



Reconfigurable electronics based on multiferroics and nanomagnetism

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Reconfigurable electronics based on multi-ferroics and nano-magnetism

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I. Background and Introduction

Multifunctional magnetoelectric materials with high exchange represent a *missing “holy grail”* of materials physics. To combine polarization and magnetization in the same solid is nothing short of actually *controlling the fundamental nature of electromagnetism in matter*. Although magnetoelectricity (ME) is an intrinsic phenomenon in some natural materials at low temperature, such single-phase materials suffer from an extremely weak ME exchange. In contrast, composites consisting of magnetostrictive and piezoelectric phases can feature dramatically larger ME coefficients. *This proposed program focuses on achieving the disruptive potential of emerging multifunctional magnetoelectrics, and in so doing lay the foundations for their use as a materials platform that would benefit future AFOSR applications.*

The purpose of this program is to develop new ME thin-layers. Efforts focus on heterostructures grown on piezoelectric single crystal substrates. Our ***program objectives are*** to (i) optimize epitaxial ME thin layers with regards to the influence of film composition, epitaxy, deposition parameters, defects and substituents; and influence of substrate composition with proximity to the morphotropic phase boundary (MPB) and crystallographic orientation; (ii) study the reconfigurable properties of these ME heterostructures and nanostructures under multiple fields for application in logic, memory, and tunable microwave applications; and (iii) understand EM interactions on the nanometer scale in these two phase systems.

The anticipated outcome and impact of this effort will be realized in the development of new materials with large magnetoelectric (ME) coupling for next-generation multifunctional devices, including, multi-state (neuromorphic-like) circuits and memories, and E-field tunable microwave resonators for secure communications.

II. Vertically Integrated BiFeO₃ Nanocomposites.

II.1 Nanopillars with E-field accessible multi-state ($N \geq 4$) magnetization with giant magnetization change in self-assembled BFO-CFO/PMN-38PT heterostructures

Summary: We have deposited self-assembled BiFeO₃-CoFe₂O₄ (BFO-CFO) thin films on (100) Pb(Mg_{1/3}Nb_{2/3})_{0.62}Ti_{0.38}O₃ (PMN-38PT) single crystal substrates. These heterostructures were used for the study of real-time changes in the magnetization with applied DC electric field (E_{DC}). With increasing E_{DC} , a giant magnetization change was

observed along the out-of-plane (easy) axis. The induced magnetization changes of the CFO nanopillars in the BFO/CFO layer were about $\Delta M=80\%$. A giant converse magnetoelectric (CME) coefficient of 1.3×10^{-7} s/m was estimated from the data. By changing E_{DC} , we found multiple ($N \geq 4$) unique possible values of a stable magnetization with memory on removal of the field.

Details: A SRO buffered BFO-CFO nanopillar structure was deposited on (100) PMN-38PT substrates, e.g. BFO-CFO/SrRuO₃/PMN-38PT, as schematically shown in Figure 1. A 65%BFO-35%CFO composition ratio was chosen. All thin films were deposited by pulsed laser deposition. The single crystal PMN-38PT substrates were grown by the Shanghai Institute of Ceramics Chinese Academy Sciences. The crystal structure was determined by X-ray diffraction (XRD, Philips X'Pert system) line and mesh scans. Magnetic hysteresis loops were recorded using a vibrating sample magnetometer (VSM, Lakeshore 7300 series) along both out-of-plane (perpendicular to the sample surface) and in-plane (parallel to the sample surface) directions. Atomic force (AFM) and magnetic force microscopy (MFM) images were obtained (Dimension 3100, Veeco), which were used to study the surface and magnetic domain structures.

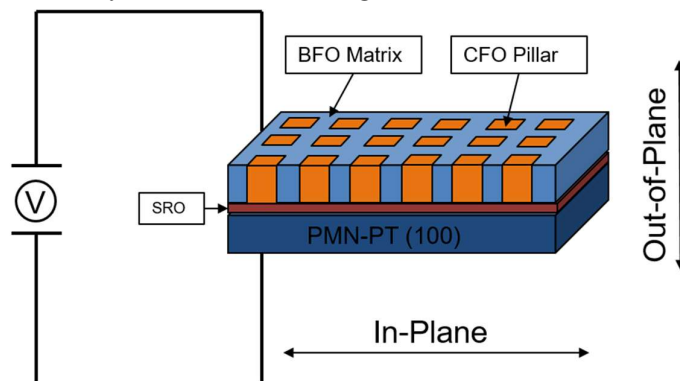


Fig. 1. Schematic of the BFO-CFO/SRO/PMN-PT heterostructure. Out-of-plane is perpendicular to the sample surface, and in-plane is parallel to the sample surface.

Figure 2 shows a XRD line scan for a BFO-CFO/SRO/PMN-38PT heterostructure. The PMN-xPT single crystals should be tetragonal (T) for $x > 32\text{at}\%$. Figure 2 confirmed that the stable phase of our PMN-38PT substrates indeed had a T structure with d-spacings of $a_T=4.046 \text{ \AA}$ and $c_T=4.002 \text{ \AA}$. These two lattice parameters correspond to those of the 'a' and 'c' ferroelectric domains. The results in Fig. 2 also show that the BFO-CFO nanocomposite layer grows epitaxially on PMN-38PT. The 2θ value for the (400) peak of CFO was 43.17° and that for the (200) peak of BFO was 45.71° , corresponding to d-spacings of $8.376 \text{ \AA}$ and $3.967 \text{ \AA}$ respectively. Compared with bulk BFO ($3.960 \text{ \AA}$) and CFO ($8.392 \text{ \AA}$), CFO undergoes a -0.179% strain (compressive) and BFO undergoes a 1.640% strain (tensile) along the OP direction.

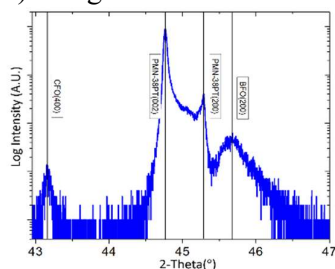


Figure 2. A 2θ scan for BFO-CFO/SRO/PMN-38PT.

Figure 3 shows AFM and MFM images for a BFO-CFO/SRO/PMN-38PT heterostructure. Part (a) shows an AFM image evidencing that a self-assembled square-like nanopillar morphology embedded in a matrix formed; and Part (b) shows a MFM image of the phase signal, demonstrating that different nanopillars have dark and light contrasts, indicating that magnetic domain orientations do not have a preferred distribution amongst equivalent directions. Part (c) shows a MFM phase image after E-field poling of the BFO matrix by positive and/or negative fields. An obvious difference between images can clearly be seen. Part (d) shows line scans extracted from the MFM phase images for both unpoled and poled nanocomposite system conditions. The line scans between these two conditions can be seen to have significant differences with respect to each other. Poling made the magnetic phase signal more intense, whether positive or negative in sign. However, outside the poling area, the line scan did not exhibit much difference between before and after poling conditions. When E_{DC} was applied by a MFM tip, the BFO matrix phase in the nanocomposite layer responded with a change of polarization. Subsequently, the magnetic domains in the CFO nanopillars elastically coupled to the E-induced shape change in the BFO matrix, resulting in a magnetization rotation and a change of the magnetic phase signal.

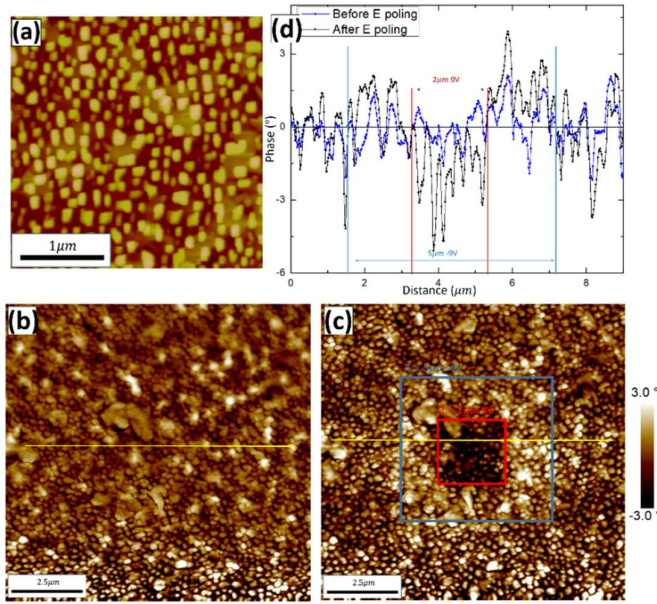


Figure 3. Scanning microscopy images for BFO-CFO/SRO/PMN-38PT. (a): AFM image. (b): MFM phase image for BFO-CFO/SRO/PMN-38PT, before E poling. (c): MFM phase image for BFO-CFO/SRO/PMN-38PT, after E poling. (d): Line scan of the phase angle before and after poling, taken along the yellow lines in the (b) and (c).

The magnetic domains were not only controllable by BFO-matrix-induced strain, but also by induced strains from the PMN-PT substrate. Magnetization measurements were then performed in response to a real-time E_{DC} applied to the substrate. The electric field was applied along the out-of-plane direction and the magnetization was measured using a VSM, as shown in Fig. 1. Figures 4 (a) and (b) show the M-H loops under particular values of E_{DC} applied along the OP and IP directions, respectively. From these data, it can be clearly seen that the easy axis of the CFO nanopillars lies along the OP direction. This is the reflection of the shape anisotropy of the nanopillar structure, which has a much larger thickness than width. The remnant magnetization (M_r) increases along OP with increasing E_{DC} , but decreases with increasing E_{DC} along IP. This is due to the combination

of the anisotropy of the magnetostriction coefficient of CFO (λ_{CFO}) and the piezoelectric coefficient of PMN-xPT. From the right hand axis of Figure 4 (c), it can be seen that the PMN-38PT substrates undergo a compressive stress along the OP direction under E_{DC} , resulting in the BFO-CFO nanocomposite layer experiencing a tensile stress along IP. Since $\lambda_{CFO} < 0$, under a tensile IP stress, the easy axis of the CFO will rotate towards the OP direction. As a consequence, the nanopillars will experience an increase in M_r with increasing E_{DC} , and vice versa a lower M_r along the IP.

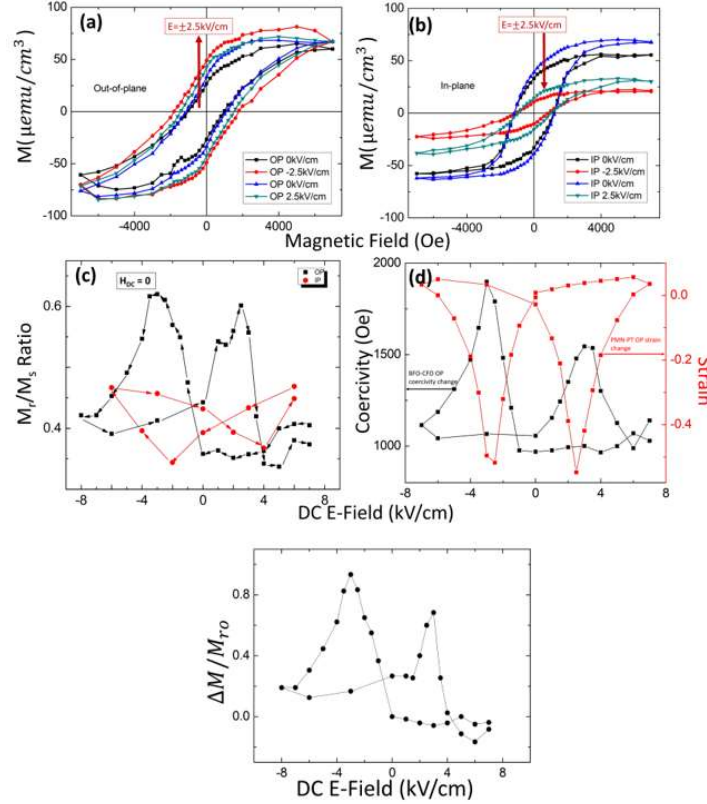


Figure 4. Magnetization measurements for BFO-CFO/SRO/PMN-38PT. (a): M - H loop under different E_{DC} , out-of-plane. (b): M - H loop under different E_{DC} , out-of-plane, in-plane. (c): M_r/M_s ratio with changing E_{DC} . (d): PMN-38PT substrate strain change with E_{DC} , and BFO-CFO/SRO/PMN-38PT coercive field change with E_{DC} . (e): $\Delta M/M_{r0}$ as a function of E_{DC} .

The remnant-to-saturation (M_r/M_s) magnetization ratio in response to $E_{DC} = 6\text{ kV/cm}$ applied to the PMN-38PT substrate is shown in Fig. 4 (c). Data are given for E_{DC} applied along the OP and IP directions. As can be seen on the right hand axis of Fig. 4 (c), the M_r/M_s ratio as a function of E_{DC} exhibited a clear butterfly-like shape, similar, but inverted to the $\epsilon - E$ response of the PMN-38PT substrate. The highest values of the M_r/M_s ratio were 0.62 under -3 kV/cm and 0.60 under 2.5 kV/cm . At fields above saturation and at $E_{DC} = 0$ (E_0), the M_r/M_s ratios were found to be nearly equal to each other with a value of about 0.40. The IP direction had an opposite trend compared to the OP, exhibiting smaller changes in the M_r/M_s ratio with increasing E_{DC} that were inverted with respect to the OP data. This inversion occurs because the easy magnetization axis is aligned with the OP direction, imparting to the IP axis relatively lower values of

both M_r and coercivity. Next, $\Delta M = M_{rDC} - M_{r0}$ (difference between M_r under $E_{DC} \neq 0$ and M_r under 0) was calculated, as shown in the Fig. 4(e). The maximum value of $\Delta M/M_{rDC}$ was found to be $\sim 80\%$. This is notably higher than the highest value (66%) previously reported for a single CoFeB layer on PMN-30PT.

The coercivity (H_C) was also found to change with E_{DC} applied on the PMN-38PT substrate, as shown in Figure 4 (d). The change of H_C along the OP direction had the same inverted butterfly-like shape as the data for the M_r/M_s ratio. The magnetic coercive field as a function of E_{DC} had similar values above the magnetization saturation point and at the origin (E_0), which was $H_C \sim 1000$ Oe. The highest magnetic coercive field (~ 1800 Oe) was found near $E_{DC} = \pm 3$ kV/cm, which corresponds to the electric coercive field of PMN-38PT (see right axis in Fig. 4 (d)). This evidences that BFO-CFO/SRO/PMN-38PT heterostructures have the strongest E_{DC} induced ME coupling when the polarization reverses.

Figure 5 (a) shows the induced magnetization response to changes in E_{DC} as a function of time taken along the OP direction while $H_{DC} = 0$. Data are given at various E_{DC} between 1 kV/cm and 3 kV/cm, beginning from a condition where the CFO nanopillars had been previously magnetized. In Figure 5(a), six distinguishable states were induced under different positive (1, 2, 3 kV/cm) and negative (-1, -2, -3 kV/cm) E_{DC} . The largest response was found for $E_{DC} = -3$ kV/cm, which corresponded to the point of maximum M_r/M_s in Figure 4(c). The magnetization direction with positive or negative E_{DC} did not switch, but increased in value following a trajectory corresponding to the M-H loop (see Fig. 4(a)). After removing E_{DC} , two stable magnetization states were accessible depending on E_{DC} direction.

These data in Fig. 5(a) reveal a strong coupling between the PMN-PT substrate and the BFO-CFO nanocomposite layer. The magnetic domains in the nanocomposite layer may rotate under $E_{DC} < 3$ kV/cm, resulting in good E_{DC} tunable properties. The converse magnetoelectric coefficient (α) was then calculated from the data in Fig. 5(a), using the equation: $\alpha = \mu_0 \frac{\Delta M}{\Delta E}$, where μ_0 is the permeability of free space, and α is in units of s/m.

The value of α was estimated to be 1.3×10^{-7} s/m again under $H_{DC} = 0$ in a previously magnetized state. This magnetization coupling coefficient is much higher than that previously reported (about 10^{-10} s/m) for BiFeO₃-CoFe₂O₄/SrRuO₃/SrTiO₃ heterostructures, and is close to values reported by Eerenstein et al for LSMO/PMN-PT (2×10^{-7} s/m). However, this prior investigation found such high values only over a limited temperature range. Our results show a large magnetoelectric coupling tunable under E_{DC} , which could be used over a wide range of temperatures below 375K.

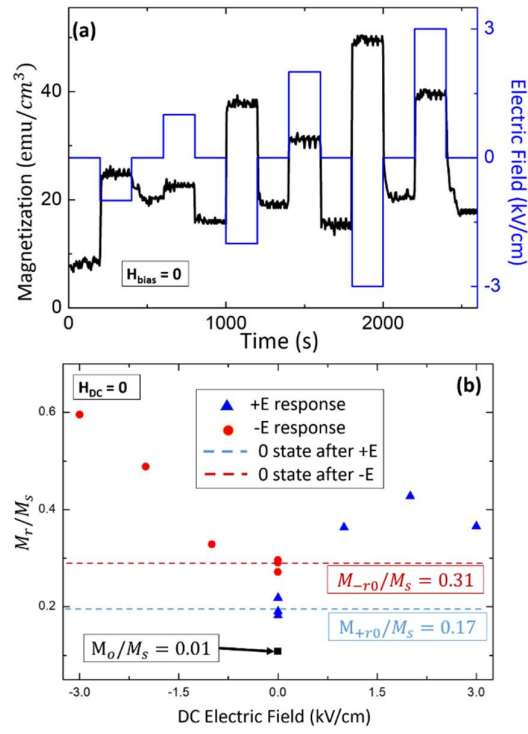


Fig. 5. (a): Time vs. magnetization measurement under different magnetic fields. (b): Calculated M_r/M_s ratios under different E_{DC} . $H_{DC} = 0$ Oe. Insert figure at upright corner shows the calculated coefficient under different magnetic field.

Two different magnetization values were found to be stable upon removing E_{DC} , whose value were dependent on E_{DC} histories (see Fig. 5(a)). To better illustrate these two states, the value of the M_r/M_s ratio is shown as a function of E_{DC} in Fig. 5(b). We note that these data were taken under $H_{DC} = 0$, beginning from a condition previously magnetized to M_r . The two different stable values of the M_r/M_s ratio found on removal of E_{DC} were $\frac{M_{-0}}{M_s} = 0.31$ (after negative E_{DC}) and $\frac{M_{+0}}{M_s} = 0.17$ (after positive E_{DC}), as illustrated by dashed lines in Fig. 5(b). After subsequent application of different E_{DC} (between 1 and 3kV/cm), these values did not change. The M_r/M_s ratio between M_{-0} and M_{+0} was 0.14, which was similar to the difference in the M_r/M_s ratio value in Fig. 4(c). The trends were also consistent with the data in Fig. 4(d), where it can be seen upon removing E_{DC} that the E-induced strain relaxed, but its value under $E_{DC} = 0$ was different between positive and negative bias sweeps. The highest M_r/M_s ratio value was found between M_{-0} and M_{-3} was found to be ~ 0.60 . The original state (M_0) is slightly larger than zero, which was due to equipment measurement error. These two different stable magnetization states accessible by E_{DC} histories after removal of E_{DC} offer a unique multi-state magnetization devices for logic and memory. The semi-volatile nature of the magnetostriction of the CFO nanopillars is due to changes in the phase stability of the PMN-PT substrate.

These M_r/M_s ratio data clearly reveal three different states before and after E_{DC} (under $H_{DC} = 0$): M_0 , M_{+0} and M_{-0} , as shown in Fig. 6. These states were for a previously magnetized condition, beginning from M_0 . The dual combination of H_{AC} (or H_{DC}) followed by E_{DC} will allow for access for two additional oppositely magnetized states: $\overline{M_{+0}}$ and $\overline{M_{-0}}$. Thus, four ($N = 4$) or more stable remnant different magnetization states could be potentially accessed by field. Previous studies of single phase magnetostrictive thin films on PMN-PT, such as CoNi/PMN-32PT, have shown only two stable magnetization states; although, one study of FeAl/PIN-PMN-PT heterostructures reported four different states on removal of E_{DC} and H_{DC} that were accessed by $E_{DC} > 4kV/cm$. We note that our investigations were done in a vertically integrated two phase ME layer on PMN-PT for $E < 3kV/cm$. This vertically integrated heterostructure with multistate ($3 \leq N \leq 5$) values tunable by E_{DC} are more relevant to integrated memories and logic than layer-by-layer ones. They have a high number of magnetic nanopillar; offer more than two states, which are accessible by E_{DC} ; and consume little power (passive). These multi-state heterostructures have the potential for neuromorphic applications.

