Complex functional oxide heterostructures

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This article presents a review of some salient aspects of a broad class of functional materials, namely complex oxides. These materials, exemplified by the rare earth manganites, superconducting cuprates and more recently multiferroics, are characterized by a complex crystal chemistry, that is central to competing/cooperating spin, charge, orbital and lattice degrees of freedom. In addition to this, a fundamental defining feature of such materials is the complex nanoscale phase coexistence that appears to be central to the appearance of large responses. The emergence of pulsed laser deposition as a tool to create artificially engineered heterostructures has provided researchers with a powerful approach to create new states of matter at such heterointerfaces. This combined with modern X-ray, electron, neutron and proximal probes (such as conducting AFM, piezoresponse SPM, etc) and *ab initio* theoretical studies has provided us with deep insight into the various physical phenomena that manifest themselves in such materials.

Keywords: Complex oxides, heterostructures, materials, power of epitaxy.

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 multiferroic 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. These materials are characterized by a strong interplay between the fundamental degrees of freedom, namely the electronic spin, charge, orbital and their interplay with the lattice (Figure 1). New states of matter have emerged as a consequence of competition/cooperation between these degrees of freedom. Second, nanoscale complexity, driven by chemical/ionic/electronic inhomogeneities is a key feature that underpins large physical responses (for example, piezoelectric/dielectric responses in relaxors, colossal magnetoresistance in doped manganites, high

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temperature superconductivity in cuprates), as illustrated schematically in Figure 2. Finally, the use of state-of-the-art thin film deposition tools (such as RHEED assisted pulsed laser deposition (also known as laser MBE), conventional MBE and chemical vapour deposition) has driven the synthesis of atomically sharp, artificial heterostructures that have exhibited novel physical phenomena, especially at the heterointerfaces. It appears to be an impossible task to review all the progress in the past two decades in this field. Instead, I will use examples from the most recent work on multiferroics to highlight various aspects.

