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Chap. 18 : Artificial laminar oxide multiferroic magnetoelectric thin film structures

Elaboration methods and study by synchrotron radiation techniques

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Abstract: Nanometric laminar two-dimensional artificial multiferroic oxide thin films can be elaborated using spinel ferrites and perovskite ferroelectrics like CoFe_2O_4 and BaTiO_3 . Such materials can retain their individual ferromagnetic or ferroelectric properties. In the thin epitaxial film regime a cross coupling of these properties is possible thanks to strain engineering. After introducing the concepts supporting artificial multiferroic laminar structures, the growth of strained BaTiO_3 thin films and the growth of subsequent Co-ferrites layers will be detailed. With respect to the relative film thickness, a detailed understanding of the elastic behavior of these films will be proposed based on the characterization using several synchrotron radiation techniques including x-ray specular and off-specular diffraction, x-ray absorption spectroscopy, as well as x-ray magnetic circular dichroism.

Keywords : MULTIFERROICS, MAGNETOELECTRIC, NANOMATERIALS, OXIDES, SYNCHROTRON RADIATION

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I. Introduction

Multiferroic materials, in which, at least two ferroic orders (ferroelectricity, ferromagnetism, etc.) exist simultaneously [1-4] have attracted a great number of studies in recent years. The main reason is that the coupling between ferroic orders opens a great perspective for new devices with additional or enhanced multifunctionalities [5].

One of the most interesting and studied couplings is the magneto-electric effect, since it enables the electric field control of magnetism and conversely, the control of the electric polarization by magnetic fields [6-13]. However, single-phase materials with robust magnetoelectric multiferroicity at room temperature are rare [14] since cooperative cation off-centering and magnetic long range ordering are antagonist properties (in bulk compounds) [15,16]¹. The non-availability of such single-phase compounds appeared as a major and limiting issue until the advent of novel elaboration techniques enabling the growth of high quality single crystalline oxide thin films. Artificial multiferroic systems combining ferroelectric and ferro-, ferri-, antiferromagnetic oxides, in the form of thin films, constitute a promising approach to overcome the lack of intrinsic multiferroics [17-23]. Such systems make promise for the realization of usable multiferroic multifunctional device structures [24], but this last process remains, at present, very challenging

Laminate composites consisting of alternating ferroelectric and ferromagnetic thin films were already considered [25-31]. For thin films, *i.e.* for laminar [29,30] artificial combinations, direct [13] as well as indirect interface strain mediated magnetoelectric coupling have been identified [27,28,32-34]. Epitaxial strain and substrate clamping can indeed be exploited [4,35,36] to enhance the ferroelectric performance of a ferroelectric layer as well as to modulate the strain induced in an adjacent ferromagnetic layer [28].

We will detail in this work the properties measured for model epitaxial thin film bilayer interfaces (CoFe_2O_4 / BaTiO_3) (CFO/BTO) prepared on single crystalline SrTiO_3 (STO) (001) oriented substrates. After detailing the preparation of the samples, we will briefly describe the investigation techniques performed using Synchrotron radiation [37-39] and what specific information they can bring for such particular systems. The results obtained on several bilayered samples, of various relative thicknesses of the constituting layers, will be then shown and discussed, before concluding remarks.

¹ For transition metal compounds, ferroelectricity requires insulating properties while magnetism requires itinerant electrons.

II. Sample preparation & characterization techniques

Perovskite structured barium titanate (BaTiO_3 , BTO) is a prototypical ferroelectric material, which is also well known for its ferroelectricity at room temperature, high permittivity, wide band gap, and for numerous dielectric-based applications [40-43]. Bulk BTO is a typical displacive ferroelectric below 395 K. It undergoes several phase transitions with decreasing temperatures, namely $\text{Pm}3\text{m} \rightarrow \text{P}4\text{mm} \rightarrow \text{C}2\text{mm} \rightarrow \text{R}3\text{m}$ at 401.8 K, 299.5 K, and 216.1 K, respectively. We focus in the present work on the tetragonal room temperature form. Considering thin BTO films is particularly relevant. The stress mechanisms occurring during epitaxial growth can be favorable. Choi *et al.* [35] demonstrated that, by growing BTO layers on substrates imposing increasing lattice misfit stresses, the ferroelectric - paraelectric transition Curie temperature T_c can be increased by approximately 500 K when the growth is realized on DyScO_3 substrates. However, the possible T_c improvement due to epitaxial strain will depend on both, the lattice mismatch and film thickness, as a matter of fact lower lattice mismatch situations favor larger possible thicknesses due to slower structural relaxation.

Cobalt ferrite (CoFe_2O_4 , CFO) is a ferrimagnetic material of spinel structure and with high Curie temperature, that was considered already in a number of previous studies [27,28,44,45]. Bulk CFO has important properties such as strong magneto-crystalline anisotropy, high magnetostriction and saturation magnetization, and high coercive fields at room temperature [46]. It crystallizes in the spinel structure with a lattice parameter of 0.838 nm. The cubic unit cell contains 8 formula units and the spinel space group is $F\bar{d}3m$. The cations can occupy either tetrahedral Td or octahedral Oh sites of the oxygen sub-lattice. Their distribution can be described by the formula $[\text{Fe}_y\text{Co}_{1-y}]\text{T}_d[\text{Fe}_{2-y}\text{Co}_y]\text{O}_h\text{O}_4$, with y the spinel inversion factor ($y = 0$ for a normal spinel and $y = 1$ for an inverse one). Calculations [47] predict an inverse spinel structure for CFO because Co^{2+} ions are more stable in Oh sites. However, especially for thin films the structure is seldom purely inverse spinel and y is usually smaller than 1 [48].

II.1 Growth of epitaxial thin films

The $\text{CoFe}_2\text{O}_4/\text{BaTiO}_3$ (CFO / BTO) bilayer films were grown using a molecular beam epitaxy setup equipped with a high power (up to 600 W) radio frequency (RF)-plasma source allowing for the production of highly reactive atomic oxygen as described in [49, 50]. The base pressure of the growth chamber lies typically in the low 10^{-10} mbar

pressure range. SrTiO₃ (STO) (001) substrates can easily be made conductive through Nb doping. Thus Nb 1 at.% doped STO(001) substrates were used in some cases to avoid charge build-up effects and to allow for ferroelectric polarization of the overlayers. The substrates were 10 × 10 mm² squares, of 1 mm thickness, supplied, aligned, cut, and polished by Crystal GmbH (Berlin, Germany). Prior thin films growth, samples were air annealed (T = 1223 K during 3 h) in order to recrystallize the top surface crystalline plane and heal polishing damages. Before starting the thin film deposition, the substrates were exposed to a high brilliance oxygen plasma (RF power 350 W) at 723 K during 60 min at least to remove any residual surface contamination (as could be checked by *in situ* Auger Electron Spectroscopy (AES) measurements). The oxide layers were formed by evaporating high purity metals (99.99 % grade) by thermal evaporation from dedicated Knudsen cells, while exposing the sample to high brilliance (RF power 350 W - 10⁻⁷ mbar oxygen) atomic oxygen plasma corresponding to highly oxidizing conditions. During growth, the samples were permanently kept at a temperature of 723 K. The BTO layers were grown first, followed by the ferrite layer. The growth rates were around 0.083 nm / min for BTO and 0.125 nm / min for CFO.

II.2 Characterization during the growth process

The structural quality of the growing layers was monitored during growth by *in situ* reflection high-energy electron diffraction (RHEED) using electrons of 30 keV primary energy. *In situ* Auger Electron Spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were systematically recorded just after deposition to determine the oxide layer composition and check the cleanliness of the final surface. All XPS spectra were taken by an ALPHA110 (Thermo Scientific) hemispherical analyzer using an Al (respectively Mg) anode to characterize BTO (respectively CFO) layers.

