Multiferroics: progress and prospects in thin films

Multiferroic materials, which show simultaneous ferroelectric and magnetic ordering, exhibit unusual physical properties — and in turn promise new device applications — as a result of the coupling between their dual order parameters. We review recent progress in the growth, characterization and understanding of thin-film multiferroics. The availability of high-quality thin-film multiferroics makes it easier to tailor their properties through epitaxial strain, atomic-level engineering of chemistry and interfacial coupling, and is a prerequisite for their incorporation into practical devices. We discuss novel device paradigms based on magnetoelectric coupling, and outline the key scientific challenges in the field.

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The past few years have seen a tremendous flurry of research interest in materials that show simultaneous ferromagnetic order (or any other kind of magnetic) and ferroelectric ordering (Fig. 1). Such ‘magneto-electric multiferroics’ were studied to some degree in the 1960s and 1970s (ref. 1) but then languished, in large part because single-phase materials with both properties could not be widely produced. The renaissance of magneto-electric multiferroics1-4 has been fuelled by developments in, and collaborations between, many areas of theory and experiment. First, the production of high-quality single-crystalline samples, in some cases through high-pressure routes, has led to the identification of new types of multiferroics5,6 with fundamentally new mechanisms for ferroelectricity. Second, improved first-principles computational techniques have aided in the design of new multiferroics, and provided understanding of the factors that promote coupling between magnetic and ferroelectric order parameters7,8. Finally, advances in thin-film growth techniques have provided routes to structures and phases that are inaccessible by traditional chemical means, and have allowed the properties of existing materials to be modified by strain engineering9. This availability of high-quality thin-film samples, in conjunction with a broad spectrum of analytical tools, has improved our ability to accurately characterize multiferroic behaviour, and has opened the door to the design of practical devices based on magnetoelectric coupling. In our opinion, these developments will prevent a recurrence of the downturn in interest that occurred in the 1970s, as thin-film multiferroics begin to reveal a range of fascinating phenomena as well as stimulate exploration of new device heterostructures.

Here we review recent progress in, and future prospects for, thin-film, heterostructure and nanostructure multiferroics; the accompanying review by Cheong and Mostovoy (page 13 of this issue) focuses on the corresponding bulk materials10. We discuss three types of thin-film architectures (Fig. 2): single-phase thin films, in which heteroepitaxial strain and crystal chemistry are the key variables in controlling and improving magnetoelectric coupling; horizontal heterostructures, in which the principles of heteroepitaxy at the interfaces can be used to control and initiate magneto-electric coupling at the atomic scale; and nanoscale ‘vertical heterostructures’, in which coupling occurs through vertical heteroepitaxy. The remainder of this review is organized as follows. First, we review the basic chemistry underlying the scarcity of magnetic ferroelectrics and the routes to combining magnetism and ferroelectricity that have overcome their contra-indication. Then we focus on multiferroics that are based on the three types of model thin-film architectures shown in Fig. 2. Finally, we discuss device architectures based on magnetoelectric coupling in thin films, before summarizing the prospects for research and technology in thin-film multiferroics.

