Engineering the microstructure and magnetism of $\text{La}_2\text{CoMnO}_{6-\delta}$ thin films by tailoring oxygen stoichiometry

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We report on the magnetic and structural properties of ferromagnetic-insulating $\text{La}_2\text{CoMnO}_{6-\delta}$ thin films grown on top of (001) SrTiO_3 substrates by means of RF sputtering technique. Careful structural analysis, by using synchrotron X-ray diffraction, allows identifying two different crystallographic orientations that are closely related to oxygen stoichiometry and to the features (coercive fields and remanence) of the hysteresis loops. Both Curie temperature and magnetic hysteresis turn out to be dependent on the oxygen stoichiometry. *In situ* annealing conditions allow tailoring the oxygen content of the films, therefore controlling their microstructure and magnetic properties.

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Bulk $\text{La}_2\text{CoMnO}_6$ (LCMO) double perovskite has been the subject of strong interest during the last years^{1–7} due to its ferromagnetic insulating character. Besides its perspectives as magnetodielectric material, LCMO is a good candidate for active insulating barriers in spin filters. For these devices, insulating barriers must be thin enough to enable tunneling conduction. The properties of epitaxial LCMO thin films have been the subject of some theoretical and experimental works in the recent years.^{8–11} Previous experimental reports based on films prepared by pulsed laser deposition (PLD) suggest that magnetic properties are strongly dependent on growth conditions. When samples are grown under low oxygen pressure the Curie temperature (T_C) is around 100 K while increasing oxygen pressure (0.2 Torr and above) T_C values around 230 K can be achieved. Nevertheless, there is no clear consensus on whether this variation of T_C comes from differences on the Co/Mn cationic ordering¹⁰ or from changes in the oxygen stoichiometry.⁹ On the other hand, low temperature hysteresis loops reported in the literature present anomalies and “biloop” features that have been attributed to the existence of a bidomain structure in the films. However, these “biloop” features of hysteresis cycles are present up to $T_C = 230$ K and, therefore, cannot be linked to the persistence of regions with low T_C phase.¹⁰

Previous studies report low temperature hysteresis loops with a saturation magnetization close to $6 \mu_B/\text{f.u.}$,^{8–10} i.e., the expected value of spin-only saturation magnetization in the case of ferromagnetic (FM) ordering of Mn^{4+} and Co^{2+} (in high spin state) ions. The existence of disorder in the cation's occupancy of the double perovskite structure, namely, the presence of Mn ions placed in Co sublattice and *vice versa* (antisites), will introduce t_{2g} - t_{2g} (Mn^{4+} - Mn^{4+}) and e_g - e_g (Co^{2+} - Co^{2+}) superexchange interactions that according to Goodenough-Kanamori-Anderson rules^{12–14} are antiferromagnetic (AF). Therefore, it is expected that the existence of antisites will reduce the saturation magnetization from $6 \mu_B/\text{f.u.}$ Thus, the departure of the saturation magnetization of a given sample from this saturation value can be interpreted as a measure of the degree of Co/Mn disorder in the structure.

The effect of Co/Mn disorder on the magnetic properties has been previously studied in bulk samples (where it can be precisely quantified by means of neutron powder diffraction).⁶ These studies show that hysteresis loops become wider (with higher coercive field and lower remanence) in the presence of disorder.^{2,4,6} Co/Mn ordering temperature is around 1125 °C and the ordering process is blocked below 1000 °C due to extremely large relaxation times.³ The reported valences for Co and Mn are 2+ and 4+, respectively, and barely change with the degree of cationic ordering.^{3,6}

In this work, we have studied the growth conditions of high quality LCMO epitaxial thin films to explore their suitability as spin filters. Samples have been prepared on top of (001) oriented SrTiO_3 (STO) substrates by means of RF magnetron sputtering. The target was prepared by solid state reaction according to the details published elsewhere.⁶ Films have been grown at heater temperatures between 800 °C and 900 °C (substrate temperature must be slightly below heater temperature) with partial oxygen pressure ranging from 0.2 to 0.4 Torr and with different *in situ* thermal treatments after deposition. Sample names and preparation conditions are listed in Table I. Structural properties of thin films were studied by X-ray diffraction and reflectivity using a Rigaku Rotaflex RU200B diffractometer equipped with a rotatory anode. The thickness of LCMO films, determined by X-ray reflectivity, depends on the oxygen partial pressure (p_{O_2}) during growth and spans from 35 nm (0.2 Torr) to 20 nm (0.4 Torr). Additionally, some selected samples were analyzed by means of synchrotron radiation at KMC2 beamline (BESSY-II at Helmholtz-Zentrum, Berlin), which is equipped with a two dimensional General Area Detector Diffraction System (GADDS), for a deeper structural characterization. Magnetization measurements were performed using a superconducting quantum interference device (SQUID, Quantum Design) as a function of temperature and magnetic field applied along (100)_{STO} crystallographic direction. Transport measurements were carried out in a Physical properties Measurement System (PPMS, Quantum Design) by using the standard four probe method. Topography of films was investigated by atomic force microscopy (AFM),

TABLE I. Growth conditions of the $\text{La}_2\text{CoMnO}_{6-\delta}$ films prepared by RF magnetron sputtering.