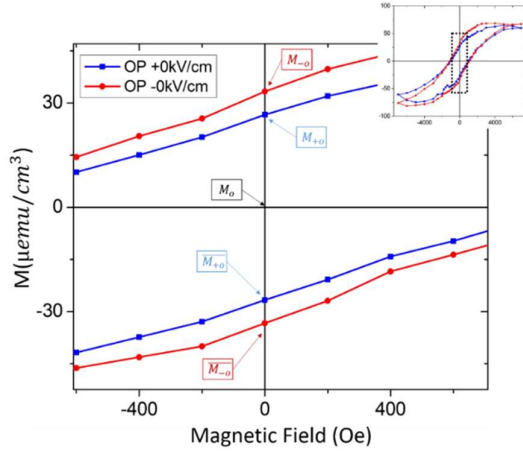


Figure 6. Enlargement of M-H curve illustrating four different remanent states before and after dual application of magnetic and electric fields.

II.2 Non-volatility using materials with only volatile properties: vertically-integrated magnetoelectric heterostructures

Different (1-3) heterostructures, such as $\text{BiFeO}_3\text{-CoFe}_2\text{O}_4$ (BFO-CFO) and $\text{BiFeO}_3\text{-CuFe}_2\text{O}_4$ (BFO-CuFO) on $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.74}\text{Ti}_{0.26}\text{O}_3$ (PMN-26PT), were selected for study as possible materials for magnetoelectric random access memory. The (1-3) heterostructures were deposited, and multi-magnetic states found under different E-field (E) conditions. Upon removal of E, two possible remnant magnetization states remained stable. If an H-field (H) was also applied, an additional two stable remnant magnetization states were found. Our investigations demonstrate (1-3) heterostructures with non-volatility, even though the individual phases/substrates had only volatile properties. This simplifies materials selection for multi-state systems based on these heterostructures, averting difficulties with compositional non-uniformity and property repeatability in particular with regards to PMN-xPT crystal substrates. With such $N \geq 4$ magnetic state systems, an MLC memory device could readily be built with high ME coupling and numerous accessible magnetic states.

Multiferroic materials have been studied for various applications, because of the existence of multiple order parameters that can interact²⁴⁻²⁶. Such applications include electric-field-controlled magnetoelectric (ME) random access (MeRAMs)²⁵ memories, which are novel approaches to overcome the density and reading limits of present generations of magnetic memories^{27,28}. Most potential materials that can be used for a component in MeRAMs, such as Metglass^{29,30}, suffer from a volatile nature, failing a critical required materials aspect for memory devices. To approach a solution for this deficiency, vertically-integrated nanopillars (designated as 1-3) heterostructures have previously been investigated, which combine magnetostrictive and piezoelectric phases with a dramatically higher ME couplings³¹⁻³⁴. Previously, (1-3) nanopillar heterostructures of $\text{BiFeO}_3\text{-CoFe}_2\text{O}_4$ (BFO-CFO) or $\text{BiFeO}_3\text{-CuFe}_2\text{O}_4$ (BFO-CuFO) deposited on $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ (PMN-xPT) single crystal substrates have been shown to have giant ME effects, which have the 3 order of magnitude larger converse magnetoelectric coefficient (α) comparing with traditionally (1-3) heterostructures on SrTiO_3 single crystal substrates^{35,36}.

The PMN-xPT substrates in these previous studies had large piezoelectric responses,

where strain was transferred to deposited films. This offers possibilities in various tunable multifunctional applications³⁵. However, the composition of PMN-xPT crystals can often suffer from problems with spatial uniformity. The strain-induced properties of PMN-xPT can be non-volatile ($x > 35\%$) or volatile ($x < 31\%$)³⁷. In the vicinity of the morphotropic phase boundaries or MPB ($x \approx 32\%$), a maximum piezoelectric response is found due to induced phase changes; however, the degree of volatile/non-volatile features can vary across a sample or between crystals of similar composition, due to the various mixed phases³⁸. This non-uniformity is in part due to the crystal growth process³⁹, and to the mixed B-site cation site. This non-uniformity result in variability in multifunctional layers deposited on PMNxPT, with regards to non-volatility for memory or logic applications.

Previously⁴⁰, the nanopillar structure of BFO-CFO vertically integrated layers was shown to pin the rotation of magnetic domains. This pinning enables the possibility for $N > 2$ remnant magnetization states. In fact, there have been reports of $N \geq 4$ different magnetic states in BFO-CFO/PMN-PT upon removal of $E^{33,15,38,41}$. This pinned domain rotation can result in non-volatile magnetization in the CFO nanopillars. When the composition of PT in PMN-PT crystal locates near the MPB, the volatile properties become unpredictable. For example, single CFO layers deposited on PMN-30PT have been shown to have volatile magnetization changes³⁸, whereas Mn-doped CFO deposited on PMN-30PT exhibits non-volatile ones⁴². The unpredictability of these induced property changes hinders their potential for applications. Previously reported BFO-CuFO on PMN-33PT¹³ and BFO-CFO on PMN-30PT⁴³ reported non-volatile changes. Both PMN-33PT and PMN-30PT are close to the MPB, and thus these results indicate such (1-3) heterostructure might have non-volatility, even though they consist of phases that individually have volatile ones.

Here, we report a self-assembling two-phase vertically integrated (1-3) heterostructure as illustrated in Figure 7 (a). Vertically integrated two-phase BFO-CFO and BFO-CuFO layers were epitaxially deposited on SrRuO₃ buffered (100) oriented Pb(Mg_{1/3}Nb_{2/3})_{0.74}Ti_{0.26}O₃ (SRO/PMN-26PT). These PMN-26PT substrates were found to possess relatively large but volatile strain changes with E_{DC} . Our results demonstrate that (1-3) heterostructure can hinder the rotation of magnetic domains, resulting in non-volatile E-field induced magnetization changes, even on a piezoelectric substrate whose own properties are clearly volatile. This offers these heterostructures potential as MLC memory devices.

The BFO-CFO thin films were epitaxially deposited on SRO-buffered (100) oriented PMN-26PT substrates by pulsed laser deposition (PLD), experimental procedures were reported previously³⁵. The BFO-CuFO thin films were deposited by switched PLD (SPLD)^{36,44}, also as previously reported³⁶. Crystal structures were determined by X-ray diffraction (Philips X'Pert system) scans. Magnetic hysteresis curves were recorded using a vibrating sample magnetometer (VSM, Lakeshore 7300 series). Atomic force microscopy (AFM) images were obtained (Dimension 3100, Veeco), which were used to study the film surface quality. The thickness of all films was 130nm, and had electrodes attached to them, as illustrated in Fig. 7 (a).

Figures 7 (b) and (c) show the morphology of both BFO-CFO and BFO-CuFO (1-3)

heterostructures on PMN-26PT substrates. The BFO-CFO layer had a typical square-like nanopillar morphology, as previously shown³⁵. BFO-CuFO exhibited a mixed nanopillar and nanobelt structure, similar to that recently reported³⁶. Figure 7(d) shows an XRD line scan for both heterostructures, revealing CFO peak at 43.29°, CuFO peak at 44.10°, and BFO peak around 46°. These data of peaks correspond to the CFO (400), CuFO (400) and BFO (200) peak, indicating a well-oriented thin film orientation as previously reported^{35,36}. Part (d) shows the XRD line scan around 45°, and the insert figure on the upright corner demonstrates the XRD line scan from 20° to 60°. This line scan of full XRD range illustrated the (100) peak of PMN-26PT around 22.18°, and BFO (100) peak at 22.60°. The XRD scans illustrate good epitaxial growth of both matrix (BFO) and nanostructure (CFO and CuFO) phases on the substrates.

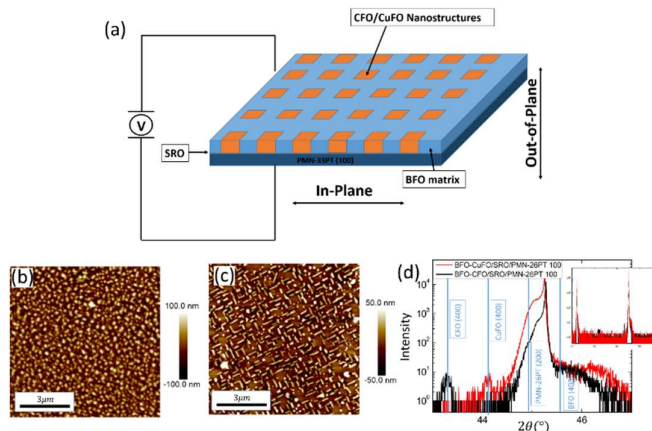


Figure 7. (a) Demonstration of (1-3) heterostructure of BFO-CFO(CuFO)/SRO/PMN-26PT, and direction of applied DC E-field. AFM images morphology of (b) BFO-CFO/SRO/PMN-26PT and (c) BFO-CuFO/SRO/PMN-26PT. (d) XRD line scan of both (1-3) heterostructures. The insert of part (d) shows the XRD line scan from 20° to 60°.

A DC electric field (E_{DC}) was applied on the sample along the out-of-plane (OP) direction as shown in Fig. 7(a). Figure 8 shows how the ratio of the remnant (M_r) to saturation magnetizations (M_r/M_s) changed with applied E_{DC} . The value of M_r at $E=0$ was measured after E_{DC} was removed for $-6\text{ kV/cm} \leq E_{DC} \leq 6\text{ kV/cm}$. The heterostructures were measured as a cycle: $0 \rightarrow E_{DC} \text{ kV/cm} \rightarrow 0 \rightarrow -E_{DC} \text{ kV/cm} \rightarrow 0$, E_{DC} ranging from 0.5 to 6 kV/cm. Figure 8(a) shows data for BFO-CFO/SRO/PMN-26PT. As can be seen, the M_r/M_s ratio increases to about 0.58 after the application of $E_{DC} = \pm 1.5\text{ kV/cm}$, and then gradually decreases to about 0.4 after removal of increasingly higher E_{DC} . These trends are similar to those recently reported for BFO-CFO heterostructures¹². The values of M_r/M_s can be categorized into several different stages: poling/de-poling (≈ 0.5), maximum (≈ 0.57), and plateau (≈ 0.41). After removal of E_{DC} , the M_r/M_s ratios were different, depending upon whether the E had previously been positive ($M_{+0} \sim 0.32$) or negative ($M_{-0} \sim 0.39$). Figure 8(b) shows $\frac{M_r}{M_s}$ vs. E_{DC} for heterostructures of BFO-CuFO/SRO/PMN-26PT. Similar results can be seen to those for BFO-CFO. The BFO-CuFO heterostructure exhibited multiple stages: poling/de-poling (≈ 0.44), maximum (≈ 0.51), plateau (≈ 0.41), $M_{+0} \sim 0.33$ and

$M_{-0} \sim 0.38$. As shown by the previously reported articles^{45,46}, the ME effect could be quantitatively described as converse magnetoelectric coefficient, which shows the change of magnetization with induced E_{DC} . The equation could be illustrated as $\alpha = \mu_0 \times \Delta M / \Delta E$; where μ_0 is the permeability of free space, ΔM is the magnetization change induce by DC electric field ΔE . By extracting the data from Figure 8 (a) & (b), $\alpha_{BFO-CFO}$ and $\alpha_{BFO-CuFO}$ could be determined as $1.5 \times 10^{-7} \text{s/m}$ and $5.6 \times 10^{-8} \text{s/m}$, respectively. These data were similar to the previous work of our group^{35,36}. Comparing with reported data of BFO-CFO on SrTiO_3 ⁴⁷, which only have $1 \times 10^{-10} \text{s/m}$, these numbers were significantly larger.

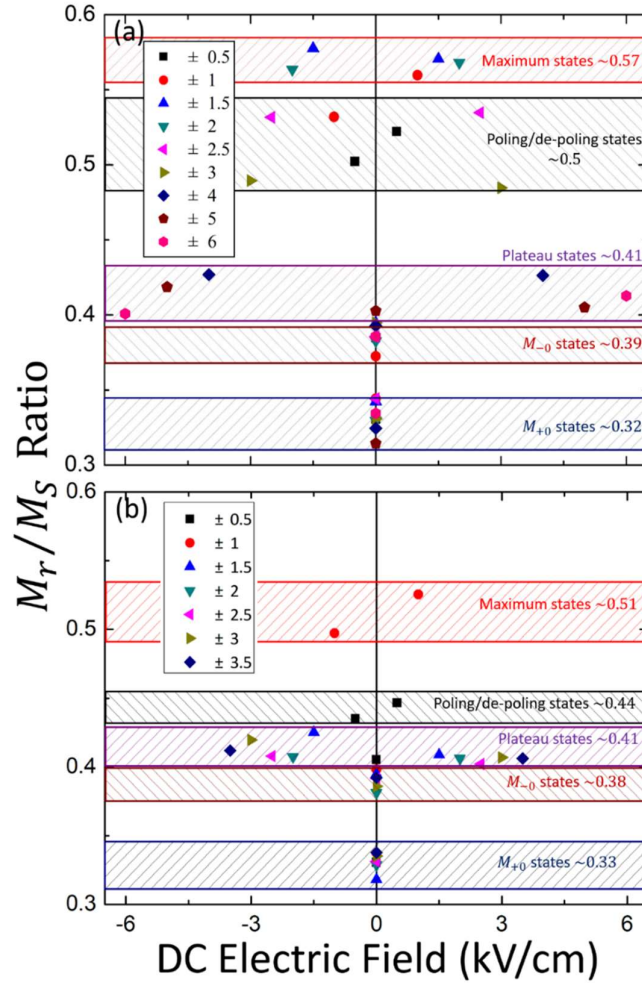


Fig.8. (a): Different magnetization states under varies E_{DC} of BFO-CFO/SRO/PMN-26PT heterostructure. Different color bar showed 5 distinguishable magnetization states: maximum states, poling states, plateau states, M_{+0} and M_{-0} states. (b) Different magnetization states under varies E_{DC} of BFO-CuFO/SRO/PMN-26PT heterostructure with similar multiple states.

It is interesting to note that M_r/M_s was dependent on the polarity of the field that had previously been applied. Even though the E-induced strain of the PMN-26PT substrate was previously reported volatile³⁷, the value of M_r/M_s of our two-phase magnetic thin film was non-volatile. To date, such non-volatility has not been reported

for heterostructures made solely of volatile materials. In fact, the piezoelectric response of PMN-30PT substrates has a volatile feature³⁷, along with the single phase CFO layers deposited on the on them⁴². The (1-3) nanostructure hinders the rotation of the magnetic domains, creating unique multiple states upon removal of E_{DC} ³⁵. This offers an approach to circumvent the issues of variability in the non-volatility of the PMN-xPT substrate imparted to deposited layers. One then has an option to use a wide range of PMN-xPT compositions on the left of the MPB, which themselves have only volatile changes.

The value of M_r/M_s depends on both E_{DC} and magnetic field (H). If the sign of E_{DC} is reversed, two remnant magnetic states are addressable for BFO-CFO/PMN-30PT ($M_{+0} \sim 0.32$ and $M_{-0} \sim 0.39$) and BFO-CuFO/PMN-26PT ($M_{+0} \sim 0.33$ and $M_{-0} \sim 0.38$). If the H-field was reversed, an additional two remnant magnetic states became accessible. Figure 9 summarizes how this four-state memory was achieved. As can be seen in Parts (a) and (b), E_{DC} and H were both used as inputs. Input fields of $E_{DC} = \pm 1 \text{ kV/cm}$ (maximum M_r/M_s) and $H = \pm 5000 \text{ Oe}$ (saturation magnetization) were used. Four different dual-field input conditions are illustrated in Figures 9 (a) and (b). Using ‘1’ to represent $E_{DC} = 1 \text{ kV/cm}$ and $H = 5000 \text{ Oe}$, and ‘0’ for $E_{DC} = -1 \text{ kV/cm}$ and $H = -5000 \text{ Oe}$, there was a combination of four different input situations which we can designate as 11, 00, 10, 01. These four input combinations resulted in the corresponding magnetization outputs for both BFO-CFO and BFO-CuFO heterostructures, as shown in Fig. 9 (c). This clearly demonstrates four distinguishable remnant magnetization states: ‘11’ input with $M_{+0} \approx 0.3$ output; ‘00’ input with $\overline{M}_{-0} \approx -0.4$ output; ‘10’ input with $\overline{M}_{+0} \approx -0.3$ output; and ‘01’ input with $M_{-0} \approx 0.4$ output. Table 1 summarizes these different inputs and outputs.

No.	Input A (E-field)		Input B (H-field)		Output M	
	kV/cm	Represent symbols	Oe	Represent symbols	M_r/M_s	Represent symbols
1	1	1	5000	1	0.3	11
2	-1	0	-5000	0	-0.4	00
3	1	1	-5000	0	-0.3	10
4	-1	0	5000	1	0.4	01

Table.1. Accessible input/output states for BFO-CuFO/SRO/PMN-26PT and BFO-CFO/PMN-26PT.

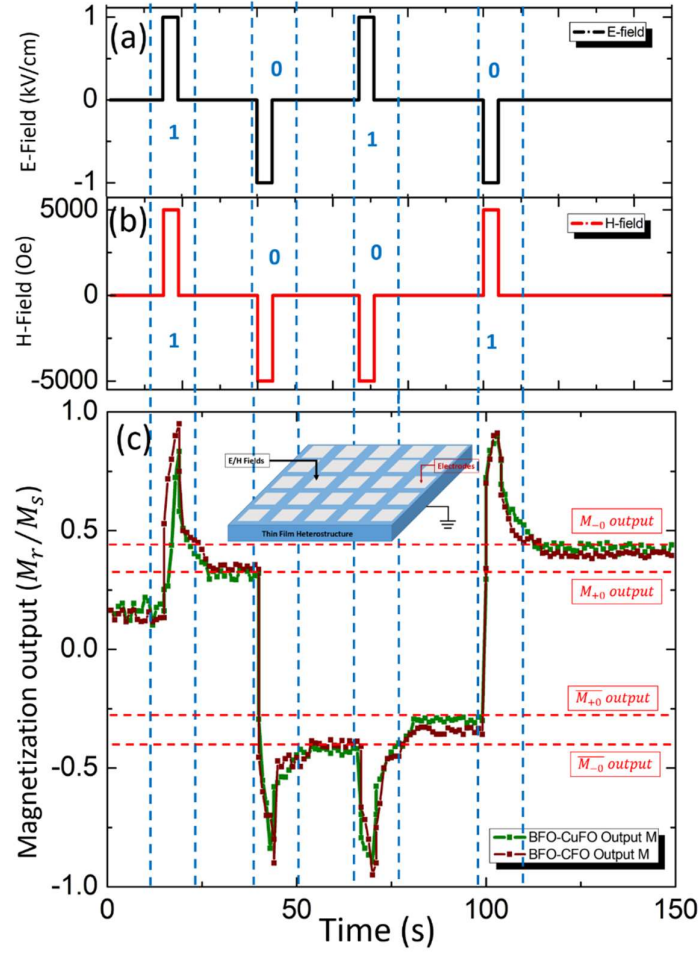


Fig.9. Schematic of magnetization outcomes using binary input: E-field and H-field. (a): Input E-field strength. (b) Input H-field strength. (c): Magnetization outcome of both BFO-CFO and BFO-CuFO heterostructure. Insert figure of (c) a schematic illustration of potential memory device application based on (1-3) heterostructure.

Traditional memory devices usually have only two (2) remnant states, which are interoperated as '1' and '0'. Reported articles⁴⁸⁻⁵² of multiferroic materials were used for this binary system, because of the easily formation of the 2 different remnant states. However, these 2-state memory devices suffer from deficiencies such as accumulated reading error, inability to corroborate with advanced algorithms and low storage densities^{53,54}. Recently, a new technique called Multi-Level-Cell (MLC) memory has been proposed^{54,55}, which can store more than one bit of information inside a single cell, resulting in a much higher storage density, and a much lower cost-per-bit⁵⁶. This MLC storage approach challenges conventional binary memory materials, because it requires more than 2 states in one unit to store information⁵⁶. By introduction binary input H-field and E-field signals, multiple magnetic states ($N \geq 2$) could be accessed. In Figure 9(c) one can see that the outcomes for BFO-CFO and BFO-CuFO heterostructures were similar to each other. If the sample surface is segregated into

different cells and coated with conductive electrodes layers, as illustrated in the insert of Fig. 9(c), a multi-bit-per-cell memory device could be built, resulting in reduced reading errors and much higher storage densities. This shows that the geometry of (1-3) heterostructures plays an important determining role. Even though the substrate and magnetic materials (CFO or CuFO) are volatile, the shape anisotropy created by the BFO matrix forced the magnetic domains to remain along the poling direction, establishing stable magnetic states.

