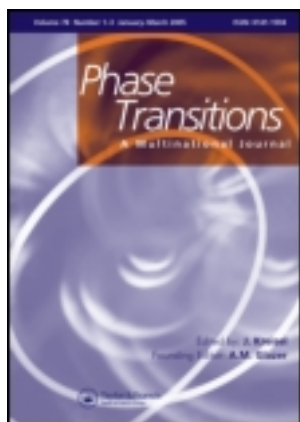


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Domain wall functionality in BiFeO₃

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Domain wall functionality in BiFeO₃

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In this article we provide an overview of phenomena involving domain walls in BiFeO₃ as nanoscale functional elements. Because ferroelectric domain walls can be routinely modified using electric fields, our results suggest a new degree of flexibility for domain boundary engineering and oxide-based nanoelectronics.

Keywords: ferroelectrics; domain walls; scanning probe methods; optics; photo-voltaics; nanoscale characterization

Recently, there has been a number of investigations showing interesting electrical transport properties at ferroelectric domain walls, in particular in multiferroic materials [1–12]. Variable levels of local electrical conductance have been measured at ferroelectric domain walls in BiFeO₃, hexagonal YMnO₃ and Pb(Zr_{0.2}Ti_{0.8})O₃. It is known that such materials often have unconventional mechanisms driving the formation of domains. Multiferroics especially are a likely source for novel domain and domain-wall properties also with regard to their magnetic properties. There are probably more materials that can exhibit similar effects, as the rich physics of transition metal oxides results in a wide variety of properties that are related to a delicate balance between charge, spin, orbital and lattice degrees of freedom. In that respect, there has been a large body of work on complex oxide materials, mainly on members of the perovskite family, which offer the advantage of very high structural quality growth. Using modern synthesis methods such as pulsed laser deposition (PLD), molecular beam epitaxy (MBE) and metal–organic chemical vapor deposition (MOCVD), among others, it is now possible to engineer interfaces between complex transition metal oxides with atomic-scale precision. Such interfaces locally break the symmetry, induce stress, and vary the bonding between ions. This in turn gives rise to changes in bandwidth, orbital interactions and level degeneracy, opening venues for modifying the electronic structure of these strongly correlated materials. Charge transfer can induce carrier densities that are different at the interface than in the bulk, resulting in physical properties at the interface which may be completely different from those of the parent bulk materials [13–17]. Tuning and controlling the physical properties of interfaces

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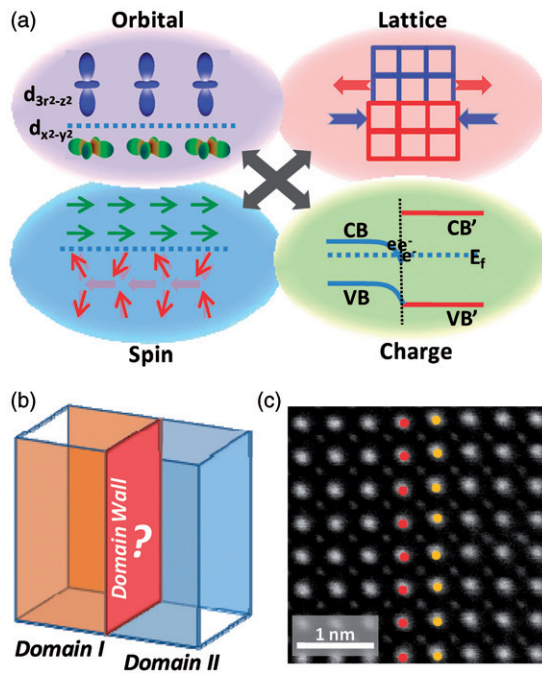


Figure 1. (a) The rich physics of transition metal oxides results in a wide variety of properties that are related to a delicate balance between charge, spin, orbital and lattice degrees of freedom. (b) Domain walls in ferroic materials can have different properties than the bulk phase. Structure and symmetry changes can give rise to different electronic and magnetic properties, they may even give rise to a local phase transition at the wall. (c) atomic resolution TEM image showing atomically sharp structural domain wall in BiFeO_3 (wall position indicated by colored dots).

and domain boundaries provides a new playground for research and offers a new nanoelectronics characterization platform for future nanotechnology [18]. Recent developments in the field of electronic and transport properties of domain walls in such materials are the subject of this article.