II.3 Synchrotron based - characterization techniques

Synchrotron radiation techniques have numerous advantages over conventional laboratory setups. They are not intended to replace them, but to complement laboratory experiments in order to obtain detailed information on specific issues or questions (very thin layers, buried diffuse interfaces, magnetometry with chemical selectivity, etc.).

Investigating very small quantities of matter (few nm thick films, possibly during *in situ* or *operando* conditions) and epitaxial layers (low crystalline defects, *i.e.* assimilated to single crystals) require in some cases very high X-ray photon flux, as well as good collimated beams, but in all cases it requires a high quality beam in terms of stability. The use of sub-mm beam sizes can also be an advantage, limiting footprint effects on

sample, especially for grazing incidence geometries (see below). X-rays generated by a synchrotron source are thus adapted to perform such studies [38,39].

For spectroscopy measurements, the x-ray energy and polarization tunability, as well as a good energy resolution and low pass, typically $\Delta E/E \sim 10^{-4}$ hereafter, are mandatory features. Although this energy tunability is not a specific requirement for the x-ray scattering experiments, it can also allow:

1. avoiding measurements in the vicinity of absorption edges and possible signal pollution by the fluorescence (parasitic signal in this case);
2. adjusting the penetration / probed depth in the sample (e.g. accessing buried layers and interfaces);
3. 'squeezing' or 'expanding' the accessible reciprocal space region (or momentum transfer values $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$, $\mathbf{k}_i$ and $\mathbf{k}_f$ being the X-ray incident and exit wave-vectors respectively, $|\mathbf{k}| = 2\pi / \lambda$, λ being the X-ray wavelength), for a given accessible scattering angle (2θ) domain.

The large photon flux, as well as handling a well collimated beam, allows for an efficient focusing of the x-ray beam down to nanometer sizes [37,39]. This also enables the realization of local probe studies [37,39,51-55], with possibilities of using as well its coherence properties in imaging experiments [37].

11.3.a X-ray specular scattering (reflectivity and diffraction)

X-ray reflectivity (XRR) is a surface/interface sensitive technique and consists in measuring the intensity of the x-ray signals reflected by the surface of a flat sample. This technique gives information concerning the thickness, interface roughness and electronic density of the layers and surfaces constituting the sample. During a XRR measurement, the sample and detector are positioned and scanned such as the incidence and emergent angles of the x-ray beams (α_i and α_f respectively, measured with respect to the optical surface of the sample) are equal, *i.e.* optical reflection condition is fulfilled ($\alpha_i = \alpha_f$) (Figure 1). The XRR phenomena can be described using Snell-Descartes law, and by considering that the refraction index (n) of any material (for the considered x-ray energies, in the ~ 10 keV range) is slightly smaller than 1 (while equal to 1 for the propagation in vacuum). As a consequence, total *external reflection* occurs at the vacuum / material interface (*i.e.* x-ray beam is totally reflected back towards the vacuum) for incident angles smaller than a critical value α_c , typically below 1° . In a XRR measurement, this leads to the low angles intensity plateau. In these conditions, the component of the transmitted wave vector normal to the surface

becomes imaginary and thus the amplitude of the refracted wave is an exponentially damped function of the depth from the interface (Figure 1 (bottom left)). As soon as $\alpha_i > \alpha_c$, the measured intensity decreases rapidly but also presents oscillations (Kiessig fringes) originating from constructive and destructive interference of the reflected x-rays having a phase shift depending on the angle (Figure 1 (right)). The result of the measurement can be modeled using for example a Parratt algorithm [56] and allows extracting and quantifying meaningful quantities mentioned above – their influence on the measured signal is illustrated in a schematic manner in Figure 1 (right). For 10 keV x-ray beams and layer thickness in the few to 10 nm range, the XRR signal typically decreases (~ 10 decades) over a range of incident angle spanning 1 to several degrees, and exhibits thickness oscillations of typical periods in the $0.1 - 1.0^\circ$ range. A more complete description and details can be found in [37,38,57].

Figure 1: principle of X-ray reflectivity

(left, top) Illustration of Snell - Descartes law for the propagation of a x-ray beam close to the optical interface between two media, of refraction index 1 (vacuum) and n ($n < 1$). (left, bottom) Similar illustration for the case of incident angle smaller than the critical one. The evanescent wave is also shown in dotted line (adapted from [37]). (right) Schematics of a x-ray reflectivity curve to illustrate the various meaningful quantities which can be accessed and extracted from the XRR measurement.

For **specular diffraction**, this measuring approach can be extended to larger scattering angles but with the specular geometry mentioned above fulfilled *with respect to the crystalline planes* of the material. If interference between the impinging and scattered x-rays can appear (Bragg law, $2 \cdot d \cdot \sin\theta = \lambda$) and the corresponding

structure factors are non-zero [37,57,58], x-ray diffraction phenomena can be observed in coplanar geometry (Figure 2). Indeed, one can consider now the regular atomic arrangement in the epitaxial layers; by orienting the sample such that the geometrical condition fulfills the Bragg law, it is possible to measure the resulting x-ray beam intensity and angular distribution, which gives information about the corresponding reticular distance d (and thus lattice spacing), the atomic arrangement, the epitaxy and the local lattice distortion.

Let us consider the case of epitaxial thin films. Performing a measurement by using the geometry depicted in Figure 2 (left panel, specular configuration with respect to the surface of the sample) gives access to the L direction in the reciprocal space [37,38,57,58] (see Figure 12, left panel, later on in the text), and thus the lattice parameter along the direction perpendicular to the surface (which is usually the c lattice parameter).

Figure 2: X-ray diffraction in coplanar geometry

Illustration of x-ray diffraction by fulfilling interference condition between the x-ray beams incident and *scattered on the crystalline planes* (adapted from [37]). The orientation with respect to the optical surface of the sample is illustrated for two cases: (left) diffraction from a set of crystalline planes parallel to the sample surface; (right) diffraction from a set of crystalline planes tilted (angle α) with respect to the optical surface of the sample. In this last case, the incident and diffracted x-ray beams are at angles of $\theta + \alpha$ and $\theta - \alpha$ respectively, with respect to the sample (optical) surface.

In the case shown in the right panel, the inter-reticular distance d is calculated as a combination of a , b and c lattice parameters. Knowledge about the crystalline structure and the epitaxy are needed, but can be obtained by searching and measuring several diffraction peaks (several scattering angles, sample azimuth, etc.). It is thus possible using these above mentioned various configurations, to extract the lattice parameters characterizing the investigated layer. Moreover, due the relatively large penetration of the hard x-rays, of several microns, buried structures / layers can be accessed and measured, provided that their crystalline structure is different.

By orienting the sample (incident angle, azimuth) and the detector angular position and recording the scattered intensity in each point, different points in the reciprocal space (H , K , L coordinates) can be accessed and reconstructed into 2D maps or 3D volumes. Not only the absolute position and intensity of the diffraction peak are important (lattice parameter, volume of the diffracting phase), but also its shape, along several directions (namely high symmetry ones) in the reciprocal space. Mapping approaches are thus interesting to perform, and benefit from the high photon fluxes x-ray beams for an accurate measurement of the diffuse scattering signal around the already low intensity diffraction peaks originating from the thin layers.