CONTRA-INDICATION BETWEEN MAGNETISM AND FERROELECTRICITY

The scarcity of ferromagnetic ferroelectrics2 is now well understood to result from the contra-indication between the conventional mechanism for cation off-centring in ferroelectrics (which requires formally empty d orbitals), and the formation of magnetic moments (which usually results from partially filled d orbitals)1. For ferroelectricity and magnetism to coexist in a single phase, therefore, the atoms that move off centre to form the electric dipole moment should be different from those that carry the magnetic moment. In principle, this could be achieved through either an alternative (non-d-electron) mechanism for magnetism, or through an alternative mechanism for ferroelectricity; in practice only the latter route has been pursued, and the exploration of multiferroics with different forms of magnetism is an open area for future research. In the magnetic perovskite-structure oxides and related materials, multiferroism is most commonly achieved by making use of the stereochemical activity of the lone pair on the large (A-site) cation to provide the ferroelectricity, while keeping the small (B-site) cation magnetic. This is the mechanism for ferroelectricity in the Bi-based magnetic ferroelectrics, the most widely studied of which is bismuth ferrite, BiFeO3 (ref. 11). (Note that BiFeO3 adopts the perovskite, not the ‘ferrite’ structure, in spite...
of its nomenclature.) A second route to multiferroism is provided by 'geometrically driven' ferroelectricity, which is compatible with the coexistence of magnetism; the antiferromagnetic ferroelectrics YMnO$_3$ (refs 12,13) and BaNiF$_3$ (ref. 14) fall into this class. A particularly appealing, recently identified mechanism occurs in TbMnO$_3$, in which ferroelectricity is induced by the formation of a symmetry-lowering magnetic ground state that lacks inversion symmetry$^1$. The resulting polarization is small, but because it is caused directly by the magnetic ordering, strong and possibly new magnetoelectric interactions should be expected. A search for the opposite effect — weak ferromagnetism that is induced by a symmetry-lowering ferroelectric distortion — is under way$^{15,16}$. Finally, certain non-centrosymmetric charge-ordering arrangements can cause ferroelectricity in magnetic materials; here LuFe$_2$O$_4$ has generated recent attention$^{16-17}$. We also point out that, to be ferroelectric, a material must be insulating (otherwise the mobile charges would screen out the electric polarization). This is an additional constraint, because many ferromagnets tend to be metallic, with many magnetic insulators having antiferromagnetic ordering. The need for insulating behaviour can also cause problems if samples are leaky, as this can suppress ferroelectric behaviour even if the structure is non-centrosymmetric. This is a common problem in the case of magnetic ferroelectrics, because magnetic transition metal ions are often able to accommodate a wider range of valence states than their diamagnetic counterparts, leading in turn to non-stoichiometry and hopping conductivity.

**SINGLE-COMPONENT THIN-FILM MULTIFERROICS**

Although the four routes to multiferroism described in the previous section have led to the identification of an array of new multiferroics, most of these have only been prepared in single crystal, ceramic or powder form. To our knowledge only two classes of single-phase multiferroics — the hexagonal manganites and the Bi-based perovskites — have been prepared as single-phase films. We summarize the literature here, highlighting where the properties of the thin films are fundamentally different from those of the corresponding bulk samples.

Perhaps the first multiferroic to be investigated in thin-film form$^{38}$ was the hexagonal manganite YMnO$_3$, which is appealing because its geometric ferroelectricity leads to a uniaxial polarization perpendicular to the plane of the film. The first study$^{39}$ used radiofrequency magnetron sputtering to obtain epitaxial (0001) films on (111)MgO and (0001)ZnO/(0001)sapphire, and polycrystalline films on (111)Pt/(111)MgO. Soon after, it was shown$^{40}$ that the metastable, non-ferroelectric cubic perovskite structure could be stabilized in thin films using appropriate conditions and substrates. Subsequently, YMnO$_3$ films have been grown on a range of substrates (Si(100), Pt/TiO$_2$/SiO$_2$/Si, Pt/(111)/Ti/SiO$_2$/Si, (111)Pt/(0001)sapphire, SiO$_2$-buffered silicon, GaN-on-sapphire) using a range of techniques (sputtering, spin coating, sol–gel processes, pulsed laser deposition, metal-organic chemical vapour deposition (MOCVD) and molecular beam epitaxy (MBE))$^{39-41}$. Although the thin-film and bulk properties are qualitatively similar, the thin-film samples show the usual reduction in ferroelectric polarizations and dielectric response compared with the corresponding single-crystal values. Preparation and characterization of other rare-earth hexagonal manganites in thin-film form, including those that form the competing perovskite phase in the bulk$^{42}$ (S. B. Ogale, personal communication), are under way.

Perovskite-structure bismuth ferrite is currently the most studied single-component multiferroic, in part because its large polarization and high Curie temperature ($\approx 820^\circ$C) make it appealing for applications in ferroelectric non-volatile memories and high-temperature electronics. An early bulk sample$^{43}$ yielded a small polarization value; measured polarizations for thin films grown by a variety of techniques$^{11,30-33}$ initially showed a large spread of values (for a summary table see ref. 34). However, the measured values are now converging to $\approx 90\mu$C cm$^{-2}$ along the [111] direction of the pseudo-cubic perovskite unit cell, consistent with first-principles calculations$^{34}$. The large difference between the thin-film and bulk values, initially attributed to epitaxial strain$^{11}$, could also result from leakage effects in crystals caused by defect chemistry or the existence of second phases, or mechanical constraints in granular bulk ceramics. There are also intriguing experimental and theoretical reports of a tetragonal phase, with $c/a = 1.26$ and an even larger ferroelectric polarization of $\approx 150\mu$C cm$^{-2}$ (refs 35,36); this is yet to be confirmed by independent reports.

