents a ferromagnetic transition at T$_c$ = 240 K, while for disordered samples a different transition occurs at T$_c$ = 150 K together with spin-glass like behavior. XAS experiments suggest that ordering implies the coexistence of Co$^{2+}$/Mn$^{4+}$ while disorder is associated to Co$^{3+}$/Mn$^{3+}$ coexistence [5,6]. From a structural point of view, Co/Mn ordering induces a P 2$_1$/n monoclinic structure (P 1 2$_1$/n 1), in front of a P bnm orthorhombic structure in the disordered case [7].
In this paper we present the structural and magnetic characterisation of two epitaxial La$_2$MnCoO$_6$ thin films grown on (001)-oriented SrTiO$_3$ (STO) substrates with very different magnetic (and structural) characteristics.

2. Experimental

Two epitaxial La$_2$CoMnO$_6$ thin films (LCMO) were grown on (001)-oriented SrTiO$_3$ (STO) substrates by pulsed-laser deposition technique by using a KrF excimer laser at energies of about 80 mJ, and stoichiometric LCMO ceramic dense pellets as target. Different growth conditions were applied with the double purpose of obtaining Co/Mn long-range ordering in the first case (LCMO-o), and maximizing the Co/Mn disorder in the second film (LCMO-d). LCMO-o film was grown at 800°C under 400 mTorr O$_2$ partial pressure. For LCMO-d the temperature was 700°C and the O$_2$ partial pressure only 50 mTorr. RHEED analysis and X-ray reflectometry confirmed that both films present a similar thickness of about 115 nm. Magnetization measurements were performed using a superconducting quantum interferometer device (SQUID, Quantum Design).

![Graph and Diagrams]

**FIG. 1** (a) Phi scan of the (1/2 1/2 3/2) reflection (taken at 2θ=38.6° and χ=25° in LCMO-o) showing four-fold symmetry (it corresponds to (103) or (211) for √2a×√2a×2a cell). (b) Reciprocal space maps around (303) STO reflection for LCMO-o and LCMO-d films. (Film reflections correspond to (336) for √2a×√2a×2a cell). (c) Reciprocal space q$_x$-scans around (303) STO reflection, parallel to the [100] in-plane direction. (d) Asymmetric 2θ scans along [111]STO direction showing (0kl) (k=1,3,5) film reflections.

3. Results and discussion

X-ray diffraction (XRD) scans of the two films grown on the STO (001) substrate showed an epitaxial growth of LCMO. Reflections from the √2a×√2a×2a structure were only observed for non-symmetric scans. q scans of characteristic reflections from the film [like the (1/2 1/2 3/2) reflection shown in Fig.1(a)] showed clear four-fold symmetry as expected for an epitaxial arrangement of the films. For simplicity we will refer to the hkl reflections related to the primitive pseudocubic cell, and the orientation of the substrate. Figures 1(b) show reciprocal space maps around a small area close to the 303 STO reflection for LCMO-o and LCMO-d films. Along with the intense substrate peak, for LCMO-d there is a clearly resolved peak at higher q$_x$ values, whereas for LCMO-o only a slight
asymmetry is observed below the substrate peak (lower q_z values). The in-plane lattice parameters of their primitive cells match that of the substrate (a=3.905 Å), as it correspond to fully-strained epitaxial films. Significantly different values for the films were obtained in out-of-plane lattice parameters: LCMO-o shows 3.917 Å, whereas it is 3.855 Å for LCMO-d. The LCMO bulk value of c/2=3.887 Å (P2_1/n: a=5.525 Å, b=5.487 Å, c=7.778 Å, β=89.95° [7]).

Some larger reciprocal space q-scans taken around (303) STO substrate reflection are shown in Fig. 1(c) (q_x- and q_z-scans are parallel and perpendicular to the [100] in-plane direction, respectively). Horizontal scans along q_x did show h=5/2, 7/2 only for LCMO-o sample. The presence of reflections with h (or l)=5/2, 7/2 are inequivocally assigned to the √2a×√2a×a structure (of either Pbnm or P2_1/n space groups), and correspond to (335), (337) reflections, respectively. Vertical scans along q_z confirmed the presence of l=5/2 and 7/2 reflections in LCMO-d sample. XRD characterization indicated (i) a c⊥-orientation of LCMO-o [epitaxial orientation [110]LCMO//[001]STO, [001]LCMO//[100]STO, corresponding to c-axis parallel to the substrate surface. (ii) For LCMO-d the orientation is [001]LCMO//[001]STO, [110]LCMO//[100]STO), that we will name c⊥ (c-axis of the film perpendicular to the substrate surface. The absence of (335) and (337) reflections in the q_z scan of sample LCMO-d indicates a pure c⊥-orientation.