The interplay between the dielectric and magnetic responses in materials is a fascinating and rich playground in condensed matter. By itself these responses are not unusual; indeed, even a spontaneous order parameter (broken time reversal symmetry leading to a spontaneous magnetization in a ferromagnet, broken spatial inversion symmetry leading to a spontaneous dielectric polarization in a piezoelectric/ferroelectric) is quite common in many materials. However, a rather limited set of materials exhibit multiple order parameters, or multiferroicity (for example, ferromagnetism and ferroelectricity, or antipolar derivatives thereof) (Figure 3 *a*). A key reason for this limited set is of course the fact that these two order parameters are 'contra-indicating', i.e. they have exactly the opposite requirements in terms of the electronic structure. Typically, ferromagnetism (especially in metallic
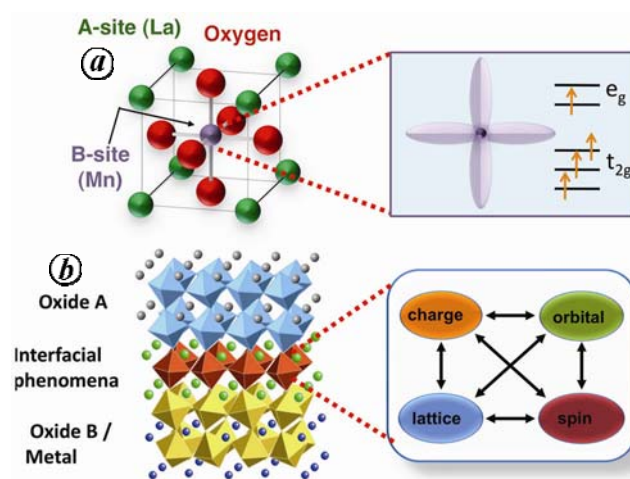
Figure 1. *a*, A schematic of the ABO_3 perovskite crystal structure, with the electronic structure of the 3d transition metal ion shown on the right side. *b*, The left side is a schematic illustration of a prototypical epitaxial oxide interface, wherein the fundamental degrees of freedom interact leading to new states of matter.
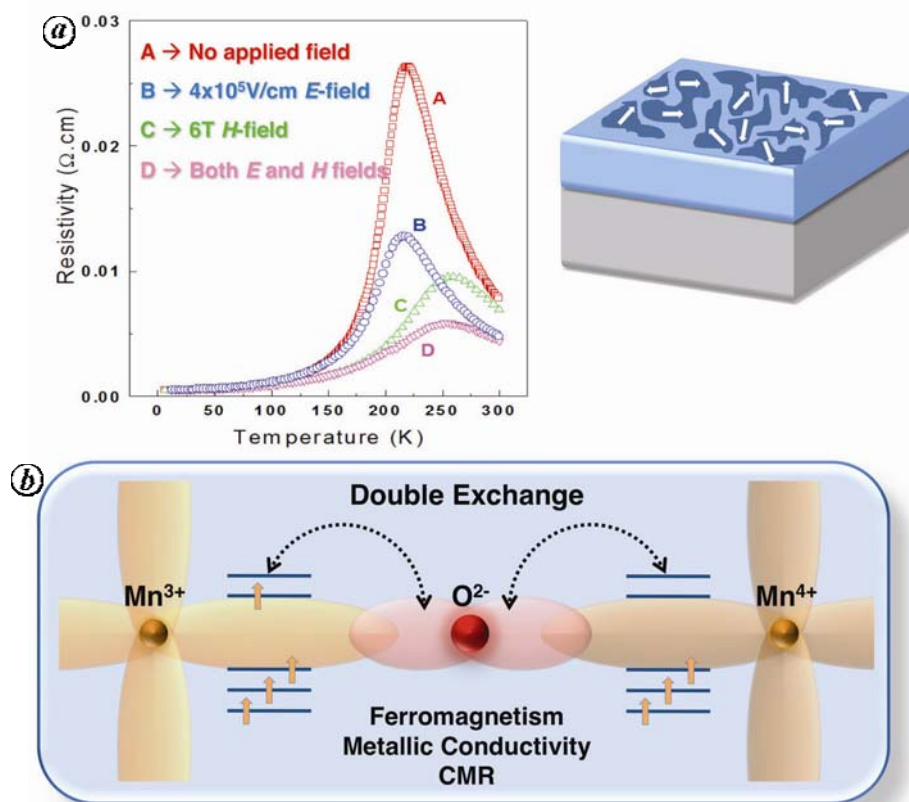
Figure 2. *a*, Large magnetic and electric field-dependent change in the transport behaviour of La–Ca–Mn–O thin films, emerging as a consequence of the nanoscale phase inhomogeneity that is depicted on the right side. *b*, A schematic illustration of how the double exchange mechanism facilitates electron transport and ferromagnetism in the manganites.

systems) arises as a consequence of exchange interactions and requires the kinetic energy of the electron to be dominant; on the other hand, stabilization of a spontaneous dielectric polarization requires a perfectly insulating state. Thus, it should be no surprise that there are not too many such examples. Indeed, it is much easier to find materials that are ferromagnetic and also have a spontaneous strain order parameter (for example, shape memory alloys). Consequently, many multiferroics typically exhibit ferroelectricity in conjunction with antiferromagnetism, as exemplified by several model systems. Finally, if there is coupling between the magnetic and dielectric degrees of freedom, then such materials are termed magnetoelectrics.

BiFeO$_3$ (BFO) is the only room temperature multiferroic (antiferromagnetic and ferroelectric) so far, which has attracted great interest and extensive studies in the past decade (Figure 3 *b* and *c*). It has a rhombohedral unit cell, built with two distorted perovskite cells connected along a pseudocubic [111] direction[1,2]. It is also a G-type antiferromagnet with a Neél temperature of ~673 K [100] and a symmetry-allowed, small canted moment due 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 octahedra along the [111] direction with a Curie temperature of 1103 K and a spontaneous ferroelectric polarization of about 90 μC/cm^2 (ref. 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.