The magnetic properties of BiFeO$_3$ thin films can also be markedly different from those of the bulk. BiFeO$_3$ has long been known in its bulk form to be an antiferromagnet with Néel temperature $T_N \approx 643$ K (ref. 37). The Fe magnetic moments are coupled ferromagnetically within the pseudo-cubic (111) planes and antiferromagnetically between adjacent planes. If the magnetic moments are oriented perpendicular to the [111] direction, as predicted by first-principles calculations$^{35}$, the symmetry also permits a canting of the antiferromagnetic sublattices resulting in a macroscopic magnetization — 'weak ferromagnetism'$^{36,37}$. However, superimposed on the antiferromagnetic ordering, there is a spiral spin structure in which the antiferromagnetic axis rotates through the crystal with an incommensurate long-wavelength period of $\approx 620$ Å (ref. 40). This spiral spin structure leads to a cancellation of any macroscopic magnetization and also inhibits the observation of the linear magnetoelectric effect$^{41}$. However, a significant magnetization ($\approx 0.5\mu_B$ per unit cell) and a strong magnetoelectric coupling have been observed in epitaxial thin films$^{38}$, suggesting that the spiral spin structure could be suppressed$^{42}$. More work is needed to characterize the magnetic behaviour of BiFeO$_3$ thin films fully — direct experimental confirmation of the spin structure would be highly desirable — and the origin of the large magnetization in ultrathin, highly strained BiFeO$_3$ (refs 11,43) is still unclear.

Finally, we mention that there has been some progress in integrating BiFeO$_3$ with silicon, desirable for Si-CMOS (complementary metal oxide semiconductor) electronics applications, and with GaN, for high-temperature electronics.

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**Figure 1** Publications per year with 'magnetoelectric' as a keyword. Reprinted with permission from ref. 2. Copyright (2005) IOP.
applications. Epitaxial growth on silicon has been helped by the use of SrTiO$_3$ as a template and a similar approach has been used to grow epitaxial BiFeO$_3$ on GaN. However, detailed characterization of the domain structure and dynamics, and reduction of the leakage current density and the coercive field, are critical challenges that need to be addressed before BiFeO$_3$-based films will be candidates for integrated microelectronic devices such as storage elements in non-volatile ferroelectric memories.

BiFeO$_3$ is unusual among the Bi-based perovskites in that it can be made under ambient conditions; most others have traditionally needed high-pressure synthesis. Recently, the stabilization of perovskite BiMnO$_3$ through thin-film growth has shown the usefulness of thin-film techniques in accessing Bi-based perovskites without high-pressure apparatus. Unlike BiFeO$_3$, the unusual orbital ordering in BiMnO$_3$ (refs 49,50) leads to ferromagnetism below $\sim 105$ K; thin-film BiMnO$_3$ is therefore being studied as a potential barrier material for magnetoelectric devices.

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orientation of the easy magnetization plane. In monoclinic BiFeO₃, however, first-principles calculations show that the six-fold degeneracy of the easy plane is lifted, and an orientation of the antiferromagnetic axis parallel to the [110] direction is preferred, that is, perpendicular to the rhombohedral axis but simultaneously parallel to the (001) plane. Because the [110] direction is perpendicular to both the [111] and [111] directions but not perpendicular to [111], in this case we expect the antiferromagnetic axis to change during the 109° ferroelectric switching but not during the 71° switching. Experimental studies are in progress to clarify the role of such strains in magnetoelectric coupling. In epitaxial thin films and heterostructures, we believe this will be a fruitful direction for research as we endeavour to understand the interactions and coupling between the order parameters.

The question of a fundamental size limit for ferroelectricity is currently of considerable interest, both in terms of understanding the basics of cooperative ferroelectric behaviour, and in response to the continued drive for miniaturization of electronic devices. Indeed it was long believed, from empirical evidence and phenomenological arguments, that there should be a critical size of the order of hundreds of ångströms below which a spontaneous electric polarization could not be sustained in a material (for a review of the early literature, see ref. 63). But more recent experimental work, corrobated by first-principles calculations, has indicated that the critical size in conventional ferroelectrics is orders of magnitude smaller than previously thought, and that ferroelectricity can persist down to vanishingly small sizes. We now need similar studies on multiferroics, in which the mechanism for ferroelectricity is unconventional, and in which coupling to the magnetism could affect the size dependence. Likewise, the size dependence of the magnetic ordering in multiferroics (be it ferro-, antiferro- or a more complicated state of order), and the behaviour of the magnetoelectric coupling with film thickness, remain to be explored.