In an attempt to distinguish between Pbnm and P2_1/n space groups we looked for the presence of characteristic monoclinic reflections and performed asymmetric 2θ/ω scans along [111]STO direction. Fig. 1(d) shows the scan for both samples in the regions where (0kk) reflections from the film with k=1,3,5 (or h0h; h=1,3,5) are expected to appear not overlapping with substrate (hhh) peaks (these reflections lay in the positions of h=1/2, 3/2 and 5/2 for (hhh) of the pseudocubic primitive cell). Only LCMO-o sample showed non negligible peaks characteristic of the P2_1/n symmetry (related to order of the cations at the B-site: rock-salt configuration). In contrast, LCMO-d is described by Pbnm group.

![Image](image_url)

FIG 2. (a) Temperature dependence of the field cooled magnetization measured in H=1 kOe (H||[100]STO direction). Inset: ZFC-FC M-T curves for LCMO-d. (b) M-H loops from LCMO-o recorded at 10K with H parallel to in-plane [100]STO and out-of plane [001]STO directions. (c) Hysteresis cycle for disordered LCMO-d (H||[100]STO ).

In Fig. 2(a) the temperature dependence of the field-cooled (FC) magnetization in LCMO-o and LCMO-d is plotted [1 kOe, H||[100]STO direction]. In LCMO-o (c⊥ and ordered) M-T shows a single ferromagnetic transition at about 220K under 1 kOe, indicating ordering at B-sites and absence of disordered phase (with characteristic Curie transitions at lower T [5]). This temperature is very close (but below) the Curie point in ordered bulk specimens (240K). Very different is the magnetization of the Pbnm disordered LCMO-d film (c⊥) of the same thickness (112 nm), which exhibits (i) about eight times less magnetization in M-T and (ii) several jumps in the M-T curve (inset of Fig. 2), at 210-220K, 150K and about 100K [5,8].
The magnetic easy axis is parallel to SrTiO$_3$ [100] in well ordered and $c_{//}$ LCMO-o film, namely parallel to the c-axis of the $P2_1/n$ La$_2$CoMnO$_6$ film. M-H hysteresis loops recorded in this film at 10K are shown in Fig. 2(b) applying the magnetic field parallel to in-plane [100] and out-of-plane [001] STO directions. The linear diamagnetic contribution from the substrate was subtracted. Well defined hysteresis loops and a coercive field of $\sim$7400 Oe was observed in LCMO-o if H$||c$ (H$||[100]$STO). Very similar coercive field is also observed when H$\perp c$ (H$||[001]$STO). These coercive field values are somewhat higher than those reported e.g. in Ref. 9 for ordered La$_2$CoMnO$_6$ films grown with the orientation $c_{\perp}$ on STO ($\sim$4500 Oe). We did not observe doubled hysteresis loops from bidomain epitaxy as reported in [9]. The relatively large coercive field seems favoured by the Co/Mn cationic ordering. The saturation value in the magnetization is about 5.8 $\mu_B$/f.u. at 10 K and 50 kOe, very close to the theoretical value of 6 $\mu_B$/f.u. expected for perfect ordering of Co$^{2+}$ HS (S=3/2) and Mn$^{4+}$ (S=3/2) ions at the B-site (Co/Mn order $>$96%).

M-H hysteresis loop corresponding to LCMO-d film is plotted in Fig. 2(c) for H applied parallel to the film surface [H$||[100]$STO]. A maximum magnetization value of 3.2 $\mu_B$/f.u. in this Co/Mn disordered film [at 10 K and 50 kOe] contrasts with the previous saturation magnetization in LCMO-o, in agreement with XRD and M(T) data. According to the slope observed in Fig. 2(c), the field of 50 kOe has not saturated the magnetization. The coercive field is also clearly lower ($\sim$2891 Oe). We recall that coercive fields of $\sim$200 Oe have been reported at 10K for disordered bulk-LCMO samples [3].

In summary, we have grown two epitaxial La$_2$MnCoO$_6$ thin films on (001)-oriented STO with opposite characteristics: a double perovskite with perfect Co/Mn order and a film with a strongly disordered distribution of B-site cations. We have reported on their different orientation, structural and magnetic properties. Our structural and magnetic characterization have shown that it is possible to obtain perfect Co/Mn cation ordering, the magnetic easy axis parallel to the c-axis of the $P2_1/n$ structure, and a single domain structure with LCMO[110]/STO[001]. Some double-perovskites of the family Ln$_2$BMnO$_6$ (Ln: Bi, La; B:metal) become promising materials in virtue of a strong coupling between the lattice and spin degrees of freedom, responsible for the coexistence in La$_2$MnCoO$_6$ of ferromagnetic ordering and magnetodielectric coupling. Further characterization using additional laboratory and synchrotron techniques is underway and will be published elsewhere.

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