To date, there are different types of MLC devices using the ME coupling effect^{27,28}. However, they have been limited either by the non-uniformity of PMN-xPT substrates for compositions near the MPB²⁷, or by the use of traditional non-volatile materials²⁸. However, the work present here, allows for the choice over a wide range of compositions to the left of the PMN-PT MPB, and also for repeatable multi-magnetic memory states accessible by E applied to the substrate.

In this work, BFO-CFO and BFO-CuFO (1-3) heterostructures were deposited on PMN-26PT substrates, and multiple magnetic states were found. Upon removal of E_{DC} , two remnant magnetization states were found to be stable. Applying an additional H-field input, two more different remnant magnetization states were found accessible and stable on removal H and E. Our investigations demonstrate (1-3) heterostructures with non-volatility, even though the materials phases/substrates have volatile properties. This opens the potential for the enhancement of the uniformity and repeatability of multifunctional layers deposited on PMN-PT crystal substrates, and also provides a much wider compositional range for choice of the PMN-xPT substrates for magnetic multi-states memory devices. For $N \geq 4$ magnetic states, an MLC memory device could be easily built with high ME coupling and multiple magnetic states.

II.3 Self-assembled epitaxial $\text{BiFeO}_3\text{-Ni}_{0.65}\text{Zn}_{0.35}\text{Al}_{0.8}\text{Fe}_{1.2}\text{O}_4$ nanobelt heterostructures on SrTiO_3 : control of magnetic anisotropy and coercivity.

Two-phase epitaxial $\text{Ni}_{0.65}\text{Zn}_{0.35}\text{Al}_{0.8}\text{Fe}_{1.2}\text{O}_4$ (NZAFO) and BiFeO_3 layers were deposited as self-assembled nanobelt-like heterostructures on (110) SrTiO_3 single crystal substrates by switching pulsed laser deposition. The magnetic anisotropy and coercivity of the low loss high magnetostriction NZAFO phase was altered by the large shape anisotropy of this nanostructure relative to that of single crystal layers. The self-assembled heterostructures exhibited strong magnetic anisotropy along the in-plane direction, resulting in an ability to tune the coercivity from 2 Oe (single crystal NZAFO layers) to ~ 650 Oe (nanobelt heterostructure). Rotation of the sample about its $[1\bar{1}0]$ direction revealed that the hard magnetic axis was along the $[001]$ with two easy directions at $\theta = \pm 30^\circ$. This magnetic anisotropy reflected the geometry of the nanobelt shape. In-plane rotation about the $[110]$ revealed a strong magnetic anisotropy along $[1\bar{1}0]$ and $[001]$, which are the two directions that defined the rectangular shape of the nanobelts. Our findings demonstrate a self-assembled nanobelt heterostructural layer whose spinel ferrite phase coercivity can be controlled by nanostructural features, which in turn modify the magnetic properties.

The magnetic properties of materials with giant magnetostriction are largely

dependent on their magnetic anisotropy¹. To date, many applications have relied on the manipulation of the anisotropy in order to optimize properties²⁻⁵. Examples include: changing the easy axis from in-plane (IP) to out-of-plane (OP) directions for electric reading⁶, and forming 2D/3D arrays with easy axes for reconfigurable electronics^{1,7,8}. Amongst all the contributions to the total magnetic anisotropy, the shape anisotropy is perhaps the most straightforward to engineer^{1,9}. A robust method that has been developed to control the shape anisotropy of epitaxial layers is the self-assembly of nanostructures of two phases^{10,11}, such as: BiFeO₃-CoFe₂O₄ (BFO-CFO) that forms vertically integrated nanopillar structures on (100) SrTiO₃ (STO) oriented substrates^{8,12}, and nanobelt structures on (110)¹³. Recently, we have reported a self-assembled mixed nanopillar/nanobelt heterostructural layer of BFO-CuFe₂O₄ (BFO-CuFO) on STO¹⁴. The magnetic anisotropy of the CuFO phase was altered by this mixed nanostructure, in a manner that enhanced its magnetoelectric (ME) effect [another my publication].

Recently, Emori et al¹⁵. reported a new Ni_{0.65}Zn_{0.35}Al_{0.8}Fe_{1.2}O₄ (NZAFO) spinel epitaxial layer that had large magnetostriction and small losses. Compared with conventional magnetic ferrites (such as CFO), the coercive field (H_c) of NZAFO was notably smaller, imparting to it higher quality factors (Q)^{16,17} and efficiencies^{18,19}. The coercivity of NZAFO layers was small (~ 2 Oe), resulting in low losses. NZAFO, CFO, and CuFO are all spinel ferrites with similar lattice parameters and structures. Thus, it should be feasible to deposit self-assembling two-phase BFO-NZAFO layers with nanopillar and/or nanobelt morphologies. In turn, this would allow changes in shape anisotropy to tune their magnetic coercivities. By controlling the relative volume fractions of the BFO and NZAFO phases, one could manipulate the shape anisotropy of the film. A new fabrication technique called switched pulsed laser deposition (SPLD), which is a technique that uses alternating targets during deposition, can simplify the fabrication of self-assembled heterostructures^{20,21}.

Here, we report self-assembled NZAFO-BFO nanobelt heterostructural layers deposited on (110) oriented SrTiO₃ (STO) single crystal substrates. The NZAFO phase formed as nanobelts embedded in a BFO matrix. The magnetic anisotropy was studied, and it was found that H_c could be manipulated by nanostructural control and its easy axis altered.

Two phase layers of BiFeO₃ (Kurt Lesker) and NZAFO (Toshiba Manufacturing Co., Ltd.) were epitaxially deposited by SPLD on (110) STO (Crystech). Prior to deposition, the substrates were cleaned with acetone and alcohol, via ultrasonication. Self-assembled BFO-NZAFO layers were deposited at a relative volume fraction of about 60:40. First, a BFO single layer was deposited at 650°C using an energy density of 1.2 J/cm² and an O₂ atmosphere of 150 mTorr for 2 min 45s. The target was then switched to NZAFO, and deposition done for 2min 15s at 650°C, 1.2 J/cm² and 150 mTorr. A bilayer structure was thus deposited. The procedure was repeated 10 times, resulting in a film with a total thickness of about 100nm. The samples were then annealed at 700°C and 100 Torr O₂. Atomic force (AFM) images were obtained (Dimension 3100, Veeco). Cross-sectional images, selected area electron diffraction patterns (SADP) and energy dispersive x-ray spectra (EDS) were measured using transmission electron microscopy (TEM, JEOL 2100). The Crystal structures were

determined by X-ray diffraction (Philips X'Pert system) and SADP. Magnetic hysteresis curves were recorded by a vibrating sample magnetometer (Microsense, EZ-9).

Figure 10 shows the surface topography of a BFO-NZAFO/STO (110) heterostructure. Part (a) shows a cross-sectional TEM image revealing a nanobelt structure, and a dashed line shows the interface between the matrix and a nanobelt. The cross-sectional image (Fig. 10(a)) reveals a clear edge line between the BFO and NZAFO phases, demonstrating that the nanobelt morphology extends throughout the entire thickness from the top surface of the film to the substrate. It is notable that the NZAFO nanobelts consisted of a dense array of nano-twin walls at the interface to the BFO matrix, as illustrated in circled dashed line in Fig. 10(a). Such a dense array of twin walls have also recently been reported for BFO-CuFO heterostructures¹⁴.

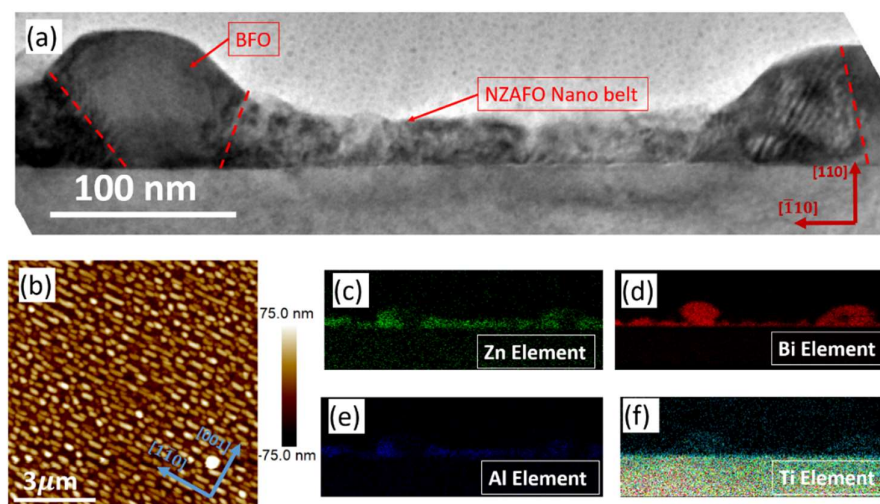


Figure 10. (a): Cross-sectional image of BFO-NZAFO heterostructure on (110) oriented STO substrate. (b): AFM image of surface of BFO-NZAFO heterostructure. (c) - (f): EDS mapping of cross-sectional image, different figures show different elements.

Figure 10(b) shows the surface morphology taken over a wider area by AFM, revealing the nanobelt distribution within BFO. The nanobelts can be seen to be oriented along the $[1\bar{1}0]$ direction, similar to that previously reported for BFO-CFO on (110) STO¹. This shows that the surface tension of NZAFO is similar to that of CFO, which favors $[1\bar{1}0]$ nanobelt formation¹¹. Parts (c)-(f) show EDS mappings of Zn, Bi, Al, and Ti respectively. The traces of Zn and Al had good overlap with each other, indicating the formation of NZAFO. The trace of Bi was found mostly in the matrix, demonstrating that it was well constrained to the BFO phase. Part (f) shows the trace of Ti, which revealed that it was constrained to the STO substrate. Overall, the EDS mapping confirmed that the nanobelts were the NZAFO phase, and that the matrix the BFO.

Figure 11 shows a XRD line scan for BFO-NZAFO/STO. The data clearly demonstrate epitaxially growth of NZAFO and BFO on (110) STO. The lattice

parameters were calculated from the scan: BFO (110) had a peak at 31.49° and a lattice parameter of $4.00\text{\AA}$, and NZAFO (220) had a peak at 30.46° and a lattice parameter of $8.29\text{\AA}$. Along the OP direction, compared to bulk lattice parameters, the BFO phase had a tensile strain of about 1% ($a_{\text{BFO-Bulk}} = 3.96\text{\AA}^{11}$), and NZAFO had a compressive strain ($a_{\text{NZAFO-Bulk}} = 8.36\text{\AA}$) of -1.2%. The insert in Fig.11 shows a selected area diffraction pattern (SADP) taken from the image in Fig. 10(a). The calculated lattice parameters from the SADP were $4.01\text{\AA}$ for BFO and $8.30\text{\AA}$ for NZAFO both consistent with that obtained by XRD.

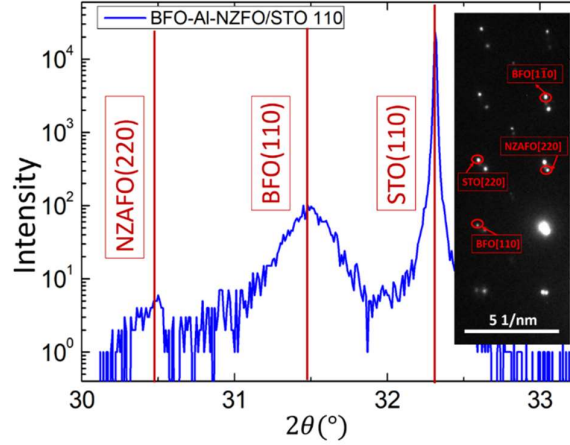


Figure 11. XRD line scan of the BFO-NZAFO/(110) STO. The insert figure shows diffraction pattern of cross-sectional area shown in Fig. 10(a).

Figure 12 (a) shows a magnetic hysteresis loop for a BFO-NZAFO heterostructure along both in-plane (IP) and out-of-plane (OP) directions. From the figure, one can see that the IP direction has a larger remnant magnetization (M_r) and coercivity (H_c). This is as expected, as the magnetic shape anisotropy lies along the IP. The insert in the lower right corner shows an enlarged figure for M_r and H_c . One can see that $M_{r-IP} = 15\text{emu/cc}$ and $M_{r-OP} = 10\text{emu/cc}$, with coercivities of about $H_{c-IP} = 650\text{Oe}$ and $H_{c-OP} = 750\text{Oe}$ respectively. Because the atomic percentage of BFO:NZAFO was about 0.6:0.4, it can be inferred that a single phase NZAFO would have M_{r-IP} and M_{r-OP} values of 40 and 25 emu/cc , respectively. This M_{r-OP} value is similar to that previously reported for NZAFO¹⁵; however, the M_{r-IP} value is notably smaller. This is probably because the nanobelt shape anisotropy results in the easy axis not lying along the [001], which is the measurement direction in Fig. 10(a). Also, the magnetic coercivity was $\sim 700\text{Oe}$, which is notably larger than the recently reported value of 2 Oe^{15} for epitaxial single phase NZAFO layers. The shape anisotropy energy density of

a NZAFO cylinder can be given by $\varepsilon_{\text{shape}} = 2\pi(N_x - N_z)M_s^2$, where $N_x = (1 - N_z)/2^{10}$ and N_z is a demagnetization factor related to the aspect ratio. From Figs. 2(a) and (b), the average aspect ratio can be determined to be 3. According to Beleggia et al.²², a value of $N_z \sim 0.15$ results when the aspect ratio is ~ 3 . Considering that $H_{\text{shape}} = 2\varepsilon_{\text{shape}}/M_s$, the coercivity induced by the shape anisotropy (H_{shape}) can be determined to be $H_{\text{shape-OP}} = 750\text{Oe}$ for the OP direction, which is close to the

experimentally measured value. This value of $H_{\text{shape-IP}}$ confirms that the magnetic shape anisotropy makes a dominant contribute to the coercive field. The results demonstrate an important method by which the value of H_c for NZAFO epitaxial layers can be controlled.

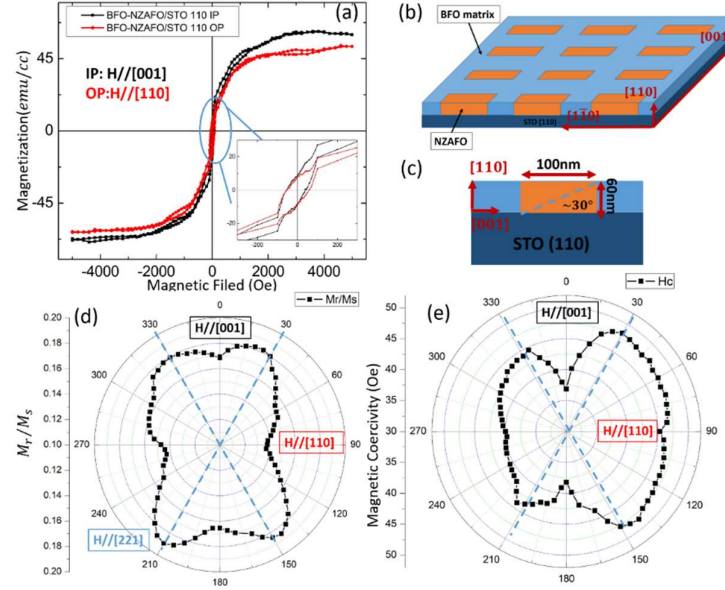


Figure 12: Magnetic hysteresis loop of BFO-NZAFO/(110) STO. (a) M-H loop of in-plane and out-of-plane direction. Insert figure of downright corner shows the enlarged area of coercivity and remnant magnetization. (b): Schematic figure of BFO-NZAFO nanobelt heterostructure with orientation labeled. (c): Schematic figure of BFO-NZAFO unit cutting along $[1\bar{1}0]$ direction. (d): M_r/M_s in response of angular, orientation of H filed was labeled. (e): H_c in response of angular, orientation of H filed was labeled.

Figures 12(d) and 12(e) show M_r and H_c as a function of rotation angle (θ) between the [001] and [110] directions. The magnetic easy and hard axes of the BFO-NZAFO/STO heterostructure can readily be identified in the figure. Smaller values of M_r and H_c can be seen along the [110] ($\theta = 90^\circ$), which is the OP direction. This indicates that the hard axis lies along the [110] ($\theta = 90^\circ$). Interestingly, the highest values were not found along the IP direction ([001], $\theta = 0^\circ$), which is the traditional easy axis for thin films. Rather, the highest values of M_r and H_c were located at $\theta = \pm 30^\circ$, yielding two easy axes for the BFO-NZAFO heterostructures. Figure 4(c) shows a schematic of the nanobelt cross section along the [001] direction, which had a length of $\sim 100\text{nm}$, a height of $\sim 60\text{nm}$, and an angle of $\sim 30^\circ$ angle between the length and the IP. According to Emori et al.¹⁵, when under a compressive epitaxial strain, NZAFO single-phase layers should have an easy axis along the face diagonal of the lattice. In the NZAFO nanobelts, the face diagonal is at about 30° from the [001] direction, which is along the [221] direction. This can be determined by considering the length and height ratio of the nanobelts in the heterostructure. Clearly, the values of M_r and H_c along $\pm 30^\circ$ from the IP direction were the highest, and these axes were the easy ones.

As mentioned in the previous section, the difference of M_r was not significant between the IP and OP directions, as can be seen in Fig. 12(a). This is because the IP

measurements were taken along the $[001]$ direction. In the heterostructure, the nanobelts form along the $[1\bar{1}0]$, and the easy axis of the plane that is parallel to the IP direction should be oriented along that of the nanobelt length due to its dominate shape anisotropy contribution. Accordingly, rotation about the IP (e.g. along $[110]$) was performed during the VSM measurements, as shown in Figure 13(a). The results demonstrate that the IP magnetic anisotropy easy axis is along the $[1\bar{1}0]$ and $[001]$ directions, which are the orientations of the nanobelts. The results show that the anisotropy had a four-fold rotational symmetry, similar to the tetragonal shape of the nanobelts embedded in the matrix. In Fig. 13(a), two points are circled in blue and red, which illustrate where the M-H loops were measured, which are then given in the insert in the lower right corner. The red and blue points designate the easy and hard axes respectively. In Figure 13(b), the M-H loops for these two points are shown. The insert shows an enhancement that better illustrates the differences in both M_r and H_c .

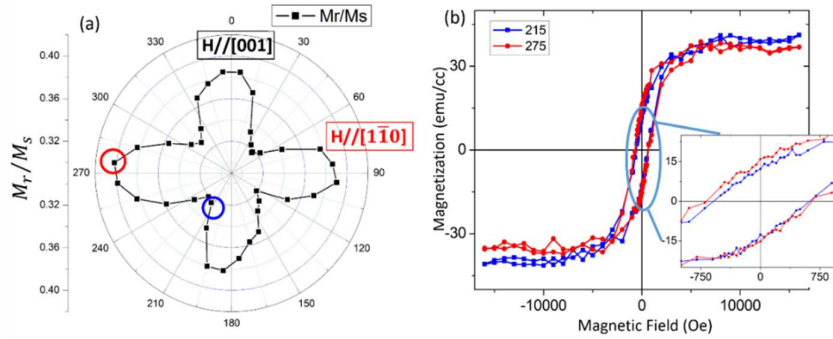


Figure 13. In-plane angle induced magnetic anisotropy of BFO-NZAFO/(110) STO heterostructure. The insert shows the M-H loops of chosen points, as shown in the blue and red circled dot in main figure.

Previously articles reported using SPLD for deposition of BFO-CFO²³ and BFO-CuFO¹⁴ nanopillar heterostructures. Here, we replaced the high loss CFO ferrite with the recently reported low loss NZAFO one, and successfully created a nanobelt heterostructures with both anisotropy and coercivity that could be controlled. The results show possibilities in self-assembling other ferrite that have similar lattice parameters as CFO, creating unique heterostructures. These heterostructures have patterned morphologies, large induced shape anisotropies, and tunable magnetic coercivities that could be useful for future applications.