II.3.b X-ray diffraction in grazing geometry

The use of low incidence angles in x-ray scattering geometry allows an increased sensitivity to surfaces and topmost thin layers [38,39,57]. If enough degrees of freedom concerning the angular movements (sample and detector) are available, a particular geometry can be used, geometry in which the incident angle (measured with respect to the optical surface of the sample) is fixed (Figure 3). It allows measuring and accessing rather large regions of the reciprocal space (in an out of plane Bragg peaks), while limiting the penetration depth down to a few 10 nm depth. By keeping the enhanced surface sensitivity and limiting bulk scattering, such an approach has clearly an advantage in measuring very small scattering signals originating from ultra-thin (epitaxial) layers.

II.3.c Mapping the reciprocal space using area detectors

We pointed out above the interest in performing mapping (2D or 3D) of the scattered signal around diffraction peaks. With the principle detailed above, the sample is oriented with respect to the x-ray beam and the detector is positioned such as to access a particular point in the reciprocal space. Then these positions are adjusted such as to access the next point to measure. Although the time of a measurement per point (exposure to x-rays) can be largely reduced at a synchrotron facility, this point-by-point measuring procedure is extremely time consuming: the accurate positioning of the motors, including acceleration, deceleration times and / or encoded position loop

regulation (~ 1 s) can be up to 10 - 100 times higher than the data acquisition times (few 10 to 100 ms). When volumes in the reciprocal space are to be measured, the total acquisition time of a dataset can thus easily raise to hours or days.

Figure 3: X-ray diffraction in grazing incidence geometry

Illustration of x-ray diffraction in grazing incidence geometry ($\alpha_i \sim 0^\circ$), for accessing (left) in plane lattice parameters ($\alpha_f \sim 0^\circ$, $q_z \sim 0$, i.e. q vector has only an in-plane component) and (right) out of plane lattice parameters ($\alpha_f > 0^\circ$, $q_z > 0$), by moving the detector (Det) position out of the sample surface plane. The (HKL) crystalline planes yielding to XRD (q vector is perpendicular on them) are sketched inside the sample by the grey shaded areas. The θ diffraction angles are measured with respect to the diffracting planes, and also schematically shown.

With the arrival on the market of reliable, fast, low noise and high dynamics detectors, approaches using them instead of the 'classical' point detector are appearing [59,60]. Indeed, each dataset is now containing a 2D slice (not necessarily along high symmetry directions) in reciprocal space. Measuring 3D volumes thus simply reduces, most of the time, to a simple line-scan of the position of the sample and / or detector. Since the data acquisition per point can be typically reduced well below 1 s (high photon flux), this acquisition is most of the time done in a continuous mode [61], during the angular movements. The result is a tremendous gain concerning not only the duration of the acquisition of large datasets, but very good resolution of the data (in reciprocal space). Mathematical algorithms [59,62] are then needed in order to properly re-synchronize datasets and angular position, as well as to reconstruct the reciprocal space and access the particular points / directions / planes.

The X-ray reflectivity and diffraction measurements reported here were realized on the SixS [63] and DiffAbs [64] beamlines at the Synchrotron SOLEIL, France. The two beamlines supply hard X-ray monochromatic photons (in the energy range $E = 5 - 20$ and $3.5 - 23$ keV respectively) with a $\Delta E/E$ resolution of 10^{-4} and are equipped with 6-circle diffractometers. The typical beam-sizes (full width at half maximum, FWHM) used during these experiments were respectively (300×100) and $(250 \times 200) \mu\text{m}^2$; the sample was placed such that the smaller dimension is perpendicular to its surface, in order to limit beam footprint effects, for low incident angles.

Sample alignment, XRR and some XRD (coplanar geometry) measurements reported hereafter were performed using a point detector. Surface XRD and reciprocal space maps (RSMs) were realized using photon energies of 15 and 19 keV (wavelength $\lambda=0.083$ and 0.065 nm) respectively on SixS and DiffAbs beamlines. When grazing incidence geometry was used, the incident angle was tuned, depending of the type of measurement, from sub-critical (0.1°) up to ~ 3 times the critical angle for total external reflection, calculated for the corresponding incident photon energy. In coplanar geometry, θ - 2θ scans (*i.e.* detector positioned at emergent angle, with respect to the incident beam, always equal to twice the incident angle), and perpendicular to the sample surface, are performed. After sample alignment and orientation using the crystalline lattice of the substrate as a reference, scanning along particular high symmetry directions in reciprocal space (*ex.* $00L$, $H00$, $HH0$, HHL , ..., see Figure 12) was performed.

A 2D silicon hybrid pixel detector [65-67] was also used in some experimental campaigns to record RSMs. Dataset was converted into reciprocal space coordinates and reconstructed towards 3D volumes using either homemade Python written code or approach described in [62]; then high symmetry 2D cuts are performed and used to extract the meaningful parameters.

II.3.d X-ray spectroscopy

X-ray Absorption Spectroscopy (XAS) is a widely used technique to study the electronic configuration of matter [68,69]. Absorption corresponds to the excitation of a core electron towards empty states. A spectrum is obtained by tuning the energy all over the absorption edges of interest while recording the absorption coefficient. The latter is done either by measuring the part of the light that is not absorbed by the sample (request thin samples) or by recording the side products of the absorption: electron and fluorescent emission. When using x-ray absorption we can distinguish two energy ranges: soft and hard X-rays. The blurred line between the two (around 3 keV) is mainly driven by the physics used in the monochromator to select one

wavelength: 2 crystals monochromator (Bragg diffraction) for hard X-rays while for the soft X-rays diffraction gratings are used. The different energy range allows to access to different edges for the same atomic species. Over the years different derivatives techniques have appeared like, for instance, XANES (X-ray Absorption Near-Edge Structure) or EXAFS (Extended X-ray Absorption Fine Structure) and also the different technique using the dichroism when one compare XAS taken with different light polarization (like XMCD (X-ray Magnetic Circular Dichroism) and XNLD (X-ray Natural Linear Dichroism), to name the two most popular (Figure 4). A dichroic spectra is obtained by subtracting two different XAS spectra measured with different light polarization or different electronic configuration (magnetic polarization, electronic configuration, light incidence angle).

Figure 4: XAS and XMCD principle

(a) Cartoon of XAS process - absorption of the X-ray photon and emission of the photoelectron (photoelectric effect). The decay from the excited state towards lower energy / ground state can happen via (b) the emission of a fluorescence photon (fluorescence decay process) or Auger electron (Auger decay process). (c) Cartoon of XMCD principle: in a magnetic material with uncompensated spin moments (up and down) in the d band, absorption edge signals measured for differently polarized X-ray photons are different, and allow, in principle, retrieving spin and orbital magnetic moments.

In the particular case of multiferroic oxide systems the soft x-rays range is ideal as the edges of interest of the magnetic 3d elements ($L_{2,3}$ edges) are located between 500 and 900 eV. Moreover, XMCD is a powerful tool when studying magnetic material as it

is a high sensitivity chemical selective magnetic probe allowing for instance to discriminate between the Co and Fe atoms when probing cobalt ferrite. In proper conditions, the application of the sum rules on a XMCD spectra allows for the determination of the orbital [70] and spin magnetic moments [71]. It is a very sensitive probe and the use of the Total Electron Yield (TEY) detection makes it appropriate when looking at thin films. Furthermore, combined with theoretical calculations, XMCD can really help to determine precisely the fine electronic structure of the measured system. In our particular case ligand field multiplet calculations permit to ascribe each feature in the XMCD spectra of Fe- $L_{2,3}$ to a defined Fe electronic configuration like the oxidation state and the symmetry which are very important information when investigating a ferrite.