Since ferroic phases can arise in two or more distinct orientations of the order parameter, they can form domains, separated by domain walls (Figure 1). Domains are a representation of long-range order with respect to at least one macroscopic tensor property of the material (order parameter). When orientation states are changed, the interfaces (domain walls) move; thus the domain structure can be manipulated by external fields, which is a central feature of ferroic materials. In general, in the vicinity of such a transition one or more macroscopic properties of the material associated with the order parameter can become large and very susceptible to external fields. Field-induced phase transitions around the transition temperature are a common feature. Subsets of ferroic phase transitions are ferroelectric, ferroelastic and ferromagnetic transitions. These involve the emergence of spontaneous polarization, spontaneous strain, or spontaneous magnetization and are commonly referred to as primary or first order ferroics. Many so-called smart materials and structures have at least one of these properties and are designed to change them in a preconceived manner through the application of external fields. Thus, given their intrinsic structure, ferroic materials are ideally suited for this purpose.

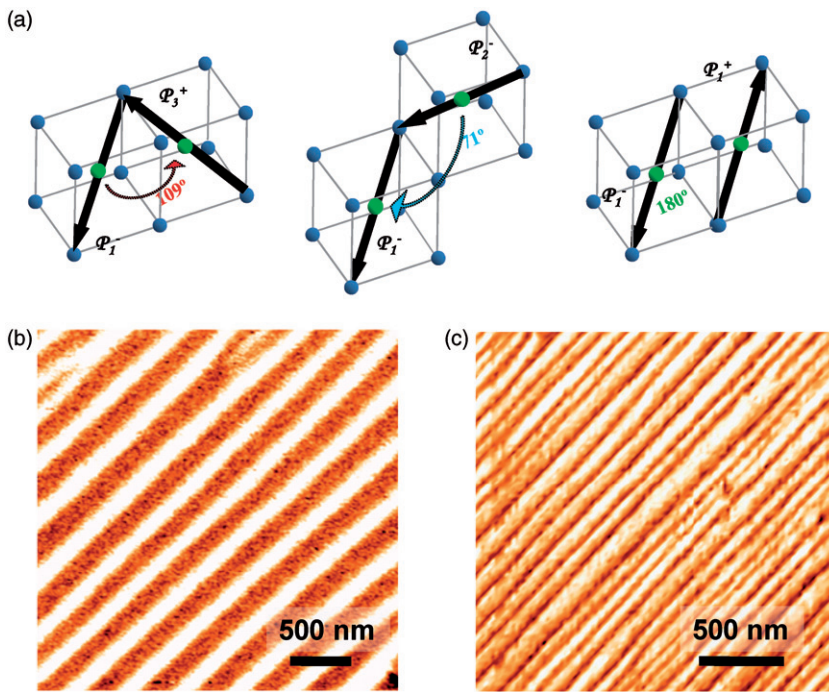


Figure 2. (a) The three different types of domain walls in rhombohedral bismuth ferrite. Arrows indicate polarization directions in adjacent domains. (b) In-plane PFM images of BFO films showing ordered stripe arrays of 71° and 109° domain walls.

The changes in structure (and as a consequence electronic structure) that occur at ferroelectric (multiferroic) domain walls can thus lead to changes in transport behavior. Indeed, domain wall conductivity has been shown in different ferroic materials, although with different transport behavior: the domain walls of BiFeO_3 (compare Figure 2) were found to be more conductive than the domains [19], while those of YMnO_3 were found to be more insulating or conductive depending on their orientation [9,10]. In YMnO_3 , a so-called improper ferroelectric multiferroic, in which ferroelectricity is induced by structural trimerization coexisting with magnetism, domain walls are found to be charged and stable. This material exhibits a conductive ‘cloverleaf’ pattern of six domains emerging from one point, and the ferroelectric state has been reported to be more conducting than the paraelectric state. The increase of the Y–O bond distance at domain walls may be responsible for the reduction of local conduction. The observed conduction suppression at domain walls at high voltages (still much less than the electric coercivity) is in striking contrast with what has been reported on BiFeO_3 .