Domains and domain walls in multiferroics

The synthesis of high quality epitaxial thin films through a variety of techniques (pulsed laser deposition (or laser MBE), sputtering, MBE, CVD) 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 of arrays of 71° domain walls and the other with an array of 109° domain walls. They both exhibit an array of
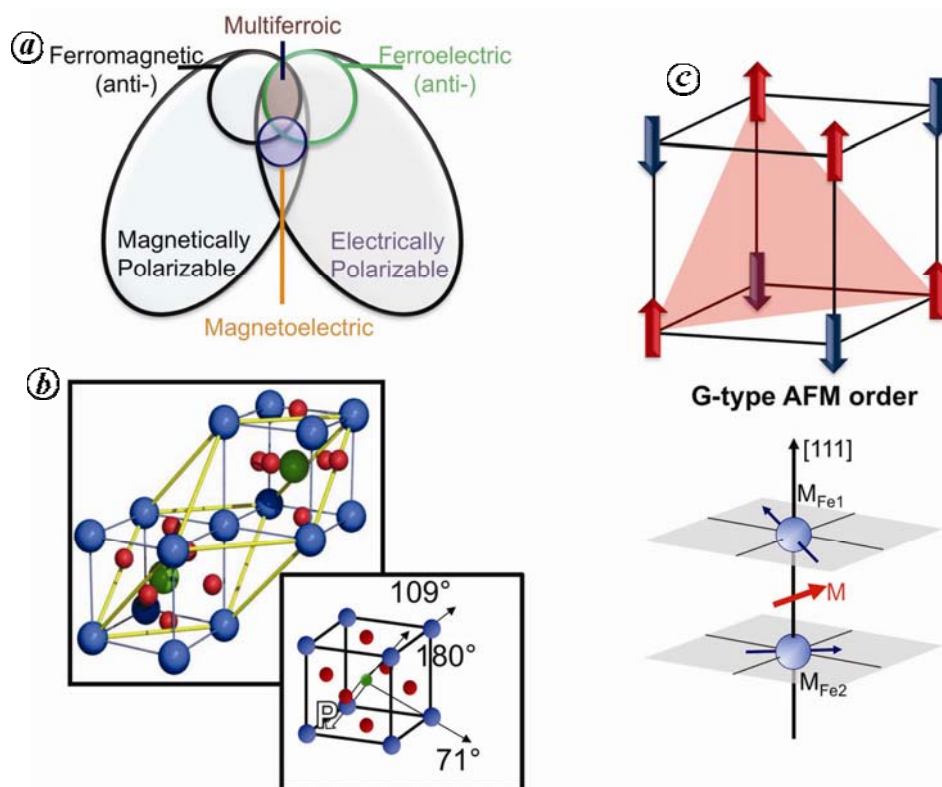
Figure 3. *a*, A schematic showing the emergence of ferromagnetic, ferroelectric and multiferroic orders from magnetically and electrically polarizable materials. *b*, A schematic of the crystal structure of the prototypical multiferroic, $BiFeO_3$ (BFO) along with the symmetry allowed polarization rotation angles. *c*, A schematic illustration of the G-type antiferromagnetic order in BFO, in which a small canted moment emerges as a consequence of a spin–orbit interaction.

fascinating electrical–optical–magnetic responses[8,9], once again highlighting the versatility of this materials system. For example, Figure 4 shows the magneto-transport behaviour of 109° domain walls, an atomic resolution image of which is shown in Figure 4 *a*. Conducting AFM-based measurements, Figure 4 *b*, shows that the walls are conducting, well above that of the domain itself, typically by 2–3 orders of magnitude[10]. Temperature-dependent measurements show that the transport is still semiconducting in nature, albeit with a smaller activation energy. Macroscopic magneto-transport studies (Figure 4 *c* and *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 magneto-transport mechanism roughly akin to that in the CMR manganites, albeit in 2-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 shown in Figure 4 *d*. Below ~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 make domain walls that are metallic (and perhaps ferromagnetic) in nature in an otherwise insulating, antiferromagnetic ferroelectric[11].

