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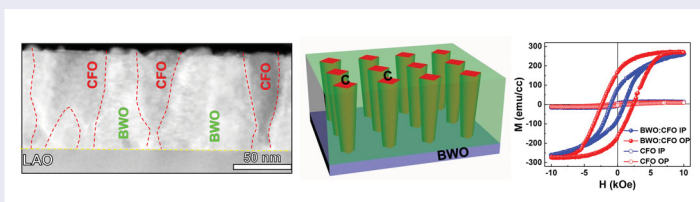
Multiferroic vertically aligned nanocomposite with CoFe_2O_4 nanocones embedded in layered Bi_2WO_6 matrix

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ABSTRACT

$\text{Bi}_2\text{WO}_6\text{:CoFe}_2\text{O}_4$ (BWO:CFO) vertically aligned nanocomposite (VAN) in epitaxial thin film form has been demonstrated on single-crystal LaAlO_3 (LAO) (001) substrates via pulsed laser deposition (PLD). CFO nanopillars exhibit a unique nanocone shape embedded in the epitaxial BWO matrix with an Aurivillius layered oxide structure. The growth direction of the CFO nanopillars is (004), different from that of its epitaxial single-phase counterpart (220), which is attributed to the interfacial strain effect. Magnetic measurements show robust and anisotropic magnetic properties from the CFO nanocone structures, and obvious ferroelectric responses are demonstrated in the BWO matrix, both at room temperature.



IMPACT STATEMENT

The BWO:CFO VAN thin film combining a ferroelectric layered oxide matrix and magnetic vertical nanocone present a new hybrid material platform for room temperature multiferroics design towards nanoscale sensors and actuators.

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KEYWORDS

Vertically aligned nanocomposite; Bi_2WO_6 ; CoFe_2O_4 ; Aurivillius layered structure; multiferroics

Introduction

Multiferroic materials which exhibit ferroelectric and ferromagnetic response simultaneously have attracted significant interest in the past few decades [1]. However, truly single-phase multiferroics are scarce, because the coexistence of magnetism (spin order) and ferroelectricity (electric dipole order) in a single-phase material may be limited. Hence, multiferroic nanocomposites that combine a ferroelectric phase and a magnetic phase have been introduced [1,2,3,4]. Various two-phase nanocomposite thin films have been demonstrated to show multiferroic properties, including $\text{BaTiO}_3\text{:CoFe}_2\text{O}_4$ [1], $\text{BiFeO}_3\text{:CoFe}_2\text{O}_4$ [2], and $\text{BaTiO}_3\text{:YMnO}_3$ [3]. Some of the above nanocomposites were designed with vertically aligned nanocomposites (VAN) structure, which is a novel thin film architecture and where two immiscible

phases co-grow epitaxially and vertically on substrates [5,6]. Furthermore, the VAN systems provide effective vertical strain coupling along the vertical two-phase interfaces, which allows the growth of highly strained films and enhanced ferroelectric/ferromagnetic properties compared to their single-phase counterparts [7]. However, the ferroelectric phases in the reported multiferroic VAN systems are mostly perovskite oxide structures [4], for example, BaTiO_3 (BTO) and BiFeO_3 (BFO). These representative ferroelectric materials have some limitations: e.g. BTO was reported to have a low Curie temperature (T_C) of 120°C to 130°C, and BFO exhibits high leakage current. Studies on the growth and property characterizations of both BTO and BFO also suggested that both films are sensitive to processing conditions and their ferroelectric properties vary significantly among different reports [8,9,10].

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Bismuth-based layered oxides (in an Aurivillius phase) have been reported as another family of ferroelectric materials, which exhibits robust polarization with low leakage current and resistant to fatigue [11]. Among various Aurivillius phases, orthorhombic Bi_2WO_6 (BWO) is one of the simplest members in the Bismuth-based layered oxide family. It is constructed by alternating $(\text{Bi}_2\text{O}_2)^{2+}$ slabs and $(\text{WO}_4)^{2-}$ perovskite layers [12], as shown in the atomic model in Figure 1(a). Because of the layered perovskite structure, it shows directional spontaneous polarization depending on the crystallinity [13]. The strong polarization anisotropy makes it unique for mastering the ferroelectric property by thin film strain effect. However, the work on BWO in thin film form is very scarce [14] and most of the BWO demonstrations have previously focused on dielectric and photocatalytic properties [15,16,17].