A useful clue for interpreting these results is perhaps the analysis of the paraphase. Whereas the high temperature, high symmetry phase of BiFeO_3 is more conducting than the ferroelectric phase [19], the converse is true for YMnO_3 [20]. This illustrates an important point: in some respects the internal structure of the walls can be considered to be in the paraelectric state; by way of a trivial example, the 180° domain walls of a ferroic are expected to be non-polar, just like its paraphase. The examples of BiFeO_3 and YMnO_3 suggest that the paraphase-like behavior can be applied to domain wall properties other than just the polarization: the insulating paraelectric state of YMnO_3 is consistent with the

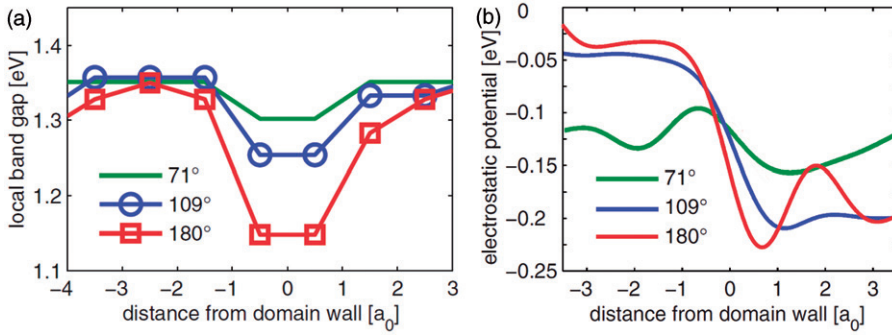


Figure 3. (a) Local band gap at domain walls in bismuth ferrite extracted from the layer-by-layer densities of states. (b) Macroscopically and planar-averaged electrostatic potential for the domain boundaries with continuous oxygen octahedral rotations. Adapted from Lubk et al. [36].

insulating nature of its domain walls, and conversely the conducting state of the paraphase of BiFeO_3 is consistent with its domain wall conductivity. Nevertheless, in the conductivity of the BiFeO_3 walls at least there are several other considerations: octahedral rotations, electrostatic steps arising from rigid rotation of the polar vector, and increased carrier density at the wall are all thought to play a role in the domain wall conductivity of BiFeO_3 and potentially also of other perovskites.

Detailed electronic properties of domain walls in bismuth ferrite have been investigated by Lubk et al. [21]. Using density functional theory the layer-by-layer densities of states was calculated. It was found that the domain walls have a significantly reduced band gap compared to the $R3c$ bulk structure. Structural changes at the wall thus lead to scenarios that approach the ideal cubic structure, in which the 180° Fe–O–Fe bond angle maximizes the Fe $3d$ -O $2p$ hybridization and hence the bandwidth of the material. Figure 3 shows the local band gap extracted from the layer-by-layer densities of states and the electrostatic potential across the domain boundaries for the three wall types. In all cases a reduction in the band gap in the wall can be seen, with the 180° wall showing the largest effect. In no case, however, does the band gap approach zero in the wall region. Similar behavior has been predicted, e.g., for LaMnO_3 [22]. The same first principles calculation also give insight into the changes in Fe–O–Fe bond angle in BiFeO_3 , in addition to the fact that walls in which the rotations of the oxygen octahedra do not change their phase when the polarization reorients are significantly more favorable than those with rotation discontinuities – i.e., antiphase octahedral rotations are energetically very costly.

The analysis of the local polarization and electronic properties also revealed steps in the electrostatic potential for all wall types, and these must also contribute to the conductivity. Steps in the electrostatic potential at domain walls are correlated with (and caused by) small changes in the component of the polarization normal to the wall [23]. These changes in normal polarization are a consequence of the rotation of the polar vector across the domain wall, and are not exclusive to BiFeO_3 . Tetragonal PbTiO_3 , for example, shows a similar effect for a 90° wall [23]. Extended phase-field calculations for tetragonal BaTiO_3 also allow calculating the intrinsic electrostatic potential drop across the 90° domain wall, regardless of the consideration of the ferroelectric as n-type semiconductor or dielectric [24]. This potential change creates a large electric field that promotes an asymmetric charge distribution around the walls, where electrons and oxygen vacancies

concentrate on the opposite sides. The increased charge density presumably promotes increased conductivity.