In summary, BFO-NZAFO nanobelt heterostructural layers was epitaxially grown on (110) STO by SPLD. This nanobelt structure extended throughout the entire film thickness, forming a BFO matrix embedded with NZAFO nanobelts, as confirmed by TEM cross-sectional imaging and EDS mapping. This self-assembled layer had good epitaxy between places and with the substrate, as shown by XRD and SADP. M-H loop measurements revealed that the magnetic anisotropy favored an easy axis along the IP, and a dramatically increased magnetic shape anisotropy. The enhanced shape anisotropy enabled controlling of the coercivity from 2 Oe (single crystal NZAFO film) to 650 Oe (self-assembled BFO-NZAFO nanostructure). Rotation along the $[1\bar{1}0]$ resulted in a $[001]$ hard axis, where the shape of the nanobelt created two different

magnetic easy axes along $\theta = \pm 30^\circ$. IP rotation about the $[110]$ revealed an easy axes along the $[1\bar{1}0]$, which aligned with the nanobelt orientation. These findings exhibit a method by which to control the coercivity and anisotropy of low loss spinel ferrites by self-assembling nanostructures.

III. Self-assembled CuFe_2O_4 - BiFeO_3 layers on $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3

III.1 Nanostructure-Enhanced magnetoelectric, magnetostrictive and Qm properties

Overview: Self-assembled two-phase heterostructures of BiFeO_3 and CuFe_2O_4 (BFO-CuFO) were deposited on (100)-oriented SrRuO_3 -buffered $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -33at% PbTiO_3 (PMN-PT), and compared to single layers of CuFO on the same single crystal substrate. The CuFO phase of the self-assembled layers had notably slimmer M-H loops than for previously reported vertically-integrated CoFe_2O_4 nanopillar ones. Notable changes in the magnetization of the CuFO nanopillars were found with applied DC electric field (E_{DC}), where M_r/M_s exhibited typical butterfly-shaped hysteresis with E_{DC} . This was in distinct difference to CuFO/PMN-PT heterostructures which did not exhibit magnetoelectric coupling. *The findings demonstrate a trade-off between /magnetostriction properties and Qm that can be controlled by nanostructure features.*

Background Vertically-integrated nanopillars (designated as 1-3) heterostructures that combine magnetostrictive and piezoelectric phases have been found to possess significant ME couplings. Vertically-integrated (1-3) heterostructures provide a much larger contact area between the matrix and nanopillar phases, allowing for intimate lattice contact and significantly reduced clamping effects with substrates. This type of (1-3) heterostructure uses the transfer of strain between piezoelectric and magnetostrictive phases to enlarge the E-field dependence of the magnetization (M). Vertically integrated (1-3) heterostructures also have a high magnetic shape anisotropy because of their nanopillar geometry. The nanopillar structure might also pin the rotation of the magnetic domains, potentially creating additional stable nonvolatile remnant magnetization states.

However, other than BiFeO_3 - CoFe_2O_4 (BFO-CFO), not too many other materials have been studied. Heterostructures of BFO-CFO have close lattice parameter matchings and suitable surface tensions that favor self-assembling (1-3) vertical integration. The spinel ferrite CFO has a large λ_m , but it also has a high coercivity that leads to high losses and low Q. High losses dramatically reduce energy/power efficiency and decrease the usefulness of their tunable features. A lower loss spinel ferrite is needed in such nanopillars to overcome these limitations.

Copper ferrite (CuFe_2O_4 , CuFO) is also a spinel ferrite. The coercivity of CuFO has been reported to be about 100-200 Oe, which is dramatically lower than that of CFO ($\sim 5000\text{Oe}$). This indicates that the losses of CuFO are smaller than that of CFO, potentially offering higher Q factors and efficiencies. Early investigations of CuFO crystals reported a high λ_m . More recently, high quality epitaxial thin layer of CuFO have been deposited on MgAl_2O_4 (MAO). However, the magnetostriction of the layers was not reported. Such CuFO thin films on MAO could suffer from mechanical clamping effects, as well as leakage currents resulting in reduced magnetostriction. In addition, CuFO has lattice

parameter that might allow matching to BFO for vertical integration, and to $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ (PMN-xPT) as a substrate. It, thus, offers an approach to make ME heterostructures with reduced losses, and significant λ_m and ME exchange.

Details: Single layer CuFO and vertically integrated CuFO-BFO layers were epitaxially deposited on PMN-33PT substrates by PLD. Self-assembled thin films were deposited by switching PLD (SPLD), where the target is switched during depositions. BFO and CuFO targets were purchased from Kurt J. Lesker Company, and both were >99.9% in purity. Single crystal PMN-33PT (100) substrates were grown at the Shanghai Institute of Ceramics Chinese Academy Sciences. Prior to deposition, the substrates were cleaned with acetone and alcohol via ultrasonication. First, a 30nm SRO layer was deposited on PMN-33PT at 700°C, using an energy density of 1.5 J/cm² and an O₂ atmosphere of 150 mTorr, which was followed by annealing at 700°C and 150 mTorr O₂ for 10min. Single CuFO layers were deposited at 700°C using an energy density of 1.2 J/cm² and an O₂ atmosphere of 150 mTorr for 50min. Self-assembled CuFO-BFO layers were deposited as a volume fraction of about 40:60. First, a BFO single layer was deposited at 700°C using an energy density of 1.2 J/cm² and an O₂ atmosphere of 150 mTorr for 2 min 48s. The target was then switched to CuFO, and deposition was done for 2min 12s at 700°C, 1.2 J/cm² and 150 mTorr to form a bilayer structure. This procedure was repeated 10 times, forming a film with a total thickness of about 130nm. The sample was then annealed at 700°C and 100 Torr O₂. Atomic force (AFM) and magnetic force (MFM) microscopy images were obtained (Dimension 3100, Veeco) to study the film surface quality and magnetic domain structures. Cross-sectional samples were fabricated by focused ion beam (FIB, FEI Helios 600 NanoLab). Cross-sectional images, selected area electron diffraction patterns (SADP) and x-ray spectra (EDS) were obtained using a transmission electron microscope (TEM, JEOL 2100). Crystal structures were determined by X-ray diffraction (Philips X'Pert system) and SADP. Magnetic hysteresis curves were recorded by a vibrating sample magnetometer (VSM, Lakeshore 7300 series).

II.1.1 CuFO single layer on PMN-33PT.

Figure. 14 summarizes the structure and ME properties of the CuFO/SRO/PMN-33PT heterostructures. Part (a) shows a cross-sectional TEM image, which exhibits formation of a single layer with no apparent nanostructures. Part (b) shows a SADP taken along the [010] zone axis. The red circled spot in the figure clearly illustrates that an epitaxial CuFO single layer formed on top of the PMN-33PT substrate. The PMN-33PT lattice parameters calculated from Fig. 14(b) were 4.03Å, which is similar to previous reports. A splitting along the (400) zone can be seen in the SADP, which are the CuFO (004) and (400) peaks. This evidences that the CuFO layer had a tetragonal (T) structure, which is different than the cubic (C) one recently reported for CuFO on MgAl₂O₄ (MAO). The lattice parameters of CuFO were determined from the splitting to be $(a_{T-\text{CuFO}}, c_{T-\text{CuFO}}) \cong (8.26, 8.67)\text{Å}$. This is similar, but not exactly the same, as the bulk CuFO lattice parameter of $c_T = 8.73\text{Å}$. The CuFO layer undergoes a compressive strain along the c-axis of ~0.68%.

Figure 14(c) shows a magnetic hysteresis loop for CuFO/SRO/PMN-33PT, along both in-plane (IP) and out-of-plane (OP) directions. The easy axis of the magnetization aligned along the IP, and exhibited a typical M-H hysteresis loop. The saturation magnetization was $M_s \approx 60 - 70 \text{ emu/cm}^3$, and the remnant magnetization was $M_r \approx 15 \text{ emu/cm}^3$.

Zhang et al. previously reported epitaxial growth of CuFO films on MAO with $M_s \sim 60 \text{ emu/cm}^3$ and $M_r \sim 20 \text{ emu/cm}^3$, similar to those reported here on PMN-33PT. The coercivity of our films was $H_c \approx 150 \text{ Oe}$ along both IP and OP. The value of H_c along the easy axis was previously reported to be $\sim 30\text{-}40 \text{ Oe}$ for CuFO powders, $\sim 23 \text{ Oe}$ for a 50nm CuFO single crystal films, and $\sim 250 \text{ Oe}$ for 450nm single crystal films. Figure. 14(d) shows an M-H loop for CuFO/SRO/PMN-33PT under various applied DC electric fields (E_{DC}), taken along OP and IP. As can be seen in the figure, the magnetization was essentially independent of E_{DC} , over the range of 0 to 4kV/cm, where PMN-33PT is known to have significant E-field induced strains. This demonstrates that the CuFO single layers have little magnetoelectric coupling, and thus it indicates negligible magnetostriction.

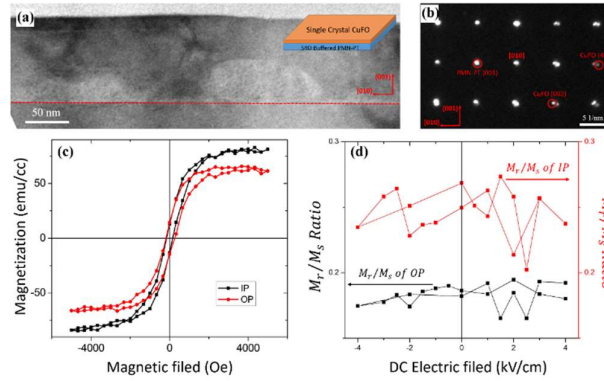


Figure 14. (a) TEM cross-section image of single crystal CuFO/SRO/PMN-33PT heterostructure. Insert figure at up right corner shows a schematic of this heterostructure. (b) Electron diffraction pattern of this cross-section. (c) VSM data for this single layer CuFO/SRO/PMN-33PT, both IP and OP directions. (d) E-field dependence of Magnetization of CuFO/SRO/PMN-33PT, both IP and OP directions.

Our findings show that CuFO layers can be epitaxially deposited on PMN-33PT. The CuFO layers have a similar T crystal structure, lattice parameters, and M_r and M_s values as bulk crystals. However, the heterostructures clearly demonstrated the lack of magnetoelectric exchange, and thus by inference the CuFO magnetostriction is very small. *Why do we show these results? This is because nanostructures of vertically-integrated layers on the same substrate will next be shown to impart to the heterostructure these missing characteristics.*

III.2. Vertically integrated CuFO-BFO layer.

Morphology and Structure.

Figure. 15 (a) shows an AFM image of a BFO-CuFO film surface. One can clearly see a nanostructure topography embedded in a matrix. The morphology consisted of an apparent mixture of nanopillars (surface dimensions of about $100\text{nm} \times 100\text{nm}$) and nanobelts (surface dimensions of about $10^3\text{nm} \times 100\text{nm}$). The nanopillars and nanobelts appeared to have similar geometries and aspect ratios, where the pillars lay vertical to the substrate plane and the belts horizontal. This mixed nanobelt-nanopillar morphology appeared stable, similar AFM topographies were obtained for heterostructures annealed at

significantly longer time (60min data not shown).

Figure. 15(b) shows corresponding MFM images for the phase response. As identified in Fig.15(b), the black circled area has a positive phase signal, whereas the white squared area has a negative one. These are the magnetic signal contributions from different magnetic domain orientations within the nanostructure. The sample was not yet poled by a magnetic field, and the magnetic domains in the CuFO nanopillars are oriented amongst symmetry equivalent directions. Most of the area is covered by the matrix phase, which is shown as green to blue colors in the phase image. These regions represent low contrast areas close to the noise level in the scale bar, which make negligible contributions to the magnetic signal. Presumably, this is due to the fact that the BFO phase magnetic signal is small. An AFM phase image scan is shown in Fig.15(c), which helps to better distinguish the presence of two phases on the surface. The AFM phase image plots a contour of the surface layer stiffness. Such contrast can be used to distinguish different phases and their distributions on the surface. In Fig.15(c), it can be seen that the phase signals of the nanopillars/nanobelts were either dark (close to -40° in the scale bar) or white (close to $+40^\circ$). This was totally different from the matrix area which is illustrated as grey in the image (middle of scale bar).

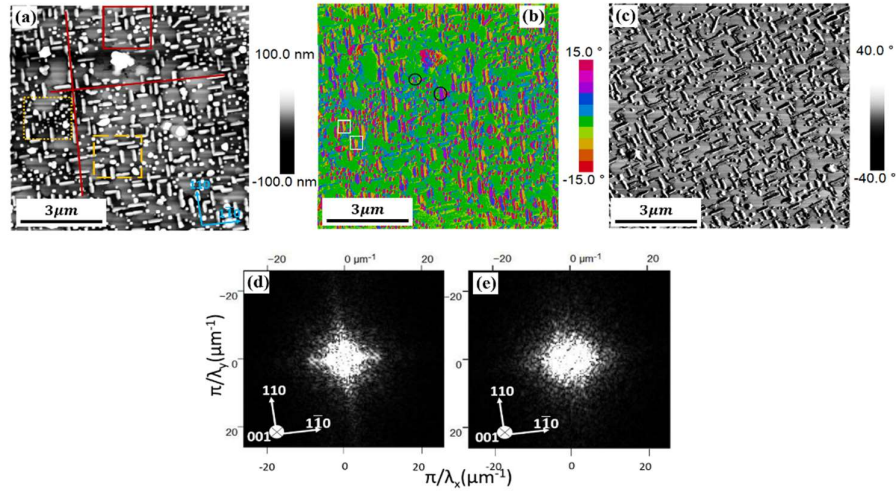


Figure 15. (a): Height information of nanopillar structure topography. (b): Magnetic phase signal of MFM scan, showing different magnetic domains in different nanopillars, and matrix without significant magnetic phase signal. (c): Phase image shows different materials of nanopillar (black or white color) and matrix (grey color). (d) & (e): FFT analysis. (d): FFT of yellow dashed area in Fig. 14(a), and (e): FFT of yellow dotted area.

Next, we considered the distribution of the nanobelts and nanorods in Fig. 15(a), which was quite regular across the surface. The belts were elongated along the $\langle 110 \rangle$ and $\langle 1\bar{1}0 \rangle$ family of directions. They were somewhat regularly spaced, with a tendency to align with neighboring belts. Fine red lines are given in the image to guide the eyes to the rectilinear regularity of the nanobelt morphology. Vertical nanorods with a square shape appeared to collect within areas surrounded by the nanobelts, and had some tendency to align with respect to each other along the $\langle 001 \rangle$ directions, as illustrated by a fine red box in the image. A fast Fourier transform (FFT) image that corresponds to the domain distribution is then given in Figure 15(d) & (e), where π/λ_x and π/λ_y are the wave-

vectors along the x- and y- directions. Fig. 15(d) was taken from the area covered by the dashed yellow box, which is a region containing mostly nanobelts. The FFT image can be seen to be strongly oriented along the $\langle 110 \rangle$ and $\langle 1\bar{1}0 \rangle$, demonstrating a significant degree of self-organization of the nanobelts into a quasi-periodic morphology. The average inter-spacing between nanobelt features π/λ_x and π/λ_y was determined to be about 174nm. We next obtained a FFT from the area defined by a dotted yellow box, which was a region containing mostly nanorods, as shown in Fig. 15(e). The FFT image revealed some degree of orientation along the $\langle 001 \rangle$, in addition to a halo that was quite diffuse and symmetric about the x- and y-axes.

A cross-sectional image of the nanopillars and nanobelts was then obtained by TEM, as given in Fig. 16 (a). From the figure, we can see that the vertically integrated two-phase layer of the heterostructure consisted of nanopillars and nanobelts. The edge of the thin film layer was distinct, exhibiting no inter-diffusion of film and substrate. The image shows that the nanobelts and nanorods extend throughout the thickness of the film from the substrate, and that the nanobelts are uniform regions rather than closely spaced nanorods. These results clearly demonstrate that the distribution of CuFO in BFO consists of a mixed morphology between nanorods vertically integrated from the substrate and nanobelts laying in the plane. From Fig. 16(a), one can also observe that the nanopillars and nanobelts of CuFO extend out from the surface of the BFO matrix. Stretching-out of nanopillars have commonly been observed for vertically-integrated nanocomposites. However, in the case of CuFO nanostructures, this extend-out was nearly half of the matrix thickness. This may be driven by relaxation of epitaxial strain due to the large lattice mismatch with the BFO matrix. As shown by the red dashed line in Fig. 16(a), the CuFO nanostructures also exhibited a particular faceted angle with respect to the matrix, which was about 55 to 60°. This angle may reflect a balance of wettability and strain interactions between nanostructures and the matrix.

Energy dispersive x-ray spectroscopy (EDS) was then performed on this sample. This allowed us to determine the composition of the nanobelts, nanorods, matrix and substrate. EDS plots for each of these regions are given in Figures 16(b)-(d), respectively. From Fig. 16 (b) and (c) one can see that there is no elemental Cu in the matrix phase, and no elemental Bi inside the nanopillar/nanobelt phase. These plots thus demonstrate that the composition of the nanobelts and nanorods are CuFO, that the matrix is BFO, and that no secondary phases form at the interfaces between nanostructures and matrix. The EDS plot in Fig. 16 (d) demonstrates the presence of elemental Pb in the substrate composition; consistent with the bright field image that the heterostructure film was clearly distinct from the PMN-33PT substrate. EDS mapping for the element Sr was also done (data not shown). The buffer layer SRO lies in-between the thin film heterostructure and substrate, which again demonstrated no mixed phases.

Figure.17 shows a high resolution TEM (HRTEM) image taken from the area labeled by the dashed red circle in Fig. 16 (a). The HRTEM image shows an area having both a CuFO nanopillar and BFO matrix, where the boundary between them is labeled by a red dash-line. Separation of the two phases was clear, demonstrating no interdiffusion of the BFO and CuFO phases or secondary phase formation at the boundaries. The HRTEM image also evidences the lattice periodicity of both phases. Two pairs of white dashed lines in Fig. 17

(a) illustrate the d-spacings of CuFO and BFO: $d_{\text{CuFO}} = 4.20\text{\AA}$ which corresponds to the CuFO (002) plane, and $d_{\text{BFO}} = 3.87\text{\AA}$ which is that of the (001) BFO. These values are consistent with those of bulk CuFO and BFO phases. The image reveals registry of the lattice phases across the interphase interfaces, demonstrating good epitaxy between CuFO and BFO phases in the self-assembled layer. The insert in the lower left corner of Fig. 17(a) shows a dark field image taken from a CuFO nanopillar. This image reveals the presence of an array of nanotwins along the (001). The nanotwins were about 5-10nm in width and 50nm in length. Such high twin wall densities can only arise when the twin wall energy $\gamma \rightarrow 0$. This type of domain engineering can play an important role in softening the elastic constant and relaxing elastic energy, in stabilizing the self-assembled nanostructure.

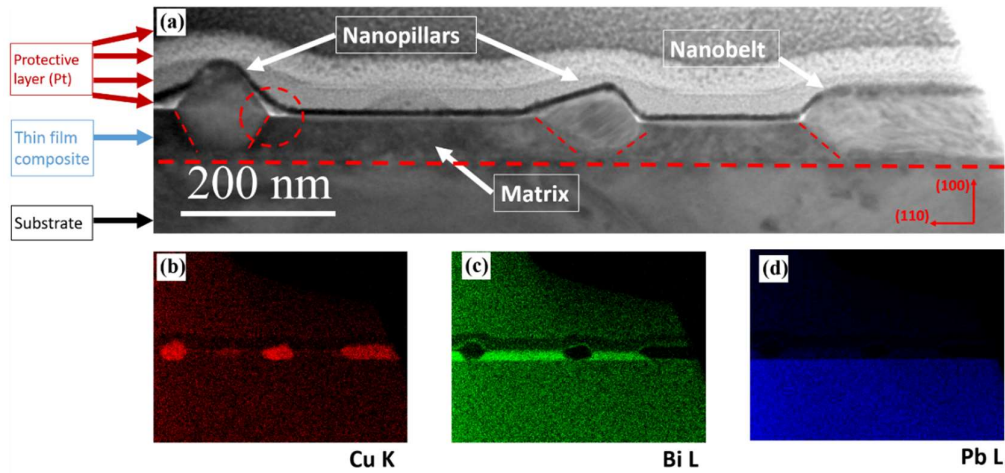


Figure 16. Cross-section images taken by TEM. (a): Cross-section bright field image containing 2 nanopillars and a nanobelt. (b). EDS mapping for element Cu, (c) Bi and (d): Pb.

