ESRF	Experiment title: Coexisting Ferro- and Antiferro-Magnetic orders in multiferroic BiMnO3 epitaxial films studied by circular and linear dichroism at Mn L2,3 and O K edges	Experiment number HE3547 :
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Report.

In the last few years, Transition-Metal oxides (TMO) showed only a part of their potentialities for the realization of electronic devices based on entire new concepts. These oxides exhibit a variety of structural, magnetic and electronic properties, ranging from metallic to semiconducting or insulating behaviors, and displaying piezoelectric, ferroelectric, or unconventional magnetic (e.g. Colossal Magneto Resistance) as well as superconducting (High Temperature Superconductivity) properties [1]. Particular interest was recently dedicated to multiferroic (MF) perovskite oxides, i.e. systems with coexisting orders, and specifically those showing ferroelectricity and magnetism, thus displaying a magnetoelectric (ME) effect. The ME effect of these materials can be used for ME memory devices (MERAM), where an electric field (a voltage) is able to switch the direction of the magnetization [2].

The reason for such low availability of suitable MF compounds is that ferromagnetism and ferroelectricity are usually mutually exclusive in TMOs [2]. BiMnO3 (BMO) could be an exception: it is ferromagnetic (FM) below 100 K and it has sizeable magnetic moments of Mn ions, but the presence of ferroelectricity is controversial. BMO ferroelectricity was originally ascribed to the electric dipoles associated to the displacements of Bi3+ , as in BiFeO3 (BFO), but recent calculations suggest an antiferroelectric (AFE) ordering [3] combined symmetry analysis and model approaches showed that the ferromagnetic state is almost degenerate with an antiferromagnetic one that breaks the inversion symmetry [4], analogous to the AF state of $HoMnO_3$ [5]; soon after the same authors suggested that the ground state could be a canted AF with a sizeable FM component, the FE being driven by the AF component [6].

Using the x-ray magnetic circular and linear dichroism (XMCD and XMLD) and X-ray linear Dichroism, on BiMnO3 epitaxial films deposited on perovskite (001) substrates (see table 1), we have investigated the balance between the complex ferromagnetic-ferroelectric states in $BiMnO_3$, that can be tuned and modulated by applying external pressure [7] or epitaxial strain [8]. By Atomic Force Microscopy in the piezo-force mode (PFM) at room T we have found that rf-sputtering grown films are ferroelectric and have at least one component of the polarization parallel to the c-axis.

In this framework, we have checked the simultaneous presence of FM and AFM phases in order to understand: 1) how these two magnetic orders are influenced by the application of external magnetic and electric field, and 2) if and how the respective order parameters are coupled so to give rise to the magnetoelectric effect (ME).

Sample	Substrate	Structure	Area
Cstrain	SrTiO3	Pseudocubic	$5x5mm^2$
POL	DySCO3	Pseudocubic	$400x400\ \mu m^2$
nPOL	DySCO3	Pseudocubic	$5x2mm^2$

Table1

In this experiment we used X-ray absorption spectroscopy, performed at the ID08 beamline of the ESRF, employing the high resolution Dragon monochromator and the XAS end-station equipped with a 6T superconducting magnet. By using simultaneously Total Electron Yield (TEY) and Fluorescence Yield (FY) detection methods – XMCD, XMLD and XLD at the Mn $L_{2,3}$ edges on $BiMnO_3$, we have determined the presence of a ME coupling, an area of $400x400\ \mu m^2$ (bigger than beam size $300x300\ \mu m^2$) polarized by Piezo Force Microscopy (PFM) technique, as sketched in figure 1 on the BMO film grown on DyScO substrate [8]. Using XMCD, XMLD and XLD techniques was possible to compare the spectra between the polarized part (POL) of the film with the part of the film as grown (nPOL) respectively. Up to 10 Mn L-edge XAS spectra, acquired with plus to minus elicities, have been averaged to eliminate any source of systematic error and to reduce the noise level. Here we show data acquired at low temperatures (5K), in normal incidence (NI) conditions and applying a magnetic field at the 0.5 Tesla, below the saturation value and above it at 4 Tesla respectively, on POL and nPOL film (figure 2).