As mentioned, the semi-rigid rotation of the polar vector across a ferroelectric–ferroelastic wall leads to an electrostatic potential that is screened by free charges which enhance the local charge density and thus, presumably, the conductivity. Since this polar rotation [25] is not exclusive to BiFeO_3 ; other perovskite ferroelectrics should also be expected to display enhanced conductivity – though to our knowledge this has not been reported. In BiFeO_3 , several other factors might be further helping the conductivity enhancement: Firstly, the magnetoelectric coupling between polarization and spin lattice is such that the magnetic sub-lattice rotates with the polarization [26,27]. Since spins rotate rigidly, they might favor a more rigid rotation of the polarization and hence a bigger electrostatic step at the wall (and of course the polarization of BiFeO_3 is itself bigger than that of other known perovskite ferroelectrics, which means that all other things being equal a rigid polar rotation in BiFeO_3 will cause a bigger electrostatic step). But perhaps the most obvious consideration is the fact that BiFeO_3 has intrinsically smaller bandgap than other prototypical perovskite ferroelectrics (~ 2.7 eV instead of 3.5–4 eV). This means that the screening charges accumulated at the wall will be closer to the bottom of the conduction band and hence will more easily contribute to the conductivity. It would be interesting to see if highly insulating single-crystal samples such as those studied by Chishima et al. [28] display the same domain-wall conductivity as do the thin-film samples studied so far. The current density of these single-crystal samples can be as low as 10^{-9} A/cm² even at electric fields in excess of 50 kV/cm, while typical resistivities of thin films are in the region of 10^6 – 10^8 Ohm cm, comparable to the resistivity of good quality BiMnO_3 [29]. How about non-ferroelectric insulators? This type of conductivity is believed to be present in materials such as LaMnO_3 as well; anytime you break the symmetry of the structure by putting in such defects, you will have a chance to change the electronic structure.

The role of defect accumulation at the walls also deserves close scrutiny. Localized states are found in the spectrum of ferroelectric semiconductors, and states localized at the walls and inside the domain but close to the wall split off from the bulk continuum. These non-degenerate states have a high dispersion, in contrast with the ‘heavy-fermion’ states at an isolated domain wall [30]. Charged double layers can be formed due to coupling between polarization and space charges at ferroelectric–ferroelastic domain walls [31]. Charged domain wall energies are about one order larger than the uncharged domain wall energies [20], and phenomenological calculations show decoration of walls by defects such as oxygen vacancies. The presence of charge and defect layers at the walls means that such walls promote electrical failure by providing a high conductivity pathway from electrode to electrode.

The control of the electronic structure at walls by doping and strain in ferroelectric and ferroelastic oxides opens a way to effectively engineer nanoscale functionality in such materials [32]. For the case of BiFeO_3 A-site doping with Ca, and magnetic B-site substitution such as Co or Ni, might prove to be a viable way to achieve new domain wall properties by manipulating the electronic structure, spin structure and dipolar moment in this material [33]. Of obvious future interest is the question of what sets the limits to the current transport behavior at walls: can one ‘design’ the topological structure of the domain wall to controllably induce electronic phase transitions within the wall arising from the correlated electron nature? Is it possible to trigger an Anderson transition by doping of domain walls or straining them? Future work has to focus on such possibilities.

Recently, the observation of tunable electronic conductivity at domain walls in La-doped BFO linked to oxygen vacancy concentration has been reported [3]. Specific growth conditions have been used to introduce varying amounts of vacancies in thin film samples [34]. The conductivity at 109° walls in such samples is thermally activated with activation energies of 0.24 to 0.5 eV. From a broader perspective, these results are a first step towards realizing the tantalizing possibility of inducing an insulator–metal transition locally within the confines of the domain wall through careful design of the electronic structure, the state of strain and chemical effects at the domain wall. For actual device applications the magnitude of the wall current needs to be increased. The choice of the right shallow-level dopant and host material might prove to be key factors in this respect. Further study of correlations between local polarization and conductivity are an exciting approach to understanding the conduction dynamics and associated ferroelectric properties in the presence of strong coupling between electronic conduction and polarization in complex oxides (Figure 4).

Recently, it was also reported that an anomalous photovoltaic effect in BFO thin films arises from a unique, new mechanism – namely, structurally driven steps of the electrostatic potential at nanometer-scale domain walls [2–4]. In conventional solid-state photovoltaics, electron–hole pairs are created by light absorption in a semiconductor and separated by the electric field spanning a micrometer-thick depletion region. The maximum voltage these devices can produce is equal to the semiconductor electronic bandgap. Interestingly, domain walls can give rise to a fundamentally different mechanism for photovoltaic charge separation, which operates over a distance of 1–2 nm and produces voltages that are significantly higher than the bandgap. The separation happens at previously unobserved nanoscale steps of the electrostatic potential that naturally occur at ferroelectric domain walls in the complex oxide BiFeO_3 . Electric-field control over domain structure allows the photovoltaic effect to be reversed in polarity or turned off (Figure 5).

