Electric field control of ferromagnetism using multi-ferroics: the bismuth ferrite story

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Since the re-emergence of multi-ferroics and magnetoelectrics almost a decade ago, bismuth ferrite has been among the most heavily studied model system. It is a multi-ferroic with robust ferroelectricity and antiferromagnetism, in conjunction with weak ferromagnetism arising primarily from spin–orbit coupling effects. This material system has generated a significant amount of discussion in the community, because many of the physical properties measured in thin films are different from the bulk. This paper summarizes some of the key observations in this versatile materials system, with a particular focus on thin films, heterostructures and interfacial phenomena.

1. Introduction

During the past couple of decades, complex oxides have attracted intense research interest especially from the condensed matter physics and materials science communities. They present a broad range of interesting functionalities, such as high-temperature superconductivity, colossal magnetoresistance, (anti-) ferromagnetic, (anti-)ferroelectric, piezoelectric and more recently multi-ferroic properties. The rich spectrum of materials physics involved has triggered extensive studies to understand the fundamental nature of existing systems, so as to control/design novel materials for applications.

BiFeO$_3$ (BFO) is the only room temperature multi-ferroic (antiferromagnetic and ferroelectric), so far, which has attracted great interest and extensive investigation in the past decade. It has a rhombohedral unit cell, built with two distorted perovskite cells connected along
a pseudo-cubic [111] direction [1,2]. It is also a G-type antiferromagnet with Néel temperature of approximately 673 K [100] and a symmetry-allowed, small canted moment owing to the Dzyaloshinskii–Moriya interaction [2,3]. The hybridization between the two 6s electrons in Bi [4] with surrounding oxygen ions leads to a large displacement of the Bi cations relative to the oxygen octahedral along the [111] direction with a Curie temperature of 1103 K and the spontaneous ferroelectric polarization of about 90 µC.m⁻² [5]. In the following, I describe three examples of the physical responses of this fascinating material; in all three cases, the focus is on novel phenomena that manifest themselves at interfaces, be they within the material or in contact with other materials.

2. Domains and domain walls

The synthesis of high-quality epitaxial thin films through a variety of techniques (pulsed laser deposition, sputtering, molecular beam epitaxy, chemical vapour deposition) has already been well established [6]. These films have become ‘model’ systems to study domain formation and to study the properties of domain walls [7]. The underlying crystallography of this system in conjunction with the elastic (through epitaxy) and electrostatic boundary conditions provides the framework for the formation of domains. Two general types of domain structures are observed, one comprising arrays of 71° domain walls and the other with an array of 109° domain walls. They both exhibit an array of fascinating electrical–optical–magnetic responses [8,9], once again highlighting the versatility of this materials system. For example, figure 1 shows the magnetotransport behaviour of 109° domain walls, an atomic resolution image of which is shown in figure 1a. Conducting atomic force microscopy (AFM)-based measurements (figure 1b) show that the walls are less resistive (compared with the domain itself), typically by two to three orders of magnitude [10]. Temperature-dependent measurements show that the transport is still semiconducting in nature, albeit with a smaller activation energy. In order to truly confirm that there is enhanced conduction through the domain walls, we carried out macroscopic transport measurements through an array of such domain walls. Macroscopic magnetotransport studies (figure 1c, d) show the existence of a large magnetoresistance when the transport direction and magnetic field direction coincide along the wall plane [10]. This suggests a possible magnetotransport mechanism roughly akin to that in the colossal magnetoresistive manganites, albeit in two dimensions, in which the magnetic moments in the domain wall plane behave like those in a spin glass; an applied magnetic field aligns the moments and thus reduces the resistance to transport. Of particular interest is the low-temperature magnetotransport data in figure 1d. Below approximately 50 K, the resistance in a magnetic field of 8 T shows a positive temperature coefficient, i.e. it decreases with decreasing temperature. We have not yet explored the transport properties at temperatures below 10 K; it would be fascinating to study the possible emergence of metallic behaviour at the domain walls. Indeed, this would be an exciting challenge for the field of complex oxides; namely, to make domain walls that are metallic (and perhaps ferromagnetic) in nature in an otherwise insulating ferroelectric, similar to the work of Aird & Salje [11].