On the other hand, CoFe_2O_4 (CFO) with a spinel structure (Figure 1(a)) is an important ferromagnetic material with excellent magnetic property such as high coercivity, moderate saturation magnetization, as well as high chemical and structural phase stability [18,19]. Furthermore, because of the high magnetostriction coefficient, it shows the possibility of tuning magnetization by lattice strain [20]. Therefore, CFO as the ferromagnetic component has been previously introduced into multiple heteroepitaxial nanocomposite systems, such as $\text{SrRuO}_3\text{:CFO}$ [21], $\text{BiFeO}_3\text{:CFO}$ [22] and $\text{PbTiO}_3\text{:CFO}$ [23].

In this study, a new VAN system composed of the ferroelectric BWO layered oxide as the matrix and the ferromagnetic CFO as the secondary phase has been proposed and illustrated in Figure 1(b). The red pillars represent the CFO phase, while the green area signifies the BWO matrix. (001)-oriented LaAlO_3 (LAO) substrates have been selected for the epitaxial growth of both phases. Compared to perovskite VAN systems such as BTO:CFO and BFO:CFO , the proposed BWO:CFO nanocomposites could present the following potential advantages: (1) high Curie temperature, low leakage current and high fatigue endurance; (2) the directional spontaneous polarization related with the layered structure; and (3) reliable ferroelectric properties presented by BWO. We thus investigated the microstructure, strain state, ferromagnetic and ferroelectric properties of the new BWO:CFO VAN system and compared it with the single-phase BWO and CFO films, with a focus on room temperature properties.

Experimental

The $\text{BWO}_{0.5}\text{:CFO}_{0.5}$ target was prepared by a conventional solid-state sintering method. The epitaxial thin

films were deposited on single-crystal (001)-oriented LAO substrates by pulsed laser deposition (PLD) using a KrF excimer laser ($\lambda = 248$ nm). The deposition rate of thin films was 2 Hz under an optimized oxygen partial pressure of 200 mTorr. Substrate temperature of 670°C was maintained during the deposition. Following the deposition, the films were cooled down to room temperature in 200 Torr oxygen atmosphere at a cooling rate of 10°C/min. 100 nm thick Au top contacts of 0.1 mm² area were deposited by a custom-built magnetron sputtering system using a 99.99% pure Au sputter target from Williams Advanced Materials.

The microstructure of as-deposited films was investigated with X-ray diffraction (XRD, PANalytical Empyrean) and transmission electron microscopy (TEM, FEI TALOS T200X) operated at 200 kV. The high-resolution scanning transmission electron microscopy (HRSTEM) images in high angle annular dark-field (HAADF) mode (also called Z-contrast imaging) were obtained using TEAM 1.0, a modified FEI Titan TEM with a Cs probe corrector operated at 300 kV. The magnetic properties of the thin films were investigated using the vibrating sample magnetometer (VSM) option in a commercial Physical Properties Measurement System (PPMS 6000, Quantum Design). During the measurements, the out-of-plane and in-plane magnetization were recorded by applying a magnetic field of 1 T perpendicular and parallel to the film plane, respectively. Ferroelectric polarization-electric field (P-E loops) measurements were conducted by Precision LC II Ferroelectric Tester (Radiant Technologies, Inc.). The phase and amplitude hysteresis loops were collected with atomic force microscopy (AFM, Bruker Dimension Icon). Bruker SCM-PIT Cr-Pt coated silicon cantilevers were adopted in the piezoelectric force microscopy (PFM) measurements.

