Unravelling the origin of the controversial magnetic properties of BiFeO$_3$ thin films

Hélène Béa,\textsuperscript{1} Manuel Bibes,\textsuperscript{2} Eric Jacquet,\textsuperscript{1} Karsten Rode,\textsuperscript{1} Peter Bencok,\textsuperscript{3} and Agnès Barthélemy\textsuperscript{1}

\textsuperscript{1}Unité Mixte de Physique CNRS/Thales, Route Départementale 128, 91767 Palaiseau, France
\textsuperscript{2}Institut d’Electronique Fondamentale, Université Paris-Sud, 91120 Orsay, France
\textsuperscript{3}European Synchrotron Radiation Facility (ESRF), 38043 Grenoble Cedex, France

(Dated: January 7, 2022)

Single phase (001)-oriented BiFeO$_3$ (BFO) thin films grown by pulsed laser deposition can only be obtained in a narrow window of deposition pressure and temperature and have a low magnetic moment. Out of the stability window Fe- or Bi-rich impurity phases form, which has a strong impact on the physical and structural properties of the films, even for impurity concentrations hardly detectable by standard X-ray diffraction measurements. By using more sensitive tools such as X-Ray absorption spectroscopy and X-ray magnetic circular dichroism and performing advanced X-ray diffraction characterization, we show that in non-optimal conditions Fe forms ferrimagnetic $\gamma$-Fe$_2$O$_3$ precipitates that are responsible for virtually all the ferromagnetic signal measured on such BFO films by standard magnetometry. This confirms that the BFO phase has a very low intrinsic moment that does not depend on strain. We also study the influence of film thickness on the nucleation of parasitic phases and find that epitaxial strain can stabilize the pure BFO phase in slightly over-oxidizing growth conditions.

PACS numbers: 75.50 Gg, 75.70 Cn, 81.15 Cd

Multiferroic materials display simultaneously several types of order, like ferroelectricity and magnetism\textsuperscript{4,5}. Beside their exciting physics, multiferroics could bring solutions for applications in many fields, like agile electromagnetics, optoelectronics or spintronics. Indeed, the magnetoelectric coupling existing in multiferroics could allow to reverse magnetization by applying an electric field instead of a magnetic field.

To achieve this, a straightforward way would be to use a ferromagnetic layer coupled to a ferromagnetic multiferroic. However, such ferromagnetic multiferroics are extremely rare, a known exception being BiMnO$_3$ that has a magnetic Curie point ($T_C$) well below room temperature. In fact, most multiferroics are antiferromagnetic or weak ferromagnets. In this context, the report of a gigantic enhancement of the magnetic moment in BiFeO$_3$ (BFO) thin films compared to bulk\textsuperscript{1} was very exciting given the high magnetic transition temperature of this compound (640K). Yet, some controversy over these results appeared shortly after publication and the intrinsic magnetic properties of BiFeO$_3$ films are still debated\textsuperscript{5,6}.

A few months ago, we reported that single-phase BFO films can only be obtained in a rather narrow range of deposition pressure $P_{O_2}$, and temperature\textsuperscript{7}. We found that films not showing indications of parasitic Fe-rich phases have a low bulk-like magnetic moment ($\sim$0.02 $\mu_B$/Fe)\textsuperscript{1} while films containing Fe oxides display a ferromagnetic behavior. Even though this suggests that in these impure films all the ferromagnetic signal comes from the Fe oxides, it is not clear whether the BFO phase in such films could not have some ferromagnetic moment. In this article, we have addressed this issue more quantitatively and demonstrate that even in Fe-oxide-rich samples the BFO phase has virtually no magnetic moment, irrespective of its strain state. We also address the influence of strain on the nucleation of extra-phases and find that in over-oxidizing conditions tending to favour the presence of Bi oxides, strain actually helps to stabilize the BFO phase.

The films were grown by pulsed laser deposition on (001)-oriented SrTiO$_3$ (STO) substrates. In order to study the structure of the films, we performed high-resolution X-ray diffraction (XRD) using a Panalytical X’pert PRO equipped with a Ge (220) monochromator. Magnetization loops were measured at 10K with the magnetic field oriented in-plane using a Superconducting Quantum Interference Device (SQUID).