If we go more into the details of a XAS / XMCD experiment on a ferrite there are several levels of analysis:

1. Recording the XAS of the different edges of interest will lead to a first analysis about the actual composition and electronic structure of our sample, in particular for the ferrite it will give an information about the stoichiometric ratio between Fe and the other 3d element (cobalt in our case) [28,72]. Playing with the detection (TEY or Fluorescence Yield (FY)) can give an information about the homogeneity of the sample with the depth. Indeed with an escape depth around 2 nm TEY is really surface sensitive while the FY give access more to the topmost 100 nm.
2. In a second step the XAS spectra recorded at the magnetic saturation will be used to obtain the XMCD signal. In practice this is done by acquiring several XAS spectra, recorded with circular left and right light polarization and the magnetic field parallel or antiparallel to the light (X-rays) propagation vector. In the case of ferrite as there is a mixing of different electronic structure it is not possible to apply the sum rules [73]. But with the knowledge of the different contributions to the XMCD signal (e.g. Fe atoms in tetrahedral and octahedral coordination respectively, Fe³⁺-Td and Fe³⁺-Oh) it is possible to describe the electronic structure in term of site occupation and compare them with reference samples [28,72]. Of course a fine comparison with proper calculations will give more precise information on the electronic structure (not only the spin and orbital magnetic moments on each type of atoms but also for instance the crystal field parameters).
3. To perform a magnetization curve it is sufficient to record the evolution of one of the intense XMCD features vs. the external applied magnetic field. On a Co ferrite by doing so on Fe and Co edges it is possible to record the magnetic behavior of the two chemical species that in some cases (core-shell nanostructure for instance) could be different. But it is also possible to record the magnetization curves for the same atomic species with different electronic

- configuration (for instance Fe^{3+} -Td vs. Fe^{3+} -Oh).
4. XNLD measurement can give access to charge anisotropies on a particular atomic species. A typical XNLD consist, for a defined beam geometry, to make the difference between XAS measured with vertical and horizontal linear polarization. With a normal incidence geometry (beam propagation vector normal to the sample plane) such technique will give an information about the in-plane anisotropy, while at grazing incidence it is the out-of-plane to in-plane anisotropy which is probed.
 5. In the particular case of our study on multiferroic systems, XAS/XMCD was also performed in order to evidence how an electrical polarization on the sample could modify the magnetic properties. To perform such experiments, one needs a proper sample environment for *operando* XAS & XMCD measurements. This includes a dedicated device allowing to apply an electric potential on a sample under Ultra High Vacuum [74] and an efficient fluorescent detector (like a Silicon Drift Detector) as the TEY signal under variable electric potential is completely distorted or even unusable. The expected results are for instance changes in the respective ratio of Fe^{2+} , Fe^{3+} -Td and Fe^{3+} -Oh with the applied electric potential. Perhaps one could also anticipate a change on the magnetization curves when an electrical voltage is applied to the film. Such results will not be presented in this work but are described in ref [24].

The XAS and XMCD measurements reported hereafter were realized at the DEIMOS [75,76] beamline (SOLEIL Synchrotron, France). The beamline provides photons in the 350 - 2500 eV energy range and is dedicated to soft x-rays dichroic measurements. It has been optimized to perform dichroism measurements that request high reproducibility in order to not introduce artefacts when making the subtraction between two XAS spectra. The beamline has been designed to ensure high spectral stability (flux and energy) and the two available undulators are used in two different ways: (i) the HU52 Apple2, which provides fully circular and fully linear polarized light, can be used for continuous scan in energy. Such scans, where the trajectories of the monochromator, the phase and gap of the undulator are synchronized, allow to perform a XAS measurement of 100 eV range in 2 - 3 minutes with a very good statistic [77]. By doing such fast scan in energy the possible instrumental instabilities (source emission, x-ray optical path) between two spectra are minimized, ensuring a proper dichroic measurement; (ii) The second undulator (EMPHU65) provides only circular polarized light but the uses of electromagnet (combined with permanent magnets) allows very fast switching of the phase at 1 Hz. This makes possible to record directly an XMCD spectra by doing a step by step energy scan where at each point in energy the circular right and left absorption signals are recorded. One such spectrum takes more time compared to a continuous scan but allows to measure directly very small XMCD signals.

A heavy duty cryo-magnet allows applying up to 7 T magnetic field along the beam direction and 2 T perpendicular to the beam direction; the sample temperature can be varied from 0.2 to 350 K due to a variable temperature dilution insert [78]. A second end-station based on a 2 T electromagnet houses several insert allowing for different sample environment and in particular the V²TI insert used for some of the measurements of this work [79]. The XAS spectra shown hereafter were measured using TEY detection.

III. Results & discussion

Two series of samples, deposited on STO(001) and on 1% Nb-doped STO(001) single crystalline substrates, have been prepared. In each set, different thicknesses of the constituting CFO and BTO layers, as listed in Table 1, have been employed. The samples have been measured by using similar XRD experimental approach, on SixS and DiffAbs, beamlines, respectively. On DEIMOS beamline, the measured samples had respective thicknesses of BTO of 7 and 14 nm, and of CFO of 2.2, 4.4, 6.6 and 15 nm. The samples details are reported in the Table 1 below; the thickness reported for each of the layers constituting the bilayer are the ones as deduced from the layer deposition time (and *in-situ* calibration).

Table 1: CFO / BTO bilayer samples

BTO \ CFO	SrTiO ₃			1% Nb - SrTiO ₃		
	2.2 nm	4.4 nm	6.6 nm	5 nm	10 nm	15 nm
7 nm	XRD / XMCD	XRD / XMCD	XRD / XMCD	XRD	XRD	XRD / XMCD
14 nm	XRD / XMCD	XRD / XMCD	XRD / XMCD	XRD	XRD	XRD / XMCD
21 nm	XRD	XRD	XRD	XRD	XRD	XRD

Samples used for the structure, crystallinity (XRD labeled, SixS and DiffAbs beamlines), XAS and dichroism (XMCD labeled, DEIMOS beamline) studies, function of the relative thickness of the respective constituting layers (CFO, reported on the horizontal direction and BTO, reported on the vertical direction).

III.1 Characterization during the growth

The bilayer structure was investigated *in situ* during AO-MBE growth and *ex situ* after completion of the ferrite overlayers. Sharp RHEED diffraction patterns from the clean STO(001) starting surface (Figure 5 (a-top)) indicate very high crystalline quality and flat initial surfaces. After cleaning the surface with atomic oxygen the starting surfaces were slightly reconstructed as expected for high quality and clean surfaces. RHEED diffraction patterns were systematically recorded along the two low Miller indices surface crystallographic directions [100] and [110]. Figure 5 (a) shows the patterns after the deposition of 15 nm BTO on STO (second line). After deposition of the BTO layer the surface cleanliness and composition were checked by AES as illustrated in Figure 6. The relative AES O_{KLL} , Ba_{MNN} / Ti_{LMM} peaks intensities provide an excellent criterion to check the composition of the layer and indicate that the BTO layer fully covers the substrate. By comparing the Ti_{LMM} and Ba_{MNN} peak heights, we can quantify the Ti/Ba ratio in the BTO layers deposited on STO(001). We obtained for all films with sharp, well contrasted and perovskite structured RHEED patterns, an AES Ti_{LMM}/Ba_{MNN} ratio, without correction by the sensitivity factor, between 1.2 and 1.9. This ratio of our films is relatively lower than the ratio expected for a homogenous flat surface of BTO. It is due to the formation of a Ba rich top layer on our sample surface as reported previously by Barbier *et al.* [50] using the same growth conditions.

