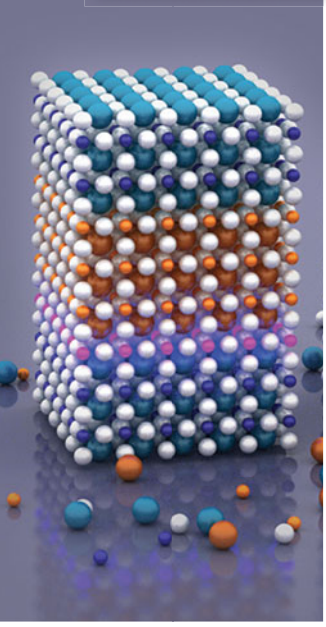




New developments in artificially layered ferroelectric oxide superlattices

Matthew Dawber and Eric Bousquet

Artificially layered superlattices of oxide materials have been intensely investigated for some time, but continue to reveal new potential as a route to advanced functional materials. As well as considering electrostatics and strain, a more complete picture of the interfaces in these systems also needs to incorporate the possibility of additional structural distortions, electronic redistributions, and complex polarization domain structures. Here we focus on superlattices composed of two perovskite oxide materials, where one is a ferroelectric, and discuss the important interactions between the component materials that determine the behavior of the new artificial material. We discuss interfaces both with and without electronic screening. The first class of interface contains technologically relevant ultrathin ferroelectric capacitors and the more recently studied ferroelectric-metal superlattices. In these systems, the influence of the ferroelectric polarization decreases rapidly with distance from the interface. By contrast, in systems where the materials adjacent to the ferroelectric layers are dielectrics, the polarization of the ferroelectric layer influences the properties of the adjacent layers over a much longer distance, setting the stage for fascinating competition between the properties of the combined materials.

Introduction

The ability to control the growth of thin films at the atomic scale afforded by modern physical deposition techniques has enabled the possibility of making new types of materials by alternating the thin-film growth of two or more materials on top of each other and repeating the process a certain number of times.[1] When the layers are on the order of a few unit cells in thickness, these structures are classed as superlattices, which refers to the fact that the predominant periodicity in the structure is the artificially produced one. Three motivations to produce these artificial materials are: (1) The possibility to modulate the properties of the two parent compounds by controlling the layer thickness ratio between the two building blocks, (2) to produce a material that has an enhancement of one or more of the initial properties of the parent compounds, and (3) to induce new properties that are completely absent in the parent compounds.

These possibilities have been explored for ferroelectricity (the property where a material develops a spontaneous electrical polarization, the direction of which can be changed by application of an electrical field) mostly in superlattices made from two building blocks, also called bi-color superlattices (see **Figure 1**; the term "color" refers to a distinct parent material within the artificial structure), which are the focus of this article. While, based on principles of electrostatics and mechanical strain, we can expect a modulation of the initial properties of the two bulk parent compounds for large layer thicknesses, present research in superlattices is especially motivated by the appearance of exotic interface effects that would induce new phenomena not present otherwise. In the field of ferroelectric perovskites (FE), several bi-color systems have been studied: FE/dielectric, FE/FE, FE/metal, and FE/incipient-FE (incipient ferroelectrics are materials that are close to being ferroelectric, but the onset of the ferroelectric order is suppressed by an external parameter). Interestingly, these systems can be roughly understood through simple electrostatic models that consider two dielectrics or a dielectric and a metal coupled by electrostatics and strain. However, these models are valid only for large thicknesses of the layers, while for small layer thicknesses, the interface effects can dominate the physics of the superlattices, and new models, explicitly taking into account these new effects, have to be built in order to understand the unexpected observed phenomena. In this article, we discuss interfaces both with and without electronic screening. The first class of interface contains technologically relevant ultrathin ferroelectric capacitors and the more recently studied