Figure. 17 (b) shows a SADP taken from Fig. 16(a) along the $[1\bar{1}0]$ zone axis. A splitting can be seen in the SADP, which evidences that the CuFO phase in the self-assembled layers had a tetragonal (T) structure. The lattice parameters of the CuFO phase was calculated from the SADP and determined to be $(a_{T-\text{CuF}}, c_{T-\text{CuF}}) \cong (8.20, 8.60)\text{\AA}$. Compared to the bulk CuFO lattice parameters, a significant compressive strain is induced along the c-axis ($\sim 1.5\%$). This compressive strain is notably larger than the strain in single CuFO layers ($\sim 0.68\%$) as mentioned above. A splitting in the diffraction pattern was also found along the (003) BFO peak, as labeled in Fig. 17 (b). The lattice parameter was calculated to be $a_{\text{BFO}} = 3.95\text{\AA}$, which is close to the bulk BFO value of the rhombohedral (R) phase ($d = 3.96\text{\AA}$). The insert in the upright corner of Fig. 17(b) shows a corresponding X-ray line scan. The BFO (200) peak was located at 46.07° ($a_{\text{BFO}} = 3.938\text{\AA}$), and the CuFO (400) was found at 44.14° ($a_{T-\text{CuFO}} = 8.200\text{\AA}$), yielding similar to those determined by SADP. However, there was no evidence of the CuFO (004) peak (i.e., c_{T-C}) in the XRD line scans.

One can presume that the self-assembly of the mixed nanostructure state is driven by minimization of the elastic strain energy, similar to that for vertically integrated nanopillar structures previously modeled by phase field theory. This mixed morphology was distinctly different than that of CFO-BFO on SRO/STO or SRO/PMN-PT, where a nanopillar structure forms on (001) substrates and a nanobelt one on (110). This difference indicates

a potentially important role of the tetragonal lattice parameters of CuFO single crystals (large $c/a \approx 1.06$), relative to the cubic ones for CFO, as a driving force for the mixed morphology.

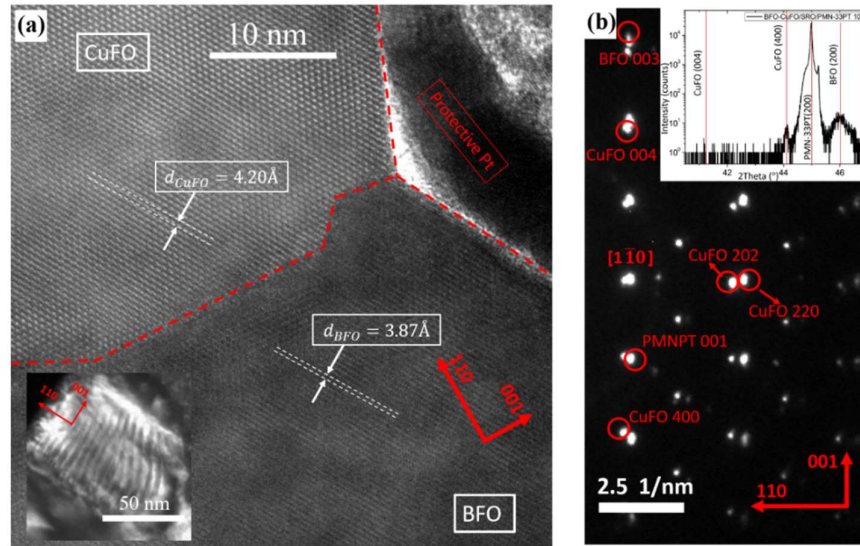


Figure 17: (a): Enlarged area of dashed circle in Fig. 16 (a). White dashed line shows the interplanar spacing of both CuFO and BFO. Insert shows dark field images of this nanopillar, illustrating a periodical line structure. (b): Corresponding diffraction pattern of selected area.

Magnetization and magnetoelectric coupling.

Figure 18 (a) shows M-H loops taken along both IP and OP directions by VSM. The saturation magnetization (M_s) was about 34 emu/cm^3 along both directions, and the remnant magnetization was $M_r = 11.3 \text{ emu/cm}^3$ and 9.7 emu/cm^3 along OP and IP respectively. Since the CuFO-BFO volume ratio was about 40:60 and since the antiferromagnetic BFO phase does not contribute to the induced magnetization, the values of M_s and M_r of the CuFO nanopillars can be estimated to be about 50 emu/cm^3 ($1.5 \times 30 \text{ emu/cm}^3$) and 15 emu/cm^3 ($1.5 \times 7.5 \text{ emu/cm}^3$), respectively. These values are nearly equivalent to those previously reported for epitaxial CuFO films on MAO, and to values shown above for CuFO/SRO/PMN-33PT. From Fig. 18 (a), the coercivity along IP and OP was determined to be 430 Oe and 700 Oe, respectively. These values are significantly larger than those for single layer CuFO/SRO/PMN-33PT, but much lower than those previously reported to CFO-BFO/SRO/PMN-PT. It was expected that the easy axis would be along IP, instead it was found along OP. This difference is undoubtedly due to nanobelt/nanopillar induced changes in the magnetic shape anisotropy. A large shape anisotropy contribution can dominate the magnetic anisotropy, changing the easy axis from IP to OP.

Figures 18 (b) and (c) show M-H loops under various applied E_{DC} , taken along OP and IP, respectively. The inserts in the figures show that M_r along OP was increased under $E_{DC} = \pm 1 \text{ kV/cm}$; whereas M_r along IP was decreased under $E_{DC} = \pm 2 \text{ kV/cm}$. The specific values of E_{DC} given in the inserts were chosen because they exhibited the largest

magnetization changes. According to Arai et al., CuFO single crystals have a negative magnetostrictive coefficient ($\lambda_{\text{CuFO}} \sim -100 \times 10^{-6} \text{m/A}$), which is a modestly large λ as can be noted by comparing with CFO ($\lambda_{\text{CFO}} \sim -250 \times 10^{-6}$). This magnetostriction for CuFO imparts to CuFO/BFO/SRO/PMN-33PT heterostructures notable magnetization changes under E_{DC} applied to PMN-PT. As shown in the right hand axis of Fig. 18(d), the PMN-33PT substrate is placed under compressive strain along OP by E, which subsequently induces the BFO-CuFO film to have a tensile strain along IP. Rotation of the easy axis by compression along OP will cause M_r to be increased, and vice versa for M_r along IP to be decreased by tension.

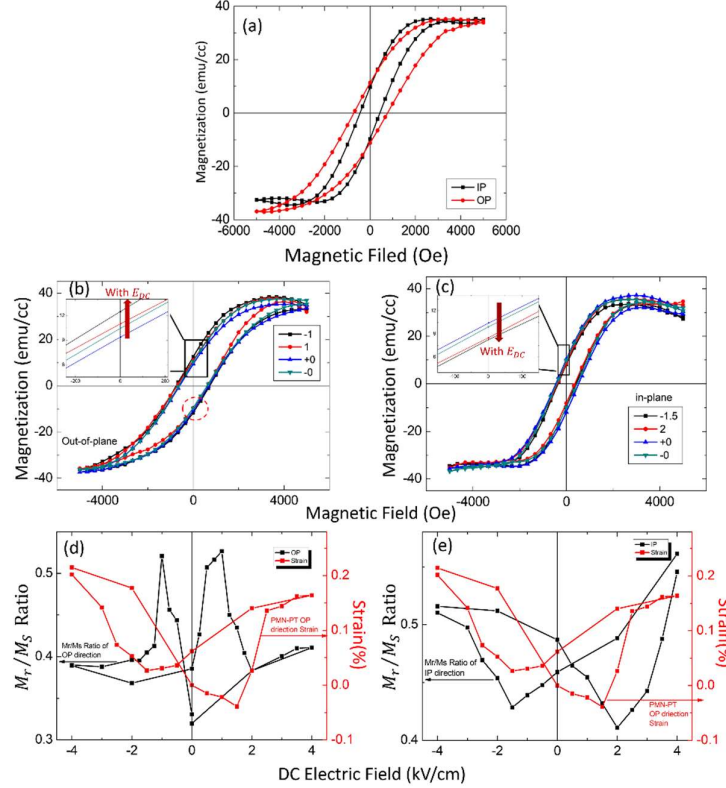


Figure 18. Magnetoelectric properties for both IP and OP direction of BFO-CuFO/SRO/PMN-33PT. (a) M-H loop of both IP and OP. (b) M-H loop of OP direction under $\pm 1 \text{ kV/cm}$ and 0 kV/cm E_{DC} . The insert figure shows the IP and OP M-H loop together at 0 Oe . (c) M-H loop of IP direction under 2 kV/cm , -1.5 kV/cm and 0 kV/cm E_{DC} . (d) and (e): M_r/M_s ratio sweep from -4 kV/cm to 4 kV/cm of OP and IP directions, respectively.

A remnant-to-saturation (M_r/M_s) magnetization ratio was then determined under various E_{DC} between $\pm 4 \text{ kV/cm}$ applied to the PMN-PT substrate. As can be seen on the left hand axis of Fig. 18 (d), the M_r/M_s ratio exhibited a butterfly-like shape, which is typical of a hysteresis loop of ferroic materials. The highest values were $M_r/M_s = 0.521$ under $E_{\text{DC}} = -1 \text{ kV/cm}$ and $M_r/M_s = 0.526$ under $E_{\text{DC}} = 1 \text{ kV/cm}$. The right hand axis of Fig. 18 (d) shows the corresponding $\epsilon - E$ curve for the PMN-33PT substrate. The $\epsilon - E$ curve also exhibited a typical butterfly-like loop, where the highest compressive strain along OP was found under $E_{\text{DC}} = \pm 1.5 \text{ kV/cm}$, corresponding to the highest value

of the M_r/M_s ratio on the left hand axis. Under higher E_{DC} , the M_r/M_s ratio became relatively constant with further increase of E_{DC} , reflecting saturation in the $\epsilon - E$ curve. Please note that there was a large difference in the value of M_r/M_s under $E_{DC} = 0$ after positive and negative poling studies. This may be due to a combination of the remnant strain of PMN-PT (right hand axis) and pinning of the magnetic domain rotation in the CuFO nanopillars. Fig. 18 (e) shows similar M_r/M_s ratio data taken along the IP direction. On the contrary, the values of M_r/M_s were decreased by compressive strain induced by applying E_{DC} to the PMN-PT substrate. The maximum decrease in M_r/M_s was found under E_{DC} of -1.5 kV/cm and 2 kV/cm .

The E-field dependence of the magnetization demonstrates the presence of ME coupling in the CuFO-BFO/PMN-33PT heterostructures. To quantify this coupling, the converse ME coefficient (α) under different conditions was calculated by $\alpha = \mu_0 \times \Delta M / \Delta E$, as given in Fig. 19; where μ_0 is the permeability of free space, ΔM is the magnetization change induce by DC electric field ΔE . The value of α was determined to be $\sim 5.5 \times 10^{-8} \text{ s/m}$ under $E_{DC} = 0.5 \text{ kV/cm}$, which decreased to $\sim 1 \times 10^{-8}$ with increasing E_{DC} . The insert in the upper right corner in Fig. 19(b) shows α for the three representative magnetic states (poling, maximum and plateau) under different H-fields. According to the insert, α dramatically decreases for $H > H_C$, due to a high degree magnetic domain alignment. Compared to previous reported values for vertically integrated BFO-CFO and STO and/or PMN-PT of $\alpha_{BFO-CuFO/ST} = 1 \times 10^{-10} \text{ s/m}$ and $\alpha_{BFO-CFO/PMN-PT} = 1.4 \times 10^{-7} \text{ s/m}$, the value for $\alpha_{BFO-CuFO/PMN-PT}$ can be seen to be significant. This demonstrates good ME coupling between the CuFO nanopillars and PMN-PT substrate. These results are in distinct contrast to our findings for CuFO/SRO/PMN-33PT heterostructures.

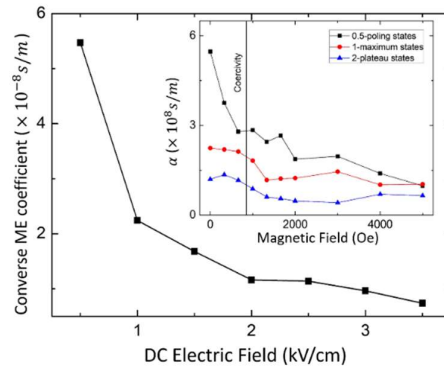


Figure 19. α_{ME} under different E_{DC} . Insert at up right corner shows the α_{ME} of three representative magnetic states under different H_{DC} .

III.3 Self-assembling two-phase vertically integrated heterostructure, including BiFeO₃-CuFe₂O₄ (BFO-CuFO)

In our previous report last year, self-assembled two-phase heterostructures of BiFeO₃ and CuFe₂O₄ (BFO-CuFO) were deposited on (100)-oriented SrRuO₃-buffered Pb(Mg_{1/3}Nb_{2/3})O₃-33at%PbTiO₃ (PMN-PT), and compared to single layers of CuFO on the same single crystal substrate. The CuFO phase of the self-assembled layers had notably slimmer M-H loops than for previously reported vertically-integrated CoFe₂O₄ nanopillar ones. Notable changes in the magnetization of the CuFO nanopillars were found with applied DC electric field (E_{DC}), where M_r/M_s exhibited typical butterfly-shaped hysteresis with E_{DC} . This was in distinct difference to CuFO/PMN-PT heterostructures which did not exhibit ME coupling. *The findings demonstrate a trade-off between magnetostriction properties and Q_m that can be controlled by nanostructure features.*

The surface topography of BFO-CuFO heterostructures displayed a mixed nanostructure—i.e., mixed nanopillars with nanobelts. We believe that the mixed nanostructures helps to relax the strain between the matrix and nanostructure phases, thereby stabilizing a complex phase distribution. CuFO is a spinel material that has similar lattice parameters to CFO. Despite their known similarities, their confirmed two phase distributions within heterostructures are quite different: BFO-CFO has a typical square nanopillar surface, whereas BFO-CuFO has a mixed nanostructure surface.

However, the physical model behind this BFO-CuFO complex surface nanostructures remained a mystery. It consisted of a quasi-periodically arranged mixture of nano-belts and nanorods. The physical mechanism behind this unusual nano-structure is important for the control of the phase distribution, and for the tuning of its properties. Accordingly, this year we have performed simulations of this mixed BFO-CuFO nanostructure. The physical model of BFO-CuFO heterostructures was performed using a phase-field model, which is a mathematical model for solving interfacial problems. We corroborated with Dr. Yipeng Gao at the Idaho National Lab (INL), who is a specialist of phase-field simulations, to establish a model for the BFO-CuFO heterostructures.

In order to use a phase-field model, it is important to have the elastic constants of the materials, which affect the surface tension. Thus, they determine the shape, size, and phase distribution of the nanostructures. However, the values of the elastic constants of CuFO were unknown. In order to obtain estimates for the elastic constant, we also corroborated with Dr. Xianming Bai (MSE, Virginia Tech). He and his student (Ziqi Xiao) used density functional theory (DFT) to calculate the elastic constant of the CuFO spinel ferrite, and the results are given in Table 2. To compare with the well-studied vertically integrated nano-structures of BFO-CFO, calculations of the elastic constants were also performed for CFO, which are given in Table 3.

Table. 2. Elastic constant of CuFO, both normal type and inverse type of CuFO.

Type	C ₁₁	C ₂₂	C ₃₃
Normal (GPa)	84.64	96.81	107.17
	C ₄₄	C ₅₅	C ₆₆
	84.50	79.54	91.66
	C ₁₂	C ₁₃	C ₂₃
	196.11	197.23	187.52
Inverse (GPa)	C ₁₁ = C ₂₂	C ₁₂	C ₁₃
	225.73	152.11	121.04
	C ₃₃	C ₄₄ = C ₅₅	C ₆₆
	185.10	67.24	88.44

Table. 3. Elastic constant of CFO, both calculated and experimental data.

Type	C ₁₁ (GPa)	C ₁₂ (GPa)	C ₄₄ (GPa)
DFT calculations	84.64	96.81	107.17
Experiment Results	225.73	152.11	121.04

Phase field simulation results are shown in Figure 20. From the calculations, one can see that the $[110]/[1\bar{1}0]$ alignment observed in experiments is strongly dominated by the long range elastic interactions between the nanostructure and matrix, which is dictated by the elastic soft directions of BFO ($[110]/[1\bar{1}0]$). The shape of the nanostructure depends on the anisotropy of CFO/CuFO. The nanostructures show a diamond shape for a Zener ratio > 1 ; where as it exhibits a pillar shape for a Zener ratio < 1 . The CFO experimental data fits the former, as shown in Fig. 20(b). Whereas, in the mixed nanopillar/nanobelt morphology of BFO-CuFO (see Fig. 20(a)), the CuFO particle shape fits the latter, as can be seen in Fig. 20(c). Clearly, the long range alignment of the mixed nanostructure of BFO-CuFO is dominated by the elastic interactions, rather than the interfacial anisotropy. The morphology difference between the phase distributions in CFO/BFO and CuFO/BFO can be attributed to the anisotropy (Zener ratio) difference.

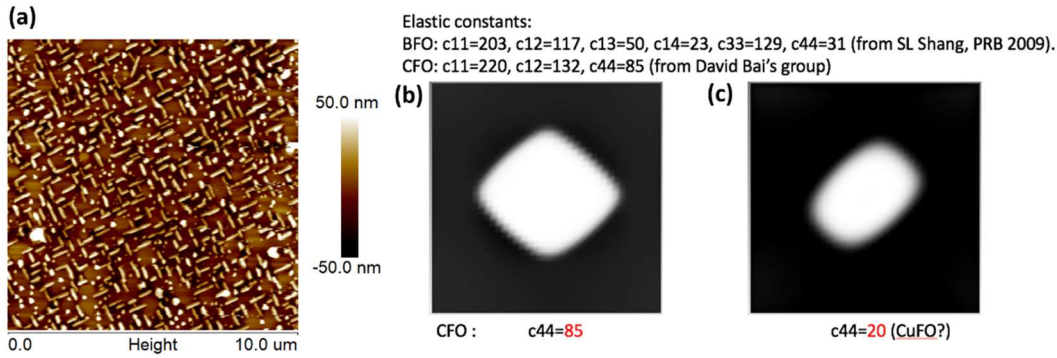


Figure 20. (a) AFM experimental scan of BFO-CuFO mix nanostructures. (b) & (c) Phase field simulations on CuFO nanostructures embedded in BFO matrix. Different size reflected different Zener ration (anisotropy). (b) $C_{44}=85$ GPa. (c) $C_{44}=20$ GPa.

IV. Inelastic neutrons scattering studies of ferrite single crystals.

We have performed preliminary neutron diffraction studies of CoFe_2O_4 magnetostrictive single crystals using the triple-axis spectrometer on BT4 at the National Institute of Standards and Technology (in Collaboration with Peter Gehring). Studies of the crystals aligned/oriented in the (HKO) scattering place (i.e., cubic $[001]$ vertical axis) were done for various constant-Q scans. The studies revealed that the crystals were of excellent quality, having mosaic spreads less than 0.5° full-width-half-maximum, and the Bragg and phonon intensities were huge. These preliminary data demonstrated much potential for the study of the dynamical structure factor of ferrite crystals. These studies could be interesting as the phonon and spin dynamics may be most important understanding what controls the Q-factor of magnetostrictive crystals and layers, via domain engineering.

We then performed scans at $Q=(4,k,0)$ for $k=0.00$ to $k=-0.50$ and from $\hbar\omega = -1$ meV to 21 meV at room temperature, as given in Figure 21. These scans are sensitive to phonons propagating along $[0 -1 0]$ and polarized along $[100]$, i.e. transverse phonons (both acoustic and optic). We also performed scans at $Q = (2+k,2-k,0)$ for the same range in k and $\hbar\omega$, which probe phonons propagating along $[1 -1 0]$ and polarized along $[110]$. We found very strong transverse acoustic (TA) modes for the scans measured at $(4,k,0)$. The TA modes are substantially weaker at $(2+k,2-k,0)$. For that reason, we then ran a test scan at $(4+k,4-k,0)$, which reflects the same phonons, and we found a much larger dynamic structure factor.

