



# A radical approach to promote multiferroic coupling in double perovskites

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## ARTICLE INFO

Available online 8 February 2009

**Keywords:**  
Double perovskite  
Multiferroics  
Property  
Structure  
Thin film

## ABSTRACT

Double perovskites provide a unique opportunity to induce and control multiferroic behaviours in oxide systems. The appealing possibility to design materials with a strong coupling between the magnetization and the polarization fields may be achieved in this family since these magnetic insulators can present structural self-ordering in the appropriate growth conditions. We have studied the functional properties of  $\text{La}_2\text{CoMnO}_6$  and  $\text{Bi}_2\text{CoMnO}_6$  epitaxial thin films grown by pulsed laser deposition. Cation-ordered  $\text{La}_2\text{CoMnO}_6$  films display a magnetic Curie temperature of 250 K while cation-disordered  $\text{Bi}_2\text{CoMnO}_6$  films present ferromagnetism up to  $\sim 800$  K. Such high transition temperature for magnetic ordering can be further tuned by varying the strain in the films indicating an important contribution from the structural characteristics of the materials. Our approach might be generalized for other oxide systems. At this end, our results are compared with other multiferroic systems. The roles of various cations, their arrangements and structural effects are further discussed.

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## 1. Introduction

Multiferroics form a surprising class of materials displaying simultaneously magnetism, ferroelectricity, and/or ferroelasticity in a single phase [1–3]. The coexistence of various electronic order parameters that can interact in a given system opens new opportunities to design unconventional spintronic devices and also poses new challenges for physics, chemistry, and technology [1–3]. However, their applicability depends on the nature of the actual coupling between the electronic, magnetic, and lattice order parameters. In this context, there are various stumbling blocks. The most challenging ones are how we can couple directly their molecular magnetic and electric fields responsible for ferromagnetism and ferroelectricity, and control eventually this coupling? Moreover, if this intimate coupling is achieved, how important is the material's response to an external applied field? Answers to these questions are hence crucial for understanding the microscopic mechanism behind the ferroic coupling and for their applicability in real devices.

In this context, double perovskites  $\text{A}_2\text{B}'\text{B}''\text{O}_6$  (where  $\text{B}'$  has partially filled  $e_g$ -orbitals while  $\text{B}''$  has empty  $e_g$ -orbitals or *vice-versa*) provide a unique opportunity to promote strong multiferroic behaviours, because they are ferromagnetic insulators governed by the  $180^\circ$  superexchange process [4] with a potential to generate a

polar character. In fact, the polar nature can be obtained if one can promote different chemical valencies for the  $\text{B}'$  and  $\text{B}''$  cations in a self-ordered phase with  $\text{B}'$  and  $\text{B}''$  alternating along specific crystallographic directions (i.e. with a  $\text{B}'\text{--O--B}''\text{--O--B}'$  sequence). Of course, such effect is absent in a disordered phase. For example, it has recently been shown that the ordered  $\text{La}_2\text{NiMnO}_6$  have a  $\text{Ni}^{2+}/\text{Mn}^{4+}$  cationic configuration leading to large dielectric constant [5] whereas the disordered phase has a  $\text{Ni}^{3+}/\text{Mn}^{3+}$  configuration [5–7]. An alternative path to induce a polar character in double perovskites may be achieved by choosing an appropriate A-site cation (e.g., Bi, Pb) that may induce a long-range molecular electric field in the system without the requirement of  $\text{B}'/\text{B}''$  self-ordering. For example, the complete substitution of  $\text{La}^{3+}$  by  $\text{Bi}^{3+}$  can induce a long-range in-built molecular electric field in  $\text{A}_2\text{CoMnO}_6$  double perovskites due to the contribution of Bi  $6s^2$  lone pair electrons similar to that observed in  $\text{BiMnO}_3$  [8]. From this perspective, comparing  $\text{La}_2\text{CoMnO}_6$  and  $\text{Bi}_2\text{CoMnO}_6$  properties in thin films becomes an interesting benchmark to understand the important ingredients required to promote useful multiferroic properties.