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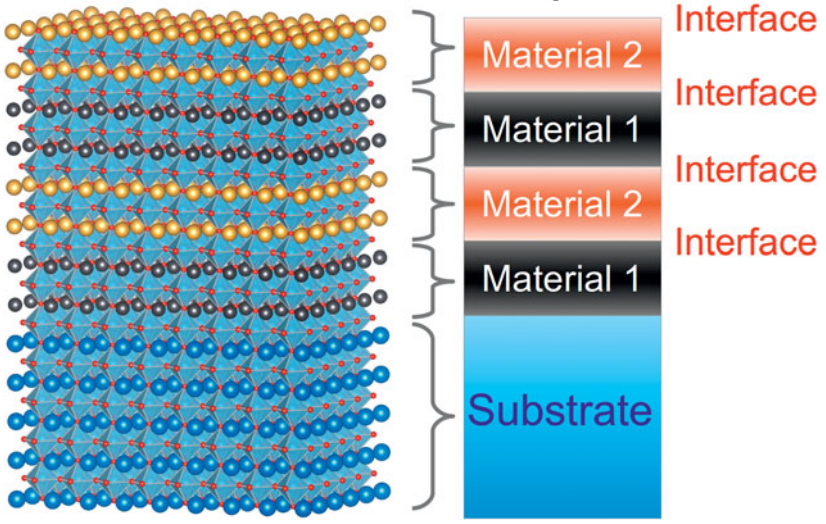


Figure 1. Schematic view of a bi-color superlattice made of two different materials epitaxially grown on a substrate.

ferroelectric-metal superlattices. In these systems, the influence of the ferroelectric polarization decreases rapidly with distance from the interface. By contrast, in systems where the materials adjacent to the ferroelectric layers are dielectrics, the polarization of the ferroelectric layer influences the properties of the adjacent layers over a much longer distance, setting the stage for fascinating competition between the properties of the combined materials.

Screening of polarization at a ferroelectric interface

The chief defining quantity of any ferroelectric material is the existence of a spontaneous polarization, or that there is some gain in free energy if the material developed aligned dipoles when it is a bulk material. While, in principle, it is favorable for the whole material to be polarized in the same direction, a ferroelectric material will more typically have regions of alternating polarization, termed domains. This is similar to the behavior in ferromagnets; however, ferromagnets and ferroelectrics are quite distinct, with the former having ordering of magnetization and the latter having involved ordering of electrical polarization. Another key difference is that typically in ferroelectrics, the domain walls are much smaller than in ferromagnets, being only one or two unit cells in size. When ferroelectrics exist as ultrathin films, or when they are a very thin layer within a larger heterostructure, many factors come into play in determining the arrangement of electrical polarization at or near the interface of a ferroelectric material with another material.

A useful starting point for considering systems of this kind is to recognize that the electric displacement (defined in Equation 2), rather than the polarization, is frequently the most relevant variable to consider across a polar interface.[2] This is because of the relationship between the electric displacement **D** and free charge ρ:

$$\nabla \cdot \mathbf{D} = \frac{\partial D_x}{\partial x} + \frac{\partial D_y}{\partial y} + \frac{\partial D_z}{\partial z} = \rho. \qquad (1)$$

The electric displacement is the combination of electric field **E** and polarization **P**:

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}, \qquad (2)$$

and it can be seen that if a polarization exists in the absence of an electric field, there will be an electric displacement. In a ferroelectric material, polarization is energetically favorable, but in other materials, the opposite is true because there is an energy cost associated with polarization. The larger the dielectric constant of the material, the smaller the energy cost associated with polarization. This cost provides a driving force to reduce or exclude the electric displacement from a ferroelectric from an adjoining material. There are a number of ways this can be achieved.

In a conventional metal-ferroelectric-metal capacitor, the metal provides a screening charge, which allows the electric displacement to be reduced across an interface, as shown in **Figure 2**a. If we consider a ferroelectric thin film with an out-of-plane polarization D_z, then the existence of a finite screening charge density allows a finite $\frac{\partial D_z}{\partial z}$ so that away from the interface, the electrical displacement is zero. For thick ferroelectric films, the amount of charge provided is finite, and therefore a finite screening length in the metal does not have a significant effect on the spontaneous polarization. However, for very thin ferroelectrics with thicknesses on the order of a few nm, the finite screening length results in a depolarization field within the film that acts to reduce or destabilize the polarization. This idea, originating in continuous dielectric models for materials, has been shown to apply down to the unit-cell length scale by the first-principles calculations of Junquera and Ghosez.[3] In one scenario in which domains do not form, the polarization of the material is reduced in a thin film with realistic electrodes (i.e., those with a finite screening length) as a result of the depolarization field. This was experimentally verified to occur using x-ray diffraction measurements of sample tetragonality in $PbTiO_3$ thin films.[4] Such a measurement is made possible through the strong coupling between strain and polarization in oxide ferroelectrics; though some care must be taken at high polarization values, the relationship between out-of plane strain and polarization weakens.[5]

While one effect of the depolarization field is to reduce the polarization, it can also be seen as a driving force that destabilizes the polarization state of the region where it exists.