X-ray Absorption Spectroscopy (XAS) and X-ray Circular Magnetic Dichroism (XMCD) were performed at the ID08 line of the European Synchrotron Radiation Facility at the Fe L$_3$ edges, at 10K. Both magnetic field ($\pm$ 6T) and propagation vector of photons were perpendicular to the sample surface with a circular polarization of nearly 100%. The spectra were collected in the total electron yield mode that has a typical probing depth of $\sim$50Å in oxides.

| Film | $P_{O_2}$ (mbar) | $t$ (nm) | %BFO | $\%\gamma$-Fe$_2$O$_3$ | $\%$Bi$_2$O$_3$ |
|------|-----------------|--------|-------|------------------------|-----------------|
| $\sharp 1$ | $10^{-4}$ | 120 | 52±1.5 | 48±1.5 | <0.4 |
| $\sharp 2$ | $10^{-3}$ | 25 | 81±2 | 19±2 | <1.7 |
| $\sharp 3$ | $10^{-3}$ | 60 | 79±2 | 21±2 | <0.7 |
| $\sharp 4$ | $10^{-3}$ | 100 | 87±1.5 | 13±1.5 | <0.5 |
| $\sharp 5$ | $6 \times 10^{-3}$ | 35 | >97.2 | <1.4 | <1.4 |
| $\sharp 6$ | $1.2 \times 10^{-2}$ | 70 | >98.7 | <0.7 | <0.6 |
| $\sharp 7$ | $1.2 \times 10^{-2}$ | 120 | 83±2 | <0.4 | 17±2 |
| $\sharp 8$ | $1.2 \times 10^{-2}$ | 240 | 79±2 | <0.2 | 21±2 |

For this study, we have fixed the deposition tempera-
Fe$_{1.25}$ for $t \geq 120$ nm, Bi$_2$O$_3$ phases are detected. This suggests different mechanisms for the appearance of Fe- and Bi-rich phases. We will study in the following the influence of these extra-phases on the structure and properties of the films.

At this point it is important to recall that all films without parasitic phases (e.g. films grown at 6 $10^{-3}$ mbar) have very low magnetic moments ($\leq 0.02 \mu_B$/Fe). In figure 1b, we show XRD spectra for films $\sharp 1$ to 4 grown at $10^{-4}$ and $10^{-3}$ mbar. In addition to the (00l) peaks due to STO and BFO, several peaks corresponding to $\gamma$-Fe$_2$O$_3$ reflections are detected. This is particularly clear for the film $\sharp 1$. At $10^{-3}$ mbar only the (800) peak of $\gamma$-Fe$_2$O$_3$ is visible but lies on the edge of the BFO (004) peak. This parasitic phase is thus not easily detectable by XRD and from these data it is not possible to conclude on the presence or absence of $\gamma$-Fe$_2$O$_3$ in the thinner film. We also note that for the $10^{-3}$ mbar series, the position of the BFO peaks varies due to strain relaxation occurring upon increasing $t$.

Figure 1c shows magnetization hysteresis cycles $M(H)$ for these four films. Remarkably, the three samples grown at $P_{O_2}=10^{-3}$ mbar show the same volumic magnetic moment. For the film $\sharp 1$, the volumic magnetic moment is larger which also corresponds to a larger proportion of $\gamma$-Fe$_2$O$_3$ as detected by XRD.

The observation of a large magnetic moment for the film $\sharp 2$ suggests the presence of $\gamma$-Fe$_2$O$_3$ even though standard XRD could not detect it. To solve this issue we performed additional XRD with much longer counting times in the $2\theta = 93$–98° range so as to increase the signal-to-noise ratio, see figure 2a. On this scan, a shoulder is clearly visible at the left of the BFO (004) peak, located at $2\theta \approx 95.5^\circ$, i.e. where the (800) reflection of $\gamma$-Fe$_2$O$_3$ shows up for the thicker films.

To better quantify the relation between the amount of maghemite and the magnetization, we have fitted the XRD spectra in the $2\theta = 90$–98° range with three pseudo-Voigt functions corresponding to the (004) BFO peak, the (004) STO peak and the (800) $\gamma$-Fe$_2$O$_3$ peak. The STO fit allows to normalize the area of the $\gamma$-Fe$_2$O$_3$ peak to that of a substrate peak. We thus obtain the area $A$ of the $\gamma$-Fe$_2$O$_3$ (800) peak, proportional to the volume of $\gamma$-Fe$_2$O$_3$ present in the film (see an example of such fits in figure 2b). As visible in figure 2a, $M$ increases linearly with $A$, which shows that the magnetic signal in these films is proportional to the amount of $\gamma$-Fe$_2$O$_3$. Of great relevance is the observation that the magnetization extrapolates to zero for $A=0$ hence demonstrating that in these films, virtually all the magnetic signal comes from $\gamma$-Fe$_2$O$_3$. In other words, the BFO phase has a very low magnetization, if any. Reciprocal space mappings collected on the films considered in the above analysis reveal a variety of strain states (see insets in fig.2a). Hence, our observation of a very low moment for the BFO phase in all these films rules out a role of strain in increasing the BFO magnetization for this range of growth pressure and temperature. This is in contrast to what was suggested...
The bold line is a fit of the (004) BFO and (800) γ-Fe$_2$O$_3$ peaks. The upper spectrum is a zoom of the fig. 1b. The lower one and XMCD measurements on films with Eerenstein state for a 100 nm film (right), both grown at 10 mbar. The reciprocal space maps of the (013) reflections reveal a fully saturated magnetization for samples grown at 10 mbar but in agreement with theoretical predictions by Wang et al. l. u. stands for reciprocal lattice units.