**HORIZONTAL MULTILAYER HETEROSTRUCTURES**

The ability to grow high-quality films with precisely controlled composition, atomic arrangements and interfaces has added to the toolbox for the creation of new functional materials, and holds particular promise for the rational design of new multiferroics. A number of routes to new multiferroics have been pursued; here we review progress in the use of atomic-level layering to engineer specific magnetic ordering through superexchange interactions, and the use of compositional ordering that breaks inversion symmetry to increase polarizations. We also outline new ideas regarding interfacial multiferroism, and describe some early demonstrations of electric field effects using multiferroics. Horizontal heterostructures consisting of alternating layers of conventional ferromagnets and ferroelectrics have been reviewed elsewhere. Motivated by the report of the possibility of single-atomic-layer superlattice ordering in double perovskite LaFeCrO₃, Baettig and Spaldin proposed the analogous Bi-based compound as a potential multiferroic material. Their density functional calculations for the (111) ordered structure included a R3c ground state with a polarization of ~80 μC m⁻², and ferrimagnetic ordering with a magnetization of ~160 e.m.u. cm⁻³ (2μ₀ per formula unit). The expansion of the set of multiferroics to include such ferrimagnets is appealing from the perspective of obtaining the robust insulating behaviour required to sustain a ferroelectric polarization, because many ferromagnetic materials are metallic, whereas magnetic insulators tend to show antiferromagnetic coupling between the magnetic ions. Although there has been considerable progress on the growth of a range of layered double perovskites (see for example refs 73 and 71), work on Bi-based double layered perovskites is in its infancy. A number of attempts are being made to synthesize Bi₅FeCrO₉, although achieving the required (111) layering of the Fe³⁺ and Cr³⁺ ions is challenging because of their similar size and charge. More promising are Bi-based double perovskites with B-site cations of different charge, such as Bi₃MnNiO₉, which has so far been synthesized only at high pressure.

The advent of MBE and related growth tools was an important step in our ability to create atomically sharp heterostructures with interfacial behaviour that is entirely different from that of the constituent materials. One example is the recent demonstration of new electronic properties at the interface between a band insulator and a Mott insulator in heteroepitaxial perovskites. Importantly for the study of ferroelectrics, the use of layer-by-layer growth to induce compositional ordering that breaks inversion symmetry has produced new heterostructures with higher polarization and large nonlinear optical response. The prototype, first predicted using density functional theory computations, is the layering of CaTiO₃, BaTiO₃, and SrTiO₃ in A–B–C–A–B–C... arrangements to lift the inversion centre. This approach has been suggested as a new route to multiferroics, as it circumvents the contra-indication between magnetism and ferroelectricity by constraining the magnetic ions in a polar arrangement in spite of their natural tendency to remain centrosymmetric (A. J. Hatt and N. A. Spaldin, manuscript in preparation).

Several interesting interfacial magnetoelectric effects have been proposed theoretically and are particularly exciting areas for future experimental study. Du et al. have used first-principles density functional theory to demonstrate a magnetoelectric effect in a ferromagnetic/ferroelectric heterostructure that arises from a purely electronic mechanism, not mediated by strain. Using a model Fe/BaTiO₃ horizontal superlattice, they showed that the magnetization at the interface due to the ferroelectric instability changes the overlap between atomic orbitals at the interface, which in turn influences the magnetization of the magnetic layer resulting in a magnetoelectric effect. Such effects, they argue, should be possible in both vertical and horizontal heterostructures. In addition, Stengel et al. used first-principles calculations of metal-insulator heterostructures in the presence of a finite electric field to show that a polarized dielectric induces an electric polarization in the adjacent metal; if the metal is ferromagnetic this should result in a region of coexisting electrical polarization and magnetization at the interface.

