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Switching ferroelectric domain configurations using both electric and magnetic fields in $\text{Pb}(\text{Zr,Ti})\text{O}_3\text{--Pb}(\text{Fe,Ta})\text{O}_3$ single-crystal lamellae

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Thin single-crystal lamellae cut from $\text{Pb}(\text{Zr,Ti})\text{O}_3\text{--Pb}(\text{Fe,Ta})\text{O}_3$ ceramic samples have been integrated into simple coplanar capacitor devices. The influence of applied electric and magnetic fields on ferroelectric domain configurations has been mapped, using piezoresponse force microscopy. The extent to which magnetic fields alter the ferroelectric domains was found to be strongly history dependent: after switching had been induced by applying electric fields, the susceptibility of the domains to change under a magnetic field (the effective magnetoelectric coupling parameter) was large. Such large, magnetic field-induced changes resulted in a remanent domain state very similar to the remanent state induced by an electric field. Subsequent magnetic field reversal induced more modest ferroelectric switching.

1. Introduction

Research into multiferroic systems has undergone a renaissance in the last decade [1,2]. This has been driven partly by renewed scientific curiosity in the topic, and partly by a strong desire to demonstrate new proof-of-principle electronic devices [3,4]. While some perceived applications might rely on distinct ferroelectric and magnetic states that can be poled separately (in four-state memory [6], for example), the majority of proposed device structures are based on a strongly coupled magnetoelectric response, in which the application of an electric field causes changes in magnetization and a magnetic field causes changes in electrical polarization [2]. A discussion of how this relates to potential device applications can be found in the research review of Pyatakov & Zvezdin [3].

There are two main strategies for obtaining strong magnetoelectric effects: (i) composite heterostructures [6–8] (in which piezoelectric or electrostrictive materials are usually intimately bonded to magnetoelastic materials) and (ii) single-phase magnetoelectric multiferroics [4,9]. Currently, for room-temperature applications, the magnetoelectric coupling performance of composites far exceeds that of single-phase systems [10], well illustrated in the graphs of Lawes & Srinivasan [11]. Significant coupling in heterostructures was shown explicitly by Heron *et al.* [12], when they demonstrated that complete reversal of magnetization in a CoFe thin film could be induced by the application of an electric field, through interfacial coupling with BiFeO₃. In addition, precise writing of ferromagnetic domains with a low electric field was shown by Lahtinen *et al.* [13] in CoFe–BaTiO₃ composites. A summary of work to date, focusing on heterostructures, is provided in the recent review by Vaz [14].

One of the key problems preventing further technological developments using single-phase multiferroic systems is that very few of them are active at room temperature [4]. BiFeO₃ is a notable exception and is the best known of all single-phase multiferroics. Ramesh and co-workers were the first to show that epitaxial BiFeO₃ films could demonstrate a large ferroelectric polarization (of the order of $100 \mu\text{C cm}^{-2}$) and saturation magnetization (reaching 150 emu cm^{-3}) [9]. However, the origin of this reported magnetization value is somewhat controversial. The bulk magnetic structure of BiFeO₃ has been shown to be a G-type antiferromagnet with only weakly canted magnetic moments; moreover, the canted moment spatially rotates, creating a cycloid structure that is incommensurate with the BiFeO₃ lattice and generates no overall net magnetization [15]. In addition, other properties of BiFeO₃ are not ideal for practical applications: the prospects of realizing useful devices are likely to be severely limited by high electrical conduction and by complications associated with a plethora of phase transitions, both in surface layers and within the bulk [15].

Very recently, several of the authors uncovered an alternative room-temperature multiferroic material. Solid solution phases between lead zirconium titanate (PZT) and lead iron tantalate (PFT) end member perovskites [16,17] (PZTFT) were shown to have both ferroelectric and ferromagnetic/ferrimagnetic hysteresis loops at room temperature. Polarization–electric field hysteresis curves were found to change, slightly but demonstrably, under applied magnetic fields [16]. This magnetoelectricity was later directly linked to magnetic field-induced alterations in the ferroelectric domain structure [18]. While changes in the ferroelectric domains were found to be sporadic and only partially reversible, it was noted that, locally, very large magnetoelectric coupling coefficients could be realized: coupling coefficient values were estimated to be of the order of $1 \times 10^{-7} \text{ s m}^{-1}$ [18]. However, whether or not such dramatic coupling coefficients might be realized macroscopically in PZTFT depends on the extent to which local sporadic domain alterations can be engineered to occur more extensively and in a controlled and reproducible manner under exposure to magnetic fields.