Currently, the overall efficiency of those photovoltaic devices is limited by the conductivity of the bulk bismuth ferrite material, which is primarily controlled by the low carrier mobility. Methods to increase the mobility, as well as induce the spatially periodic potential in an adjacent material with a lower gap than BFO are possible routes to achieve larger current densities under white light illumination, and more generally, they would

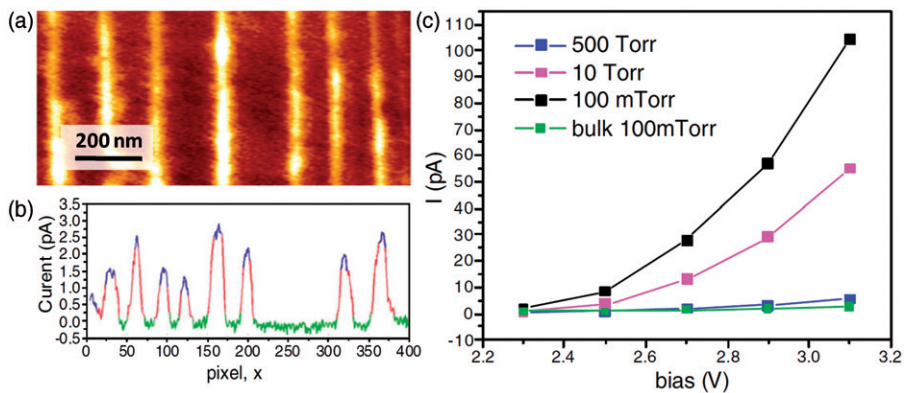


Figure 4. (a) c-AFM images of a BFO sample with 109° stripe domains showing conduction at the walls. (b) Example of a c-AFM current image cross-section. (c) Current levels for samples with different oxygen cooling pressure and thus varying density of oxygen vacancies.

demonstrate what the source of periodic potential and the PV current flow can be in different materials. Low band-gap semiconductors with asymmetric electron and hole mobilities are possible candidates to show such an effect. In addition, photo-electrochemical effects at domain walls are a possible further interesting route, e.g. for applications in water splitting [35].

Defect–domain wall interaction is a very important area of research that deserves increased attention [36]; e.g., point defects, can broaden the wall [37,38]. The width of twin walls in PbTiO_3 , for example, can be strongly modified by the presence of point defects within the wall. The intrinsic wall width of PbTiO_3 is about 0.5 nm, but clusters of point defects can increase the size of the twin wall up to 15 nm [39]. Trapped defects at the domain boundary play a significant role in the spatial variation of the antiparallel