The power of epitaxy

Epitaxy provides a powerful pathway to create new states of matter at interfaces as a consequence of the interactions between the spin, charge, orbital and lattice degrees of freedom (Figure 5). The emergence of *in situ*, surface analytical tools such as RHEED and time-of-flight ion scattering and recoil spectroscopy (TOF-ISARS) has become a key enabler of the atomic scale control of the heterostructure synthesis. Such growth studies are typically performed on carefully surface terminated single crystal substrates (such as TiO_2 terminated $SrTiO_3$). Figure 5 *a* shows RHEED intensity oscillations from an LSMO layer grown with and without a template $SrRuO_3$ layer; the oscillations correspond to the layer-by-layer growth of LSMO. The insertion of the $SrRuO_3$ template layer has the effect of flipping the surface termination from the B-site (TiO_2) to A-site (LaSrO), shown schematically in Figure 5 *b*.
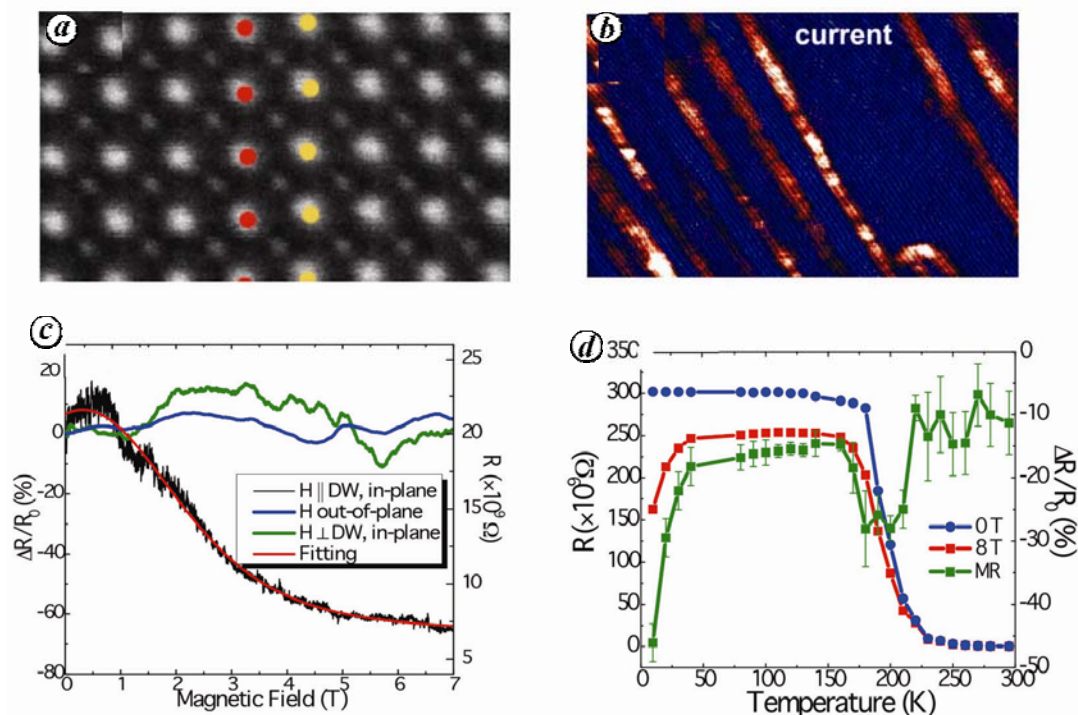
**Figure 4.** *a*, An atomic resolution image of the 109° domain wall in BFO. *b*, A conducting AFM image showing electronic conduction at such domain walls. *c*, Angle-dependent magnetotransport measurements of arrays of 109° domain walls, showing large MR values when the transport and field directions coincide, while MR is essentially negligible when the field is perpendicular to the transport direction. *d*, Temperature dependence of the resistance and MR at 8 T; note the positive slope to the transport at 8 T, below ~50 K.

The nature of the surface and interface termination can be directly discerned by atomic imaging (Figure 5 *c*) and electron energy loss spectroscopy (Figure 5 *d*).