In this article, we demonstrate that the susceptibility of ferroelectric domains to switch orientation under applied magnetic fields is enhanced after electric field-induced switching has been performed. The origin of such strong history dependence is not yet known, but the study demonstrates that coupling coefficients can certainly be manipulated in this single-phase material.

2. Experimental methods

The starting material for this research was a bulk ceramic that had been characterized in a previous study [16] of nominal composition $[\text{Pb}(\text{Zr},\text{Ti})\text{O}_3]_{0.6}-[\text{Pb}(\text{Fe},\text{Ta})\text{O}_3]_{0.4}$. Microstructural evaluation, under transmission electron microscopy, suggested that the ceramic had some second phase material at grain boundaries. Thus, in this study, as in [18], focused ion beam (FIB) milling was used to cut lamellae (approx. $8 \times 10 \times 0.3 \mu\text{m}$) from grain interiors only, such that the properties of single-phase, single-crystal sheets could be examined. The procedure was based on work by Schilling *et al.* [19].

Coplanar capacitor structures were made by patterning thin-film, sputter-deposited, platinum (on single-crystal MgO substrates) to make electrically isolated contact pads with an interelectrode gap approximately $2.5 \mu\text{m}$ wide (cut using FIB). FIB-cut PZTFT lamellae were then carefully placed across this interelectrode gap, using a sharpened glass needle and micromanipulator; this set-up is similar to that used in [20] and [21]. The entire MgO substrate and capacitor device structure was then annealed in air at 600°C for 1 h. This anneal fulfilled a dual purpose: firstly, it caused recovery of structural damage at the lamellar surfaces (and simultaneous ejection of gallium) [19]; secondly, it improved the bonding between the Pt thin-film electrodes and PZTFT to create a reasonable electrical contact. After annealing, any surface precipitates (probably gallium oxide) were removed by acid etching (2.8 mol l^{-1} HCl) to yield a pristine surface suitable for high-resolution piezoresponse force microscopy (PFM) [22]. PFM was used to directly map ferroelectric domain patterns after applying electric or magnetic fields (3 kOe magnetic field was applied by a permanent rare earth magnet placed underneath the sample).

3. Results and discussion

Schematics of the experimental arrangements used for the application of both coplanar electric and perpendicular magnetic fields are presented in figure 1*a,b*. A plot of capacitance as a function of applied bias voltage, figure 1*c*, is given for a coplanar structure. While the hysteresis in the capacitance–voltage (CV) loop is characteristic of a ferroelectric, the polarization–voltage response (PV loop), presented in figure 1*d*, makes the ferroelectricity self-evident. The PV loop was constructed by numerical integration of the capacitance (being proportional to the rate of change of polarization with respect to applied voltage) using the same approach as that used by Chang *et al.* [20] and Wang *et al.* [9]. A noteworthy feature of this ferroelectric hysteresis is that the remanent polarization is somewhat lower than the spontaneous polarization, indicating significant amounts of back-switching after the application of fully switching electric fields.

The remanent ferroelectric domain states were mapped by monitoring the component of the piezoelectric activity approximately parallel to the applied electric field, after the application and removal of the field. In this study, a relatively unusual ‘flexural’ mode of imaging was used in which the nominal ‘vertical’ PFM response (VPFM) actually results from in-plane polarization components causing buckling of the cantilever. The fingerprint for flexural dominance, in VPFM, is that the VPFM phase reverses when the sample is rotated by 180° . An archetypal example of this can be seen in figure 2, where complete phase reversal upon rotation is evident. From this, we can conclude that the ‘VPFM’ in this study actually monitors in-plane polarization components parallel to the cantilever axis, and hence parallel and antiparallel to the applied electric field: in figure 3, ‘yellow’ PFM phase data represent polarization components to the left and ‘pink’ PFM phase data represent polarization to the right.