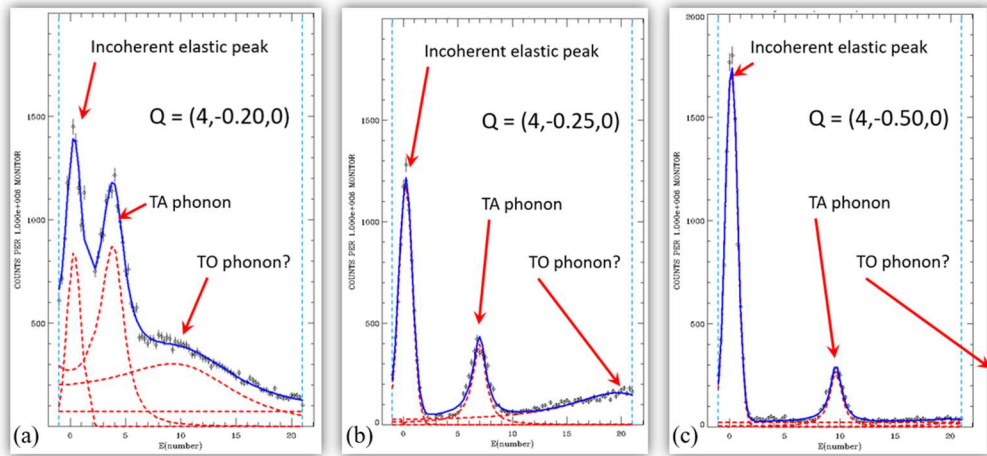


Fig.21. Inelastic neutron diffraction data for CoFe_2O_4 single crystals taken along $Q=(4,k,0)$ for $k=0.00$ to $k=-0.50$ and from $\hbar\omega = -1$ meV to 21 meV at room temperature. (a) $k=-0.20$, (b) $k=-0.25$, and (c) $k=-0.50$. The data were taken using the triple-axis spectrometer on BT4 at the National Institute of Standards and Technology (in Collaboration with Peter Gehring).

Here are a few initial and potentially interesting observations:

- For small values of k , i.e. for long wavelength TA modes, there seems to be a substantial amount of damping, i.e. the TA modes become increasingly broad in energy as $k \rightarrow 0$, which implies a shortened lifetime. This occurs for $k < 0.20$ rlu. For larger values of k , the TA modes were sharp and well-defined. These data indicate a dampening (dispersion) of the spin wave.
- There is evidence of an extremely broad transverse optic (TO) mode at higher energies in both the (400) and (220) Brillouin zones that disperses unusually rapidly to energies above 20 meV at large k . This is most likely an optic mode, but it is unusually broad and dispersive. Furthermore, this broad transverse TA mode couples to the TA or spin wave mode at smaller k . This coupling may represent the dynamics of the magnetostriction interaction.
- The elastic ($\hbar\omega=0$) incoherent scattering in the (400) Brillouin zones increases as $k \rightarrow 0.50$. This does not happen in the (220) Brillouin zone. These data indicate that there is diffuse scattering that is strongly peaked near $(4,0.5,0)$. The strong diffuse scattering along this zone is consistent with the previous report of magnetic nano-domain structures within CoFe_2O_4 .

Our preliminary data indicate that structural heterogeneity may play an important role in the dynamics of the spin and acoustic modes. Structural heterogeneity may manifest itself in a nano-twin structure, as previously reported. Similar types of effects are known in PMN-PT single crystals, where polar nano-twins control the dynamics of the acoustic phonon modes. The structural heterogeneity may provide key and important aspects by which to control and tune the

dynamics of the spin modes in magnetostrictive materials to achieve high Q factors. This maybe key for finding and developing new generations of magnetostrictive materials with enhanced magnetostriction and Q factors.

Furthermore, going forward, the findings have important ramifications to the deposition of ferrites on piezoelectric PMN-PT substrates. This is because investigations have shown that the domain structure of magnetostrictive layers grown on piezoelectric substrates have a domain pattern transfer. Thus, domain engineered PMN-PT crystal substrates can be used to template domain engineering in ferrite crystal layers. This should provide important approaches to achieving advancements in integrated multifunctionality for reconfigurable electronics.

V. Giant Energy Densities in Epitaxial engineered PLZT Layers

Overview: Thin films of 300-nm-thick $(\text{Pb}_{0.98}, \text{La}_{0.02})(\text{Zr}_{0.95}, \text{Ti}_{0.05})\text{O}_3$ (PLZT) were epitaxially deposited on (100), (110), and (111) SrTiO_3 single crystal substrates by pulsed laser deposition. X-ray diffraction line and reciprocal space mapping scans were used to determine the crystal structure. Tetragonal ((001) PLZT) and monoclinic M_A ((011) and (111) PLZT) structures were found, which influenced the stored energy density. Electric field induced antiferroelectric to ferroelectric (AFE $\rightarrow$ FE) phase transitions were found to have a giant reversible energy density of up to $30\text{J}/\text{cm}^3$. Such large energy density changes at induced phase transformations in thin films open up important opportunities in integrated multifunctional magnetoelectric nanocomposites.

Background: Many studies have focused on the electric field (E-field) induced antiferroelectric to ferroelectric (AFE $\rightarrow$ FE) phase transition. It generally exhibits unique double hysteresis loops that can increase the energy storage density and efficiency for applications in high charge energy storage devices and micro-actuators. Lead zirconate titanate (PZT) is a well-investigated ABO_3 perovskite system, whose B-site cation ratio ($\text{Zr}^{4+}/\text{Ti}^{4+}$) can significantly alter the ferroelectric properties from AFE to FE stability. The ratio of $\text{Zr}^{4+}/\text{Ti}^{4+} = 95/5$ has attracted attention as it is close to the phase boundary between AFE and FE states. La^{3+} doping onto the Pb^{2+} site is an effective way to stabilize the AFE orthorhombic (O) phase of PZT to higher titanium contents, over a FE rhombohedral (R) phase. Ten millimeter thick $(\text{Pb}_{0.88}, \text{La}_{0.08})(\text{Zr}_{0.91}, \text{Ti}_{0.09})\text{O}_3$ (PLZT, 8/91/9) ceramics have been reported to have a recoverable energy storage density of $3\text{J}/\text{cm}^3$ at an E-field of $180\text{kV}/\text{cm}$.

The induced AFE $\rightarrow$ FE phase transition in PLZT ceramics exhibits a large volume change when the applied E-field exceeds a critical value of E_{FE} . Externally imposed stress/strain can thus offer an additional approach by which to modify the AFE $\rightarrow$ FE transition and transformational pathway. Accordingly, the lattice mismatch of PZT-based films deposited on substrates may impose significant epitaxial strains on the films, changing the AFE $\rightarrow$ FE transition process. Most prior studies of epitaxial PZT (or PLZT) films have focused on compositions near the morphotropic phase boundary (MPB) between ferroelectric R and T phases ($\text{Zr}^{4+}/\text{Ti}^{4+}=1$) for actuator/sensor applications, or on the Ti-rich range (35/65, 20/80) for FE memories. Little is known about the structure and properties of AFE PLZT epitaxial films. Most prior studies focused on polycrystalline AFE PZT films. From the perspective of energy storage capacitor applications, polycrystalline films normally have large numbers of defects and/or grain boundaries that can reduce the dielectric breakdown strength, and thus decrease the recoverable energy density. Whereas epitaxial films with lower concentrations of defects and higher mobility of domain walls can be expected to exhibit improved energy storage capability and thermostability.

It is known that La-doping of the PZT system weakens the FE interaction and disrupts the long-range polar order, decomposing the conventional FE domain state into a polar nano-domain one. Such relaxor ferroelectrics (RFEs) have been shown to have slim and slanted P-E hysteresis loops. Low hysteresis and high saturation polarizations offer these relaxors as promising candidates for energy storage capacitor materials.

Here, epitaxial PLZT (2/95/5) films were deposited on different oriented SrTiO₃ (STO) substrates by pulsed laser deposition (PLD). The crystal structure, phase transition characteristics and transformational pathways, and energy storage performance from room temperature to 250°C were studied. Our results demonstrate the giant energy densities of $>30\text{J}/\text{cm}^3$ can be achieved by domain engineering in epitaxial thin layers that undergo an induced $\text{AFE} \rightarrow \text{FE}$ transition – which is an order of magnitude higher than that previously reported.

Details: Films of PLZT (2/95/5) were deposited on (100), (110), and (111) STO single-crystal substrates by PLD. An excimer laser LPX305i (Lambda Physik) with KrF radiation was used. The PLZT film thickness was set at 300nm, which was confirmed by cross-sectional scanning electron microscopy (SEM, LEO 1550, Zeiss). The crystal structure was determined using a Philips X'pert high resolution X-ray diffractometer (XRD) equipped with a two bounce hybrid monochromator, and an open three-circle Eulerian cradle (resolution: 0.0002°). To obtain more structural details of the variously oriented films, reciprocal space maps (RSM) were measured along the (002), (022), and (222) zone axes. The surface topologies were determined by a Veeco SPI 3100 atomic force microscope (AFM). A homemade Sawyer-Tower system was used to measure the polarization-electric field (P-E) hysteresis loops. The crystal structure, phase transition characteristics and pathways, and energy storage performance of the antiferroelectric (2/95/5) PLZT films were then studied from room temperature to 250°C, enabling a comprehensive understanding of films. In the following section of the text, we designate PLZT to refer to the composition 2/95/5.

Figure 22 is the RSM mesh scans of differently oriented PLZT films. For (001) PLZT, doublet peaks along both the (200) and (220) zone axes were found, indicating a T structure with 90° twin domains, where the c-domain population was dominate over the a-one. For (011) and (111) PLZT films, a doublet splitting along the (200) zone axis and a triplet along the (220) zone axis were found. These are signatures of a monoclinic A (M_A) crystal structure. The origin of these crystal structure differences is the IP strain state, which was homogenous for the (001) PLZT film but imhomogenous for the (011) and (111) PLZT ones. These result clearly demonstrate that domain engineering has a significant effect on the phase transformational characteristics, and thus the properties of epitaxial thin layers.

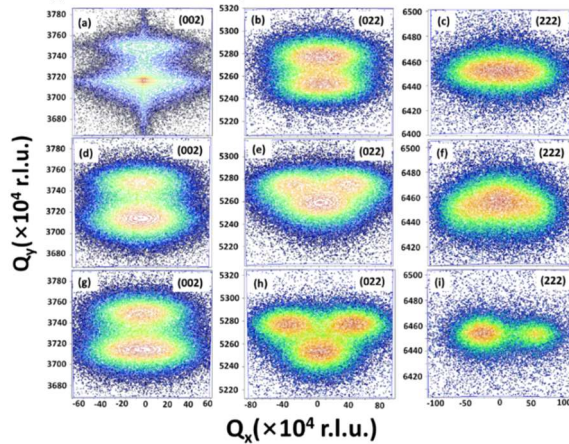


Figure 22. RSM images of (a)-(c) (001) PLZT film, (d)-(f) (011) PLZT film, and (g)-(i) (111) PLZT film. (a), (d), (g) were taken along the (002) zone axis; (b), (e), (h) along the (022) zone axis; and (c), (f), (i) along the (222) zone axis.

We next studied the polarization changes at the induced phase transformation. Figures 23 (a)-(c) show room temperature bipolar P-E loops for the PLZT films on the different STO substrates. Figures 23 (d)-(f) give the calculated energy storage density (ESD) and energy storage efficiency (ESE) as a function of E. Under low E-fields, all three samples exhibited typical AFE loops with a small remanent polarization, low P-E loop areas (i.e. low loss or high Q), and hence a relatively high ESE. As the maximum E was increased, a critical field E_{FE} was reached, where the AFE→FE phase transition was induced. Due to the FE order tending to be retained on removal of the E-field after the AFE→FE transition has been induced, the ESE values were reduced at the high E-field range. Giant reversible energy densities of $>30\text{J/cm}^3$ were found at efficiencies of about 50%. Critical going forward was the determination of how to further increase the energy storage efficiency.

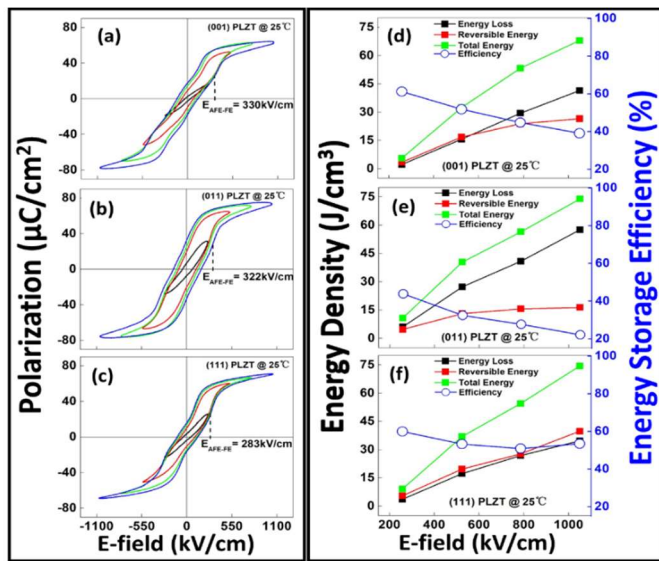


Figure 23. P-E loops of (a) (001) PLZT, (b) (011) PLZT, and (c) (111) PLZT at room temperature with increasing E-fields. Parts (d)-(f) show the corresponding energy densities and ESE values calculated from (a)-(c).

As shown in Figure 24, when the temperature was increased, the P-E curves of the samples gradually evolved into slim loops. This is indicative of a relaxor ferroelectric (RFE) state, characterized by polar nanodomains assembling via domain engineering. The calculated ESD and ESE were then mapped into contour plots as functions of both temperature and E, as shown in Figure 25. This figure summarizes the optimum working temperature ranges for the differently oriented PLZT films, where each film offers its highest ESD and ESE values: 70~200°C for (001) PLZT ($25\sim35\text{J/cm}^3$, 50~70%), 150~200°C for (011) PLZT ($12\sim18\text{J/cm}^3$, 30~50%), and both 25°C to 70°C and 200~250°C for (111) PLZT ($20\sim40\text{J/cm}^3$, 30~55%).

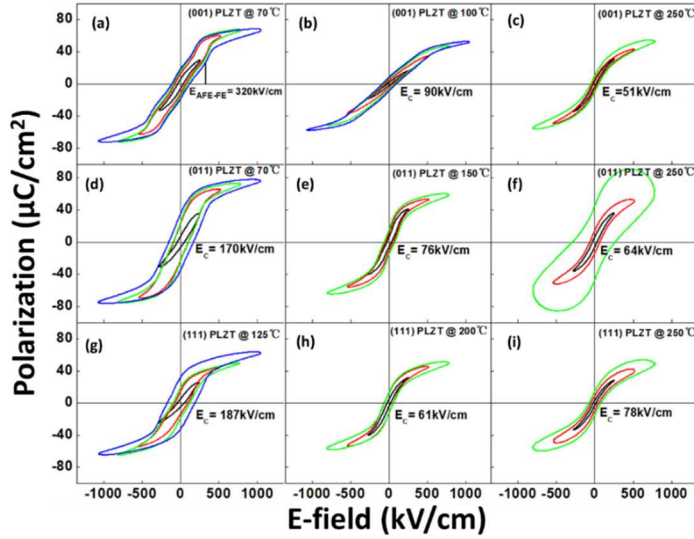


Figure 24. *P-E loops of (a)-(c) (001) PLZT, (d)-(f) (011) PLZT, and (g)-(i) (111) PLZT measured at various temperatures that reveal different ferroelectric phase stabilities: (a) AFE; (d), (g) FE, and others are RFE. The wider loops in (f) and (i) were caused by leakage currents.*

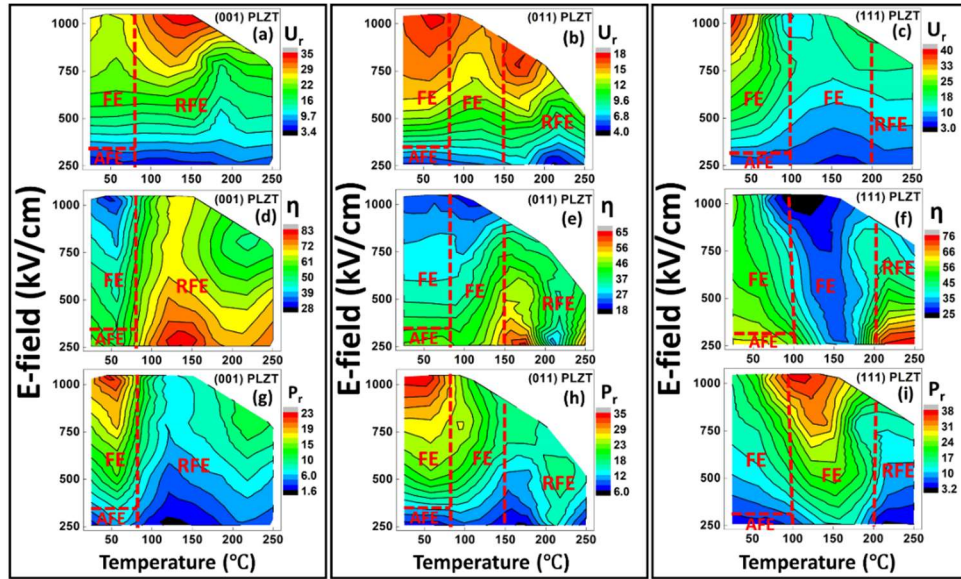


Figure 25. *(a)-(c) ESD (J/cm^3), (d)-(f) ESE (%), and (g)-(i) remanent polarization ($\mu\text{C}/\text{cm}^2$) of oriented PLZT films as functions of both E and temperature. (a), (d), (g) (001) PLZT; (b), (e), (h) (011) PLZT; and (c), (f), (i) (111) PLZT. Different phase regions are marked by red dash lines in each figure.*

Temperature variable XRD data were then taken to determine the crystal structure and lattice parameter changes. XRD line scans (see Figures 26 (a)-(b)) show that the left side of the PLZT peaks did not change much with increasing temperature. Rather, the right side of the peaks continuously shifted to smaller 2θ values with increasing temperature, and finally merged with the left peaks near 250°C . Temperature variable XRD data were then taken to determine the crystal structure and lattice parameter changes. XRD line scans (see Figures 26 (a)-(b)) show that the left side of the PLZT peaks did not change much with increasing temperature. Rather, the right side of the peaks continuously shifted to smaller 2θ values with increasing temperature, and finally merged with the left peaks near 250°C . The RSM scans demonstrated that the crystal structure did not change for any of these films over the temperature range investigated (see Figures 26 (c)-(f)).

The temperature dependence of the lattice parameters for both PLZT and STO are shown in Figures 26 (g)-(i). The lattice parameter of STO was linearly extended with increasing temperature due to thermal expansion. This may partially relax the lattice mismatch between itself and the films, reducing the IP strain of the PLZT layers. No evidence of sudden changes in the c/a ratio of the PLZT films was observed until above 200°C. On the contrary, the value of c/a gradually approached one as the temperature was increased towards 250°C. Temperature variable XRD results indicate that the changes in P-E characteristics with temperature discussed above can be attributed to the reduction of the tetragonality or monoclinicity, which are more likely strain-induced transitions rather than symmetry-related ones.