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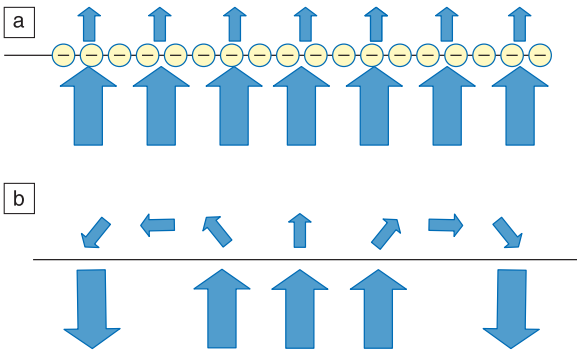


Figure 2. The two scenarios for reduction of D_z at an interface: (a) screening by free charge and (b) reorientation of the polarization.

One effect of this is to make switching to the opposite polarization state easier, reducing the coercive field necessary for switching.[6] Another result of the destabilizing effect of the depolarization field on a uniformly poled ferroelectric is that rather than suffer a reduction in the magnitude of their polarization, ultrathin films often develop an arrangement of very finely spaced stripe domains with opposing polarization directions.[7–9] The existence of these stripe domains can be inferred from x-ray diffraction measurements, where they appear as satellites in the vicinity of Bragg peaks. Measurement of domain structure by x-ray diffraction is appealing in a number of ways, first because no electrical contacts are required; second, because it allows domain periodicities, which are on the order of only a few nm to be readily identified; and third, because the particular peaks around which satellites are observed gives an indication of the polarization directions within the film.[7,10] Real space visualization of the stripe domains in ultrathin films is more challenging because with a domain size on the order of 10 nm, they are close to the resolution limit of the piezoforce microscopy technique,[11,12] which is a favored method for studies of ferroelectric domain structure in ferroelectric thin films. Under certain conditions, the domains become visible in topographic atomic force microscopy measurements,[13] and recently they have been visualized by coherent x-ray Bragg projection ptychography.[14]

The polarization state of a ferroelectric thin film without a top electrode is very sensitive to surface adsorbates, and it is likely that ferroelectric surfaces exposed to air will have their polarization at least partially screened by dissociated water molecules on their surface.[15] Indeed, it has also been shown that it is possible to control the polarization size and direction through control of the surface chemistry[16] or oxygen partial pressure of the environment around a film.[17,18]

Whether by free electrons in a metal or surface adsorbates, we have so far discussed the reduction of D_z via some sort of free charge present at an interface. However, D_z can be reduced across an interface even if there is no free charge if the sum of the in-plane derivatives increases, as in the case where $\rho = 0$:

$$\frac{\partial D_z}{\partial z} = -\frac{\partial D_x}{\partial x} - \frac{\partial D_y}{\partial y}. \quad (3)$$

This relationship allows the polarization to effectively turn around, through the development of in-plane polarization at an interface. The resulting polarization arrangement is most frequently stripes of opposite polarization in the ferroelectric material with some in-plane components of polarization at the interface, a so-called closure domain pattern as shown in Figure 2b. Such patterns have been clearly identified in first-principles simulations of $PbTiO_3$ films with $SrRuO_3$ electrodes.[19]

Ferroelectric-dielectric superlattices

Having discussed some of the key considerations at a ferroelectric metal interface, we now turn to the ferroelectric-dielectric interface that is at the core of many of the artificially layered ferroelectric materials studied today.