3. Phase control through epitaxial constraints

An interesting manifestation of the power of epitaxy is the ability to distort and eventually change the ground state of the system through epitaxial strain. The evolution of the structural state can be understood from ab initio calculations (figure 2a). As an in-plane compressive strain is imposed via the substrate, the rhombohedral (R) structure becomes progressively monoclinic (and perhaps even triclinic), until a critical strain of approximately 4.5% is reached. For substrates that impose a larger strain (such as YAlO₃), the structure changes into a ‘super-tetragonal’ (T) state (or a monoclinic derivative thereof) with a distinct jump [12]. Such an isostructural phase transition, in which the symmetry does not change but the coordination chemistry changes
Figure 1. (a) An atomic resolution transmission electron microscopy (TEM) image of the 109° domain wall (DW). (b) Conducting AFM image of transport through such domain walls. (c) Macroscopic magnetotransport data through an array of 109° walls showing the significant magnetoresistance (MR) for transport and magnetic field (H) parallel to the wall while transport and/or H normal to the wall shows very little magnetoresistance. (d) Temperature dependence of the resistance and magnetoresistant behaviour. (Online version in colour.)

dramatically, has been observed in other materials systems [13–18]. Partial relaxation of the epitaxial constraint by increasing the film thickness leads to the formation of a mixed phase nanostructure which exhibits the coexistence of both the R- and T-phases, as illustrated in the AFM image in figure 2b. This mixed phase nanostructure is fascinating from many perspectives. First, high-resolution electron microscopy shows that the interface between these two phases is essentially coherent (figure 2c). This is important because it means that movement of this interface should be possible simply by the application of an electric field, as is indeed the case [19]. Second, and perhaps more importantly, the highly distorted R-phase, in this ensemble, shows a significantly enhanced ferromagnetism. This can be discerned from the X-ray magnetic circular dichroism–photoemission electron microscopy (XMCD–PEEM) image in figure 2d. The R-phase appears in either bright or dark stripe-like contrast in such PEEM images, corresponding to the thin sliver being magnetized along the X-ray polarization direction or anti-parallel to it. A rough estimate of the magnetic moment of this highly strained R-phase (from the PEEM images as well as from superconducting quantum interference device measurements) gives a local moment of the order of 25–35 emu ml\(^{-1}\). It is noteworthy that the canted moment of the R-phase (approx. 6–8 emu ml\(^{-1}\)) is not observable by the XMCD technique owing to the small magnitude of the moment. Our work has shown that this enhanced magnetic moment in the highly strained R-phase disappears around 150°C; further, application of an electric field converts this mixed phase into the T-phase, and the enhanced magnetic moment disappears; reversal of the field brings the mixed phase back accompanied by the magnetic moment in the distorted R-phase [20]. These observations raise several questions: first, what is the magnetic state of the strained R-phase? Given that the spin–orbit coupling is the source of the canted moment in the bulk of BFO, can this enhanced moment be explained based on the strain and confinement imposed on the R-phase? What is the state of the Dzyalozhinski–Moriya vector in such a strained system?
4. Exchange bias coupling and electric field control of magnetism

By far the most exciting aspect of work on multi-ferroics is the potential to control magnetism (AFM or ferromagnetism) with an electric field. While this is of fundamental importance (i.e. how does one couple an axial vector to a polar vector with high efficiency?) and harks back to Maxwell’s equations describing electromagnetism, the potential technological implications are equally tantalizing. Specifically, if one is able to switch ferromagnetism with an electric field in a robust and repeatable manner, then the potential to create information storage and communication devices that consume much less energy than devices driven by electric currents (e.g. magnetic random access memory that embeds spin valves and tunnel junctions and is manipulated by currents). Thus, the first step is to ask the question: is there coupling between ferroelectricity and antiferromagnetism? The simplest of possibilities would be the one in which the ferroelectric polarization is switched by $180^\circ$ and this leads to a corresponding rotation of the antiferromagnetic vector, $L$. However, this does not appear to be the case, at least from a theoretical perspective [21]. On the other hand, ferroelastic rotations of the polarization vector, for example through a $71^\circ$ or $109^\circ$ switching process, do indeed change the AFM vector direction.
Figure 3. (a) A PEEM image obtained using linearly polarized X-ray showing the formation of antiferromagnetic domains that correspond to ferroelectric domains (b). (c, d) The corresponding images after a portion of the same region was electrically switched, supporting the notion that the antiferromagnetism rotates along with the ferroelectric polarization for ferroelastic switching events. (Online version in colour.)

in thin films, as captured in figure 3. This has also been confirmed by neutron scattering studies in single crystals [22]. It is interesting to note that work to explore the electric field manipulation of antiferromagnetic electromagnons is just in the early stages [23]. Thus, although electric field control of the AFM state is now well established, the inability of the AFM state to be sensed by the external world, unlike ferromagnetism, is an impediment. Therefore, a significant focus in recent years has been on exchange-coupled ferromagnetism–AFM heterostructures.