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 6 *a*). 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 ~4.5% is reached. For substrates that impose a larger strain (such as YAlO$_3$), 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 dramatically, has been observed in other materials systems[13,14]. 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 6 *b*. 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 6 *c*). 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[15]. Second, and perhaps more importantly, the highly distorted R-phase in this ensemble shows a significantly enhanced ferromagnetism. This can be discerned from the XMCD-PEEM image in Figure 6 *d*. 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 SQUID measurements) gives a local moment of the order of 25–35 emu/cc. It is noteworthy that the canted moment of the R-phase (~6–8 emu/cc) is not observable by the XMCD technique due 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[16]. These observations raise several questions: (i) 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
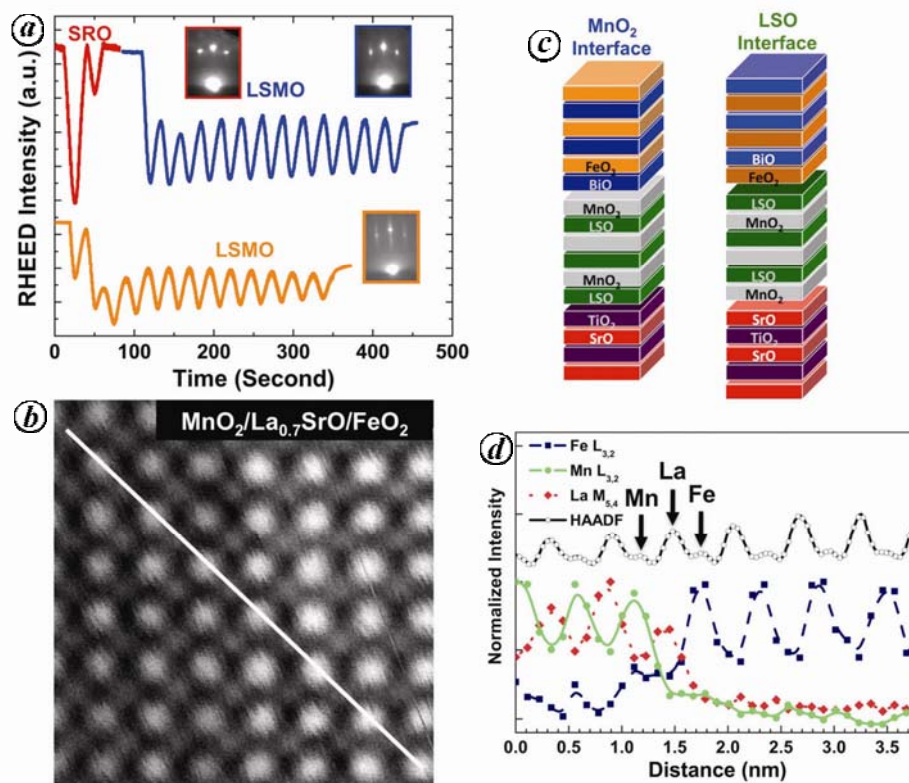
Figure 5. *a*, Layer-by-layer growth of oxide heterostructures, shown schematically in *b*, enabled by *in-situ* control using reflection high energy electron diffraction intensity oscillations. *b*, Schematic of two model heterointerfaces; the one on the left has a B-site termination (MnO$_2$) while the one on the right has an A-site (LaSrO) termination enabled through the insertion of a SrO layer. *c*, An atomic resolution image of the LaSrO interface with the corresponding atomic scale, electron energy loss (EELS) line profiles shown in *d*.

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?

## Exchange bias coupling and electric field control of magnetism

By far, the most exciting aspect of work on multiferroics is the potential to control magnetism (AFM or FM) 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 Maxwells 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 fashion, the potential to create information storage and communication devices that consume much less energy compared to devices driven by electric 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* 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[17]. On the other hand, ferroelastic rotations of the polarization vector, for example through a 71* or 109* switching process does indeed change the AFM vector direction in thin films[18]. This has also been confirmed by neutron scattering studies in single crystals[19]. It is interesting to note that recent work has demonstrated the electric field manipulation of antiferromagnetic electromagnons in this system[20]. 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 FM–AFM heterostructures.