On successfully realized BTO films, the CFO overlayers were deposited with the same method using lower temperatures and slightly higher oxidation conditions. RHEED patterns for 6 nm and 15 nm CFO deposited on 21 nm BTO are shown in Figure 5 (a) (the 2 bottom rows). The patterns are well contrasted and demonstrate the epitaxial growth of (001) layers of (i) BTO within a perovskite structure and (ii) of CFO overlayers within a spinel structure. One may note that for the growth of the CFO layers, the intermediate spinel strikes appear around 2 - 3 nm. They are particularly easy to observe in the integrated line profiles presented in Figure 5 (b, c) and are highlighted by a rectangle in the [110] profiles (Figure 5 (c)). These intermediate rods persist and intensify throughout the entire deposition duration, indicating that the desired spinel phase is maintained and is strengthened while the deposition proceeds. These extra strikes result from the fact that the spinel lattice parameter is nearly twice the one of BTO, they are thus not due to any kind of reconstruction. In our growth conditions, we obtained for both BTO and CFO layers well defined strikes with only faint eventual 3D spots indicating a mostly flat and well defined average surface.

Figure 5: RHEED characterization during growth.

(a) Examples of RHEED patterns recorded during the growth of a bilayer sample of 21 nm BTO covered by 15 nm CFO along the two low Miller indices directions. (b) and (c): line profiles extracted from the individual images. The lines were translated such as to keep the specular spot at a given central position. (d) BTO in plane lattice parameter evolution during growth on STO(001) for a 15 nm thick layer and (e) CFO in plane lattice parameter evolution during the growth of 15 nm CFO on a 21 nm BTO layer.

Figure 6: AES characterization.

AES characterization during growth after completion of a 12 nm thick BTO layer grown on STO.

The in-plane lattice parameter evolution of BTO and CFO layers has been investigated using integrated line profiles extracted from the RHEED patterns (see Figure 5 (b, c)). The STO bulk lattice parameter, at the growth temperature (723 K), was used to calibrate the reciprocal space. The thermal expansion coefficients of STO and BTO were taken from a previous work [50]. At room temperature, the in-plane lattice parameters of STO and BTO are 0.3905 nm and 0.3992 nm, we thus obtain 0.3923 nm and 0.401 nm, respectively, at 723 K. The corresponding excess lattice parameter has been corrected to determine room temperature equivalent lattice parameters. Figures 5 (d) shows an increase of the in-plane lattice parameter of BTO in the early stages of the growth. It increases up to the value of 0.401 nm, within the error bars of our measurement, after deposition of 9 nm approximately before remaining essentially constant, indicating a full lattice relaxation already at a thickness of 9 nm for a film that was grown up to 15 nm total thickness. We observe a somehow similar behavior for the growth of the CFO overlayer (see Figure 5 (e)). The lattice parameter relaxes in a more slowly manner and reaches asymptotically a steady state after the growth of about 12 nm without reaching the fully relaxed expected value at 15 nm. We observe always a slight residual in-plane contraction of our ferrite layers within the range of thicknesses we have investigated (*i.e.* below 20 nm). However most of the structural relaxation, from the RHEED analysis, occurs before 9 nm for BTO and 12 nm for CFO which are thus the thickness ranges we may be able to exploit for strain engineering.

The final composition of our films was firstly checked using *in situ* AES (Figure 6) before more quantitative *in situ* XPS measurements were realized. The control of the composition of our CFO films was performed using *in situ* XPS with a Mg K α source while an Al K α source was used for bare BTO layers. Figure 7 shows a typical example of a wide scan spectra taken after the deposition of a 5 nm CFO film. The presence of Co and Fe lines are observed as expected and only very residual Ba 3*d* and Ti 2*p* peaks appear, indicating a highly homogeneous deposition of the CFO layer consistent with the RHEED observations indicating a flat average surface.

Figure 7: XPS characterization after growth of a bilayer.

XPS wide scan of a 5 nm CFO / 12 nm BTO bilayer realized with a Mg K α source. All peaks present in the scan are attributed exclusively to CFO and BTO.

We have focused our attention on the excitation of the 2*p* levels because of their high sensitivity to the oxidation state of cations. As shown Figure 8 (right), the presence of Fe³⁺ yields a well-defined characteristic satellite structure 8 eV after the Fe 2*p*_{3/2} peak (~710 eV). The peak 2*p*_{3/2} of Co (see Figure 8 (left)) is located at 780 eV and a shake-up satellite is observed at ~7 eV toward higher binding energy typical for Co²⁺ systems. The composition was estimated from the Co 2*p*_{3/2} and Fe 2*p*_{3/2} peak intensities as indicated by the respective fits in Figure 8 using usual asymmetric Gauss-Lorentz functions and a Shirley type background. In all cases, we obtained the expected stoichiometry. The peak decomposition required moreover the introduction of 2 species of Co and Fe related to the site occupancy in the lattice, *i.e.* Oh and Td sites, indicating a mixed spinel composition which laid typically always to around 80% inverse spinel.

Figure 8: XPS characterization after growth of a bilayer Co-2p and Fe-2p.

XPS scans of a 5 nm CFO / 12 nm BTO bilayer realized with a Mg K α source and centered on the Co-2p (left) and Fe-2p (right) lines which were decomposed in individual contributions.

III.2 Synchrotron based - characterization techniques

All the samples reported in Table 1 were measured using the same systematical experimental approach. For the x-ray diffraction approach, once the sample is aligned with respect to the x-ray beam, the following datasets were acquired: (i) x-ray reflectivity, (ii) specular x-ray diffraction ($00L$ direction) line-scans, (iii) in plane grazing incidence XRD line-scans (along 2 symmetry directions, $[H00]$ and $[HH0]$), and (iv) Reciprocal Space Maps (RSMs) at particular positions (containing both an in plane and an out of plane component) in fixed grazing incidence geometry [38,39]. For the (ii) and (iii) situations, rocking scans at the positions of diffraction peaks characteristic to BTO and CFO (several diffraction orders) were also recorded.

III.2.a X-ray reflectivity (XRR)

X-ray reflectivity (XRR) measurements were performed on several particular samples, with the aim of (i) confirming the relative thickness of the constituting layers, cf. the aimed thickness during the AO-MBE process, and (ii) confirming the relative low roughness (< 1 nm r.m.s.) of the constituting films at the end of the growth process [24]. The period of the oscillations (in q coordinates, measured directly on the dataset or extracted after a Fourier Transform [60 and references therein,79,80]) can be converted into thickness of the corresponding layer. A more quantitative approach involves modelling and fitting the whole dataset [24,50,79], case in which other

meaningful parameters are accessed.

Several reflectivity curves for increasing thickness of the bilayer are shown in Figure 9 along with an example of fitted dataset.

Figure 9: X-ray reflectivity curves

Measured x-ray reflectivity datasets for several increasing bilayer thickness (the relative thickness of the constituting layers is maintained constant). The thicknesses of the BTO / CFO layers are reported for each curve. Datasets were corrected for x-ray beam footprint effects, normalized to unity with respect to the total external reflectivity plateau and vertically shifted for better visibility. The inset shows the fit of the XRR curve for the 10 nm CFO / 14 nm BTO / STO sample.

These measurements confirm the thickness of the layers (within 10% of the aimed value, and topped to about 0.8 nm) and show that the manufacturing approach and conditions are granting well defined layers with very low roughness ($\sim 0.2 - 0.3$ nm r.m.s. for the buried interfaces and slightly increased to ~ 0.4 nm r.m.s. for the topmost surface). Note also that there is a slight increase of the interfaces roughness with the increase of the thickness of the constituting layers. Although the presence of extra interfacial layers of thickness < 1 nm cannot be completely out-ruled from these datasets, if present, they are in very limited / low quantity. Thus, we can exclude a significant intermixing of the oxide layers.