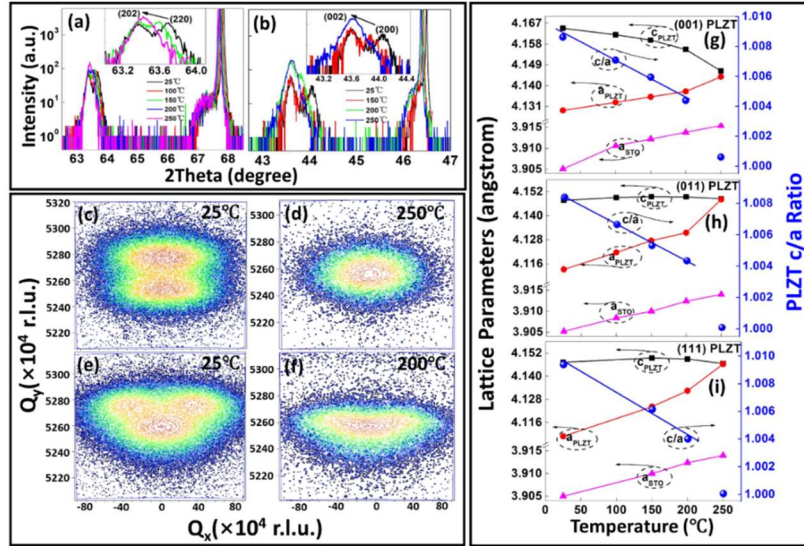


Figure 26. Temperature dependent XRD line scans of (a) PLZT/SRO on (001) STO, and (b) PLZT/SRO on (111) STO. Parts (c)-(f) RSM images of (c), (d) (001) PLZT; and (e), (f) (011) PLZT. The zone axis is along the (022) in (a), (c)-(f); and along the (002) in (b). (g)-(i) Calculated lattice parameters of STO substrate (a_{STO}) and PLZT film (a_{PLZT} , c_{PLZT}), as well as the c/a ratio of PLZT, as a function of temperature. The orientations of the substrate in (g), (h), and (i) are (100), (110), and (111), respectively. The c/a ration of PLZT was linearly fitted to temperature in the range from 25°C to 200°C.

Unipolar drive and increased efficiency: The PLZT films contained a mixed AFE/FE phase stability, after bipolar drive, as evidence by the large values of P_r for $E=0$. Thus, on reversal of applied E-field polarity, the polarization rotation in the FE regions may consume more energy. This, in turn, diminishes the ESE. In domain-engineered piezoelectric crystals, unipolar drive has been shown as an effective way to decrease hysteretic losses and energy consumption. Furthermore, under unipolar drive, since the polarity of E does not switch, defects such as oxygen vacancies will not continuously migrate, favoring to improve fatigue limits for high-frequency charging/discharging cycles, and accordingly reducing the leakage current's reduction of the ESE value.

As shown in Figures 27(a)-(c), under unipolar drive, the remanent polarization was noticeably smaller than those under bipolar drive. At the same time, the ESD values (see Figures 27 (d)-(f)) were considerably more stable than the bipolar ones over the entire temperature range studied. The maximum ESD values were about 19J/cm³, 15J/cm³, and 17J/cm³ for (001) PLZT, (011) PLZT, and (111) PLZT, respectively. These are comparable to the bipolar results, when considering the fact that the unipolar cycle was half of the bipolar one. Due to the lower remanent polarization values in the unipolar cases, the ESE values in Figures 27 (g)-(i) were significantly higher than the

bipolar ones, in particular for the (011) film. The efficiency at the maximum ESD value reached 77%, 60%, and 70% for (001), (011), and (111) PLZT, respectively. All three samples exhibited a gradual AFE/FE-RFE transformation with increasing temperature.

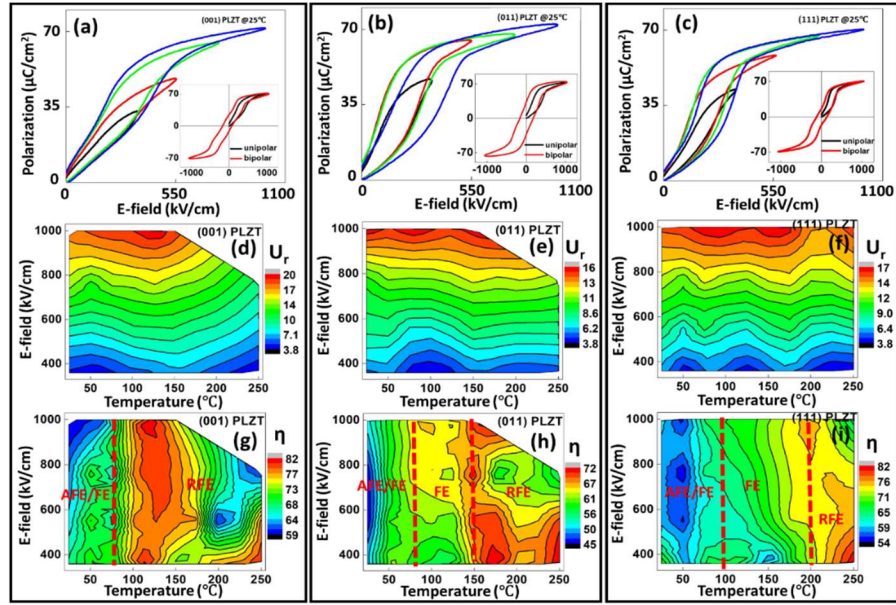


Figure 27. Unipolar P-E loops of (a) (001) PLZT, (b) (011) PLZT, and (c) (111) PLZT. The insets exhibit a comparison between unipolar and bipolar loops. (d)-(f) and (g)-(i) are the corresponding ESD (J/cm^3), and ESE (%), respectively. The red dash lines in (g)-(i) divides different phase regions based on the bipolar result characteristics.

With respect to applications, *fatigue limit tests of these PLZT films revealed that the energy storage performance characteristics could be maintained after 10^8 charging/discharging cycles* under a maximum field of 765kV/cm and at room temperature, as shown in Figure 28. This is different from induced AFE→FE transitions in bulk, where large c/a ratio changes result in rapid deterioration of the samples' mechanical intensities with cycles. Clearly, unipolar drive may be a promising way to enhance the energy storage capability of AFE thin film materials.

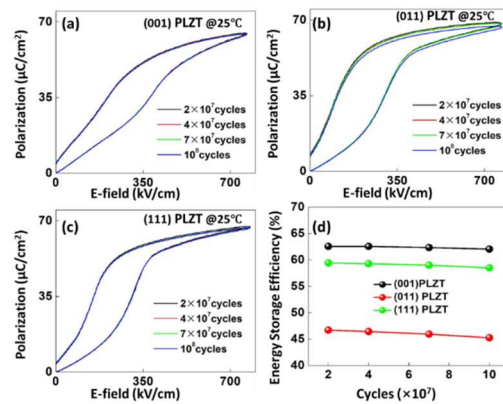


Figure 28. Unipolar P-E loops of (a) (001) PLZT, (b) (011) PLZT, and (c) (111) PLZT at room temperature with increasing numbers of charge/discharge cycles. (d) is the calculated energy storage efficiency as a function of the running cycles.

Summary: Thin films of PLZT (2/95/5) were epitaxially deposited on (100), (110), and (111) STO substrates. An orientation effect imparted to the PLZT films, via diverse values of the IP strains, resulted in either T phase stability for PLZT on (100) STO or M_A phase for PLZT on (110) and (111) STO. The interrelationship amongst crystal structure, dielectric phase transitions, and energy storage performance was studied over the temperature range from 25 to 250°C. The (001) PLZT films exhibited an $AFE_T/FE_T \rightarrow RFE_T$ transition under E, where the bipolar drive resulted in an ESD of $\geq 35 \text{ J/cm}^3$ and an ESE of $\geq 70\%$. The (011) and (111) PLZT films exhibited an $AFE_{MA}/FE_{MA} \rightarrow FE_{MA} \rightarrow RFE_{MA}$ transition, where their ESD (ESE) values reached $\leq 18 \text{ J/cm}^3$ (50%) and $\leq 40 \text{ J/cm}^3$ (55%), respectively. *Investigations under unipolar drive were also performed, revealing notably higher ESE values due to low energy losses.*

Such large energy density changes at induced phase transformations in thin films open up important opportunities in integrated multifunctional magnetoelectric epitaxial films and nanocomposites. Large induced strains and energy densities will result in significantly increased ME coefficients and power transfer capabilities with tunable characteristics, which is one of the important goals that we are working towards

VI. Progress.

Articles:

Primary support

1. X. Tang, M. Gao, Jiefang Li, and D. Viehland, “Self-assembled epitaxial $\text{BiFeO}_3\text{-Ni}_{0.65}\text{Al}_{0.8}\text{Fe}_{1.2}\text{O}_4$ nano-belt heterostructures on SrTiO_3 : Control of magnetic anisotropy, easy axis, and coercivity”, Journal of Applied Physics, Volume: 126, Issue: 12, Article Number: 123905 (Sept 2019).
2. X. Tang, C.M. Leung, M. Gao, Jiefang Li, and D. Viehland, “Nanostructure-enhanced magnetoelectric/magnetostreictive properties and reduced losses in self-assembled epitaxial $\text{CuFe}_2\text{O}_4\text{-BiFeO}_3$ layers on $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-33at\%PbTiO}_3$ crystals”, Journal of the American Ceramic Society, Volume: 102, Issue: 9, Pages: 5192-5202 (Sept. 2019).
3. X. Tang, M. Gao, C.M. Leung, Jiefang Li, and D. Viehland, “Non-volatility using materials with only volatile properties: Vertically integrated magnetoelectric heterostructures and their potential for multi-level-cell devices”, Applied Physics Letters, Volume: 114, Issue: 24, Article Number: 242903 (June 2019).
4. Tang X, Viswan R, Gao M, et al. Nanopillars with E-field accessible multi-state ($N \geq 4$) magnetization having giant magnetization changes in self-assembled $\text{BiFeO}_3\text{-CoFe}_2\text{O}_4/\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-38at\%PbTiO}_3$ heterostructures[J]. Scientific reports, 2018, 8(1): 1628.
5. X. Tang, YT. Gao, z. Xiao, X. Bai, M. Gao, H. Luo, Jiefang Li, and D. Viehland, “Mixed nanopillar/nanobelt morphology in $\text{BiFeO}_3\text{-CuFe}_2\text{O}_4$ self-assembled epitaxial layers on PMN-PT substrates” simulations by phase field modelling and density functional theory” (in preparation).

Partial support

1. M. Gao, X. Tang, C.M. Leung, J.F. Li, and D. Viehland, "Phase transition and energy storage behavior of antiferroelectric PLZT thin films epitaxially deposited on SRO buffered STO single crystal substrates", Journal of the American Ceramic Society, Volume: 102, Issue: 9, Pages: 5180-5191 (Sept. 2019).
[Work was part of Min Gao's PhD thesis, whom was supported by a DOE grant. It was primarily his work. However, Xiao Tang gave supplementary support in some TEM measurements, and he was supported by AFOSR].
2. M. Gao, X. Tang, S. Dai, J.F. Li, and D. Viehland, "Depth dependent ferroelectric to incommensurate/commensurate antiferroelectric phase transition in epitaxial lanthanum modified lead zirconate titanate thin films", Applied Physics Letters, Vol: 115, Issue: 7, Article Number: 072901 (August 2019).
[Work was part of Min Gao's PhD thesis, whom was supported by a DOE grant. It was primarily his work. However, Xiao Tang gave supplementary support in some TEM measurements, and he was supported by AFOSR].
3. M. Gao, R. Viswan, X. Tang, C. Leung, J.F. Li, and D. Viehland, "Magnetoelectricity of CoFe₂O₄ and tetragonal phase BiFeO₃ nanocomposites prepared by pulsed laser deposition", SCIENTIFIC REPORTS Volume: 8, Article Number: 323, DOI: 10.1038/s41598-017-18788-8, Published: JAN 10 2018.
[Work was part of Min Gao's PhD thesis, whom was supported by a DOE grant. It was primarily his work. However, Xiao Tang gave supplementary support in some TEM measurements, and he was supported by AFOSR].
4. M. Gao, R. Viswan, X. Tang, C. Leung, J.F. Li, and D. Viehland, "E-field controlled phase transformation in bismuth ferrite thin films, and effect of laser energy density", APPLIED PHYSICS LETTERS **Volume:** 111, **Issue:** 15, **Article Number:** 152905, **DOI:** 10.1063/1.4997017 (Oct. 2017).
[Work was part of Min Gao's PhD thesis, whom was supported by a DOE grant. It was primarily his work. However, Xiao Tang gave supplementary support in some TEM measurements, and he was supported by AFOSR].
5. D. Viehland, Jiefang Li, and Yaodong Yang, "Tutorial: Product properties in multiferroic nanocomposites", Journal of applied Physics, Volume: 124, Issue: 6, Article Number: 061101 (August 2018).
[This was a Tutorial paper that concerned many years of work on multiferroic materials. Part of this effort was supported by AFOSR].

Conferences:

1. MS&T 2017, Pittsburgh, PA, 10/09/2017. Presentation entitled: 'E-field Induced Giant Dynamic Magnetization Change in Self-assembled'.
2. MS&T 2018, Columbus, OH, 10/15/2018. Presentation entitled: 'Novel two phase self-assembled nanopillar heterostructures with E-field induced magnetization manipulation'.
3. EMA 2018, Orlando Florida, 1/20/2018. Presentation entitled: "Vertically Integrated Nanostructures with E-field Accessible Multi-state (≥ 4) Magnetization in BFO-CFO/PMN-PT Heterostructures".
4. CIMTEC 2018, Perugia, Italy, 6/5/2018. Presentation entitled: "Magnetoelectric Nanocomposites for Tunable Electronics".
5. MS&T 2018, Columbus, OH, 10/15/2018. Presentation entitled: 'Novel two phase self-assembled nanopillar heterostructures with E-field induced magnetization manipulation'.

Current and Pending (D. Viehland, as of June 2019)

Investigator: Dwight Viehland	Other Agencies to which this proposal has been/will be submitted:
Support (<u>C</u> urrent, <u>P</u> ending, <u>S</u> ubmission Planned in Future or <u>T</u> ransfer of Support): Current	
Project/Proposal Title and grant number, if appropriate: Magnetic Sensors for Detection Award number: N00014-15-1-2457 (with Jiefang Li, VT)	
Source of Support: Office of Naval Research	Location of Project: Virginia Tech
Award Amount: \$326353 Total Award Period Covered: 7/1/2015-9/30/2019	
Award Amount to PI's Research: \$326353	
Person-Months Per Year Committed to Project: <u>0.15</u> Pers. Months; Specify: <u>Cal.</u> , <u>Acad.</u> , or <u>Sumr</u> : Sumr	
Describe Research Including Synergies and Delineation with Respect to this Proposal/Award: Development of magnetic sensors based on magnetoelectric composites that have the ability to reject acoustical/mechanical vibration noise sources. No overlap with present proposal.	

Investigator: Dwight Viehland	Other Agencies to which this proposal has been/will be submitted:
Support (<u>C</u> urrent, <u>P</u> ending, <u>S</u> ubmission Planned in Future or <u>T</u> ransfer of Support): Current	
Project/Proposal Title and grant number, if appropriate: Reconfigurable Electronics based on Multi-Ferroids and Nano-magnetism (with Jiefang Li, VT) Award number: FA9550-16-1-0001	
Source of Support: AFOSR	Location of Project: Virginia Tech
Award Amount: \$434085 Total Award Period Covered: 11/30/2015-10/31-2019	
Award Amount to PI's Research: \$434085	
Person-Months Per Year Committed to Project: <u>0.3</u> Pers. Months; Specify: <u>Cal.</u> , <u>Acad.</u> , or <u>Sumr</u> : Sumr	
Describe Research Including Synergies and Delineation with Respect to this Proposal/Award: Investigation of vertically integrated magnetoelectric nanostructures epitaxially deposited on substrates, and testing of their tunable properties under DC electrical and magnetic biases for applications in next generation electronics. There are some synergies with a DOE program. This synergy concerns property and TEM measurements. It is distinct from this AFOSR program, as it focused on a wide variety of nanostructures for tunable properties, whereas the DOE project focused on E-field control of BiFeO ₃ . They were also clearly delineated in student thesis, as the AFOSR grant supported Xiao Tang and the DOE grant supported Min Gao.	

Investigator: Dwight Viehland	Other Agencies to which this proposal has been/will be submitted:
Support (<u>C</u> urrent, <u>P</u> ending, <u>S</u> ubmission Planned in Future or <u>T</u> ransfer of Support): Current	
Project/Proposal Title and grant number, if appropriate: Nano-Domain and Defect Engineering of Binary and Ternary-modified PMN-PT Textured Ceramics and Crystals (with Jiefang Li, VT) Award number: N00014-17-1-2234	
Source of Support: Office of Naval Research Virginia Tech	Location of Project:
Award Amount: \$382573 Total Award Period Covered: 3/1/2017- 2/28/2020	
Award Amount to PI's Research: \$382573	
Person-Months Per Year Committed to Project: ____ Pers. Months; Specify: <u>C</u> al., <u>A</u> cad., or <u>S</u> umr:	
Describe Research Including Synergies and Delineation with Respect to this Proposal/Award: Investigations of nanodomain engineering in single crystals and textured piezoelectric ceramics. Determination of how the phase transformation sequence and domain conditions are effected by such compositional modifications. No overlap with present proposal.	

Investigator: Dwight Viehland	Other Agencies to which this proposal has been/will be submitted:
Support (<u>C</u> urrent, <u>P</u> ending, <u>S</u> ubmission Planned in Future or <u>T</u> ransfer of Support): Current	
Project/Proposal Title and grant number, if appropriate: Mesoscale interfacial dynamics in magnetoelectric nanocomposites (with Jiefang Li, VT) Award number: DE-FG02-06ER46290	
Source of Support: DOE	Location of Project: Virginia Tech
Award Amount: \$1866262 Total Award Period Covered: 8/1/2006-7/31/2018	
Award Amount to PI's Research: \$1866262	
Person-Months Per Year Committed to Project: <u>0.3</u> Pers. Months; Specify: <u>C</u> al., <u>A</u> cad., or <u>S</u> umr: Sumr	
Describe Research Including Synergies and Delineation with Respect to this Proposal/Award: Deposition and investigation of phase transitions in epitaxially deposited BiFeO ₃ on PMN-PT substrates. Engineering of magnetic phase transitions through strain engineering. This is the program for which the report was written. There were some synergies with the AFOSR program listed and detailed above. It is distinct from this AFOSR program, as the AFOSR program focused on a wide variety of nanostructures for tunable properties, whereas the DOE project focused on E-field control of BiFeO ₃ . They were also clearly delineated in student thesis, as the AFOSR grant supported Xiao Tang and the DOE grant supported Min Gao.	

Investigator: Dwight Viehland	Other Agencies to which this proposal has been/will be submitted:
Support (<u>C</u> urrent, <u>P</u> ending, <u>S</u> ubmission Planned in Future or <u>T</u> ransfer of Support): Current	
Project/Proposal Title and grant number, if appropriate: A MATRIX Solution to Solid State Devices for Scalable, Integratable, and Efficient Signal and Power (with Jiefang Li, VT) Award number: W911NF-15-1-0616	
Source of Support: Army Research Office Virginia Tech	Location of Project:
Award Amount: \$1499980 Total Award Period Covered: 10/1/2015-6/30/2019	
Award Amount to PI's Research: \$902887	
Person-Months Per Year Committed to Project: <u> 1 </u> Pers. Months; Specify: <u> Cal. </u> , <u> Acad. </u> , or <u> Sumr </u> : Sumr	
Describe Research Including Synergies and Delineation with Respect to this Proposal/Award: Development and studies of gyrators based on magnetoelectric heterostructures. Gyrators have a unique ability to convert current into voltage, and offer important features with regards to electrical and magnetic property inversion. No overlap with present proposal.	

Investigator: Dwight Viehland	Other Agencies to which this proposal has been/will be submitted:
Support (<u>C</u> urrent, <u>P</u> ending, <u>S</u> ubmission Planned in Future or <u>T</u> ransfer of Support): Current	
Project/Proposal Title and grant number, if appropriate: Material Solution for Electron Transpiration Cooling of Leading Edges: E.T-cooling (with Jiefang Li)	
Source of Support: Defense Advanced Research Projects Agency Location of Project: Virginia Tech	
Award Amount: \$1,815,000 Total Award Period Covered: 12/09/19-12/08/23	
Award Amount to PI's Research: \$1,815,000	
Person-Months Per Year Committed to Project: <u> 0.15 </u> Pers. Months; Specify: <u> Cal. </u> , <u> Acad. </u> , or <u> Sumr </u> : 0.15 Sumr	

Current and Pending (Jiefang Li, as of June 2019)

Investigator: Jiefang Li	Other Agencies to which this proposal has been/will be submitted:
Support (<u>C</u> urrent, <u>P</u> ending, <u>S</u> ubmission Planned in Future or <u>T</u> ransfer of Support): Current	
Project/Proposal Title and grant number, if appropriate: Magnetic Sensors for Detection Award number: N00014-15-1-2457 (with D. Viehland, VT)	
Source of Support: Office of Naval Research	Location of Project: Virginia Tech
Award Amount: \$326353 Total Award Period Covered: 7/1/2015-9/30/2019	
Award Amount to PI's Research: \$326353	
Person-Months Per Year Committed to Project: <u>1</u> Pers. Months; Specify: <u>C</u> al., <u>A</u> cad., or <u>S</u> umr: Sumr	
Describe Research Including Synergies and Delineation with Respect to this Proposal/Award: Development of magnetic sensors based on magnetoelectric composites that have the ability to reject acoustical/mechanical vibration noise sources. No overlap with present proposal.	