Two types of ferromagnets can be envisioned. The first is a conventional ferromagnet, such as CoFe (or other such metallic ferromagnets). A significant amount of exchange coupling studies between such ferromagnets and multiferroics 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 109*
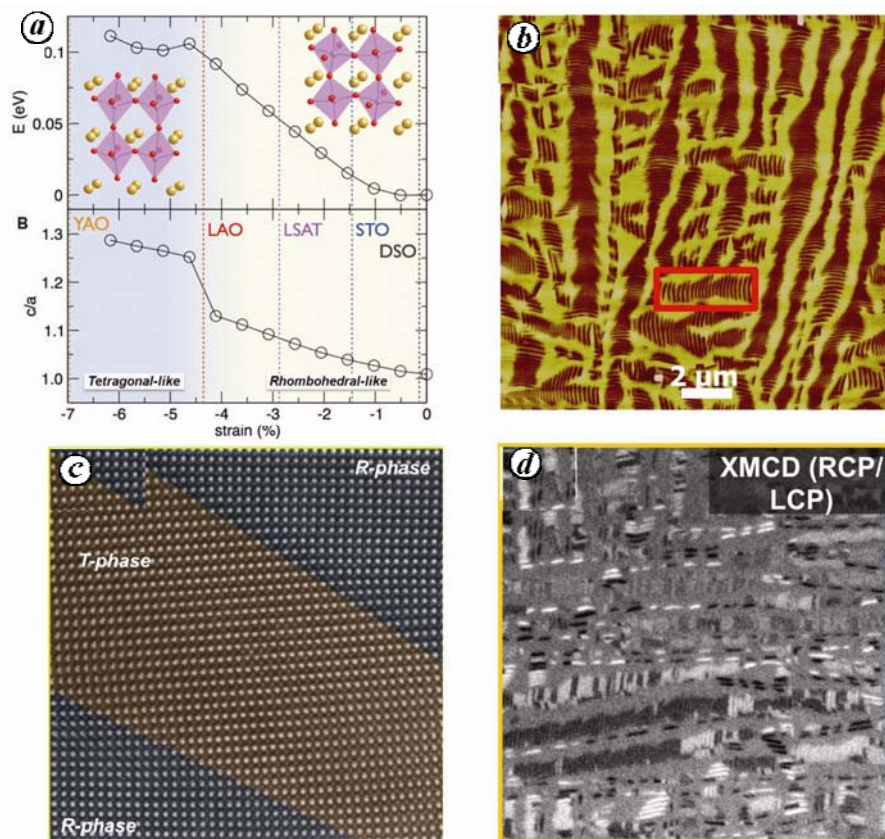
Figure 6. *a*, Phase evolution in the BFO system as a function of in-plane compressive strain, evolving from pure rhombohedral (R-phase) to super-tetragonal (T-phase). *b*, An AFM image of the mixed T/R phase nanostructure. *c*, A high resolution TEM image of the mixed phase nanostructure; note the absence of any dislocations at the interface. *d*, An XMCD-PEEM image showing that the nanoscale R-phase regions are ferromagnetic (black and white stripes).
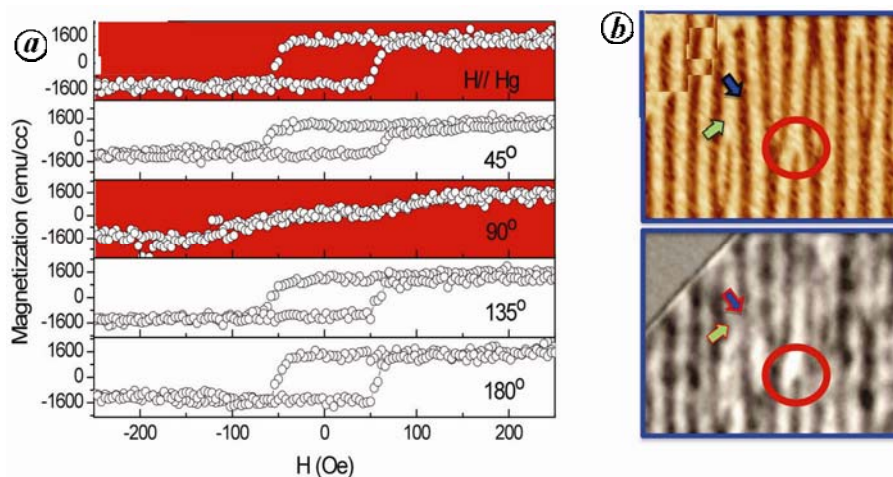