Name	T_g ($^{\circ}\text{C}$)	p_{O_2} (Torr)	T_C (K)	<i>In situ</i> thermal treatment (after deposition)
A	800	0.4	130	Fast Cooling (25 $^{\circ}\text{C}/\text{min}$, $p_{\text{O}_2} = 0.4$ Torr)
B	800	0.4	140	Annealing 1 h at 800 $^{\circ}\text{C}$, $p_{\text{O}_2} = 400$ Torr; cooling 10 $^{\circ}\text{C}/\text{min}$
C	900	0.3	120	Fast cooling (25 $^{\circ}\text{C}/\text{min}$, $p_{\text{O}_2} = 0.3$ Torr)
D	900	0.4	160	Fast cooling (25 $^{\circ}\text{C}/\text{min}$, $p_{\text{O}_2} = 0.4$ Torr)
E	900	0.4	225	Annealing 1 h at 900 $^{\circ}\text{C}$, $p_{\text{O}_2} = 400$ Torr; cooling 10 $^{\circ}\text{C}/\text{min}$
F	900	0.4	230	Annealing 1 h at 900 $^{\circ}\text{C}$, $p_{\text{O}_2} = 400$ Torr; cooling 1 $^{\circ}\text{C}/\text{min}$
G	900	0.4	150	Annealing 1 h at 900 $^{\circ}\text{C}$, $p_{\text{O}_2} = 2 \times 10^{-6}$ Torr; cooling 10 $^{\circ}\text{C}/\text{min}$

using an Asylum Research MFP-3D microscope in tapping mode, revealing a flat surface with terraces-and-steps morphology which follows the STO surface morphology (see the inset in Fig. 2).

Fig. 1 shows the magnetization vs. temperature curves, measured following a zero-field-cooling field-cooling process under $H = 1$ kOe, for the most representative samples. Top panel illustrates the dependence of magnetic properties on growth temperature (T_g): increasing T_g from 800 $^{\circ}\text{C}$ to 900 $^{\circ}\text{C}$ promotes an increase of T_C from ~ 130 K to ~ 160 K. The dependence of T_C on p_{O_2} at a fixed T_g ($=900$ $^{\circ}\text{C}$) is evidenced in

Fig. 1(b), which reveals that lowering p_{O_2} from 0.4 to 0.3 Torr promotes the reduction of T_C down to ~ 120 K.

To further enhance T_C , we have performed different *in-situ* annealing processes and depicted the results in Fig. 1(c). This figure shows that by annealing at 900 $^{\circ}\text{C}$ and $p_{\text{O}_2} = 400$ Torr we obtain T_C values of about 225 K, close to that reported for bulk samples^{2,4} and films grown by PLD.^{8–10} However, we note that in some reported cases, PLD films were grown at 800 $^{\circ}\text{C}$ and no annealing process, further than a relative fast cooling down to room temperature, was needed, whilst for RF sputtered films $T_g = 800$ $^{\circ}\text{C}$ is not enough to obtain a high T_C , even after an *in-situ* annealing at $p_{\text{O}_2} = 400$ Torr (sample B, not shown). Furthermore, we have evaluated the influence of lowering the cooling rate after the annealing (sample F), observing a slight increase of T_C (~ 230 K). We have measured the temperature dependence of the resistivity of different samples, all of which display insulating behavior. As an example, resistivity of sample F is displayed in the inset of Fig. 2.

Fig. 2 plots the $M(H)$ hysteresis loops corresponding to samples with low and high T_C (C, E, and F) measured at $T = 10$ K. The diamagnetic contribution of the substrate has been corrected by subtracting the corresponding $M(H)$ loops measured at 350 K. In the case of sample C (low T_C), we find a coercive field of $H_C \sim 5200$ Oe, with saturation magnetization $M_S \sim 5.0 \mu_B/\text{f.u.}$ at $H = 70$ kOe. For sample F (high T_C), a loop with a higher value of the coercive field ($H_C \sim 7500$ Oe) is found but irreversibility extends up to

FIG. 1. Normalized magnetization vs. temperature of different films, measured under 1 kOe. (a) Effect of growth temperature; (b) effect of oxygen partial pressure, and (c) effect of annealing at 400 Torr and effect of lowering cooling rate.