We first consider the case where development of an in-plane polarization component does not occur. In such a case, if there is no free charge at the interface, the electric displacement is continuous across the interface or equivalent if we denote the ferroelectric material with a subscript F and the dielectric material with a subscript D:

$$P_F^0 + \varepsilon_0 \varepsilon_F = P_D^0 + \varepsilon_0 \varepsilon_D. \quad (4)$$

Here the electric fields in each layer are denoted by $\varepsilon_F, \varepsilon_D$, and the zero field polarizations are P_F^0, P_D^0 . Another condition is that the change in electrostatic potential across each bi-layer in the superlattice structure should be zero, implying that

$$l_F \varepsilon_F = -l_D \varepsilon_D, \quad (5)$$

where the thicknesses of the layers are denoted by l_F, l_D . The electrostatic energy of a given layer in the presence of a finite electric field is, to leading order in the field, given by $E_{elec} = -l\varepsilon P^0$. When the previous equations are taken into account, one finds that the electrostatic energy of a bi-layer in a superlattice can be expressed as

$$E_{elec}\left(P_F^0, P_D^0\right) = \frac{l_F l_D}{\varepsilon_0 \left(l_f + l_D\right)} \left(P_D^0 - P_F^0\right)^2. \quad (6)$$

This equation shows that there is an energy cost for a difference in polarization between adjacent layers in a ferroelectric dielectric superlattice. If the dielectric layer is fairly easy to polarize, then the system tends to avoid discontinuities in the polarization (as shown in **Figure 3**a). This idea was convincingly shown to be the case in first-principles simulations performed on $BaTiO_3/SrTiO_3$ superlattices,[22] and formed the basis for a Landau theory approach to describe the properties of $PbTiO_3/SrTiO_3$ superlattices, which works well in the limit of a thin dielectric layer.[20]

Both $BaTiO_3$ and $PbTiO_3$ are under considerable compressive strain when grown on $SrTiO_3$ substrates. This leads to a

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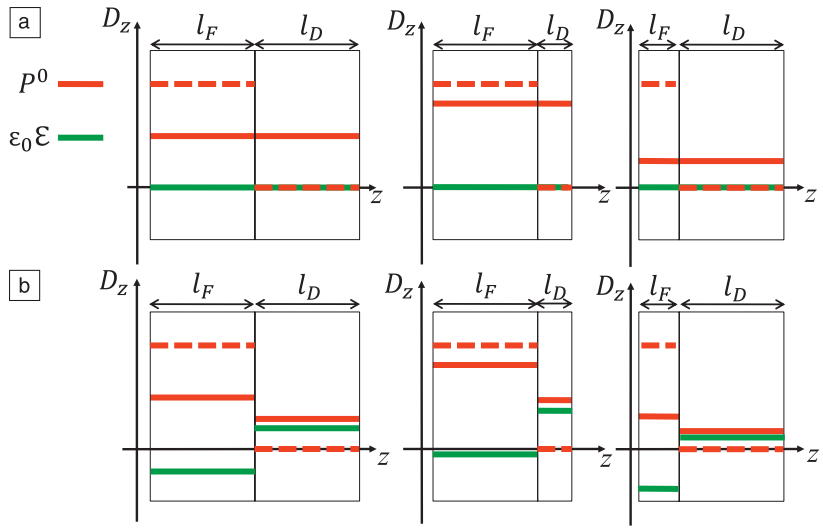


Figure 3. Diagrammatic representation of the two components of the electrostatic displacement field in a ferroelectric dielectric bi-layer with polarization in the growth direction. The vertical axis represents the electric displacement; the horizontal axis is length in the superlattice growth direction. Red lines show the zero field electric polarization; green lines show the field component of the electric displacement, which comes from an electric field. The dashed lines show the polarization the materials would have if they were stand-alone epitaxially strained films. (a) Ferroelectric-dielectric bilayers with a readily polarizable dielectric. Here it can be seen that the electric field is negligible, and polarization is essentially continuous through the structure. The value of the polarization is determined by the relative volume fractions of the two materials.[20] (b) Ferroelectric-dielectric bilayers with a dielectric that is not readily polarizable. Here polarization is not continuous, and there is an electric field present in each layer. As it is in the opposite direction to the polarization in the ferroelectric layer, there is an associated energy cost, and the system may opt to reduce the size of the polarization, either by a direct reduction of the polarization in the ferroelectric material, or by forming either stripe domains or an antiferroelectric.[21]

strong preference for out-of-plane polarization in these materials. If the epitaxial constraint on the in-plane lattice parameter of the superlattices is maintained, then so long as the dielectric layers are kept thin, the previous considerations dominate the evolution of polarization from one layer to the next. However, if the dielectric layer is thicker than a few unit cells and development of an in-plane polarization is not too costly for the material, then the electric displacement in the out-of-plane direction need not be constant throughout the superlattice, rather a domain structure can form where the polarization rotates at the interface between the materials leaving the interior of the ferroelectric materials strongly polarized and the interior of the dielectric material weakly polarized. In this configuration, the layers are described as being weakly coupled. The transition from superlattices, where the layers are strongly electrostatically coupled in the thin layer limit (which applies to thicknesses below a few unit cells), to being weakly coupled in the thick layer limit has been studied in $KTaO_3/KNbO_3$ superlattices[23–25] and $PbTiO_3/SrTiO_3$ superlattices.[26–28]