Figure 7. *a*, Angle-dependent ferromagnetic hysteresis loops for a 2.4 nm CoFe layer deposited on an epitaxial BFO thin film; the easy axis of the CoFe layer is along the in-plane projection of the canted moment of the BFO. *b*, the top panel is the piezoforce microscopy image of the BFO layer showing the set of 2 domains in which the polarization vector is rotated by 71°; the corresponding XMCD-PEEM image is in the bottom panel and shows that the magnetic domain structure of the CoFe layer is directly aligned with that of the BFO layer.

domain walls invariably show a strong exchange bias, suggesting that the uncompensated moments at the domain walls 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[21,22]. Angle-dependent magnetic measurements clearly show that the externally applied magnetic field is
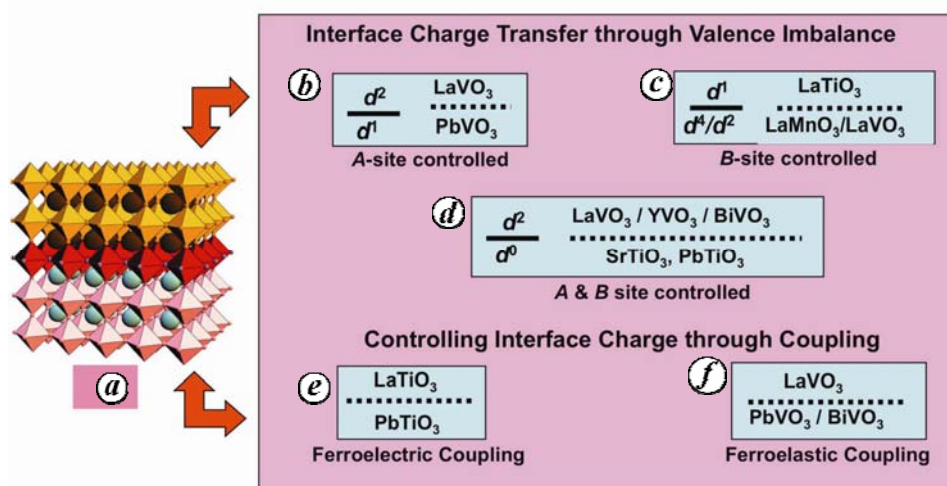
Figure 8. *a*, A schematic showing the formation of the interface (shaded red) between two perovskites. *b*, *c*, *d*, Examples of interface electronic states driven by charge transfer through valence imbalance for (*b*) *A*-site, (*c*) *B*-site and (*d*) *A* and *B* site substitutions. *e*, *f*, Examples of interface charge control through ferroelectric/ferroelastic coupling.
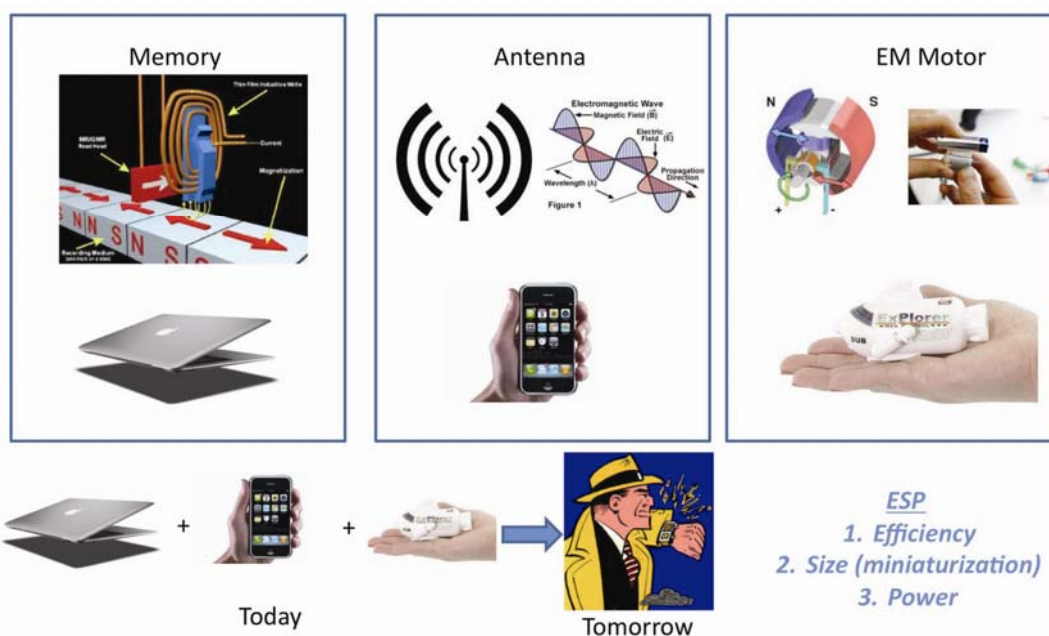
Figure 9. A schematic summary of the three focus areas in a new programme, TANMS, that has been recently funded to explore device applications of multiferroics and magnetoelectrics.