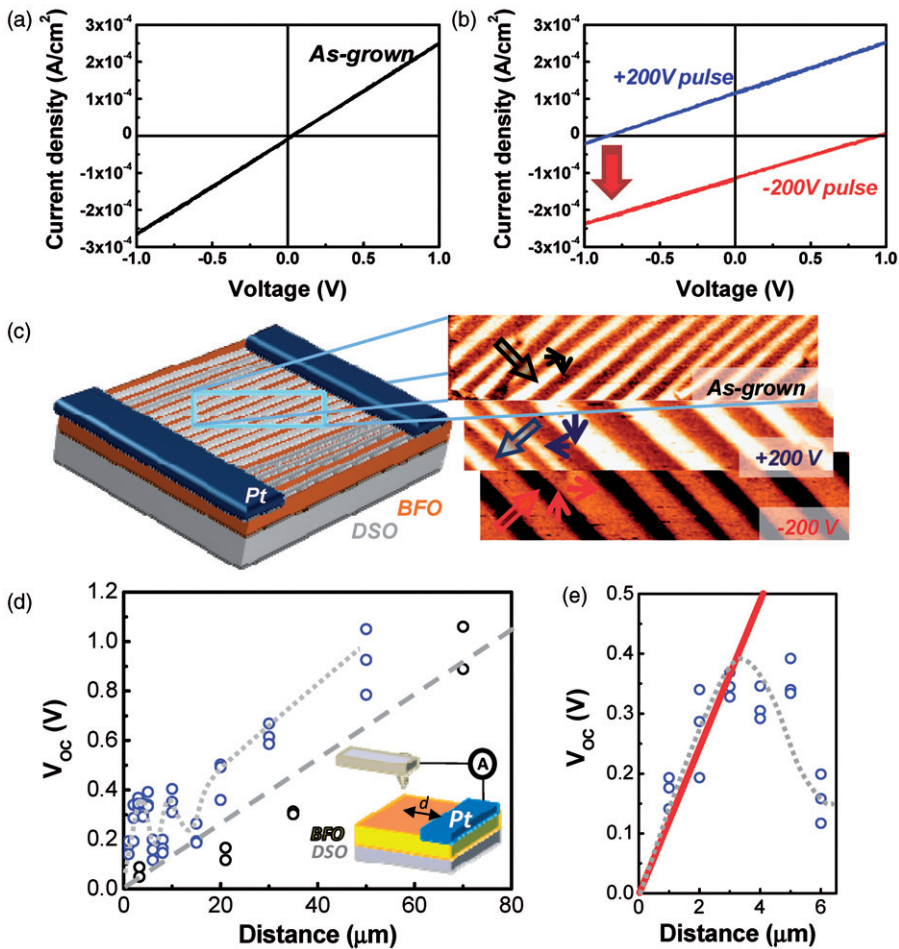


Figure 5. Switchable domain-wall PV effect and c-AFM based PV characterization. (a) Photovoltaic I–V curve for as-grown sample, (b) same after switching, (c) corresponding PFM images of the as-grown and poled device structures. Arrows indicate the in-plane projection of the polarization and the net polarization direction, (d) local measurements of V_{OC} , (a) 109° domain walls (blue) show different, oscillating behavior of V_{OC} with distance as compared to 71° domain walls (black). Inset: schematic nanoscale PV measurement setup, (b) initial large slope (red line) indicating large PV effect at 109° walls.

polarization width in the BaMgF₄ single crystal as seen by PFM [40], and asymmetric charge distribution around 90° domain walls in BaTiO₃ have also been reported, where electrons and oxygen vacancies concentrate on the opposite sides [38]. Interaction between the order parameter and the point defect concentration causes point defects to accumulate within twin walls [37]; conversely such defects contribute to the twin-wall kinetics and hysteresis [41], as they tend to clamp the walls. Oxygen vacancies in particular have been shown to have a lower formation energy in the domain wall than in the bulk, thereby confirming the tendency of these defects to migrate to, and pin, the domain walls [42]. This leads to a mechanism for the domain wall to have a memory of its location during annealing [31].

Domain wall (super)conductivity was studied by Aird and Salje [43]. Exposing WO₃ to sodium vapor, they observed preferential doping along the ferroelastic domain walls. Transport measurements showed superconductivity with a critical temperature of 3 K, while magnetic measurements did not, suggesting that superconductivity was confined to the domain walls only, which provided a percolating superconductive path, while occupying a very small volume fraction of the crystal. Later, Bartels et al. [44] used c-AFM to show the converse behavior. The domain walls of a calcium-doped lead orthophosphate crystal were found to be more resistive than the domains.

The concept of doping has also been applied to bismuth ferrite in an attempt to modify the electronic and magnetic properties and to reduce leakage currents [14,45]. B-site doping of BFO with Ti⁴⁺ has been shown to reduce leakage by over three orders of magnitude while doping with Ni²⁺ lead to a higher conductivity by over two orders of magnitude [46]. Likewise, doping with Cr or Mn has also been shown to greatly reduce leakage currents in BFO films [47]. Yang et al. investigated Ca doping of BFO with results showing strong similarity to phase diagrams of high-*T_C* superconductors and colossal magnetoresistive manganites where a competition between energetically similar ground states is introduced by hole doping [32]. Control of the conductive properties by band-filling was observed in Ca-doped BFO. Application of an electric field enabled this control to the extent that a p–n junction can be formed, erased and inverted in this material. A ‘dome-like’ feature in the phase diagram is observed around a Ca concentration of 1/8, where a new pseudo-tetragonal phase appears and the electric modulation of conduction is found to be the largest. Conductive-AFM measurements reveal that the material exhibits resistive switching and that subsequent application of electric fields can reverse the effect. The observed reversible modulation of electric conduction accompanied by the modulation of the ferroelectric state is a consequence of the spatial movement of naturally produced oxygen vacancies under an electric field that act as donor impurities to compensate Ca acceptors and maintain a highly stable Fe³⁺ valence state. This observation might lead to new concepts for merging magnetoelectrics and magnetoelectronics at room temperature by combining electronic conduction with electric and magnetic degrees of freedom [48–50]. This doping concept of Ca and Mn, among others, might also be applicable to domain walls in BiFeO₃.