Early experimental studies on heterostructures comprising a ferro- or piezoelectric and a carrier-mediated magnet (such as a diluted magnetic semiconductor or a double-exchange manganite) suggest the possibility of artificially engineered multiferroics in which the coupling is mediated through an electric field effect at the interface. The prototypical examples of such ‘field-effect multiferroic heterostructures’ are Co-doped TiO₂/PZT (ref. 82), and lanthanum calcium manganite/PZT (ref. 83). In both cases, the piezoelectric PZT influences the magnetic behaviour by modulating the carrier density in the magnetic layer through a conventional electric field effect. Much more detailed work needs to be done in this promising area. In particular, the origin of magnetism in Co-doped TiO₂ is a controversial topic, with a considerable spread of experimental data in the published literature.

Finally, we mention that the field of horizontal heterostructure multiferroics is starting to benefit immensely from the use of a variety of surface-sensitive electronic probes such as angle-resolved photoemission (ARPES). An emerging area of research involves the probing of surface and near-surface interface electronic structure in situ. For this, the deposition process must be connected in situ to the probe; although this is common in semiconductor heteroepitaxy, it is only just evolving in complex oxide heteroepitaxy. Such systems, shown schematically in Fig. 3, are currently being designed in several laboratories around the world, and promising preliminary results are emerging.
Vertical heterostructures such as the nanopillar geometry shown in Fig. 2c offer numerous advantages over the conventional ‘horizontal’ heterostructures discussed above. First, they have a larger interfacial surface area and are intrinsically heteroepitaxial in three dimensions; this should allow for stronger coupling between ferroelectric and magnetic components. In addition, substrate-imposed mechanical clamping, which is known to suppress both the piezoelectric response and the magnetoelectric coupling mediated by lattice deformation in thin-film-on-substrate geometries, should be reduced in the vertical architecture. The prototypical multiferroic vertical nanostructure consists of a magnetic spinel phase which is epitaxially embedded into the ferroelectric matrix. The first example contained CoFe$_2$O$_4$ pillars in a BaTiO$_3$ matrix, but many different combinations of perovskites (BaTiO$_3$, PbTiO$_3$, BiFeO$_3$, and SrTiO$_3$) and spinels (CoFe$_2$O$_4$, NiFe$_2$O$_4$, and Fe$_3$O$_4$) have since been grown. However, the design and control of such heterostructures remains a challenge.

Recent work has demonstrated very strong magnetoelectric coupling in such nanostructures, through switching of the magnetization on reversal of the ferroelectric polarization. Detailed studies in progress suggest that the switching is mediated by strong mechanical coupling between the two lattices, which leads to a time-dependent modulation of the magnetic anisotropy in the nanopillar. The strength of the coupling suggests a key role for heteroepitaxy, but does not lead to controllable switching of the magnetization; control can only be achieved if an additional weak magnetic field is superimposed to lift the time-reversal symmetry.

This approach of using vertically heteroepitaxial nanostructures is relatively new, and much research is still needed to understand the nature of the heteroepitaxy as well as the coupling mechanisms. In terms of nanostructure assembly, controlling the degree of order among the nanopillars is possibly the most interesting, albeit difficult problem. Indeed, this has been an ongoing quest in the field of semiconductor quantum dot nanostructures, with recent progress also driven by directed assembly processes. The formation of self-assembled, vertical nanostructures with long-range ordering will undoubtedly have great impact, not only in the field of multiferroics, but in a broad range of photonic applications. In addition, many open questions regarding the magnetoelectric coupling remain: what is the timescale of the coupling process? How does the time dependence of the magnetism relate to the ferroelectric switching? What is the smallest value of magnetic field that can lead to full switching of the magnetization? How does the behaviour depend on the chemistry of the nanopillars? Is there a critical dimension below which the coupling will disappear or change in nature? These areas are ripe for future research.

**COUPLING PHENOMENA AND DEVICE STRUCTURES**

Given the successful incorporation of magnetic and ferroelectric materials into a variety of technologies, the question arises: what are the applications that are uniquely made possible through multiferroic materials and/or magnetoelectricity? Earlier reviews outlined many possible applications of bulk multiferroics, with a strong emphasis on high-frequency devices such as filters and oscillators that could be tuned by magnetic fields. Indeed, recent work on bulk multilayers indicates their promise in electrically tuneable microwave applications such as filters, oscillators and phase shifters (in which the ferri-, ferro- or antiferro-magnetic
resonance is tuned electrically instead of magnetically), and as low-frequency, high-resolution magnetic field sensors. Coupling in this case is believed to result from the macroscopic mechanical coupling of the two materials at the bonded interface. In such bilayers, coupling coefficients (which are proportional to the magnetoelectric susceptibilities) as large as 1–5 Oe cm kV$^{-1}$ at microwave frequencies have been reported; these are an order of magnitude higher than in polycrystalline composites, pointing to the key role of crystallographic orientation control in optimizing the magnetoelectric response.