Going one step beyond the case where an in-plane polarization is possible in the dielectric layer, one can consider superlattices, where one layer has a preference for out-of-plane polarization, and the other has a preference for an in-plane polarization. An example of such a system is $PbTiO_3/CaTiO_3$ on a $SrTiO_3$ substrate. While bulk $CaTiO_3$ is not ferroelectric, when grown on $SrTiO_3$, it is under considerable tensile strain, and the competition between its tendency toward in-plane polarization and the desire of $PbTiO_3$ to be out-of-plane polarized allows rotation of the polarization and an enhanced piezoelectric response for particular ratios of the layer thicknesses of the two materials.[29]

In contrast to the previously discussed materials that involve readily polarizable dielectric layers, superlattices that involve dielectrics that have fairly modest dielectric constants may arrange themselves in such a way as to have no overall polarization rather than suffer the energy cost associated with polarization discontinuity (depicted in Figure 3b). For example, $(BaTiO_3)_m/(BaO)_n$ superlattices made of alternating m unit cell layers of FE perovskite $BaTiO_3$ and n unit cell layers of rock salt BaO have been studied from first principles,[21] and it was found that (1) when $m<<n$, the superlattice remains an insulator, and (2) when the ratio m/n reaches a critical value, the system prefers to stabilize in an antiferroelectric state, where adjacent unit cells have opposite polarizations that best minimize the electrostatic energy (global anti-polar displacements will not couple with the depolarizing electric field). Antiferroelectric materials are of high interest for energy storage applications, because their double hysteresis loop characteristic results in a larger amount of energy stored for a given polarization value when compared to linear dielectrics.[30]

Hybrid improper ferroelectricity

So far, the only structural distortions we have considered have been the polar distortions most commonly associated with ferroelectricity. Recently, a significant revival of interest in improper ferroelectrics has occurred, motivated in part by the discovery that it is present in $PbTiO_3/SrTiO_3$ superlattices.[31] Levanyuk proposed the concept of improper ferroelectricity in order to describe some ferroelectric phase transitions, where the polarization P is no longer the primary order parameter that governs the phase transition.[32] (An order parameter is an artificial variable used in the so-called Landau phenomenological theory. The aim of the Landau theory is to describe the temperature evolution of this order parameter around phase transitions.) In this case, Levanyuk considered a non-polar two-dimensional order parameter $\Phi = (\Phi_1, \Phi_2)$, for which the symmetry transformations are such that the product $\Phi_1.\Phi_2$ has the same symmetry as P. When this condition is satisfied, the term $\Phi_1.\Phi_2.P$ is invariant under all the symmetry operations of the crystal. As a result, when the order parameter Φ condenses (becomes non-zero) at its critical temperature T_c, it will

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induce a spontaneous polarization through the tri-linear term $\Phi_1.\Phi_2.P$, even if P is unstable (i.e., P would not develop if Φ is absent). In crystals, presenting such a tri-linear coupling with P, a spontaneous polarization can be driven by nonpolar distortions. Because of its scarcity in bulk materials and the small reported spontaneous polarization in known compounds, the mechanism of improper ferroelectricity has not historically attracted a lot of attention.