Another interesting aspect of nanoscale oxide materials and the domain walls therein is their potential usage in tunneling devices. Control of the growth of these materials on the unit cell level has led to research on the application of high quality ultra-thin ferroelectric films as switchable tunnel barriers for various applications [51]. The polarization reversal of a ferroelectric barrier has been predicted to show large changes in tunneling resistance [52] due to the control of polarization charges at the interface. Using this effect may lead to the development of novel resistive memory devices. STM and STS measurements in cross-sectional samples have been used to directly investigate the nature

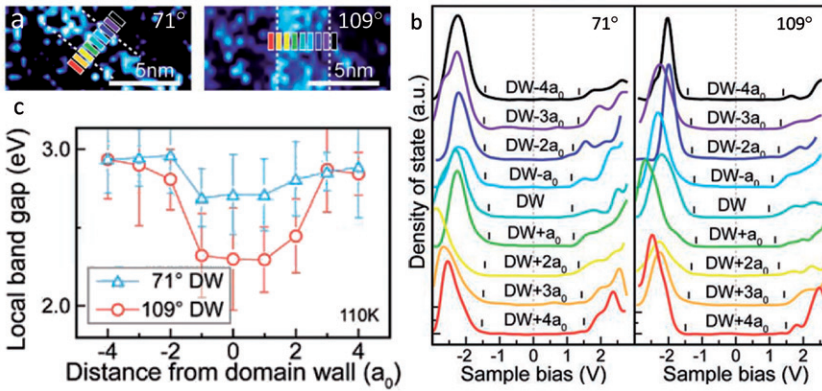


Figure 6. Layer-by-layer dI/dV measurements across 71° and 109° domain walls in BiFeO_3 acquired at 110 K. Bars in (a) denote positions where the electronic spectra are probed, and (b) show the corresponding STS spectra. The band edges are indicated by black tick marks in (b). (c) Extracted local band gap across the domain walls. Adapted from Ref. [47].

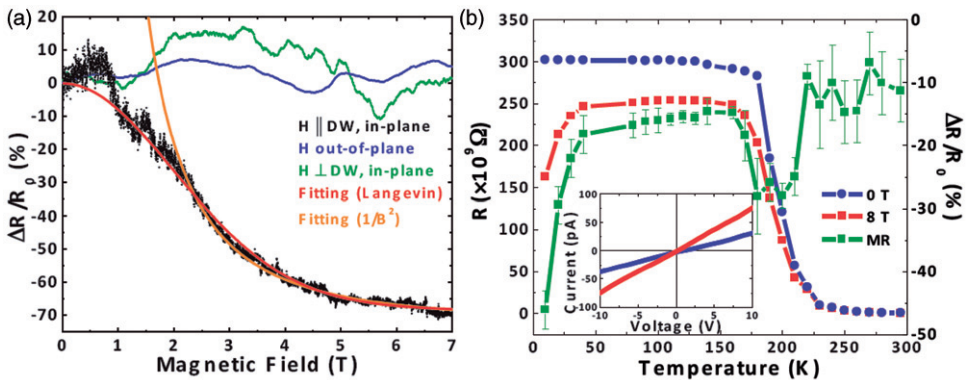


Figure 7. Magnetotransport study on 109° domain wall samples. (a) Anisotropic magnetoresistance in different directions of external magnetic field at a temperature of 10 K. (b) Resistance–temperature curves at two different external magnetic fields showing in red (8 T) and blue (0 T). The corresponding magnetoresistance is shown in green. Adapted from Ref. [7].

of the unusual local electronic conductivity at ferroelectric domain walls in multiferroic BFO [53]. *In situ* cleaved samples with ordered stripe arrays show decreases of the bandgap at the domain boundaries. In addition, a shift towards the Fermi level in the band edges of 109° and 71° domain walls have been measured (Figure 6). The demonstrated approach in this work serves as a model technique to investigate and understand electronic structure at oxide interfaces.

An important aspect of multiferroic domain walls concerns the true state of magnetism at such a wall. Temperature-dependent transport measurements are a possible route to follow to understand the actual spin structure and whether it exhibits a glass-like or ordered ferromagnetic state [7]. Of interest is the effect of extra carriers introduced into the system, e.g., by doping or electric gating, on magnetism. Is there a way to change the magnetic interaction from superexchange to double exchange? The strength of the

coupling between the ferroelectric and antiferromagnetic walls in BiFeO_3 is an issue that still needs to be resolved from both a theoretical and an experimental perspective, although initial measurements have been performed (Figure 7). The role of the dimensionality on electrical and magnetoelectrical transport needs to be elucidated and compared to known systems, such as manganites [22,54]. The interaction between ferroelectric and antiferromagnetic domain walls has been studied in model multiferroics such as YMnO_3 [55] and BiFeO_3 [56]. In both cases it has been shown that the antiferromagnetic domain walls are significantly wider (by $\sim 1\text{--}2$ orders of magnitude) compared to the ferroelectric walls. This is also in agreement with the phenomenological predictions of Daraktchiev et al. for coupling-mediated wall broadening [57].