Results and discussion

XRD analysis was first carried out to check the crystallinity of the BWO:CFO film. Pure BWO and CFO films were also deposited and measured for comparison, as shown in Figure 1(c). The pattern of nanocomposite BWO:CFO presents BWO (00 l) and CFO (004) peaks. The BWO (00 l) peaks indicate the layered structure and are identical to that of the pure BWO on LAO. The lattice parameter of BWO (004) is calculated to be 8.213 Å, which is almost half of the bulk parameter 16.427 Å [24]. It indicates nearly perfect matching between BWO and CFO phases in the out-of-plane direction. In addition, it is clearly observed that BWO (004) matches with CFO (004) in the out-of-plane direction. However, the pure CFO on LAO shows (220) and (440) as the textured

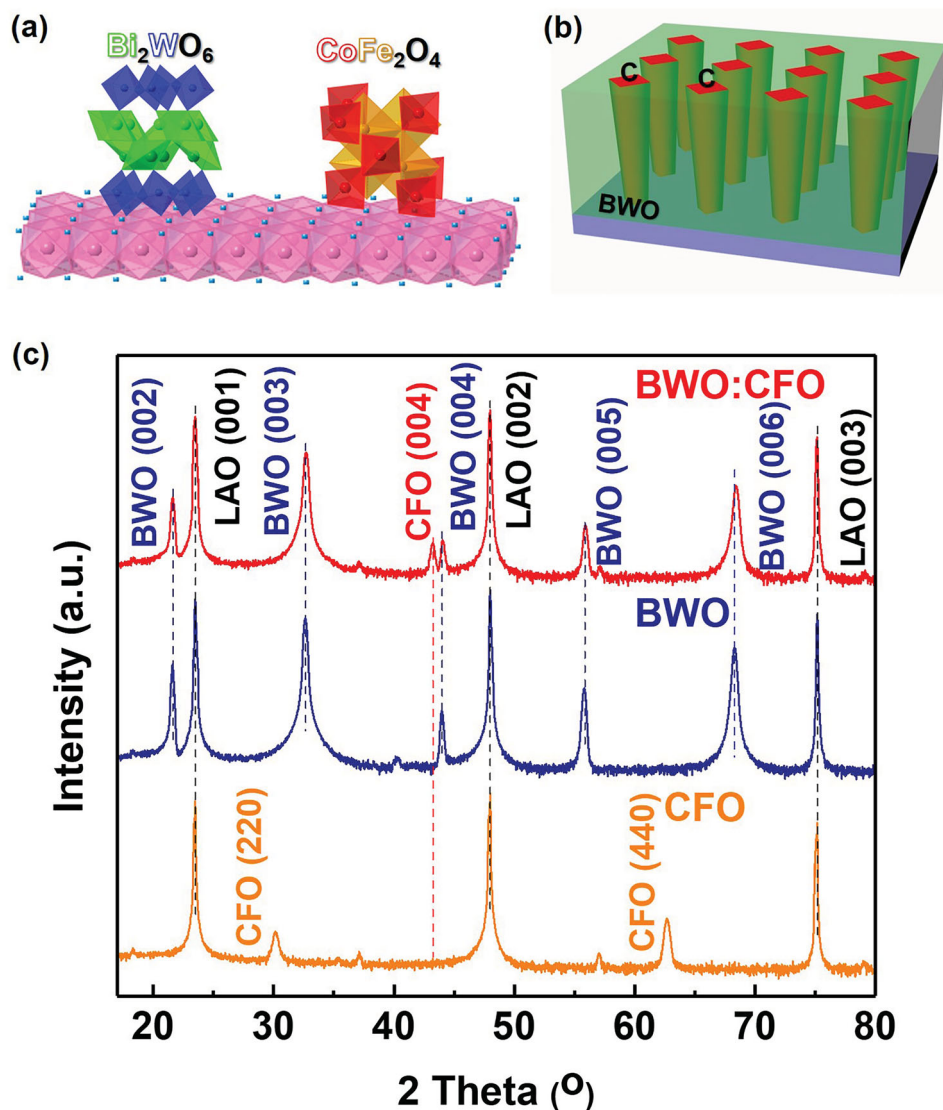


Figure 1. (a) Atomic models of Bi₂WO₆ (BWO), CoFe₂O₄ (CFO) and LaAlO₃ (LAO). (b) Schematic diagram of VAN structure. CFO phase is represented by red pillars and denoted with C, while BWO is the rest green area. (c) $\theta-2\theta$ XRD scans of BWO:CFO, BWO and CFO on LAO substrates, respectively.