Investigator: Jiefang Li	Other Agencies to which this proposal has been/will be submitted:
Support (<u>C</u> urrent, <u>P</u> ending, <u>S</u> ubmission Planned in Future or <u>T</u> ransfer of Support): Current	
Project/Proposal Title and grant number, if appropriate: Reconfigurable Electronics based on Multi-Ferrioxs and Nano-magnetism (with D. Viehland) Award number: FA9550-16-1-0001	
Source of Support: AFOSR	Location of Project: Virginia Tech
Award Amount: \$434085 Total Award Period Covered: 11/30/2015-10/31-2019	
Award Amount to PI's Research: \$434085	
Person-Months Per Year Committed to Project: <u>1</u> Pers. Months; Specify: <u>C</u> al., <u>A</u> cad., or <u>S</u> umr: Sumr	
Describe Research Including Synergies and Delineation with Respect to this Proposal/Award: Investigation of vertically integrated magnetoelectric nanostructures epitaxially deposited on substrates, and testing of their tunable properties under DC electrical and magnetic biases for applications in next generation electronics. No overlap with present proposal. Does have some synergy with respect to property measurements.	

Investigator: Jiefang Li	Other Agencies to which this proposal has been/will be submitted:
Support (<u>C</u> urrent, <u>P</u> ending, <u>S</u> ubmission Planned in Future or <u>T</u> ransfer of Support): <u>Current</u>	
Project/Proposal Title and grant number, if appropriate: Nano-Domain and Defect Engineering of Binary and Ternary-modified PMN-PT Textured Ceramics and Crystals (with D. Viehland) Award number: N00014-17-1-2234	
Source of Support: Office of Naval Research Virginia Tech	Location of Project:
Award Amount: \$382573 Total Award Period Covered: 3/1/2017- 2/28/2020	
Award Amount to PI's Research: \$382573	
Person-Months Per Year Committed to Project: <u>1</u> Pers. Months; Specify: <u>Cal.</u> , <u>Acad.</u> , or <u>Sumr</u> :	
Describe Research Including Synergies and Delineation with Respect to this Proposal/Award: Investigations of nanodomain engineering in single crystals and textured piezoelectric ceramics. Determination of how the phase transformation sequence and domain conditions are effected by such compositional modifications. No overlap with present proposal.	

Investigator: Jiefang Li	Other Agencies to which this proposal has been/will be submitted:
Support (<u>C</u> urrent, <u>P</u> ending, <u>S</u> ubmission Planned in Future or <u>T</u> ransfer of Support): <u>Current</u>	
Project/Proposal Title and grant number, if appropriate: A MATRIX Solution to Solid State Devices for Scalable, Integratable, and Efficient Signal and Power (with D. Viehland) Award number: W911NF-15-1-0616	
Source of Support: Army Research Office Virginia Tech	Location of Project:
Award Amount: \$1499980 Total Award Period Covered: 10/1/2015-6/30/2019	
Award Amount to PI's Research: \$902887	
Person-Months Per Year Committed to Project: <u>1</u> Pers. Months; Specify: <u>Cal.</u> , <u>Acad.</u> , or <u>Sumr</u> : <u>Sumr</u>	
Describe Research Including Synergies and Delineation with Respect to this Proposal/Award: Development and studies of gyrators based on magnetoelectric heterostructures. Gyrators have a unique ability to convert current into voltage, and offer important features with regards to electrical and magnetic property inversion. No overlap with present proposal.	

Investigator: Jiefang Li	Other Agencies to which this proposal has been/will be submitted:
Support (<u>C</u> urrent, <u>P</u> ending, <u>S</u> ubmission Planned in Future or <u>T</u> ransfer of Support): Current	
Project/Proposal Title and grant number, if appropriate: Material Solution for Electron Transpiration Cooling of Leading Edges: E.T.-cooling (with D. Viehland)	
Source of Support: Defense Advanced Research Projects Agency Location of Project: Virginia Tech	
Award Amount: \$1,815,000 Total Award Period Covered: 19/01/19-12/08/23	
Award Amount to PI's Research: \$1,024,071	
Person-Months Per Year Committed to Project: <u>6</u> Pers. Months; Specify: <u>Cal.</u> , <u>Acad.</u> , or <u>Sumr</u> : Sumr	

Cost status:

All Funds expended

References

1. Wang, Z. *et al.* Engineered Magnetic Shape Anisotropy in BiFeO₃-CoFe₂O₄ Self-Assembled Thin Films. *Acs Nano* **7**, 3447-3456 (2013).
2. Brivio, S., Petti, D., Bertacco, R. & Cezar, J. C. Electric field control of magnetic anisotropies and magnetic coercivity in Fe/BaTiO₃(001) heterostructures. *Applied Physics Letters* **98**, 092505, doi:Artn 092505 10.1063/1.3554432 (2011).
3. Geprags, S., Brandlmaier, A., Opel, M., Gross, R. & Goennenwein, S. T. B. Electric field controlled manipulation of the magnetization in Ni/BaTiO₃ hybrid structures. *Applied Physics Letters* **96**, 142509, doi:Artn 142509 10.1063/1.3377923 (2010).
4. Venkataiah, G., Shirahata, Y., Itoh, M. & Taniyama, T. Manipulation of magnetic coercivity of Fe film in Fe/BaTiO₃ heterostructure by electric field. *Applied Physics Letters* **99**, 102506, doi:10.1063/1.3628464 (2011).
5. Zhang, W. R. *et al.* Strain relaxation and enhanced perpendicular magnetic anisotropy in BiFeO₃:CoFe₂O₄ vertically aligned nanocomposite thin films. *Applied Physics Letters* **104**, 062402, doi:Artn 062402 10.1063/1.4864405 (2014).
6. Wei, Y. *et al.* Four-state memory based on a giant and non-volatile converse magnetoelectric effect in FeAl/PIN-PMN-PT structure. *Sci Rep* **6**, 30002, doi:10.1038/srep30002 (2016).
7. Gao, M. *et al.* E-field controlled phase transformation in bismuth ferrite thin films, and effect of laser

- energy density. *Applied Physics Letters* **111**, 152905, doi:Artn 152905 10.1063/1.4997017 (2017).
- 8 Tang, X. *et al.* Nanopillars with E-field accessible multi-state ($N \geq 4$) magnetization having giant magnetization changes in self-assembled BiFeO₃-CoFe₂O₄/Pb(Mg_{1/3}Nb_{2/3})-38at%PbTiO₃ heterostructures. *Sci Rep* **8**, 1628, doi:10.1038/s41598-018-19673-8 (2018).
 - 9 Ma, J., Hu, J., Li, Z. & Nan, C. W. Recent progress in multiferroic magnetoelectric composites: from bulk to thin films. *Adv Mater* **23**, 1062-1087, doi:10.1002/adma.201003636 (2011).
 - 10 Zheng, H., Kreisel, J., Chu, Y.-H., Ramesh, R. & Salamanca-Riba, L. Heteroepitaxially enhanced magnetic anisotropy in BaTiO₃-CoFe₂O₄ nanostructures. *Applied Physics Letters* **90**, 113113, doi:10.1063/1.2713131 (2007).
 - 11 Zheng, H. *et al.* Multiferroic BaTiO₃-CoFe₂O₄ Nanostructures. *Science* **303**, 661-663, doi:10.1126/science.1094207 (2004).
 - 12 Rafique, M., Herklotz, A., Dorr, K. & Manzoor, S. Giant room temperature magnetoelectric response in strain controlled nanocomposites. *Applied Physics Letters* **110**, 202902, doi:Artn 202902 10.1063/1.4983357 (2017).
 - 13 Yan, L., Bai, F. M., Li, J. F. & Viehland, D. Nanobelt Structure in Perovskite-Spinel Composite Thin Films. *Journal of the American Ceramic Society* **92**, 17-20, doi:10.1111/j.1551-2916.2008.02825.x (2009).
 - 14 Tang, X. *et al.* Nanostructure-enhanced magnetoelectric/magnetostrictive properties and reduced losses in self-assembled epitaxial CuFe₂O₄-BiFeO₃ layers on Pb(Mg_{1/3}Nb_{2/3})O₃-33at%PbTiO₃ crystals. *Journal of the American Ceramic Society* **0**, 1-11, doi:doi:10.1111/jace.16387 (2019).
 - 15 Emori, S. *et al.* Coexistence of Low Damping and Strong Magnetoelastic Coupling in Epitaxial Spinel Ferrite Thin Films. *Adv Mater* **29**, doi:10.1002/adma.201701130 (2017).
 - 16 Bian, L. X., Wen, Y. M., Li, P., Gao, Q. L. & Zheng, M. Magnetoelectric transducer with high quality factor for wireless power receiving. *Sensors and Actuators a-Physical* **150**, 207-211, doi:10.1016/j.sna.2009.01.003 (2009).
 - 17 Ohnuma, S., Kobayashi, N., Masumoto, T., Mitani, S. & Fujimori, H. Magnetostriction and soft magnetic properties of (Co_{1-x}Fe_x)-Al-O granular films with high electrical resistivity. *Journal of Applied Physics* **85**, 4574-4576, doi:10.1063/1.370412 (1999).
 - 18 George, S. & Sebastian, M. T. Microwave dielectric properties of novel temperature stable high Q Li₂Mg_{1-x}Zn_xTi₃O₈ and Li₂Al_{1-x}CaxTi₃O₈ (A=Mg, Zn) ceramics. *Journal of the European Ceramic Society* **30**, 2585-2592, doi:10.1016/j.jeurceramsoc.2010.05.010 (2010).
 - 19 Tay, K. W. & Wu, W. F. Pure Oxygen Atmosphere Sintering Behavior and Microwave Dielectric Properties of x(Mg_{0.96}Co_{0.04})TiO₃ - (1-x)SrTiO₃ Ceramics. *Iumrs International Conference in Asia 2011* **36**, 462-467, doi:10.1016/j.proeng.2012.03.067 (2012).
 - 20 Li, L. *et al.* Direct Observation of Magnetic Field Induced Ferroelectric Domain Evolution in Self-Assembled Quasi (0-3) BiFeO₃-CoFe₂O₄ Thin Films. *ACS Appl Mater Interfaces* **8**, 442-448, doi:10.1021/acsami.5b09265 (2016).
 - 21 Aimon, N. M., Kim, D. H., Choi, H. K. & Ross, C. A. Deposition of epitaxial BiFeO₃/CoFe₂O₄ nanocomposites on (001) SrTiO₃ by combinatorial pulsed laser deposition. *Applied Physics Letters* **100**, 092901, doi:10.1063/1.3690957 (2012).
 - 22 Beleggia, M., De Graef, M. & Millev, Y. T. The equivalent ellipsoid of a magnetized body. *Journal of Physics D-Applied Physics* **39**, 891-899, doi:10.1088/0022-3727/39/5/001 (2006).
 - 23 Li, Y. *et al.* Magnetoelectric quasi-(0-3) nanocomposite heterostructures. *Nat Commun* **6**, 6680, doi:10.1038/ncomms7680 (2015).

24. Gao, M. *et al.* E-field controlled phase transformation in bismuth ferrite thin films, and effect of laser energy density. *Applied Physics Letters* **111**, 152905, doi:Artn 152905 10.1063/1.4997017 (2017).
25. Khalili Amiri, P. *et al.* Electric-Field-Controlled Magnetoelectric RAM: Progress, Challenges, and Scaling. *IEEE Transactions on Magnetics* **51**, 1-7, doi:10.1109/tmag.2015.2443124 (2015).
26. Wang, W. G., Li, M., Hageman, S. & Chien, C. L. Electric-field-assisted switching in magnetic tunnel junctions. *Nat Mater* **11**, 64-68, doi:10.1038/nmat3171 (2011).
27. Shen, J. *et al.* A multilevel nonvolatile magnetoelectric memory. *Sci Rep* **6**, 34473, doi:10.1038/srep34473 (2016).
28. Yao, Y. P. *et al.* Multi-state resistive switching memory with secure information storage in Au/BiFe_{0.95}Mn_{0.05}O₃/La_{5/8}Ca_{3/8}MnO₃ heterostructure. *Applied Physics Letters* **100**, 193504, doi:Artn 193504 10.1063/1.4714514 (2012).
29. Bibes, M. & Barthelemy, A. Multiferroics: towards a magnetoelectric memory. *Nat Mater* **7**, 425-426, doi:10.1038/nmat2189 (2008).
30. Ma, J., Hu, J., Li, Z. & Nan, C. W. Recent progress in multiferroic magnetoelectric composites: from bulk to thin films. *Adv Mater* **23**, 1062-1087, doi:10.1002/adma.201003636 (2011).
31. MacManus-Driscoll, J. L. *et al.* Strain control and spontaneous phase ordering in vertical nanocomposite heteroepitaxial thin films. *Nat Mater* **7**, 314-320, doi:10.1038/nmat2124 (2008).
32. Yan, L. *et al.* Review of magnetoelectric perovskite–spinel self-assembled nano-composite thin films. *Journal of Materials Science* **44**, 5080-5094, doi:10.1007/s10853-009-3679-1 (2009).
33. Wang, Z. *et al.* Engineered Magnetic Shape Anisotropy in BiFeO₃–CoFe₂O₄ Self-Assembled Thin Films. *Acs Nano* **7**, 3447-3456 (2013).
34. Wang, Z. G. *et al.* Electrical and thermal control of magnetic coercive field in ferromagnetic/ferroelectric heterostructures. *Physical Review B* **89**, 035118, doi:ARTN 035118 10.1103/PhysRevB.89.035118 (2014).
35. Tang, X. *et al.* Nanopillars with E-field accessible multi-state ($N \geq 4$) magnetization having giant magnetization changes in self-assembled BiFeO₃-CoFe₂O₄/Pb(Mg_{1/3}Nb_{2/3})-38at% PbTiO₃ heterostructures. *Scientific reports* **8**, 1628 (2018).
36. Tang, X. *et al.* Nanostructure-enhanced magnetoelectric/magnetostrictive properties and reduced losses in self-assembled epitaxial CuFe₂O₄–BiFeO₃ layers on Pb(Mg_{1/3}Nb_{2/3})O₃–33at%PbTiO₃ crystals. *Journal of the American Ceramic Society* **0**, 1-11, doi:doi:10.1111/jace.16387 (2019).
37. McLaughlin, E. A., Liu, T. Q. & Lynch, C. S. Relaxor ferroelectric PMN-32%PT crystals under stress and electric field loading: I-32 mode measurements. *Acta Materialia* **52**, 3849-3857, doi:10.1016/j.actamat.2004.04.034 (2004).
38. Wang, Z., Wang, Y., Luo, H., Li, J. & Viehland, D. Crafting the strain state in epitaxial thin films: A case study of CoFe₂O₄ films on Pb(Mg, Nb)O₃–PbTiO₃. *Physical Review B* **90**, 134103 (2014).
39. Lim, L., Shanthi, M., Rajan, K. K. & Lim, C. Flux growth of high-homogeneity PMN–PT single crystals and their property characterization. *Journal of crystal growth* **282**, 330-342 (2005).
40. Li, Y. *et al.* Magnetoelectric quasi-(0-3) nanocomposite heterostructures. *Nat Commun* **6**, 6680, doi:10.1038/ncomms7680 (2015).
41. Wang, Z. *et al.* Domain rotation induced strain effect on the magnetic and magneto-electric response in CoFe₂O₄/Pb(Mg,Nb)O₃-PbTiO₃ heterostructures. *Journal of Applied Physics* **111**, 034108, doi:10.1063/1.3684546 (2012).
42. Wang, Z., Wang, Y., Ge, W., Li, J. & Viehland, D. Volatile and nonvolatile magnetic easy-axis rotation in epitaxial ferromagnetic thin films on ferroelectric single crystal substrates. *Applied Physics Letters*

- 103**, 132909, doi:Unsp 132909 10.1063/1.4823539 (2013).
43. Wang, Z., Yang, Y., Viswan, R., Li, J. & Viehland, D. Giant electric field controlled magnetic anisotropy in epitaxial BiFeO₃-CoFe₂O₄ thin film heterostructures on single crystal Pb(Mg_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}O₃ substrate. *Applied Physics Letters* **99**, 043110, doi:10.1063/1.3619836 (2011).
 44. Li, L. *et al.* Direct Observation of Magnetic Field Induced Ferroelectric Domain Evolution in Self-Assembled Quasi (0-3) BiFeO₃-CoFe₂O₄ Thin Films. *ACS Appl Mater Interfaces* **8**, 442-448, doi:10.1021/acsami.5b09265 (2016).
 45. Nan, T. *et al.* Quantification of strain and charge co-mediated magnetoelectric coupling on ultra-thin Permalloy/PMN-PT interface. *Sci Rep* **4**, 3688, doi:10.1038/srep03688 (2014).
 46. Wang, F., Zhou, C., Gesang, D. & Jiang, C. Electric field control of magnetization reorientation in Co/Pb (Mg_{1/3}Nb_{2/3})-PbTiO₃ heterostructure. *Nanoscale Res Lett* **12**, 104, doi:10.1186/s11671-017-1866-6 (2017).
 47. Zavaliche, F. *et al.* Electric field-induced magnetization switching in epitaxial columnar nanostructures. *Nano Lett* **5**, 1793-1796, doi:10.1021/nl051406i (2005).
 48. Wei, Y. *et al.* Four-state memory based on a giant and non-volatile converse magnetoelectric effect in FeAl/PIN-PMN-PT structure. *Sci Rep* **6**, 30002, doi:10.1038/srep30002 (2016).
 49. Yang, Y. J. *et al.* Electric-Field-Control of Non-Volatile Magnetization Switching in Multiferroic CoFeB/(011)-PMN-PT Heterostructures. *Materials Science Forum* **848**, 675-681, doi:10.4028/www.scientific.net/MSF.848.675 (2016).
 50. Zhang, C. *et al.* Electric field mediated non-volatile tuning magnetism at the single-crystalline Fe/Pb(Mg_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}O₃ interface. *Nanoscale* **7**, 4187-4192, doi:10.1039/c4nr05847j (2015).
 51. Zhou, Z. *et al.* Interfacial charge-mediated non-volatile magnetoelectric coupling in Co(0).(3)Fe(0).(7)/Ba(0).(6)Sr(0).(4)TiO(3)/Nb:SrTiO(3) multiferroic heterostructures. *Sci Rep* **5**, 7740, doi:10.1038/srep07740 (2015).
 52. Yang, Y. J. *et al.* Electric-field control of non-volatile magnetization switching without external-magnetic-field bias in CoFeB/(011)-PMN-0.3PT heterostructures. *Epl* **109**, 17008, doi:Artn 17008 10.1209/0295-5075/109/17008 (2015).
 53. Soares, B. F., Jonsson, F. & Zheludev, N. I. All-optical phase-change memory in a single gallium nanoparticle. *Phys Rev Lett* **98**, 153905, doi:10.1103/PhysRevLett.98.153905 (2007).
 54. Zheludev, N. I. & Kivshar, Y. S. From metamaterials to metadevices. *Nat Mater* **11**, 917-924, doi:10.1038/nmat3431 (2012).
 55. Avci, C. O., Mann, M., Tan, A. J., Gambardella, P. & Beach, G. S. D. A multi-state memory device based on the unidirectional spin Hall magnetoresistance. *Applied Physics Letters* **110**, 203506, doi:Artn 203506 10.1063/1.4983784 (2017).
 56. Bedeschi, F. *et al.* A Bipolar-Selected Phase Change Memory Featuring Multi-Level Cell Storage. *Ieee Journal of Solid-State Circuits* **44**, 217-227, doi:10.1109/Jssc.2008.2006439 (2009).