III.2.b X-ray diffraction (XRD) in specular geometry

X-ray diffraction (XRD) measurements in specular geometry (aligned on the crystalline lattice) were performed for all samples. As an example, the datasets measured for the samples already shown in XRR are presented in Figure 10. The data are represented using reciprocal lattice units (r.l.u.) of STO, *i.e.* the XRD peaks of the substrate will appear at integer coordinates. Due to the particular crystalline structure of the BTO and CFO (at room temperature slightly tetragonal with $c/a \sim 1.01\%$ and cubic - inverse spinel respectively), as well as to the approximately double lattice parameter of the CFO (compared to BTO and STO), CFO XRD characteristic peaks appear only close to even L coordinates (r.l.u. of STO), while BTO characteristic peaks appear close to each integer L coordinate, as illustrated in Figure 10. The BTO and CFO peak separation is increasing with increased reciprocal space (L) coordinate.

Figure 10: XRD in specular geometry, along the [00L] direction

Measured x-ray diffraction datasets (specular geometry, *i.e.* along [00L] direction) for several increasing bilayer thickness (the relative thickness of the constituting layers is maintained constant). The thicknesses of the BTO / CFO layers are reported for each curve. Datasets are vertically shifted for better visibility. The inset shows a measurement performed on the thickest available sample, close to $L \sim 4$ r.l.u. of STO, with well separated XRD peaks originating from BTO and STO.

The oscillations (Laue oscillations) originating from the finite thickness of the film (crystalline part, BTO film) are present and correspond, within the experiment data quality, to the thickness measured in XRR.

For each of the characteristic peaks of CFO and BTO, and for several orders of them, rocking scans were performed: the detector is maintained at fixed position (2θ , characteristic of the corresponding diffraction peak) while the sample angular position (incident angle) is scanned. Without entering into details (see also Section III.2.d below), the measured width is, in this case, limited by the corresponding size broadening (*i.e.* the very low thickness of the films, in the few to 15 nm range). The agreement between the total film thickness (the one aimed at, or deduced from XRR) and the crystalline part (period of the oscillations in Figure 10) supports the statement that our films are epitaxial and of high crystalline quality over their whole thickness, with a low (negligible) interface intermixing.

III.2.c X-ray diffraction (XRD) in grazing incidence geometry, in the plane of the surface

This approach has the advantage of measuring *only* the in-plane lattice parameters (a and b) of the constituting layers. By maintaining the angles of incidence and emergence very close to 0, in the case of the epitaxial layer the diffraction can originate only from crystalline planes which are perpendicular to the sample surface (*i.e.* $L \sim 0$). Performing the measurements at incident angles close (or slightly inferior) to the critical one ensures that the scattered signal originating from the bulk substrate is largely diminished. Figure 11 shows the results obtained for CFO / BTO bilayers of increasing CFO thickness (same thickness ratio). Like before, for each of the characteristic peaks of CFO and BTO, and for several orders of them, rocking scans were performed: the detector is maintained at fixed position (in the plane of the sample surface, characteristic of the corresponding diffraction peak) while the sample angular position (azimuth angle in this case) is scanned.

III.2.d X-ray diffraction (XRD) in grazing incidence geometry, out of the plane of the surface

This approach has the advantage of measuring *both* the in-plane and out-of-plane lattice parameters ($a = b$ and c) of the constituting layers. Like before, the angle of incidence is maintained very close to 0, thus the sample probed volume is limited (low penetration depth of the X-rays). Consequently, the scattered signal originating from the bulk substrate is largely diminished. By properly positioning the detector (see Figure 3) various (hkl) coordinates in the reciprocal space can be accessed. Either line scans (along L direction, for fixed H and K) or 2D maps can be performed, these

last ones offering more complete information. For the samples investigated here, typically (*HHL*) and (*HOL*) RSMs ($H \sim 2$, $L \sim 2$ r.l.u. of STO) were performed.

Figure 11: XRD in grazing incidence geometry, along the in-plane [H00] direction

X-ray diffraction datasets (grazing incidence geometry, in-plane along [H00] direction) for several increasing bilayer thickness (the relative thickness of the constituting layers is maintained constant). The thicknesses of the BTO / CFO layers are reported for each curve. Datasets are vertically shifted for better visibility. XRD peaks originating from BTO and CFO are pointed out.

Figure 12 schematically illustrates the signal distribution in the reciprocal space for a CFO / BTO / STO(001) system, as well as a 2D measurement around a particular region ((222)STO Bragg peak in this case, for the 15 nm CFO / 21 nm BTO / STO(001) sample), region in which both CFO and BTO will yield to significant scattered signal.

The measured RSMs for all the available samples are reported in Figures 13 and 14. From such datasets, each of the characteristic XRD peaks (CFO and BTO) are fitted using a 2D Gaussian function (see e.g. Supplementary Material in ref. [24]) and the corresponding parameters are extracted.

Figure 12: Reciprocal space for a CFO/BTO epitaxial layer deposited on STO(001) single crystalline substrate.

(left) Illustration of the reciprocal space for a CFO / BTO / STO(001) system, considering the particular crystalline structure and lattice parameters of the constituting layers. (right) Measured reciprocal space map (HKL plane) close to the (222)STO reflection (circled region on the left panel).

The H and L positions for each peak are converted to lattice parameters. As it can be seen in Figure 13, in some cases (mainly thinnest CFO layers), the scattered signal in the maps is too low in intensity to allow for a reliable mathematical fitting procedure. In this case, the peak positions were pointed out by hand on the RSM (and enhanced / saturated contrast & color levels were used).

Figure 13: Reciprocal space maps around (202) position

Reciprocal space maps around the (202) STO diffraction peak, for the samples on undoped STO substrate / SixS beamline measurements (logarithmic color scale, from white to black). Both H and L ranges are 1.6 - 2.2 r.l.u. of STO (grid = 0.1 r.l.u. of STO). The layer thickness (CFO / BTO) are reported for each panel. The extracted positions of the CFO and BTO peaks are marked by $\times$ and $+$ symbols respectively². The position of the (202)STO substrate peak is marked by an empty dot (o).

² For some samples exhibiting faint XRD signals in the map, RSMs around (222)STO peak were performed as well (not shown here); in such cases, the reported peak positions are deduced from these last mentioned measurements.

Figure 14: Reciprocal space maps around (222) position

Similar to Figure 13, reciprocal space maps around the (222) STO diffraction peak, for the samples on 1% Nb - doped substrate / DiffAbs beamline measurements. H and L ranges are respectively 1.65 - 2.15 and 1.6 - 2.1 r.l.u. of STO (grid = 0.1 r.l.u. of STO).

Figure 15 reports the CFO lattice parameter evolution vs. its thickness, for the thinnest (7 nm) BTO layer available [72]. The observed trend shows that for thicker CFO films, the in-plane strain is released and the film relaxes towards its bulk lattice parameter (0.838 nm). This relaxation is also happening in the direction perpendicular to the surface of the sample, and the c/a ratio approaches 1, *i.e.* the value in the bulk material. Importantly, the thinner ferrite films adopt a tetragonal lattice due to the epitaxial strain. A similar trend can also be observed for the BTO layers, for the fixed CFO thickness of 6.6 nm (Figure 16). The evolution is though more complex, since the

BTO layer is sandwiched between the STO substrate and the CFO film. This last one will try to impose its lattice parameter as well (in plane expansion), of amplitude depending of the actual CFO thickness used. The situation is also illustrated for CFO films thinner and thicker than this particular value of 6.6 nm.

Figure 15: CFO lattice parameters evolution

In-plane (a) and out-of-plane (c) CFO lattice parameters function of the layer thickness, for a fixed thickness of the BTO layer (7 nm). Adapted from [72]. The points corresponding to the thinnest layers were either omitted or extracted from positions pointed out by hand on the RSMs. The reported points for the 3.5 nm and 12 nm CFO thickness correspond to particular samples manufactured and measured (but not completely) in a different experimental campaign.