In this section we discuss recent progress in the development of thin-film multiferroic devices, and illustrate the potential of multiferroic/magnetoelectric thin films and heterostructures with a few key examples. Although less advanced than the bulk multilayers mentioned above, large coupling effects have been observed in thin films; for example in nanopillar heterostructures, switching of the ferroelectric polarization by an applied electric field leads to a reversal of the magnetization direction (Fig. 4). We focus specifically on approaches by which magnetic responses can be controlled through the application of an electric field in thin-film heterostructures and nanostructures. Although the number of studies has been small, we expect this to change in the immediate future, as the integration of thin-film heterostructure devices with conventional silicon electronics provides impetus. Of course, the converse effect, tuning electrical behaviour with a magnetic field, is also an enticing possibility, although the need to generate and apply large magnetic fields (of several tesla) is an issue that must be resolved before this approach is practical.

First we review experimental methods for measuring magnetoelectric coupling in thin films. The classical method for probing magnetoelectric coupling is to measure the magnetoelectric response, $\partial P / \partial H$ or $\partial M / \partial E$ (where $P$ is electric polarization, $H$ is magnetic field, $M$ is magnetization and $E$ is electric field), directly as a function of temperature; this is analogous to the measurement of dielectric or magnetic susceptibilities. In thin films, however, such measurements are often complicated by leakage in the dielectric and other parasitic effects. Furthermore, the magnetoelectric coefficients are often small, leading to response signals that are only a few nanovolts and therefore require lock-in detection. Because of these difficulties, a variety of approaches has been developed to probe magnetoelectric coupling, many of which offer high spatial resolution; these approaches take advantage of the diversity of interactions between magnetoelastic materials and a broad spectrum of electromagnetic radiation (X-rays, visible optics, infrared optics, microwave and millimetre waves). A particularly important development is the evolution of chemical and magnetic state-specific imaging using photo-excited electrons in photoemission electron microscopy (PEEM). State-of-the-art PEEM systems have spatial resolution of the order of 20–50 nm, and with the PEEM 3 microscope at the Advanced Light Source at Lawrence Berkeley Laboratory, the possibility of 10-nm resolution is imminent. This technique has been used successfully by Scholl and co-workers to probe the exchange bias coupling between ferromagnetic cobalt and antiferromagnetic LaFeO$_3$. Using a combination of X-ray magnetic circular dichroism PEEM to probe the domain structure of the ferromagnet, and linear dichroism PEEM to probe the antiferromagnet, they have demonstrated the existence of exchange bias coupling in this system. A similar approach in our laboratory will explore the coupling between a range of ferro- and ferrimagnets (Co, CoFe$_2$O$_4$, NiFe$_2$O$_4$) and ferroelectric BiFeO$_3$. Magneto-optic measurements in the visible range using the Kerr effect (MOKE) provide another route to exploring magnetoelectric coupling in thin films. These studies are conceptually similar to conventional MOKE measurements, but the modulation of the MOKE response is through an electric field. In addition, ferro- and antiferromagnetic resonance spectroscopy is a powerful technique for probing coupling effects at microwave or millimetre wave frequencies, and, as mentioned above, presents the most obvious route to practical applications.

Next we discuss two routes to controlling the magnetic behaviour using electric fields: through modifying the amount or direction of spin canting, and through influencing the exchange bias coupling. A common feature of antiferromagnetic oxides, including the multiferroic perovskites, is the presence of canted magnetism on the transition metal sublattice. Such a canting arises primarily from the Dzyaloshinskii–Moriya interaction, and its existence and magnitude are determined by the symmetry of the crystal and the strength of the spin–orbit interaction respectively. Typical canting angles are ~0.5°, which can lead to weak ferromagnetism with modest remanent magnetization of around 1 to 10 e.m.u. cm$^{-3}$. Because the direction of the canting is determined by the symmetry of the crystal, it has been suggested that it should be possible to find multiferroics in which reversal of the ferroelectric polarization using an electric field causes a simultaneous reversal of the canting and hence of the magnetization. First-principles calculations on BiFeO$_3$ showed that it is not a suitable candidate; here the spin canting couples to the antiferrodistortive rotations of the FeO$_6$ octahedra rather than to the ferroelectric distortion of the lattice, and therefore 180° switching of the ferroelectric polarization should not affect the magnetic state.

