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## Multiferroic perovskites under epitaxial strain

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## Summary

This dissertation presents the experimental investigation of the structure and physical properties of thin films of the multiferroic  $\text{TbMnO}_3$  under compressive epitaxial strain. Multiferroic compounds are a class of material exhibiting both spontaneous electrical polarization and magnetization, within the same phase. These materials are rare in nature and efforts are devoted to the discovery/synthesis of new multiferroics. Multiferroics are good candidates to display high magnetoelectric response. This class of materials, in which the electrical and magnetic orders are coupled, has great potential in spintronics or non-volatile 4-state memories. However, the reported couplings are usually too weak to be implemented for applications. Possible ways to enhance the materials' response, are to use an appropriate dopant, to apply an external pressure or to apply epitaxial strain. While the understanding of the fundamental mechanisms related to the appearance of multiferroicity in some materials has greatly improved over the last few years, many theoreticians and experimentalists are working towards finding new systems with enhanced magneto(-di)electric response, or modifying an existing material in an attempt to enhance the magnetoelectric coupling or to create new multiferroics.

The scope of this thesis is to study the role of epitaxial strain on a multiferroic material. We focus on one of the most popular multiferroics,  $\text{TbMnO}_3$ , in which the spontaneous electrical polarization is due to a spiral spin ordering, giving rise to a large magnetoelectric coupling. Moreover, large strain effects can be expected in such system because of the subtle balance between the magnetic interactions and its large magnetic frustration. Despite its interest, no reports on  $\text{TbMnO}_3$  under epitaxial strain were available at the beginning of our study. We have investigated the structure and

properties of compressively strained thin films of  $\text{TbMnO}_3$ , with thickness below 100nm.

In chapter 1, we introduce multiferroic and magnetoelectric materials and their interest from the fundamental and from the applications point of view, as well as the compound subject of this thesis,  $\text{TbMnO}_3$ , describing the crystallographic and magnetic structure of the bulk material. We motivate the interest of growing thin films of these materials, in general, and of  $\text{TbMnO}_3$ , in particular. Finally, we present several recent reports on epitaxially grown rare earth manganites, specially the manganites that show a splitting between the field-cooled and the zero-field-cooled magnetization curves, absent in the antiferromagnetic bulk materials. We point out that several explanations have been offered for these observations but no clear answer exist.

In chapter 2, we introduce the experimental tools used for the growth and study of the thin films. These include the growth of the films by pulsed laser deposition, high resolution x-ray diffraction from laboratory and synchrotron sources, x-ray photoelectron spectroscopy, atomic force microscopy and magnetic and dielectric characterization. Other techniques employed in this thesis but used by our collaborators, such as transmission electron microscopy (TEM) and embedded cluster calculations, are not included.

In chapter 3, we discuss the growth and the structure of the  $\text{TbMnO}_3$  thin films under compressive strain on single crystals of atomically flat  $\text{SrTiO}_3$  substrates. We show that the initial stage of the growth is 2D in the case of low oxygen pressures of 0.25mbar and 3D in the case of the films grown at 0.9mbar. However, in both cases, the structure of the films has been revealed to show the same evolution: A tetragonal unit cell is observed only for films as thin as 2nm ( $\approx 3$  unit cells). Above that thickness, the orthorhombic distortion starts appearing, increasing with increasing thickness but keeping the out-of-plane spacing constant. Above a critical thickness of about 60-80nm (depending on the oxygen pressure during growth), the films suddenly relax to

their bulk lattice parameters, showing a coexistence of a strained and a relaxed part. Moreover, we found that the four-fold symmetry of the cubic SrTiO<sub>3</sub> substrate leads to the formation of four equivalent orthorhombic domains, as confirmed by TEM experiments. The TEM images reveal a large density of domain walls and small domains, whose sizes increase with increasing thickness. The density of domain walls has been estimated from the images and it is found to scale with the inverse of the thickness for the fully-strained films, and to deviate from that behavior for the partially relaxed films. The main results in this chapter are: The successful stabilization, for the first time, of TbMnO<sub>3</sub> films under compressive strain on SrTiO<sub>3</sub> substrates; the tunability of the orthorhombicity with thickness; and the control of the size of the domains (or the density of domain walls) with thickness.