The discovery of a similar mechanism in $PbTiO_3/SrTiO_3$ superlattices[31] and work on $YMnO_3$, an important multiferroic (a multiferroic material is defined as a crystal that possess more than one ferroic order parameter, such as ferroelectricity, ferromagnetism, or ferroelasticity) that is an improper ferroelectric,[33] refocused attention on improper ferroelectrics.[34–39] It has been found that at the interface between two perovskites ABO_3 and $A'BO_3$, the order parameters Φ_1 and Φ_2 related to the out-of-phase antiferrodistortive (AFD) distortion ($a^0a^0c^-$ in the so-called Glazer notation)[40] and in-phase AFD distortion ($a^0a^0c^+$), respectively, have their product, $\Phi_1.\Phi_2$, that symmetrically transforms with the polarization along the z-direction P_z (see **Figure 4** for a schematic view of the distortions). This means that the tri-linear term $\Phi_1.\Phi_2.P_z$ is invariant under all the symmetry transformations of the crystal, and thus if one has both Φ_1 and Φ_2 condensed in $ABO_3/A'BO_3$ superlattices, spontaneous polarization will be induced in a manner similar to the mechanism of improper ferroelectricity. By taking into account such a tri-linear coupling in $PbTiO_3/SrTiO_3$ superlattices, it has been possible to explain the anomalous experimental measurements presenting a linear dependence of the polarization with temperature (while it should be a square root dependence for a regular ferroelectric) and a nearly temperature independent dielectric constant (while a divergence around T_c should be observed for a regular ferroelectric phase transition). The crucial point is that the tri-linear coupling with P is induced by the interface and cannot be observed in the bulk parent crystals. In $PbTiO_3/SrTiO_3$ superlattices, the resulting ferroelectric and dielectric properties are large, and thus of great interest for technological applications.[31]

We note, however, that in the definition of improper ferroelectricity given by Levanyuk,[32] the components of the two-dimensional order parameter will condense together at the same critical temperature T_c. This makes a difference for the mechanism reported in $PbTiO_3/SrTiO_3$ superlattices, where the two order parameters Φ_1 and Φ_2 are different and independent, and thus there is no reason to have the condensation of these two order parameters at the same T_c. Moreover, in $PbTiO_3/SrTiO_3$ superlattices, first-principles calculations show[31] that the polarization can develop alone without the need of the AFD distortions. To distinguish between the two possibilities, the tri-linear coupling inducing polarization with two independent order parameters has been subsequently called "hybrid improper ferroelectricity."[34] Going further, a rationalization of improper ferroelectricity has been proposed in terms of electric displacements.[35] From this analysis, it appeared that a regular improper ferroelectric as defined by Levanyuk is nearly unaffected by the electrical boundary condition, a very interesting property for applications.[36]

This is, however, not the case in the hybrid improper ferroelectric state present in $PbTiO_3/SrTiO_3$ superlattices, where sensitivity to the electrical boundary conditions depends on the interaction strength between the two non-polar AFD modes. If this interaction is not strong (if the two AFD distortions are not in competition) and if the AFD distortions are dominant with respect to P, then we can expect a similar response to the electrical boundary conditions as for a regular improper ferroelectric. This, however, does not explain why experimentally the temperature dependence of the ferroelectric properties of the $PbTiO_3/SrTiO_3$ superlattice is observed to be as a regular improper ferroelectric, while first-principles calculations predict an unusual hybrid improper ferroelectric behavior.

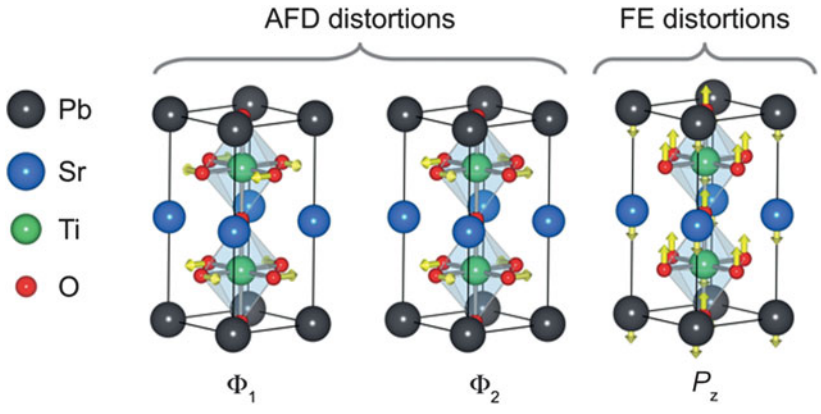


Figure 4. Schematic of the three distortions present in the hybrid improper ferroelectric state observed in $PbTiO_3/SrTiO_3$ superlattices. The yellow arrows represent the direction of the atomic displacement related to the distortions. The symmetry breaking of the interface between the two compounds allows these three competing instabilities at the bulk level to be associative in the superlattices through a tri-linear coupling $\Phi_1.\Phi_2.P_z$.