Two types of ferromagnets can be envisioned. The first is a conventional ferromagnet, such as CoFe (or other such metallic ferromagnets; figure 4a). A significant amount of exchange coupling studies between such ferromagnets and multi-ferroics have already been carried out in previous work. Magnetic coupling, manifested as a combination of a directional, exchange bias as well as an enhancement of the coercive field, has now been well established. An interesting aspect of the interfacial coupling is the role of domain walls in influencing the coupling mechanism; for example, samples with a high density of \(10^9\)° domain walls invariably show a strong exchange bias, suggesting that the uncompensated moments at the domain walls (figure 1) are likely to be possible sources for exchange bias. More recent work using a combination of element-specific X-ray spectromicroscopy, magnetotransport and scanning electron microscopy polarization analysis has demonstrated the direct coupling between the canted moment in a domain and the moment in the CoFe ferromagnet (figure 4b) [24,25]. Angle-dependent magnetic measurements clearly show that the externally applied magnetic field is not the most important parameter; instead, the internal coupling between the canted moment in the BFO and the ferromagnetic moment in the CoFe appears to be more important (figure 4c). This coupling is also evident from direct PEEM imaging of the CoFe layer (figure 4d). There is a direct, one-to-one correlation of the ferroelectric domains (shown at the top) and the magnetic ‘domains’ in the ferromagnet (shown at the bottom). Such a correlation is useful in establishing the notion that the ferromagnetic moment in the CoFe layer is coupling to the canted moment in the BFO layer (which incidentally projects normal to the domain long axis). Having established the coupling, many critical questions remain...
Figure 4. (a) A high-resolution TEM image of a CoFe/BFO interface showing the abrupt nature of this interface. (b) A piezo force microscopy (PFM) image along with a schematic of how the canted moment ($M_{\text{canted}}$) aligns in such a two-domained BFO structure. $P_{\text{net IP}}$, net in-plane polarization. (c) Easy and hard axis ferromagnetic hysteresis loops for the CoFe layer, with the field applied parallel and normal to the canted moment direction. Note that the easy axis is always along the direction of the canted moment in the BFO layer. (d) PFM image (top) and the corresponding Co-XMCD–PEEM image (bottom) showing the one-to-one correlation of the ferroelectric domains in the BFO and magnetic domains in the CoFe layer. (Online version in colour.)

to be answered. For example, how robust is this interfacial coupling, particularly with respect to repeated switching of the ferroelectric? Can the magnetic moment in the CoFe layer be indeed switched by $180^\circ$ by switching the ferroelectric out of plane by a commensurate $180^\circ$?

In oxide ferromagnets, such as La–Sr–Mn–O (LSMO), we observe several fascinating interfacial phenomena. At such epitaxial interfaces, all the degrees of freedom, namely the spin, charge, orbital and lattice degrees, are likely to be active, especially in materials such as BFO, as illustrated in figure 5a, b. As recent reviews have already dealt with the possible origins of the magnetic coupling and the electric field control of this magnetic coupling [26], the reader is requested to refer to them to explore these topics. Most interestingly, an enhanced magnetic moment in the BFO layer is observed right at the interface (figure 5c) and is one of the key indicators that the charge, spin and orbital structure at such interfaces can be quite different from the bulk. Similar enhancements of the magnetic moment in BFO have also been observed in BFO/LSMO superlattices [27]. Of interest as well is the recent proposal of a suppression in the oxygen-octahedral tilt at the BFO/LSMO interface [28] (figure 5d). These results, coupled with the observation of magnetism and magnetotransport at domain walls (figure 1), strongly indicate that interfaces do indeed have significantly different magnetic behaviour.
Figure 5. Orbital reconstruction and origin of emergence of novel interface magnetic structures. (a) Interface orbital reconstruction owing to the electronic hybridization. (b) Schematic of the origin of the interface magnetism owing to the strong magnetic coupling across the interface and (c) the proposed spin structures across the interface. CB, conduction band; VB, valence band. (d) The experimentally measured (using scanning TEM) rotation angles [24] for a BFO/LSMO interface. (Online version in colour.)

electromagnetic devices

Figure 6. A schematic summary of the three focus areas in a new programme, TANMS, that has been recently supported to explore device applications of multi-ferroics and magnetoelectrics. (Online version in colour.)
Where are we going? So, in the current reincarnation, we have seen almost 10 years of basic science on multi-ferroics and magnetoelectrics and have learnt a huge amount about the intricacies of such coupled phenomena, especially in complex systems such as BFO. It is also clear that these fundamental discoveries need to be translated into meaningful technologies. Thus, it is critical that applied programmes be initiated and supported to make progress towards useful technologies. Within the USA, we have launched an Engineering Research Center that is squarely focused on the possible device manifestations of these materials. The central focus of this centre, called the Center for Translational Applications of Nanoscale Multiferroic Systems (TANMS), is shown in figure 6. This centre focuses on three application areas, namely memories, antennae and nanoscale motors in which multi-ferroics and magnetoelectrics will play a key role. Stay tuned for progress reports from TANMS. The Defense Advanced Research Projects Agency (DARPA) has also initiated programmes on multi-ferroics and magnetoelectrics, albeit on a smaller scale (see the article by Viehland [29] for a good summary of some of the research and development (R&D) activities supported by DARPA). Other agencies, such as the Semiconductor Research Corporation, have also initiated R&D activities leading to devices based on multi-ferroics, primarily focused on electric field control of magnetism. So, the next few years should be quite promising in terms of possible device manifestations of multi-ferroics and magnetoelectrics.

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References