**Figure 4** Thin-film multiferroic nanostructures. **a**, AFM image of the surface of self-assembled BiFeO$_3$–CoFe$_2$O$_4$ nanoparticles in which the CoFe$_2$O$_4$ nanopillars appear in bright contrast; **b**, schematic illustrating the four possible polarization directions in the matrix BiFeO$_3$ phase; **c**, magnetic force microscopy image of the nanostructure that has been pre-magnetized in a magnetic field of 2 T. Note the bright contrast in all the nanopillars, indicating that they are all magnetized in the same direction; the magnetic coercive field of the nanopillars is ~3 kOe (not shown); **d**, MFM image of the same region as in c, after the application of a 16 V d.c. field to the central boxed area along with a small magnetic field of about 700 Oe. Note that all nanopillars have switched their magnetization direction to the black state. Reprinted from ref. 88. Copyright (2005) American Chemical Society.
In addition, calculations showed that epitaxial strain does not significantly affect the canting angle in BiFeO$_3$, although a change in crystal symmetry induced by heteroepitaxy would of course change the allowed canting directions. More interestingly, the effects of non-180° polarization reorientation in BiFeO$_3$ thin films have recently been examined, and the orientation of the antiferromagnetic vector has been manipulated using an electric field; this could be a promising route to orientation control of weak ferromagnetism. And electric-field switching of weak antiferromagnetism has been demonstrated computationally in BaNiF$_2$; this could lead to electric field control of magnetization through the exchange bias routes discussed below. The most important open question here is whether the canting angle can be increased, because an order of magnitude increase in canting angle would yield magnetizations that are comparable to those in existing magnetic devices. The dependence of canting angle on epitaxial strain, on symmetry modification through heteroepitaxy, on the chemistry of the non-magnetic ions, and on the crystal structure are ripe areas for further study.

The concept of exchange bias coupling in magnetic materials is well known, and is extensively used in magnetic sensing and storage applications. Exchange bias occurs when the strong magnetic exchange interactions at the interface between an antiferromagnet (typically a metal such as Mn or a semiconductor such as MnO) and a ferromagnet pin the orientation of the spins in the ferromagnetic layer. The availability of ferroelectric antiferromagnets, such as the multiferroic perovskites, presents an exciting opportunity for modulating or controlling the magnetic structure by the application of an electric field as follows. Coupling between ferroelectricity and antiferromagnetism provides permanent, non-volatile control of the orientation of the antiferromagnetic axis, then coupling between the antiferromagnetic component and an adjacent ferromagnet should allow switching of the ferromagnetism through the application of an electric field. This promises to be an exciting area of research and suggests the possibility of new device technologies, particularly in the spintronic applications discussed below. Many laboratories worldwide have taken up the challenge, and although these efforts are in their infancy, it is likely that the topic will be extensively researched in the immediate future. Of course, such effects do not necessarily require a multiferroic; a large magnetoelastic coupling would also be sufficient.

The use of magnetoelastic coupling and multiferroics in spintronics is a rapidly emerging area of research, and a number of possible device architectures have been proposed. This theme, related to the one above, focuses on controlling and manipulating the spins of carriers in a ferromagnet using an electric field. One specific manifestation is a multiferroic tunnel junction which is used as a spin filter device with the potential to control both electrically and magnetically. Experimentally, this seems to be difficult to accomplish because so many variables affect behaviour at such length scales. First, the multiferroic tunnel barrier must be thin; of the order of 1–2 nm thick. The growth of epitaxial thin-film multiferroics with high structural quality containing only a few unit cells is challenging and will undoubtedly be a focal point in the coming years. In addition, the stability of both magnetic and ferroelectric order parameters must be maintained down to these small thicknesses. As we discussed earlier, the robustness of ferroelectricity in thin films is of tremendous current interest, with state-of-the-art experiments and first-principles computations indicating a critical thickness of a few unit cells, strongly dependent on the screening properties of the electrodes. How the critical behaviour is affected by the simultaneous presence of magnetic ordering in multiferroics is an open question.