In chapter 4, we present the magnetic measurements performed on the films described in chapter 3, together with x-ray photoelectron spectroscopy (XPS) measurements and embedded cluster calculations. The XPS measurements showed an increase of the Mn<sub>3s</sub> exchange splitting compared to the expected splitting for Mn<sup>3+</sup>. The origin of the increase of the splitting has been investigated by means of embedded cluster calculations and it was attributed to an increase of ionicity in the thin film with respect to the bulk material. We show that the dominant magnetic interactions in the thin films are antiferromagnetic, similar to the bulk material, but that ferromagnetic interactions are present in the films below the Néel temperature, evidenced by a splitting between the field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves. The induced magnetization, or the magnitude of the FC-ZFC splitting,  $M$ , has been investigated as a function of thickness ( $d$ ) and it has been found to follow the same dependence than both the density of domain walls and the orthorhombic distortion (pseudo-cubic angle):  $\propto d^{-1}$ . In principle, both are good candidates to explain the origin of the induced ferromagnetism in the films. However, the out-of-plane magnetization also shows a splitting between the field-cooled and zero-field-cooled conditions, at around 40K, which is different from the expectation of an antiferromagnetic

coupling along this direction, strongly suggesting that it is not the structural distortion but, instead, the presence of domain walls, that causes the ferromagnetism.

In chapter 5, we present the dielectric characterization of the films. The anomaly in the dielectric constant that is observed in the bulk material at about 27 K, related to the onset of the electrical polarization and linked to the transition from a sinusoidal to an spiral spin state, was not observed in the fully-strained thin films. However, the anomaly was recovered for films showing coexistence of a strained and a relaxed part. We postulate that the small size of the domains and the large number of domain walls prevent the long-range spin order and, therefore, also the associated ferroelectric order. Impedance analysis allowed us to separate the different contributions to the dielectric response and revealed two Debye-like relaxation mechanisms. One of them is related to polaron hopping, while the other is attributed to relaxation of domain walls. Magnetocapacitance measurements showed that the films are magnetoelectric due to the large magnetoresistance of the domain walls. The domain wall relaxation times show a change of slope at the bulk ferroelectric transition temperature ( $T_C \simeq 27\text{K}$ ), suggesting that there is local ferroelectric order, modifying the relaxation of the domain walls. The results in this chapter show the wealth of information extracted from the dielectric measurements in the films, which reveal that the functional properties of the films are determined by their domain walls. This opens the interesting possibility to utilize domain walls for applications (specially for applications requiring miniaturization).

In chapter 6, we present preliminary results on the growth and characterization of  $\text{TbMnO}_3$  films grown on  $\text{SrRuO}_3$ -buffered (001)- $\text{DyScO}_3$  in an attempt to have a finer control of the structure of  $\text{TbMnO}_3$ . (001)- $\text{DyScO}_3$  has the same space group as  $\text{TbMnO}_3$  and should impose tensile strain on  $\text{TbMnO}_3$ . The films are epitaxial, single-phase and have an orthorhombic structure. However, due to the relaxed  $\text{SrRuO}_3$  layer, needed for the electrical characterization of the films, the strain state of the films is

not imposed by the substrate, but by the electrode. The dielectric behavior of the films show little influence of the domain walls, as expected, since the isomorphism of the substrate, electrodes and film should prevent the formation of domains.

In conclusion, we show that epitaxial growth on high-symmetry substrates offers a way to control the structure and properties of  $\text{TbMnO}_3$  and other orthorhombic perovskites, allowing tuning the orthorhombic distortion with increasing thickness. We have shown that the films consist of fine domains and a large density of domain walls, which can be asymptotically increased with decreasing thickness, allowing domain engineering. Due to this microstructure, the properties of the films are very different from those of the bulk material. The magnitude of induced ZFC-FC hysteresis, or induced magnetic moment, absent in bulk, is found to have the same thickness dependence as the domain wall density and the orthorhombic distortion (these two being naturally linked). Although a direct effect of the epitaxial strain (decrease of the orthorhombic distortion) cannot be totally ruled out, this cannot explain the observed out-of-plane magnetization. Our results suggest that the observed ferromagnetism, below the spin ordering temperature, is due to the domain walls. The relaxation of the crystallographic domain walls could be evidenced in the dielectric investigation of the films. Magnetocapacitance and magnetoresistance effects were observed and also linked to the domain walls that are believed to pin the antiferromagnetic domain walls when the system orders magnetically.

This work shows the importance of domain walls in multiferroic and magnetoelectric materials and their potential for device implementation when the miniaturization becomes limited by materials' size effects. This idea of using domain walls as functional objects, is creating a new field of research associated with the study and manipulation of the properties of designed domain wall structures in multiferroics and other functional materials (see very recent works in references [141, 149, 161]). The present work represents significant advance in this direction.