There are several reports on the structural and magnetic properties of bulk  $\text{La}_2\text{CoMnO}_6$  double perovskites while very little information can be found on bulk  $\text{Bi}_2\text{CoMnO}_6$  (BCMO) [4–7,9,10]. Nevertheless, the available data have clearly demonstrated that the cation-disordered materials exhibit multiple magnetic transitions while the ordered ones are characterized by a single ferromagnetic-to-paramagnetic transition (FM- $T_c$ ). For example,  $\text{La}_2\text{CoMnO}_6$  in its cation-ordered phase displays a unique FM- $T_c$

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around 245 K, while disordered samples present also a second magnetic transition around 145 K [4–7,9,10]. From a structural point of view, it has been also established that a cation-ordered La-based double perovskite displays monoclinic  $P2_1/n$  symmetry while the disordered system presents the orthorhombic  $Pnma$  symmetry [5–7]. The recent demonstration of magnetodielectric effects in the La-based self-ordered double perovskites in the vicinity of their ferromagnetic transition close to room temperature is a clear indication of their potential for novel multifunctional devices [6]. However, they still remain challenging materials and the observation of a coupling between the magnetization and the polarization needs to be correlated to microscopic models. Thus, a deeper understanding and a meticulous correlation between their physical and structural properties become crucial.

Unlike the study of the bulk phases, growth of double perovskite thin films is quite recent [11–18]. Obviously, these films are of great interest since they represent the first step toward their integration in multifunctional applications for spintronic devices. This has motivated us to compare the functional properties of LCMO and BCMO films. In this paper, we present our results on epitaxial LCMO and BCMO double perovskite thin films grown by pulsed-laser deposition. The impact of the growth parameters on the Co/Mn ordering is presented as well as the functional magnetic properties of the films. The results reveal that the ordered LCMO films display ferromagnetism up to about 250 K while the disordered BCMO films remain ferromagnetic up to anomalously large temperature of 800 K. We present a possible scenario to explain the surprising enhancement of the FM- $T_c$  of disordered BCMO films with respect to LCMO. This mechanism is based on the increase of the superexchange strength arising from the overlap between the Bi  $6s^2$  lone pair electrons and the Co–O–Mn, Mn–O–Mn, and Co–O–Co electronic wave functions aided by the structural changes.

## 2. Experimental details

Epitaxial films of  $\text{La}_2\text{CoMnO}_6$  and  $\text{Bi}_2\text{CoMnO}_6$  films were grown in the temperature range of 600–850 °C under 10–800 mTorr  $\text{O}_2$  pressure by ablating the respective targets using a KrF laser ( $\lambda = 248$  nm) [15,18]. Polycrystalline stoichiometric LCMO and off-stoichiometric BCMO (with 20 wt% excess Bi) targets were synthesized by standard solid-state chemistry route. Unlike LCMO, BCMO films could be grown only in a very limited parameter window due to the high vapour pressure of Bi and a resulting low melting temperature. Films were grown on (100)  $\text{SrTiO}_3$  (STO), (100)  $\text{LaAlO}_3$  (LAO) and (100)  $\text{Nb:SrTiO}_3$ .