FIG. 2. Magnetization vs. applied field measured at 10 K with H applied along $(100)_{\text{STO}}$ crystallographic orientation. Curves have been corrected for the diamagnetic contribution from the STO substrate. Insets show the AFM image (top left) and resistivity dependence on temperature (bottom right) corresponding to sample F.

very high fields (~ 50 kOe). In fact, magnetization attains a value near $4.33 \mu_B/\text{f.u.}$ (at $H = 70$ kOe) but it is still far from reaching the saturation regime. In the case of sample E ($T_C \sim 225$ K, slightly below that of sample F), which was annealed in the same conditions as sample F but cooled down at a faster cooling rate, coercive field is $H_C \sim 7100$ Oe and magnetization does not saturate at the highest attainable field. Interestingly, this sample presents a biloop; this behavior has been previously reported for PLD films and considered as evidence of the existence of a bidomain structure.¹⁰

To clarify the possible relation between the magnetic behavior and the structure of the samples, we have carefully analyzed samples C, D, and F by means of synchrotron diffraction. First, we have examined the reciprocal space maps of the (103) diffraction peak (indexed with respect to STO). These maps (not shown) reveal that the films are epitaxial with the same in-plane lattice parameters as the STO substrate. Therefore, no relaxation of the tensile strain due to lattice mismatch with the substrate occurs during annealing processes. Rods along Q_Z show thickness fringes revealing the high crystal quality of the prepared films. To elucidate if LCMO grows with c -axis parallel or perpendicular to the substrate surface (sketch at the top of Fig. 3), we measured

FIG. 3. Reciprocal space maps measured by synchrotron X-ray diffraction for samples with the lowest and higher T_C ; (right column) $(0 \bar{3} \frac{5}{2})$ reflection, only present for $\text{La}_2\text{CoMnO}_{6-\delta}$ with c -out of plane, (left column) $(0 \bar{5} \frac{3}{2})$ reflection, only present for $\text{La}_2\text{CoMnO}_{6-\delta}$ with c -in plane. The sketch at the top of the figure illustrates the two possible orientations of the film on top of STO.

the $(0 \bar{3} \frac{5}{2})$ and $(0 \bar{5} \frac{3}{2})$ diffraction peaks (referred to STO reciprocal lattice) which appear exclusively when the c -axis of LCMO is out-of-plane or in-plane, respectively. We performed phi-scans around their positions in reciprocal space and plot the projections along Q_x of the collected intensity in Fig. 3. The orientation of c -axis strongly varies with preparation conditions. For sample C, reflection $(0 \bar{3} \frac{5}{2})$ is much stronger than the $(0 \bar{5} \frac{3}{2})$ one (see Figs. 3(a) and 3(b)), proving that both orientations coexist but that the c -in plane orientation is predominant. For sample E, both peaks present similar intensities, thus indicating that both orientations coexist in similar proportions. Finally, sample F presents only the $(0 \bar{5} \frac{3}{2})$ reflection, representative of a unique crystallographic orientation (c -out of plane). For the phase with c -out of plane, the c lattice parameter decreases monotonically with the fraction of that phase: 7.803(5), 7.762(5), and 7.736(5) Å for samples C, E, and F, respectively. However, this change of c parameter cannot be attributed to a relaxation of structural strain, as mentioned above.

The differences in the growth conditions of the studied samples are the thermal treatment and p_{O_2} in the chamber. In order to discern which of these two factors determines the change in T_C , we have prepared a new sample (G) that was annealed at 900°C during 1 h but under vacuum conditions (2×10^{-6} Torr), in contrast to the 400 Torr used for samples E and F. This sample exhibits low T_C (~ 150 K) very similar to that of sample D, even when its thermal history is identical to sample E, but with reduced p_{O_2} during the annealing. Therefore, we attribute the increase of T_C to the larger oxygen content in the films annealed at high p_{O_2} (and at high enough temperature, vide ultra). This result is in accordance with previous studies in bulk $\text{La}_2\text{CoMnO}_{6-\delta}$ samples (Ref. 2) where low T_C (~ 150 K) was reported for samples with $\delta \geq 0.05(1)$ but high T_C (~ 225 K) was found when the oxygen deficiency is $\delta \leq 0.02(1)$, and also in agreement with the conclusions derived in Ref. 9 for thin films grown by PLD, where the change in T_C is attributed to variations of oxygen stoichiometry. However, the annealing temperature also plays a relevant role. As in the case of sample B, an annealing process at 800°C (and $p_{\text{O}_2} = 400$ Torr) is not enough to increase T_C , which indicates low oxygen content in the film, even for high p_{O_2} . This result proves that oxygen diffusion proceeds slowly at 800°C but much faster at 900°C . Hence, a threshold temperature, between these two values, must be surpassed to reach an efficient oxygen uptake and diffusion inside the films. The behavior shown by sample F (slowly cooled from 900°C) can be explained when considering that the slow cooling process implies a longer time above this threshold temperature, resulting in a larger oxygen uptake. In fact, samples with prolonged annealing time (two hours or more) and fast cooling exhibit magnetic behavior similar to that of sample F. In other words, final oxygen content of the sample depends on the oxygen pressure and temperature during the annealing (and its duration).