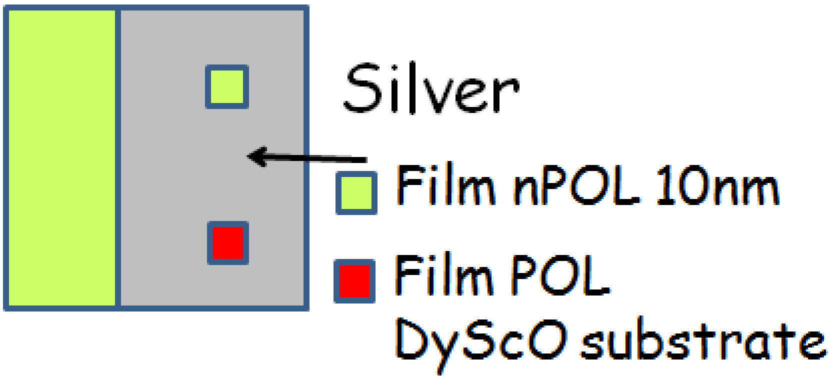


Figure 1: Schematic view of the BMO film 10 nm thick, grown on DyScO substrate, red square correspond to the 400x400 μm^2 area polarized by PFM technique.

In figure 2 we can notice, striking differences between Mn $L_{2,3}$ edge XMCD spectra for 10 nm of POL and nPOL BMO film, where B is applied along the z-axis corresponding to the polarized direction using PFM technique (NI configuration). The differences observed between the two spectra could be a first indication of a ME coupling in our compounds.

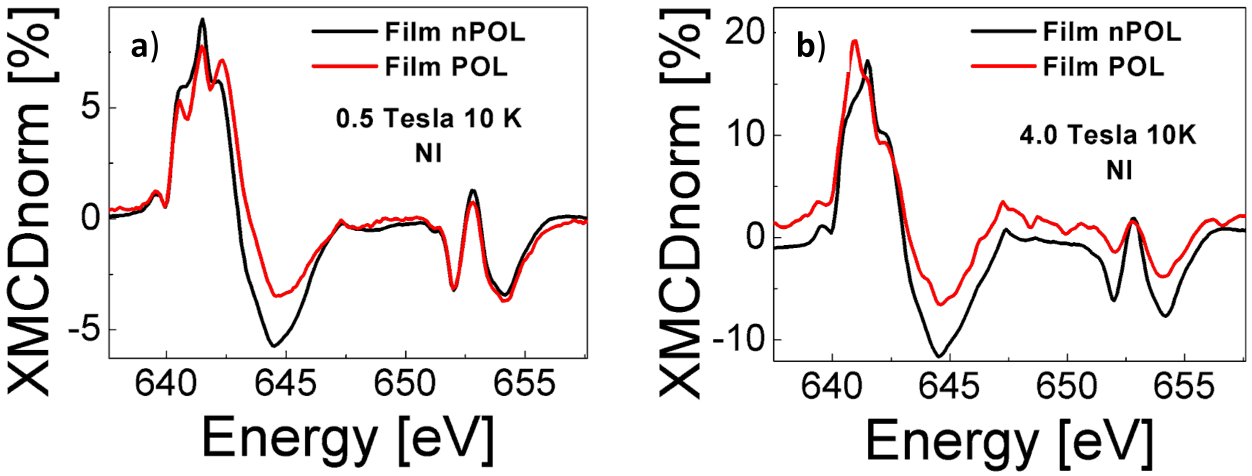


Figure 2 Mn edge XMCD spectra on BMO acquired in normal incidence for nPOL (black line) and POL (red line) as function of the magnetic field: 0.5 Tesla a) and 4 Tesla b) respectively .

By using fully linear polarized light and grazing incidence (GI) conditions (ϑ = 60° from the surface normal), we have studied the orbital anisotropy of Mn 3d states, with particular attention towards the differences between POL and nPOL electronic properties, comparing with the electronic properties of BMO under compressive strain (Cstrain), when it is grown on STO. In Fig. 3, we show XAS spectra at the Mn L_{23} edges of POL, nPOL and Cstrain samples(see table1) measured in TEY mode, at room temperature.