Nanoscale conduction phenomena in complex oxide domain walls form an exciting and growing field of interest in functional materials. With the current developments surrounding their conductive properties there are many remaining questions and some new ones. For example, the investigation of dynamic conductivity at domain walls is an exciting aspect [6]. This addresses important factors: a possible electric-field induced distortion of the polarization structure at the domain wall; the dependence of conductivity on the degree of distortion; and weak-pinning scenarios of the distorted wall. The domain wall is very likely not a rigid electronic conductor, instead offering a quasi-continuous spectrum of voltage-tunable electronic states. This is different from ferroelectric domains, where switching may give rise to discrete (often only two) conductance levels. The intrinsic dynamics of domain walls and other topological defects are expected not only to influence future theoretical and experimental interpretations of the electronic phenomena, but also pose a possibility to find unique properties of multiferroic domain walls, e.g., magnetization and magnetoresistance within an insulating antiferromagnetic matrix [7], also due to order parameter coupling and localized secondary order parameters [38]. Of obvious future interest is the question of what sets the limits to the current transport behavior at walls: can one ‘design’ the topological structure of the domain wall to controllably induce electronic phase transitions within the wall arising from the correlated electron nature? Is it possible to trigger an Anderson transition by doping of domain walls or straining them? The observation of superconductivity in ferroelastic walls of WO_3 certainly points to various exciting and unexplored areas of domain boundary physics [40].

The investigation of topological defects beyond the classic domain walls are also a new exciting area of research. Recent work by Hong et al. shows that arrays of ferroelectric nanowires have switchable quadrupoles and thus potential as nanodevices [58]. Exotic topological defects in nanostructures (vertices, vortices, quadrupoles, etc.) are currently a very active area of research. For example, vortex cores in BiFeO_3 have been demonstrated to be dynamic conductors controlled by the coupled response of polarization and electron–mobile-vacancy subsystems with external bias [59].

Several applications have been suggested to make use of domain walls in ferroelectric materials based on their additional functionalities as well as their effects on existing devices. Uses that have been mentioned are as a local strain sensor incorporated on an AFM probe or a multilevel resistance-state device that is written by an electrical current [60]. Other possibilities include nonvolatile memories, piezoelectric actuators, ultrasound transducers, surface acoustic wave devices and optical applications [50]. For existing devices, the discovery of conducting domain walls stimulates engineers to prevent their products from having the ‘wrong’ domain walls that could cause leakage and prevent its use in ferroelectric memories.

Experimental results and theoretical investigations in recent years have convincingly demonstrated that certain transition metal oxides and some other materials have dominant

properties driven by spatial inhomogeneity. Strongly correlated materials incorporate physical interactions (spin, charge, lattice and/or orbital hybridization), allowing complex interactions between electric and magnetic properties, resulting in ferromagnetic, anti-ferromagnetic phase transitions. Of even higher interest are the hetero-interfaces formed between correlated materials showing new state properties. Domain walls are only one example of ‘naturally’ occurring interfaces in such materials. The challenge is to determine whether such complex interactions can be controlled in those materials or heterointerfaces at sufficiently high speeds and densities to enable new logic device functionality at the nanometer scale. Parameters such as interface energy, switching speed and threshold, tunability, dynamics of the states, and size dependencies need to be quantified to determine if domain boundary materials could be employed as a building block for information processing systems.

In summary, we have provided an overview on nanoscale electronic conduction phenomena in domain walls in BiFeO_3 . The ferromagnetic properties of ferroelectric walls in paramagnetic and antiferromagnetic materials suggest that much more R&D should be done on domain walls in multiferroics as well as for the dynamics of domain walls in these materials [55,57,61]. Artificially engineered oxide interfaces may pave the way to novel tailored states of matter with a wide range of electronic properties, including domain walls. Many ferroelectric relaxor-like systems nanoscale phase separated materials are interesting as well since they have intrinsic nanodomains. Domain-wall electronics, particularly with ferroelectrics and multiferroics, may become interesting for nanotechnology [12].

Acknowledgements

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