orientation, which is different from the preferred (004) texture of the CFO phase in the nanocomposite. Similar preferred (004) CFO growth orientation has been reported in the BFO:CFO system [1,25], where the interface of CFO (004) shares the {110}-type interface with BFO matrix, due to the low interface energy between the octahedrons in the perovskite and those in the spinel phase. Thus, the preferred orientation of (004) CFO in BWO:CFO nanocomposite compared with the pure CFO is due to the strain effect from BWO matrix. The out-of-plane lattice parameter of CFO in BWO:CFO can be calculated to be 8.367 Å compared to the bulk parameter of 8.39 Å [26], which indicates a minor compressive strain of -0.27% in out-of-plane direction. The effect of deposition rate on the nanocomposite microstructure has also been explored. Figure S1 shows the XRD pattern of

BWO:CFO deposited under the laser frequency of 10 Hz. CFO phase shows the (004) growth orientation and the out-of-plane lattice parameter is calculated as 8.359 Å, which is also under compressive strain. However, BWO phase shows more peaks, besides the primary (00 l) peaks, which are marked by ‘*’. It indicates other orientations of BWO phase have grown in the high deposition frequency sample. This result is similar to the previous bismuth-based oxides work that the layered structure is sensitive to the deposition rate [27]. Similarly, the film composition (i.e. two-phase molar ratio) could also affect the overall film microstructure and the resulted film properties. It thus shall be further explored as future work.

TEM was applied to further investigate the microstructure and strain status of the nanocomposite films. The cross-sectional TEM image (Figure 2(a))

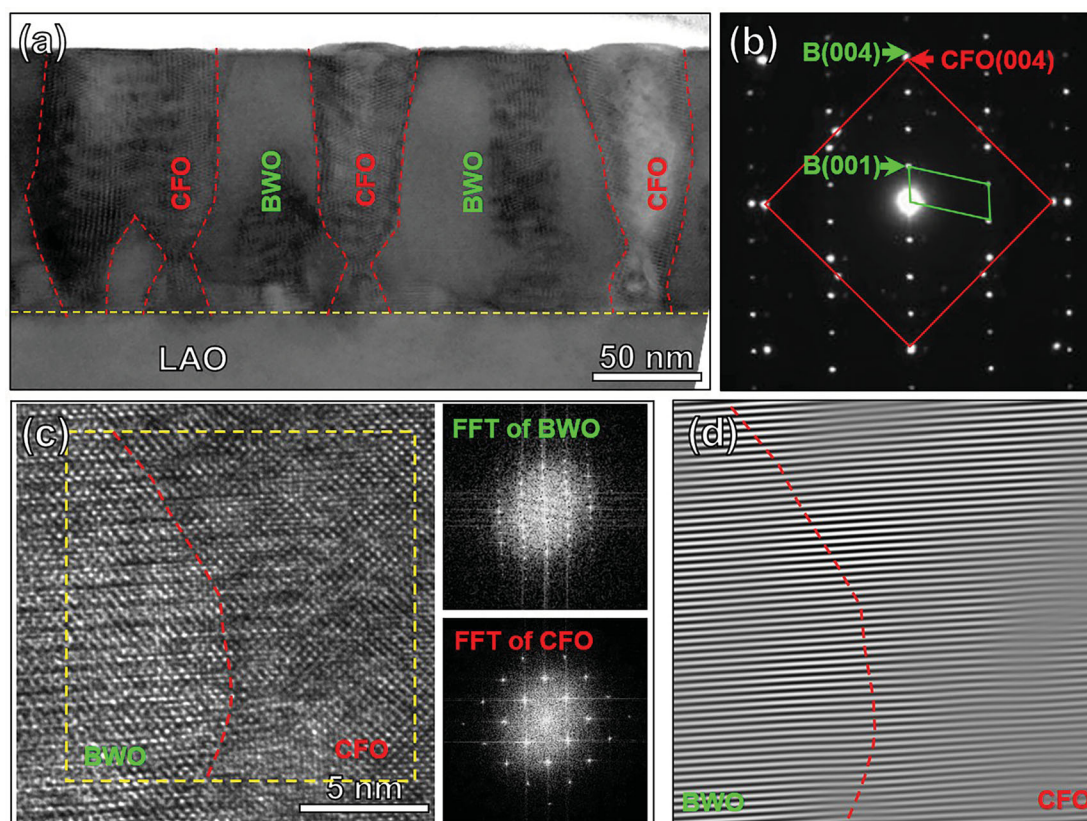


Figure 2. (a) Cross-sectional TEM image of BWO:CFO. (b) The corresponding SAED pattern from thin film area. BWO phase is denoted with B. (c) HRTEM image along the interface between BWO and CFO. The insets show the fast Fourier transformed (FFT) images from BWO and CFO phases. (d) The corresponding FFT filtered image (the dashed line guides the interface).