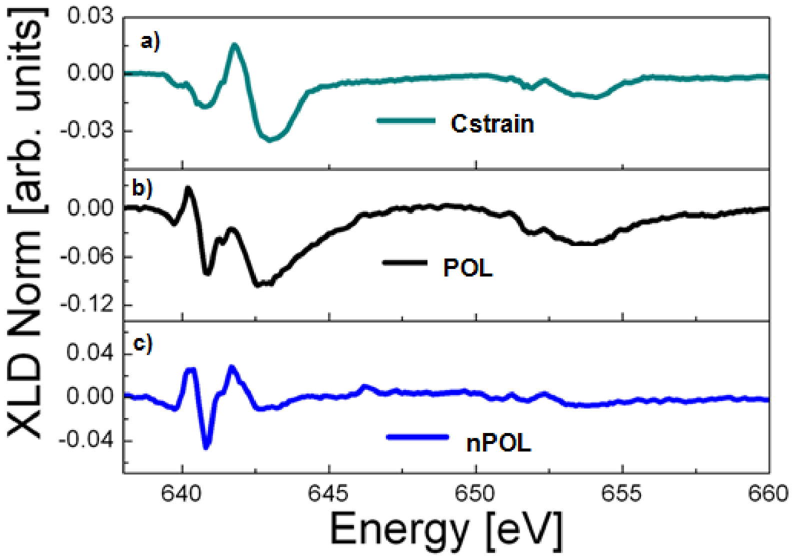
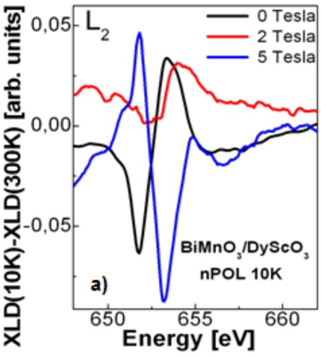
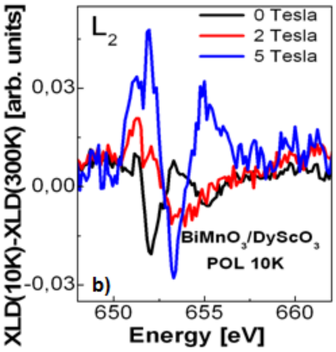


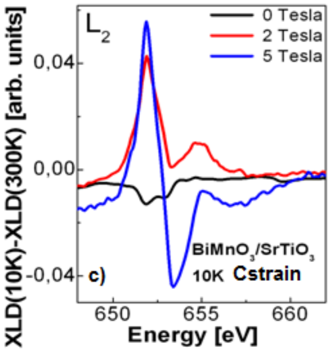
Figure 3: X.ray linear dichroism (I_c-I_{ab} normalized to the max of the average spectral) on Cstrain, POL and nPOL samples measured in TEY and room temperature.

It is clear, that all of the XLD spectra are different. In particular, a preferential occupancy of $3d_{x^2-y^2}$ orbitals is observed only for nPOL sample performing an integral of the XLD spectra. In the other two cases (Cstrain and POL) a $d_{3z^2-r^2}$ orbital order is obtained. What is surprisingly in this result, is not only the change of the orbital for Cstrain sample, that we already expect due to the strain, but the same effect observed even on polarized film (POL). This indicates that the polarization of the film is changing its magnetic response, (see figure 1), but also the electronic structure of the sample, that could be compared to a strain effect.

Recently in ref. [9] has been demonstrated that is possible to evaluate the magnetic contribution in linear dichroism spectra through XMLD, determining the presence of an AFM order. Since, at low temperature there are both contributions: magnetic (characterized by FM and/or AFM order) and orbital, in the hypothesis that the orbital order does not depend by the temperature, the 300K XLD spectra has been subtracted to the XLD at 10K (figure 4), in order to obtain a spectrum with only the magnetic contribution. In figure 4 XMLD for only Mn L_2 edge spectra is shown, changing the magnetic field from 0 to 5 Tesla for all the configurations POL, nPOL and Cstrain. The reverse of the spectra (figure 4) is observed applying the magnetic field, related to the appearance of a different symmetry when the ferromagnetic spin are saturating. The change of symmetry is due to an AFM component [9].
However, observing figure 4, for all the configurations POL, nPOL and Cstrain the weight of the AFM order seems different. Indeed for nPOL film the reverse of the XLD spectra is clear at 5 Tesla, while the same effect is already coming at 2 Tesla for Cstrain and Pol films. This is an additional proof of the effect on the magnetic properties polarizing the compound and it is the first time that a proof of a ME coupling is found in a BMO compound.







In conclusion, with this experiment it was observed that an antiferromagnetic (AFM) and ferromagnetic (FM) co-existence order in our pseudocubic ultrathin films as function of strain, temperature, electric and magnetic field, with a clear evidence of a ME coupling, similar to what is expected for an improper system.

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