Figure 3*a* presents a series of flexure mode images in which the phase information has been superposed over the PFM amplitude signal. In previous work [18], it was established that the microstructure in PZTFT should be considered across a hierarchy of length scales, with sets of fine fundamental domains, of order 10 nm in width, grouped into bundles (or ‘superdomains’) on length scales approximately 100 nm, with further groupings of these ‘superdomain’ bundles into regions of the order of micrometres in size. The PFM used in this study only resolves features above approximately 20 nm in size, and hence is not imaging the smallest length scales associated

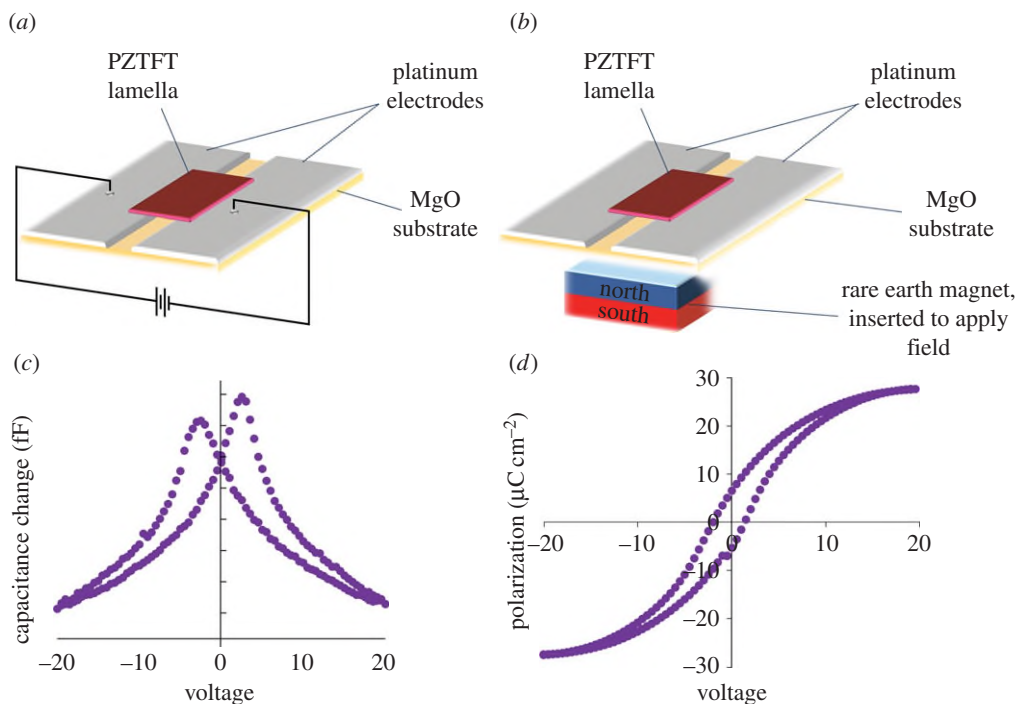


Figure 1. Schematic illustrations of the single-crystal PZTFT lamella integrated into a simple coplanar electroded capacitor structure during (a) electric field-induced and (b) magnetic field-induced switching. (c) The capacitance as a function of voltage shows maxima at finite values of applied bias and hysteresis characteristic of ferroelectric behaviour; (d) this is illustrated further in the integrated polarization–field loop derived from the data in (c).