shows that both phases grew as vertical domains from the substrate surface to the top of the film. The distinguished dots in the corresponding selective area electron diffraction (SAED) pattern (Figure 2(b)) exhibit only (00 l)-orientated BWO and (004)-oriented CFO phases, which agrees well with the previous XRD results. The in-plane lattice parameter of CFO is then calculated to be $a = b = 8.404 \text{ \AA}$ and the corresponding in-plane strain is determined as 0.17%. It indicates that the CFO phase in BWO:CFO is under out-of-plane compressive strain (ε_{001}), which is calculated as -0.44% . As a comparison, pure BWO and CFO phases were also characterized and shown in Figure S2(a,c) by TEM. BWO wets the substrate completely and follows a layer-by-layer growth, which is identified by the satellite diffraction pattern (Figure S2(b)). In comparison, the pure CFO thin film follows island growth with (044) as the out-of-plane orientation in the SAED pattern (Figure S2(d)). It suggests that the BWO phase in the nanocomposite facilitated the nucleation and growth of CFO (004). BWO:CFO heterointerface was investigated with high-resolution TEM (HRTEM) (Figure 2(c)). The two phases show excellent epitaxial quality. The BWO phase exhibits clear layered structure along the out-of-plane direction (c -axis). The

insets are fast Fourier transform (FFT) images obtained from local BWO and CFO areas. They agree well with the SAED pattern. The corresponding fast Fourier filtered image (Figure 2(d)) confirms the well matching between 4 of BWO (00 l) and CFO (004) along the vertical interface, which is energetically favorable saving with small residual strain.

Further microstructure analysis has been conducted to reveal the chemical composition distribution and the out-of-plane strain status of BWO:CFO. Figure 3(a) presents the plan-view low-mag STEM image, and Figure 3(b) shows the corresponding EDS mapping data. The top view of CFO nanopillars shows a rectangular shape. Based on the high-resolution STEM (HRSTEM) (Figure 3(c)) and EDS results, the interfaces between the two phases are very sharp without any obvious inter-diffusions. Cross-sectional STEM (Figure 3(d)) and corresponding EDS mapping (Figure 3(e)) were also carried out to explore the 3D nature of the film. The diameter of the CFO nanopillars increases along the growth direction and the pillars form an inverted cone shape, which could be related to that the strain effects on CFO pillars from BWO matrix decrease as the film grows thicker. Similar inverted cone shape of CFO nanopillars has been