not the most important parameter; instead, the internal coupling between the canted moment in BFO and the ferromagnetic moment in CoFe appears to be more important (Figure 7 *a*). This coupling is also evident from direct PEEM imaging of the CoFe layer (Figure 7 *b*). There is a direct, one-to-one correlation of the ferroelectric domains (shown on 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 to be answered.

For example, how robust is this interfacial coupling, particularly with respect to repeated switching of the ferroelectric?

In the case of heterostructures involving oxide ferromagnets such as La–Sr–Mn–O, we observe several fascinating interfacial phenomena that are driven by spin, charge and orbital reconstructions at the interface. 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 Figures 1 and 5. As recent reviews have already dealt with the possible origins of the magnetic coupling and the electric field control of this magnetic

coupling[23], the reader is referred to them to explore these topics. Most interestingly, an enhanced magnetic moment in the BFO layer is observed right at the interface, 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[24]. Of interest as well is the recent proposal of a suppression in the oxygen octahedral tilt at the BFO/LSMO interface[25]. These results, coupled with the observation of magnetism and magnetotransport at domain walls, strongly indicate that interfaces do indeed have significantly different magnetic behaviour.

On the basic science of oxide interfaces, a lot remains to be understood. The ability to heteroepitaxially engineer interfaces with almost atomic perfection is the key to opening up new directions in exploring electronic structure, phase equilibrium and the interplay between the fundamental degrees of freedom, as illustrated in Figure 8. In the current reincarnation, we have seen almost ten years of basic science on multiferroics 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 funded to make progress towards useful technologies. Within the US, NSF has launched an Engineering Research Center that is squarely focused on the possible device manifestations of these materials. The central focus of this center, named Translational Applications of Nanoscale Multiferroic Systems (TANMS), is shown in Figure 9. This center focuses on three application areas, namely memories, antennas and nanoscale motors in which multiferroics and magnetoelectrics will play a key role. Progress reports from TANMS are awaited. DARPA has also initiated programmes on multiferroics and magnetoelectrics, albeit on a smaller scale. Other agencies, such as the Semiconductor Research Corporation (SRC) have also initiated R&D activities leading to devices based on multiferroics, primarily focused on electric field control of magnetism. So, the next few years should be quite promising in terms of possible device manifestations of multiferroics and magnetoelectrics.

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