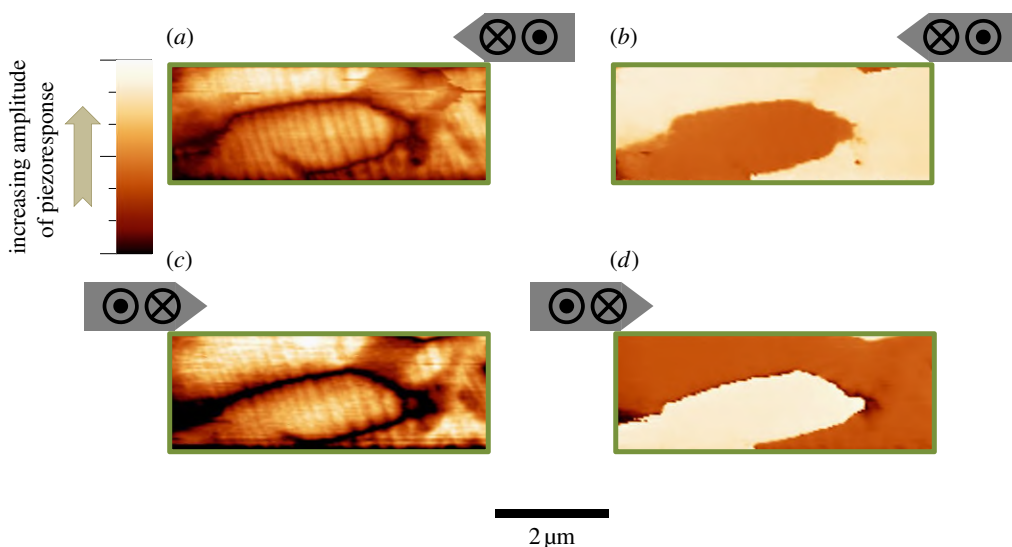


Figure 2. In PFM, two modes of cantilever distortion can lead to a vertical displacement of the laser on the photodiode detector: genuine vertical deflection of the PFM tip and in-plane movement of the tip parallel to the cantilever axis (so-called buckling or flexure). To distinguish between these two distortion modes, images can be taken of the same area before and after rotating the sample by 180°; true vertical deflection is not sensitive to sample rotation, while flexural distortion leads to a reversal in the phase of the image. As can be seen, the amplitude images (a,c) remain unchanged after rotation, but the phase images (b,d) are completely reversed. Flexural distortion is therefore dominant, so that changes in phase can be used to distinguish between in-plane polarization components either parallel or antiparallel to a vector along the axis of the cantilever. The cantilever orientation is given by the grey tip schematic.