Systematic studies have been performed from symmetry analysis and first-principles calculations in order to understand the conditions to reproduce the hybrid improper ferroelectricity in superlattices other than $PbTiO_3/SrTiO_3$.[35,37,38,41,42] The results are the following: A tri-linear coupling between $a^0a^0c^-$, $a^0a^0c^+$, and P_z is possible only if the perovskite superlattice is built by alternating A sites ($ABO_3/A'BO_3$), and it is completely forbidden if one alternates the B site ($ABO_3/AB'O_3$). Another hybrid improper coupling is also possible between the in-plane polarization P_{xy} and the tilt pattern $a^-a^-c^+$ in $ABO_3/A'BO_3$ superlattices. The chemistry choice of the A, A', and B cation is important since, depending on the composition, they will favor different tilt patterns that can or cannot energetically favor the tri-linear coupling with the polarization. It is possible to tune the two hybrid improper ferroelectric states

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(the one inducing P_z and the one inducing P_{xy}) by playing with epitaxial strain, even when the propensity of the two parent compounds to induce such a state in the superlattice is not high.

The fact that having the tilt pattern $a^-a^-c^+$ in the parent compounds favors a hybrid improper ferroelectric state in $ABO_3/A'BO_3$ superlattices is particularly attractive since the $a^-a^-c^+$ tilt pattern (*Pnma* space group) is by far the most common distortion present in bulk perovskites, thus opening up possibilities to numerous superlattice candidates.

Extension to electric control of magnetization

Tuning the direction of magnetic moments with an electric field in magnetic materials is one of the main objectives toward lower energy consumption of electronic memory and spintronic applications.[43,44] Current magnetic memories use an electric current to write the information. This process requires much more energy (several order of magnitudes) than if one applies an electric voltage instead. Finding bulk materials exhibiting such a property (the magnetoelectric property) appeared very difficult in view of the rarity of the compounds that are magnetoelectric, but also because the discovered materials doing so often displayed very small magnetizations that only occurred at very low temperatures and were thus useless for technological applications.

One approach proposed to tune the magnetization with an electric field is through a magnetic-metal/ferroelectric interface.[43,45–47] The idea is to exploit possible magnetoelectric coupling at the interface between a ferromagnetic metal and a regular ferroelectric. Successful experimental evidence of such interfacial coupling has been shown in prototypical Fe/$BaTiO_3$ and Co/$BaTiO_3$ heterostructures, where the magnetization at the interface can be reversed by reversing the spontaneous polarization of the ferroelectric layer.[48] The interest in such combinations is that the magnetoelectric coupling is observed at room temperature. A similar reversal of the magnetization of a CoFe magnetic alloy grown on top of the multiferroic material $BiFeO_3$ has been observed experimentally at room temperature.[49] In this case, the mechanism responsible for electric switching of the magnetization is related to the magnetic coupling between $BiFeO_3$ and CoFe at the interface and thus through the intrinsic magnetoelectric coupling present in $BiFeO_3$. Going further, a similar mechanism has been proposed by means of first-principles calculations in a $PbTiO_3$ layer covered by a Fe/Au/Fe trilayer.[50] In such a system, it is predicted that the amplitude of the magnetization switching of the top Fe layer when reversing the polarization in $PbTiO_3$ can be modulated by the thickness of the Au layer through interlayer exchange coupling in the Fe/Au/Fe trilayer.

Beyond these systems, a different approach to an effective magnetoelectric device is to build artificial magnetoelectric-layered systems, an approach that has already had some success in the context of giant magnetoresistance.[51]

The hybrid improper ferroelectric mechanism suggests there is high potential for tuning the magnetic properties with an electric field through tri-linear coupling between the polarization and the oxygen octahedral rotation. Magnetic interactions are strongly affected by the binding between the transition-metal cation and the surrounding oxygens. If one induces a distortion of the oxygen octahedra in a magnetic perovskite AMO_3 (through the AFD distortions, for example), the strength of the super-exchange interaction between the magnetic action's *M* may be modified. Moreover, it is also well established that the spin orientation (linked to single ion anisotropy, which is the spatial orientation anisotropy seen by a magnetic moment on a given atom) and the spin canting (in most cases due to the Dzyaloshinsky–Moriya interaction, which involves the cross product between two spins and tends to favor orthogonal orientation of two successive magnetic moments in a crystal) are strongly affected by the AFD distortions.[52] Then, if one wants to tune the magnetic interactions by an electric field, coupling of the AFD distortion with the electric field is required. This coupling is nevertheless extremely small if the AFD distortions are present alone since they are nonpolar distortions. It is here that the interest in having a direct coupling between AFD and polarization becomes apparent, and this exists in the case of the hybrid improper ferroelectricity phases reported in $ABO_3/A'BO_3$ superlattices.