Finally, we discuss the potential applications of multiferroics in electrically controlled spin wave devices. The excitation of spin waves by an alternating electric field, and of ferroelectric oscillations by a magnetic field, was discussed theoretically in a landmark 1982 review by Smolenskii and Chupis. They proposed that such excitations, which should be strongest in ferroelectric ferrimagnets, could be used to produce magnetoelastic generators or spin wave amplifiers driven by electric field or current. However, there has been very limited subsequent work on the influence of electric fields on spin waves. Experimental results are just beginning to emerge, with the first demonstration of hybrid excitations in multiferroic manganese nanogranites recently reported. We believe that this should be an area of strong focus in future.

We hope that this review has captured the sense of excitement and anticipation that is prevalent in the field of magnetoelastic multiferroics, and indeed in the entire area of complex oxide thin-film heterostructures. Discoveries are being made and reported almost weekly; we have attempted to put these developments into perspective, with a particular focus on their prospects for thin-film-based devices. Thin-film multiferroic systems provide an outstanding opportunity for making use of a rich spectrum of physical responses. Among these, the potential to electrically control magnetism in its many manifestations to create new devices within the framework of spintronics, information storage and communication, forms the spur that is energizing worldwide research activity.

As in any rapidly evolving field, it is impossible to do justice to all that is going on. We apologize in advance for any omissions, and hope that they will provide the motivation for additional articles and commentaries.

References
12. van Aken, B. B., Palstra, T. T. M., Filipeetti, A. & Spaldin, N. A. The origin of ferroelectricity in
20. Yoo, D. C., Lee, J. Y., Kim, S. K. & Kim Y. T. Microstructure control of YMO$_3$, thin films on Si (100)
FeRAM. Integr. Ferroelectr. 68, 75 (2004).
28. Balasubramanian, K. R. Phase Competition and Thin Film Growth of Layered Ferroelectrics and
29. Teague, I. J., Rerson, R. & James, W. J. Dielectric hysteresis in single crystal BaFeO$_3$, Solid State
30. Li, J. et al. Dramatically enhanced polarization in (001), (101), and (111) BaFeO$_3$, thin films due to
32. Xi, Q., Diou, J., Tomov, R., Blamire, M. G. & MacManus-Driscoll, I. J. Gravely reduced leakage
33. Xi, Q. et al. High resolution X-ray diffraction and transmission electron microscoy of multiferroic
34. Neaton, J. B., Ederer, C., Waghmare, U. V., Spaldin, N. A. & Rabe, K. M. First-principles study of
35. Yun, K. Y., Ricchini, D., Kanasahima, T., Noda, M. & Okumura, M. Giant ferroelectric polarization
36. Ederer, C. & Spaldin, N. A. Effect of epitaxial strain on the spontaneous polarization of thin film
37. Kisiel, S. V., Ozrov, R. P. & Zavodnov, G. S. Detection of magnetic order in epitaxial BiFeO$_3$, by
38. Dryaloshinskii, I. E. Thermodynamic theory of “weak” ferroelectromagnetism in antiferromagnetic
42. Bai, F. et al. Destruction of spin cycloid in (111)-oriented BiFeO$_3$, thin films by epitaxial
49. Anou, T., Chiba, H., Ohoyama, K., Yamaguchi, Y. & Sono, Y. Structure determination of ferromagnetic
50. dos Santos, A. M. et al. Orbital ordering as the determinant for ferromagnetism in biferroic


Acknowledgements

Clearly, this work represents the cumulative efforts of many researchers around the world. Specifically, we acknowledge several key collaborators (in alphabetical order): L. Q. Chen (Pennsylvania State Univ. (PSU)), L. E. Cross (PSU), C. Ederer (Columbia Univ.), C. B. Eom (Univ. Wisconsin), M. Fiebig (Univ. Bonn), V. Gopalan (PSU), J. Kreisel (Univ. Grenoble), S. Ogale (Univ. Maryland), K. M. Rabe (Rutgers Univ.), D. Schlom (PSU), H. Schmid (Univ. Geneva), A. Scholl (ALS-LBL), J. F. Scott (Univ. Cambridge), D. Viehland (Virginia Tech.), M. Wuttig (Univ. Maryland), F. Zavaliche (Seagate Technologies) and T. Zhao (Seagate Technologies). We also thank past and present members of our research groups at Berkeley and Santa Barbara. We thank the following funding agencies: ONR, DOE and NSF (R.R.) and NSF (N.A.S).

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