In pure BFO, Fe is octahedrally surrounded and the iron valence is also 3+ but 5 of the 8 Fe ions contained in a unit-cell are in octahedral (Oh) sites while the other 3 are in tetrahedral (Td) sites. In γ-Fe$_2$O$_3$ the iron valence is also 3+ but 5 of the 8 Fe ions are in tetrahedral (Td) sites in this latter sample. Consistent with this observation is the lower XAS signal measured at the 721.5 eV peak. We conclude that film #2 has a larger proportion of Fe$^{3+}$ in Td sites, as expected in the presence of γ-Fe$_2$O$_3$.

In film #5 no clear XMCD signal was measured, suggesting a very low magnetic moment, in agreement with SQUID results. On sample #2 we find a large dichroic signal (see figure 3d), very similar to that of γ-Fe$_2$O$_3$. More quantitatively, we can calculate the spin moment $M_S$ and the orbital moment $M_L$ using the sum rules, which yields $M_S = 0.22 \pm 0.05 \mu_B$/Fe and $M_L = 0.02 \pm 0.005 \mu_B$/Fe. The total magnetic moment is $M = M_S + M_L = 0.24 \pm 0.06 \mu_B$/Fe, in very good agreement with the magnetization measured by SQUID, 40 emu.cm$^{-3}$ or 0.27 $\mu_B$/Fe. Since bulk maghemite has a magnetic moment of 1.25 $\mu_B$/Fe, the proportion of γ-Fe$_2$O$_3$ near the surface (probed by XMCD) is thus close to the 20% calculated for the volume (see table I). Therefore, the distribution of this extra phase in the film seems to be homogeneous, which is consistent with the presence of γ-Fe$_2$O$_3$ for all thicknesses, particularly for the lower ones.

We now examine in more detail the high-pressure region of the diagram shown in figure 1a. In figure 1b, XRD spectra of samples grown at 1.2 $10^{-2}$ mbar with different thicknesses are shown. For the thinner film, no parasitic phases are observed, even for long counting rates (not shown), while at larger $t$ Bi$_2$O$_3$ lines show up. On the AFM images of fig. 1d, we can see that the detection of Bi$_2$O$_3$ is accompanied by the nucleation of square outgrowths on the surface for $t \geq 120$ nm. Auger electron spectroscopy confirmed that these hillocks are Bi-rich and Fe-poor, thus likely corresponding to Bi$_2$O$_3$ (Ref. 4). When $t$ increases, these outgrowths become higher (as high as the film thickness).
groups phases by strain has indeed been reported by several different $\Delta g$ phase is given by:

$$\Delta g = t\left[\Delta g_S - \Delta g_M\right] - \frac{\mu}{1 - \nu} \epsilon^2 + \left(\sigma_S^2 - \sigma_M^2\right)$$  

(1)

$\Delta g_S$ and $\Delta g_M$ are the stable and metastable phase formation energies, respectively, $\mu$ and $\nu$ the shear and Poisson coefficients of the metastable phase, $\epsilon$ the strain and $\sigma_S^2$ and $\sigma_M^2$, the interface energies for the stable and metastable phases, respectively. In principle the first term is always negative. The second term is positive if, for instance, the interface between the metastable phase and the substrate is coherent (i.e. the metastable phases grows in a fully strained state) while the interface between the stable phase and the substrate is not (e.g. if the mismatch between the stable phase and the substrate is large). Thus, when $t$ is small $\Delta g$ can be positive and the growth of the metastable phase is favoured but there is a critical thickness $t_c$ above which $\Delta g$ becomes negative which leads to the formation of the stable phase. On the other hand, if the structure of the metastable phase relaxes (hence enhancing its interface energy) the formation of the stable phase can become more favourable for $t < t_c$.

In our case, we have seen that BFO grows fully strained on the STO substrate up to $t \approx 70 \text{ nm}$ so that the BFO/STO interface energy $\sigma_{BFO/STO}$ is low and the conditions for the growth of the metastable BFO phase are met. The formation of $\text{Bi}_2\text{O}_3$ occurs when BFO relaxes, hence increasing $\sigma_{BFO/STO}$. It is thus tempting to conclude that this relaxation unbalances equation (1) and favours the formation of the stable $\text{Bi}_2\text{O}_3$ phase. However, since many parameters in equation (1) are unknown, it is not possible to calculate $t_c$. Thus we cannot be fully conclusive on whether the formation of $\text{Bi}_2\text{O}_3$ is just related to the thickness increase or directly due to the observed structural relaxation.