Through the tri-linear coupling $\Phi_1.\Phi_2.P$ discussed in the previous section, if one applies an electric field to switch the polarization, one of the two other order parameters Φ_1 and Φ_2 will have to switch in order to keep the energy invariant. This mechanism has been explored in detail from first-principles calculations, and the preliminary results indicate that the most favorable case is when the P_{xy} orientation of the polarization is coupled with the $a^-a^-c^+$ tilt pattern.[34,42,52] However, the inversion mechanism of the magnetization with P_{xy} is not straightforward.[42] It appears that the electric field has to reverse the $a^-a^-c^0$ tilt pattern (Φ_1) and not the $a^0a^0c^+$ tilt pattern (Φ_2) because the magnetization is more strongly coupled to the $a^-a^-c^0$ tilt pattern.[42,52] Systems exhibiting such a coupling have not yet been found because in most analyzed magnetic superlattices, it appears to be more energetically favorable to reverse $a^0a^0c^+$ when P_{xy} is reversed by an electric field rather than reversing $a^-a^-c^0$.

Ferroelectric metal superlattices

An interesting variation on the ferroelectric-metal interface is the special case of an ultrathin metallic layer within a ferroelectric superlattice. Recently, layered heterostructures combining dielectrics such as $SrTiO_3$ with metallic magnetic perovskite oxides such as $SrRuO_3$, $SrFeO_3$, and $SrVO_3$ have been recognized to be rich in new physics,[53–60] particularly as the thickness of the metallic perovskite layer decreases. For example, in $SrTiO_3/SrRuO_3$, a single unit cell layer of $SrRuO_3$ embedded within $SrTiO_3$ maintains a metallic character and is expected to behave like a two-dimensional electron gas (2DEG).[57] In this system and the related $PbTiO_3/SrRuO_3$ system,[60] the fact that $SrRuO_3$ layers retain their metallic character as their thickness is reduced allows the anisotropy

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of the conductivity of the overall superlattice structure to be tuned, which presents a potential route for enhancing the thermoelectric figure of merit.[58] By contrast, in $SrTiO_3/SrFeO_3$[54] and $SrTiO_3/SrVO_3$,[55] a transition from metallic to insulating behavior is observed as the metallic layer is reduced in thickness. The origin of the suppression of metallicity is quite different in the two cases, but in general, systems that have a critical thickness for their metallic layer can be considered to become novel insulators that may have distinctive dielectric properties and/or a tunable bandgap for solar energy conversion applications.[61]

Tri-color superlattices

While in this article we have focused on bi-color superlattices, alternating between the growth of three different materials (tri-color superlattices) has also been explored.[62–67] In such tri-color dielectric systems, the inversion center is broken irrespective of the composition of the layers, and thus the tri-color superlattices will always be polar materials. An appealing aspect of these material systems is that it is possible to control the "amplitude" of the inversion-symmetry breaking by varying the thickness ratio between the different constituents.[66] Tri-color superlattices also appear to be an extremely promising route to obtain large magnetoelectric responses.[64,65] Alternating more than three different compounds has not (yet) been explored, though we might expect very interesting and complex phenomena to appear in these systems due to the increasing number of different interfaces.

Conclusion

The possibilities offered by the complex interplay of structural considerations, electrostatics, and strain at interfaces between ferroelectric oxides and other materials are exciting. A key feature of both past research and future progress in this area is that a combination of computation and cutting edge experimental tools are required to uncover the mechanisms that are active at an interface. The ability to harness nonstructural distortions through hybrid improper ferroelectricity is just one possible route to new materials, but one that appears to have great potential. One issue still to be explored fully is the temperature dependence of this mechanism, and a first-principles investigation of this would be especially welcome. As the understanding of these complex interfaces progresses, we predict we will soon see materials that go beyond two or three component materials, and that in the not too distant future, the lessons learned in these carefully crafted epitaxial structures will make their way into the next generation of high performance dielectric, ferroelectric, piezoelectric, and pyroelectric devices.

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