The very thin films of CFO (2.2 nm, Figure 16, left panel) could be expected to have very little effect, and the BTO lattice parameters to be found as the ones from RHEED measurements at the end of the deposition process (Figure 5). For the considered BTO thicknesses (7, 14 and 21 nm), RHEED data show that the in-plane lattice parameter of the film achieves the relaxed bulk value, ~ 0.4 nm [24,50]. Though, the measurement of the 2.2 nm CFO capped samples show that the in- and out-of-plane BTO lattice parameters are almost constant, amounting ~ 0.391 and 0.406 nm respectively (tetragonality $c/a \sim 1.038$). These values are significantly different from

the ones expected for the relaxed bulk, showing that even the thin 2.2 nm CFO films do have a significant effect.

Figure 16: BTO lattice parameters evolution

In-plane (*a*) and out-of-plane (*c*) BTO lattice parameters function of its thickness, for several CFO layer thicknesses. The reported points for the 3.5 nm CFO (first panel) and 20.5 nm BTO thickness (third panel) correspond to particular samples manufactured and measured (but not completely) in a different experimental campaign.

For thicker CFO samples (5 and 10 nm), the in-plane BTO lattice parameter ($a \sim 0.398$ nm) approaches the value found at the end of the growth of the BTO film (see above). One should note anyhow the larger *c* lattice parameter found for the thinnest (7 nm) BTO layer, amounting to a value similar to the one found for thinnest CFO capping. In this case, the 7 nm CFO layer seems to act already on the in-plane lattice parameter, but the BTO film mostly deforms in the plane of the surface. It is only when the CFO thickness is increased to 15 nm (Figure 16, right panel), that the *a* and *c* BTO lattice parameters seem to reach a “stable” and “relaxed” situation, which is closer to, but not exactly equal to, the bulk structure. The BTO tetragonality amounts in this case to a value of $c/a \sim 1.01$.

We mentioned earlier that for diffraction peaks characteristic to each of the 2 layers, and for several orders of them, their azimuthal and radial widths were measured

(either in separate line-scan measurements or from the RSMs datasets). The reciprocal space Bragg peak width is expected to be the result of the convolution of several contributing components: (i) a mosaic spread (angular mis-orientation between the crystallites constituting the epitaxial film) that is a constant angular azimuthal opening at any reciprocal momentum q value; (ii) a domain size that leads to a finite width Δq in reciprocal space for any peak, and (iii) a lattice parameter dispersion (micro strain) that will spread linearly with q . The azimuthal peak width, in a direction parallel to the sample surface, is significantly large and corresponds to mosaicity. In the direction perpendicular to the surface, the small finite thickness of the layer is dominating and is considered as domain size. The azimuthal width will be dominated by the first two effects and the radial one by the last two. Knowing the experimental widths for at least two peaks at different momentum transfer values is thus a minimum in order to determine these three contributions. Even if in some cases only one XRD peak was measured, data can be extracted by assuming some of the contributions as dominant, and the other(s) being neglected.

Table 2: structural parameters for CFO / BTO bilayers deposited on undoped STO(001) single crystalline substrates

BTO CFO			2.2 nm	4.4 nm	6.6 nm
7 nm	mosaicity (°)	CFO	1.06 ± 0.17	1.97 ± 0.15	1.72 ± 0.19
		BTO	1.20 ± 0.22	1.07 ± 0.22	0.86 ± 0.20
	domain size (nm)	CFO	147 ± 22	234 ± 13	237 ± 172
		BTO	209 ± 50	273 ± 118	172 ± 31
14 nm	mosaicity (°)	CFO	2.14 ± 0.18	1.74 ± 0.34	1.70 ± 0.05
		BTO	1.01 ± 0.07	0.99 ± 0.18	0.98 ± 0.10
	domain size (nm)	CFO	208 ± 131	114 ± 66	209 ± 61
		BTO	293 ± 121	255 ± 34	275 ± 135
21 nm	mosaicity (°)	CFO	1.35 ± 0.21	1.34 ± 0.28	1.07 ± 0.31
		BTO	0.98 ± 0.15	1.20 ± 0.07	1.05 ± 0.08
	domain size (nm)	CFO	224 ± 95	70 ± 14	61 ± 11
		BTO	300 ± 107	320 ± 164	144 ± 18

Mosaicity and crystalline domain size, values in the plane of the surface of the sample deduced from the XRD datasets (from [72]).

Table 2 reports the results for the bilayers prepared on the undoped STO substrates (SixS beamline measurements) [72]. The in-plane mosaicity, of both BTO and CFO films, seems to be rather low, in the 1.0 - 1.2° and 1.5 - 2.1° ranges respectively, showing the good crystalline quality of the epitaxial layers. The in-plane crystalline domain size has rather dispersed values and error bars, which does not allow pointing

out clear trends with respect to the thickness of the layers. Nevertheless, we can note a typical BTO domain size of about 250 nm (and not clearly dependent of the layer thickness) while this size becomes about half for the CFO films. The dispersion in the domain size data could also be a consequence of slightly different quality of the STO substrates used for preparing each sample.

The in-plane lattice parameters during growth of BTO showed that, at the early stages of the growth, because of the lattice mismatch, the BTO film undergoes a compressive biaxial in-plane stress generated by the substrate and adopts the in-plane lattice parameter of STO, with the deformation being in the elastic limit. Above 2 nm thickness, the strain relaxation proceeds in BTO / STO and the in-plane lattice parameter of BTO increases and reaches a full relaxation at about 8 nm thickness. These results are consistent with previous studies [28,50,81]. If the CFO film is grown on a fully relaxed (*i.e.* thick) BTO film, we observe again lattice relaxation occurring at the very first stages of growth [28], with a residual compressive stress. It is this one which seems to be ensuring the magnetoelectric coupling, enhanced *via* the ferroelasticity.

III.2.e XMCD / magnetism

XAS, XMCD and XNLD investigations have been performed on our CFO / BTO samples. The main idea was to characterize the electronic and magnetic structure of the ferrite layers. Such results, especially when correlated to the structural study, will allow to link electronic and magnetic properties with the structure of our films. The final aim was to optimize the preparation of our sample in order to improve their multiferroic properties.

With the XAS technique we are looking explicitly to the ferrite electronic properties as we are recording the $L_{2,3}$ edges of Fe and Co atoms. In the following figure 17 we have represented XMCD measurements taken on a 4.4 nm CFO / 7 nm BTO sample at the Co- $L_{2,3}$ edges. At first sight several observations can be made: additionally to the Co- $L_{2,3}$ edges showing multiplet features, as expected for cobalt oxides, 2 other strong features are visible. They correspond to the $M_{4,5}$ edges of barium from the BTO under layer. Actually the CFO layer is thin enough to allow the signal coming from BTO to be visible. We can also observe that the XMCD signal of the $M_{4,5}$ edges is zero as expected for this non-magnetic element. On figure 17 (left) we have represented the XMCD signals taken at saturation ($H = 5$ T magnetic field) and at $H = 0$ T corresponding to the signal at remanence. This remnant signal is approximately 50% less than the saturation one and confirms that the CFO is ferrimagnetic with a sizeable non-zero magnetization at remanence.