In summary, we have found that epitaxial BFO films grown at 6 $10^{-3}$ mbar are single-phase for thicknesses up to at least 240 nm. For lower pressures, all the films contain $\gamma$-Fe$_2$O$_3$, as evidenced by XRD, XAS and XMCD. We showed that this extra phase is responsible for all the magnetic moment in the film so that, at least in all the range of growth conditions we have explored, the BFO phase has a very low magnetic moment, if any. At 1.2 $10^{-2}$ mbar BFO films are also single-phase for $t \leq 70 \text{ nm}$ while $\text{Bi}_2\text{O}_3$ appears in the film above that thickness. Reciprocal space maps analysis suggests a role of strain in stabilizing a metastable BFO phase at this pressure.

Acknowledgments

Enlightening discussions with F. Petroff, V. Cros and K. Bouzehouane are gratefully acknowledged. This work has been supported by the E.U. STREP MACOMUFI (033221) and the contract FEMMES of the Agence Nationale pour la Recherche. H.B. also acknowledges financial support from the Conseil Général de l’Essonne.

---

* Electronic address: manuel.bibes@iee.u-psud.fr
† Now at Physics Department, Trinity College, Dublin 2, Ireland

1 N.A. Hill, J. Phys. Chem. B 104, 6694 (2000).
2 G.A. Smolenskii and I.E. Chupis, Sov. Phys. Usp. 25, 475 (1982).
3 V.E. Wood and A.E. Austin, Int. J. Magn. 5, 303 (1974).
4 I. Žutić, J. Fabian, and S. Das Sarma, Rev. Mod. Phys. 76, 323 (2004).
5 M. Fiebig, J. Phys. D.: Appl. Phys. 38, R123 (2005).
6 Ch. Binek and B. Doudin, J. Phys.: Condens. Matter 17, L39 (2005).
7 Ch. Binek, A. Hochstrat, X. Chen, P. Borisov, W. Klemann and B. Doudin, J. Appl. Phys. 97, 10C514 (2005).
8 J. Wang, J.B. Neaton, H. Zheng, V. Nagarajan, S.B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D.G. Schlom, U.V. Waghmare, N.A. Spaldin, K.M. Rabe, M. Wuttig and R. Ramesh, Science 299, 1719 (2003).
9 H. Béa, M. Bibes, A. Barthélémy, K. Bouzehouane, A. Khodan, J.-P. Contour, S. Fusil, F. Wyczisk, A. Forget, D. Lebeugle, D. Colson and M. Viret, Appl. Phys. Lett. 88, 062502 (2005).
10 W. Eerenstein, F.D. Morrison, J. Dho, M.G. Blamire, J.F. Scott and N.D. Mathur, Science 307, 1203a (2005).
11 F. Bai, J. Wang, M. Wuttig, J. Li, N. Wang, A.P. Pyatkov, A.K. Zvezdin, L.E. Cross and D. Viehland, Appl. Phys. Lett. 86, 032511 (2005).
12 C.P. Hunt, B.M. Moskowitz, and S.K. Banerjee, Rock Physics and Phase Transitions, a Handbook of Physical Constants (1995).
13 C. Ederer and N.A. Spaldin, Phys. Rev. B 71, 224103 (2005).
14 J.M.D. Coey, Phys. Rev. Lett. 27, 1140 (1971).
15 S. Czekaj, F. Nolting, L.J. Heyderman, P.R. Willmott, and G. van der Laan, Phys. Rev. B 73, 020401(R) (2006).
16 P. Morrall, F. Schedin, G.S. Case, M.F. Thomas, E. Dudzik, G. van der Laan and G. Thornton, Phys. Rev. B 67, 214408 (2003).
17 J.P. Crocombette, M. Pollak, F. Jollet, N. Thromat, and M. Gautier-Soyer, Phys. Rev. B 52, 3143 (1995).
18 S. Brice-Profeta, M.-A. Arrio, E. Tronc, N. Menguy, I. Letard, C. Cartier dit Moulin, M. Noguès, C. Chanéac, J.-P. Jolivet and Ph. Sainctavit, J. Magn. Magn. Mater. 288, 354 (2005).
19 M.A. Novojilov, O.Y. Gorbenko, I.E. Graboy, A.R. Kaul, H.W. Zandbergen, N.A. Babushkina and L.M. Belova, Appl. Phys. Lett. 76, 2041 (2000).
20 S.V. Samoylenkov O.Y. Gorbenko, I.E. Graboy, A.R. Kaul, H.W. Zandbergen and E. Connolly, Chem. Mater. 11, 2417 (1999).