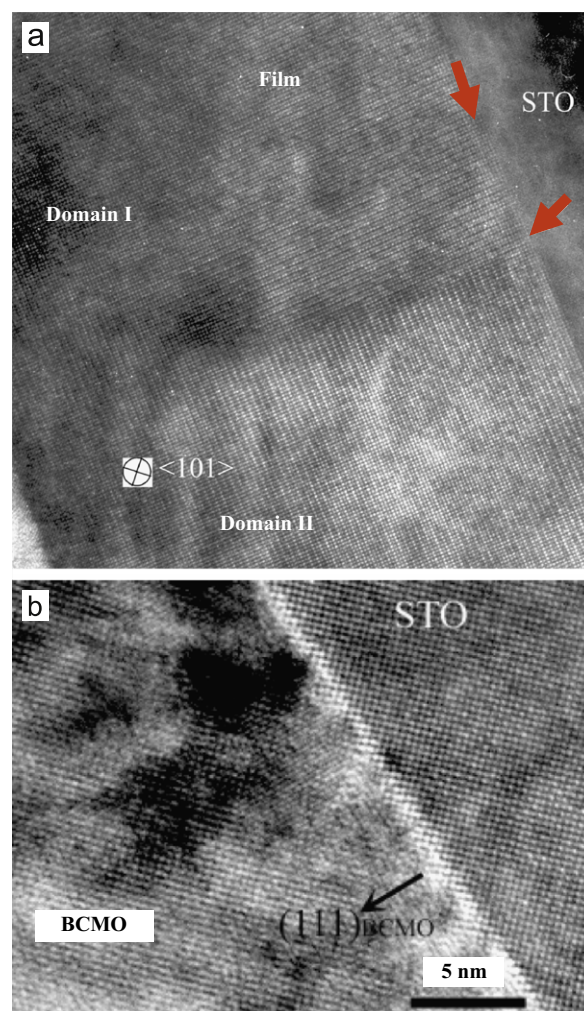
The crystallinity and epitaxial nature of these films were examined in detail using X-ray diffraction (XRD) with  $\text{Cu-K}\alpha$  radiation in the  $\theta$ – $2\theta$ , rocking curve, and  $\phi$ -scan modes. Moreover, the microstructure, crystallinity, and film–substrate interface quality were studied using a transmission electron microscope Hitachi H-9000 NA operating at 200 kV and equipped with an energy dispersive spectrometer (EDS). Magnetic properties of the films in the range of 10–400 K were studied using a SQUID magnetometer from Quantum Design. High-temperature magnetic properties are studied using a vibrating sample magnetometer. Temperature and magnetic field dependence of the dielectric properties of the films were measured in a physical property measurement system (PPMS) from Quantum Design using on a capacitor structure realized by depositing simply indium dots directly onto the LCMO/Nb:SrTiO<sub>3</sub> films.

## 3. Results and discussion

XRD studies show that the LCMO films on STO (001) grow in the (001) directions while the BCMO films on STO (001) grow in

the (111)-direction [15,18]. Furthermore, LCMO films are characterized by sharper rocking curve peaks than the BCMO films. For example, the LCMO films grown under optimized conditions exhibit about 0.2° full width at half maximum (FWHM) while it is about 0.7° for BCMO films. Compared to LCMO, the relatively large FWHM for BCMO films can be interpreted as the natural outcome of the large strain expected from the important mismatch between cubic STO (001) and monoclinic BCMO (111). Despite the apparent incompatibility between STO substrate and the monoclinic crystal structures of LCMO and BCMO, we find that both LCMO and BCMO are growing coherently on STO.

The coherent can be confirmed in Fig. 1a showing the high-resolution transmission electron microscopy (HRTEM) image of the LCMO/STO. The sharpness of the LCMO/STO interface can be directly inferred from the high-resolution transmission electron microscopy images and the film is free from extended defects. Furthermore, LCMO films are also displaying a bi-domain microstructure growth, with domains rotated by 90° from each other. These resulting domains have the same growth directions but a different (in-plane) epitaxial relationship with the substrate: their tilt angle lies in perpendicular directions as confirmed from their respective electron diffraction patterns (not shown here). These patterns also display superlattice peaks confirming the presence of long-range Co/Mn ordering in LCMO. Similarly, the



**Fig. 1.** Cross-sectional HRTEM images of (a)  $\text{La}_2\text{CoMnO}_6/\text{SrTiO}_3$  (001) illustrating a sharp interface and the presence of bi-domains structure (red arrows) and (b)  $\text{Bi}_2\text{CoMnO}_6/\text{SrTiO}_3$  (001) sharp interface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

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