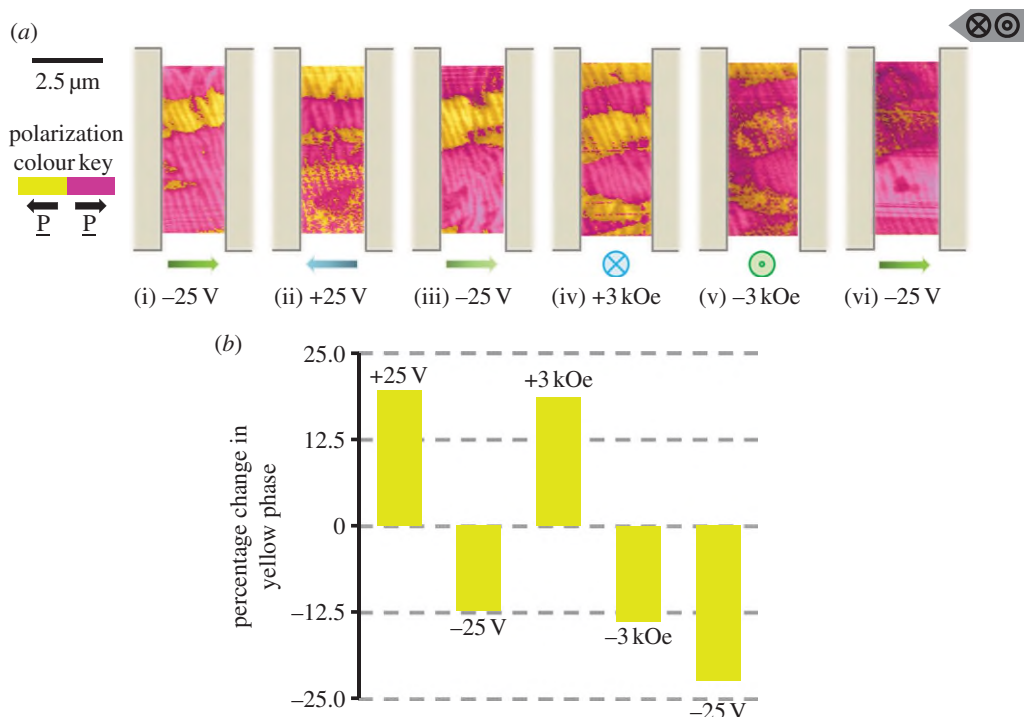


Figure 3. (a) Images of the ferroelectric domain states after the application of successive electric and magnetic fields; amplitude and phase maps have been superimposed on each other. Yellow is associated with polarization components pointing to the left of the images and pink to the right. The remanent states have been imaged after sample exposure to the following succession of bias voltages/magnetic fields: -25 V (i), +25 V (ii), -25 V (iii), +3 kOe (iv), -3 kOe (v) and -25 V (vi). The electric fields (blue and green arrows) cause consistent changes in the in-plane remanent domain orientations resolved along the axis of the PFM cantilever. The initial application of a magnetic field largely mirrors electric field-induced switching, but subsequent reversal of the magnetic field leads to much more subtle changes. Some attempt at quantifying the domain changes has been done by counting the 'yellow' phase pixels in each image. (b) The changes in the populations of 'yellow' phase pixels are plotted after each successive bias voltage and magnetic field has been applied and removed. The cantilever orientation is again given by the grey tip schematic.

with the fundamental domains in PZTFT. Nevertheless, changes in the polar microstructure with applied fields can be monitored over the coarser two levels of length-scale hierarchy. In the first three PFM images in figure 3a(i-iii), it is clear that the successive application of -25 and +25 V across the electrodes causes significant levels of polar reorientation. For -25 V (figure 3a(i)(iii)), the predominant phase colour is 'pink', while switching with +25 V (figure 3a(ii)) introduces new micrometre-scale bands of domains and causes significant overall phase reversal from 'pink' to 'yellow' (associated with a change in the remanent polarization from right to left as the polarization switches to align with the applied field).

It was found that, once the PZTFT had been switched with -25 V, the application of a magnetic field perpendicular to the lamellar surface (figure 3a(iv)) could induce quite dramatic changes in the remanent domain orientation. In fact, the resultant microstructure, after the magnetic field had been applied and then removed, was remarkably similar to the remanent state induced by the application and removal of a +25 V bias voltage. This comparability in remanent states suggests that the level of ferroelectric switching induced by the applied magnetic field is similar to that caused by electric fields, known to induce complete polar reorientation prior to field removal (see the CV and PV behaviour in figure 1). This observation is reminiscent of the ridged coupling, observed during switching, of the magnetic order and the induced electrical

polarization witnessed at cryogenic temperatures by Hoffmann *et al.* [23] on MnWO_4 . However, the further application of a magnetic field in the opposite sense (figure 3a(v)) did not cause as dramatic a change in the remanent ferroelectric domain state, at least upon visual inspection. In figure 3b, changes in domain orientations have been quantified by directly counting the numbers of pixels assigned to a particular phase colour. According to this analysis, the number of ‘yellow’ phase pixels has been significantly reduced by the reversal of the magnetic field (figure 3a(iv)(v)). Indeed, it suggests that magnetic fields can induce domain reorientations that are completely comparable with those produced by electric fields. However, pixel count changes in this case resulted from a reduction in the yellow phase signal within the mesoscale domain bands, without any obvious change in the size of the bands themselves. This could indicate change occurring at a lower level in the microstructural hierarchy. In the authors’ opinion, the change in domains induced by the reversal of the orientation of the applied magnetic field is less dramatic than the unequivocal change caused by the application of magnetic field after electrical switching; the latter creates genuine new domain bands. Figure 3a(vi) demonstrates that the domains can still be switched electrically, after the sample had been exposed to the magnetic fields.

4. Summary and conclusion

Single-crystal lamellae of a new room-temperature magnetoelectric multiferroic (PZTFT) have been integrated into simple capacitor devices to allow the effects of electric and magnetic fields on the domain configurations to be evaluated. Overall, there are two major points that arise from our observations:

- that a magnetic field applied perpendicular to the PZTFT lamella can induce switching of the ferroelectric domains that is comparable to that produced by electric fields—clearly there is significant room-temperature magnetoelectric coupling; and
- that although pixel counting suggests a significant change in domain states induced by magnetic fields applied in opposite senses, visually the data are much less compelling than that associated with the application of a magnetic field directly after a switching electric field has been applied.

This kind of experiment has been repeated several times on different samples and consistently we observe that significantly greater levels of magnetic field-induced switching in ferroelectric domains occur the first time the magnetic field is applied after conventional electrical switching of the domain states. Subsequent changes in magnetic field orientation produce much less dramatic effects. This interplay between the magnitude of the magnetoelectric coupling and the history of the sample, in terms of prior exposure to electric or magnetic fields, is not yet understood, but could be a clue in determining the fundamental mechanism of magnetoelectricity in this material.

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