Figure 17: XMCD spectra: measurement and calculated

(left): XMCD spectra at the Co- $L_{2,3}$ edges on 4.4 nm CFO / 7 nm BTO. XAS spectra at the Co- $L_{2,3}$ edges including the $M_{4,5}$ edges of the barium from the BTO under layer. In green the XMCD curves done at 5 T (dark) and at 0 T (light). The XMCD signal on the Ba edges is null as expected for this non-magnetic material. The XMCD spectrum is the difference between two XAS spectra recorded with opposite orientation of the magnetic field and of the helicity of the light, which we will call XAS(+) and XAS(-) for simplicity. XAS(+) (XAS(-)) corresponds to the absorption coefficient of left- (right-) circularly polarized light, taking the direction of the magnetic field as the quantization axis. In practice a XMCD curve is obtained by averaging several XMCD signal taken by field and polarization reversal; (right) Calculated XMCD spectra, obtained using ligand field multiplet calculations, for the different Fe contributions found in a ferrite. From the calculation it can be seen that the general shape of the XMCD is similar for all coordinations and symmetries. The main differences are coming from the energy position of the peaks and the sign: ferromagnetic atoms are giving a dominant negative XMCD contribution at the L_3 edge. The main feature of Fe³⁺-Td at the L_3 -edge is positive because the Fe³⁺-Td atoms are antiferromagnetically coupled to the other contributions in a ferrite.

In order to go beyond these first conclusions it is mandatory to perform additional treatments. In the case of an oxide where the XMCD signal, for an atomic species, is actually coming from different electronic configurations, it is not possible to apply the

sum rules [73] and the only solution is to de-convolute the experimental spectra using experimental reference spectra of single phases or calculated spectra. We have used the second approach in order to interpret the different Fe and Co XMCD spectral features on the basis of ligand field multiplet calculations or on the basis of the configuration-interaction model, after taking into account the $3d$ electron configuration of the cation, the crystal field for each type of site, the spin-orbit coupling, the electron-electron interaction, and the hybridization effects [28]. For iron ferrites the different features are Fe^{2+} , $\text{Fe}^{3+}\text{-Td}$ and $\text{Fe}^{3+}\text{-Oh}$ and the ligand field multiplet calculations of each individual contribution are represented on figure 17 (right).

Figure 18: Deconvolution of the experimental XMCD spectra in terms of contributions of the ligand field multiplet XMCD spectra.

Results for (left) CFO films deposited on 7 nm BTO with the thickness ranging from 2.2 nm to 15 nm. (right) for a 14 nm BTO film and similar CFO thicknesses. The experimental XMCD spectra are plotted with open block symbols and the fits with a continuous line.

Using these reference curves it is now possible to fit the experimental XMCD spectra and express each of these spectra in terms of percentage of Fe^{2+} , $\text{Fe}^{3+}\text{-Td}$ and $\text{Fe}^{3+}\text{-Oh}$. Moreover, as these calculated spectra represent a single electronic configuration it is allowed to apply the sum rules [70,71] on it and deduce the orbital and spin

magnetic moment of Fe in the ferrite. Figure 18 presents the result of the deconvolution for different CFO thickness deposited on 7 nm and 14 nm film of BTO.

Looking at these XMCD spectra for the BTO film of 7 nm we can observe that the Fe^{2+} contribution (negative feature at lower energy) is more present for the lower coverages. This over-representation of Fe^{2+} indicates a reduction of the ferrite at lower coverages. This tendency is also present for the CFO films on 14 nm of BTO, but is less marked. This means that not only lower coverages of CFO favor the reduction of the ferrite at the interface but this Fe reduction is also increased for thin BTO layer. All these results are summarized in figure 19.

Figure 19: Dependence with the CFO thickness of the different Fe species (Fe^{2+} , Fe^{3+} -Td and Fe^{3+} -Oh) in the CFO overlayer.

Evolution of the percentage of Fe^{2+} (black), Fe^{3+} -Td (green), Fe^{3+} -Oh (red) with the CFO thickness. The blue curves correspond to the spinel inversion factor deduced from the percentage of Fe^{3+} -Td. (see formulae Section II). The full symbols are for the 7 nm BTO films and the open symbols for the 14 nm BTO films.

Figure 19 clearly illustrates the fact that low CFO thickness favor Fe^{2+} to the detriment of Fe^{3+} . The relative Fe^{3+} -Td and Fe^{3+} -Oh contributions indicate a typical ~80-90% inverse spinel configuration for the CFO films thicker than 4 nm (see formulae Section II). This reduction of Fe at lower coverage can be interpreted as an interface reactivity occurring during growth. However, it results from a more complex mechanism since it

is also dependent on the BTO thickness.

Figure 20: XMCD vs. XNLD: evidence of the lattice distortion of the ferrite cell for different CFO thickness.

(a) XMCD at the Co- L_3 edge (taken at $H=5T$), (b) XNLD at the Co- L_3 edge, (c) XNLD at the Fe- $L_{2,3}$ edge. The XNLD is obtained by taking the difference between XAS spectra taken with linear horizontal and vertical polarized light. In our case the sample is at 60° grazing angle meaning that we are probing the charge anisotropy between the surface and the direction perpendicular to the surface (while with the a geometry with the beam normal to the surface plane we would probe the in plane anisotropy).

In parallel to what is observed on the Fe edge the XNLD on the Co $L_{2,3}$ -edges bring other additional information. From the XMCD (see figure 20 (a)) we clearly see that the magnetic signal at 5 T for 2.2 nm CFO films is 5 to 6 times smaller than the one measured for 4.4 nm and 6.6 nm CFO films. If we compare the XNLD at the Co L_3 -

edge (see figure 20 (b)) we also observe a strong dependence with the CFO coverage: for the thin sample (2.2 nm) we measure a strong XNLD signal that is correlated to the tetragonalization of the lattice as also put into evidence by the diffraction experiments. This lattice distortion more strongly impacts the Co sites as it is not observed any significant change of the XNLD signal at the Fe $L_{2,3}$ -edges (see figure 20 (c)).

The XAS at the Co $L_{2,3}$ -edges allow to directly link the disappearance of the magnetism at the Co sites with the lattice distortion of the ferrite unit cell as to the large XNLD signal correspond a very small XMCD.

IV. Conclusion

In this review chapter we have presented a series of results concerning laminar artificial multiferroic structures realized with CoFe_2O_4 and BaTiO_3 thin films on $\text{SrTiO}_3(001)$ single crystalline substrates. AO-MBE has been successfully used to realize fully epitaxial structures with respective film thicknesses in the 2 - 21 nm range. Detailed synchrotron radiation x-ray diffraction measurements were conducted to investigate the internal strain in the samples. Within our thickness range the epitaxial strain is progressively released for both layers. Notably, the strain state of a stack is found depending on both thicknesses demonstrating that the sandwiched BaTiO_3 layers experience epitaxial stress from the substrate and from the overlayer, the latter being itself strained by the BaTiO_3 layer. The final lattices parameters result from the balance between all elastic deformations.

The magnetic properties of these bilayers were investigated by synchrotron x-ray magnetic dichroism measurements, an element sensitive technique that allows determining the ions site occupation with high sensitivity as well as the magnetic moment carried by ions in specific sites. The layers were found mainly ($\sim 80\%$) of inverse spinel type. The total magnetization results from the subtle interplay between several antagonist phenomena: chemical interface reduction leads to an increasing amount of more magnetic Fe^{2+} and less magnetic Co^{2+} for the thinnest layers. Importantly the CoFe_2O_4 spinel layer experiences a strong tetragonal deformation in the early stages of growth that explains well the loss of magnetization for the strained thin layers.

This study exemplifies the possibility to use strain engineering to produce

nanomaterials with new and tunable properties. Our results demonstrate the key role of structural strain in the onset of artificial multiferroicity stressing the need to use films thin enough to experience elastic epitaxial strain. All phenomena were found dependent on both, the CoFe_2O_4 and BaTiO_3 film thicknesses, highlighting strong cross-correlations in such laminar systems and the need for a careful investigation of the structural and ferroic properties in an unified approach in order to understand the underlying multiferroic coupling mechanisms.

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