In order to confirm the correlation between oxygen content and crystallographic orientation, we must discard that only the increased time at high temperature (so, the thermal history of the samples) might lead to the change from mostly

c-in plane (sample C) to only *c*-out of plane (sample E). High-resolution X-ray diffraction on $(0\bar{3}\frac{5}{2})$ and $(0\frac{5}{2}3)$ diffraction peaks of sample G (not shown) evidences a clear predominance of *c*-in plane orientation. Therefore, samples C and G have very similar oxygen content and the same crystallographic orientation, while samples G and E have the same thermal history but different orientations. This clearly indicates that on increasing the oxygen content, the amount of phase with *c*-out of plane increases.

The variation of the *c*-cell parameter (of the phase with *c*-out of plane) also supports the idea of a progressive increase of the oxygen content. The variation of the cell volume (59.494, 59.181, and 58.983 Å³) for samples C, E, and F, respectively, also tends to that reported for the bulk value (58.771 Å³ (Ref. 6)). This shrinkage of the *c*-parameter (and cell volume) with the oxygen content is coherent with the reduction of the cationic radii under oxidation (ionic radii of Mn³⁺ and Mn⁴⁺ are 0.785 and 0.670 Å respectively^{15,16}).

As mentioned previously, cationic ordering is a key parameter for controlling the magnetic properties of bulk LCMO.^{3,4,6} In previous works on thin films prepared by PLD, cationic ordering was inferred in base of *M_S* values at low *T* close to 6 μ_B/f.u., the expected value for spin-only fully ordered La₂Co²⁺Mn⁴⁺O₆ ferromagnet.^{8–10} Our study evidences that magnetization at high fields depends on the oxygen stoichiometry. Sample C, with low oxygen content, saturates clearly below 6 μ_B/f.u., which could be due to some degree of Co/Mn disorder, or from the oxygen off-stoichiometry. For films with high *T_C*, i.e., those with high oxygen content, *M(H)* curves do not reach saturation, therefore, we cannot establish the degree of order following this criterion.

At this point, it is important to recall that similar *T_C* values were found in bulk samples with different degree of Co/Mn cationic ordering.^{2,6} However, bulk samples with high degree of Co/Mn ordering exhibit hysteresis loops with low *H_C* values and high remanence, whilst samples with low Co/Mn ordering present high *H_C* values and low remanence.^{2,4,6} Nevertheless, in LCMO bulk material, the Co/Mn ordering process is blocked below 1000 °C,³ so no change of cationic order can be expected during annealing processes at 900 °C. Therefore, the high *H_C* and low remanence of samples E and F would not be related with the degree of Co/Mn ordering.

In conclusion, we have prepared epitaxial thin films (~20 nm) of the ferromagnetic insulating LCMO compound by RF magnetron sputtering with high *T_C* values. Synchrotron diffraction studies show that films grow epitaxially on top of (001) STO substrate and are fully strained and of high crystalline quality. A strong dependence of *T_C* on the oxygen content

was detected. Only samples annealed at high enough temperature (~900 °C) in oxygen rich atmosphere (*p*_{O₂} = 400 Torr) exhibit *T_C* values well above 200 K. On the other hand, we have evidenced that oxygen content also controls the abundance of the two different crystallographic orientations existing in the films; high oxygen content (sample F) leads to a single crystallographic orientation (with *c*-axis out of plane), while for low oxygen content, both crystallographic orientations coexist. Although at this point we have achieved ferromagnetic, insulating, flat-surface thin (~20 nm) films of high crystalline quality, further studies are required in order to ensure good capabilities of LCMO films as spin filter barriers.

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¹⁶From a Co²⁺/Mn⁴⁺ valence scheme that has been confirmed by XANES measurements on samples with high and low *T_C*⁴ and by neutron powder diffraction⁶ on samples with high and low degree of Mn/Co ordering, oxygen vacancies can only be compensated by reducing from Mn⁴⁺ to Mn³⁺. Reduction from Co²⁺ to Co⁺ is very unlikely.