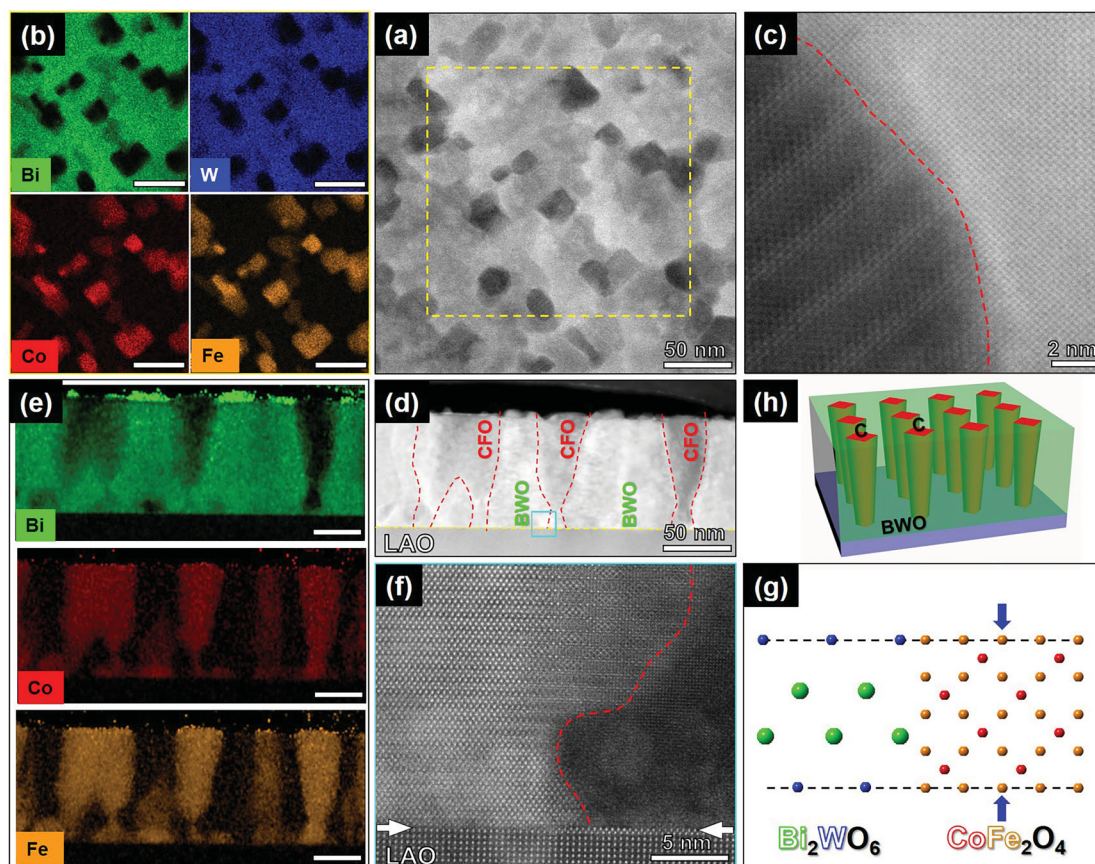


Figure 3. Microstructure study of BWO:CFO. (a) Plan-view STEM image of a selected area of the film, with (b) EDS mapping of the marked area and (c) atomic-scale high-resolution image of one pillar interface. (d) Cross-sectional STEM image of a selected area of the film with (e) the corresponding EDS mapping and (f) atomic-scale high-resolution STEM image of BWO:CFO interface. (g) The atomic models of the coupling between BWO and CFO. (h) 3D construction of the film.

reported in the BFO:CFO nanocomposite, in which CFO nanopillars also grow along (001) direction [2]. Hence, the overall 3D structure of BWO:CFO VAN thin film is illustrated in Figure 3(h). HRSTEM was applied to explore the triple-phase interface area between the substrate and the two phases, as shown in Figure 3(f). BWO shows very clear layered structure along the growth direction (*c*-axis). It is noted that four layers of BWO (a half unit cell thickness) are coupled with CFO (004) (a unit cell thick of CFO). The coupling is illustrated by the atomic model in Figure 3(g). Based on the above strain and structure analysis, parts of the octahedrons in the CFO phase are shown under out-of-plane compressive strain. The strain effect from BWO on CFO phase could lead to a pronounced change in the coupling behaviors.

To demonstrate the multiferroic nature of the two-phase nanocomposite film, both magnetic and ferroelectric measurements have been conducted at room temperature. Figure 4(a) shows the in-plane (IP) and out-of-plane (OP) magnetic hysteresis (M-H) loops of BWO:CFO film measured at 300 K. The magnetization

values were normalized to the volume fraction of CFO ($\sim 29\%$) approximately after subtracting the diamagnetic signals from the LAO substrates. This demonstrates the effectiveness of CFO as the secondary phase into VAN systems to introduce ferromagnetic property. The ratio of remanence to saturation magnetization (M_r/M_s) for the out-of-plane ($(M_r/M_s)_\perp$) is 61%, which is larger than that for the in-plane ($(M_r/M_s)_\parallel$) value of 37%. Meanwhile, the coercive field (H_c) in out-of-plane direction is 2.39 kOe, which is also much larger than that of the in-plane direction of 1.07 kOe. The high magnetic anisotropy can be attributed to the anisotropic microstructure of the nanocomposite film, i.e. the CFO nanocone structures in the BWO matrix. The IP and OP magnetic hysteresis (M-H) loops of pure CFO are also shown in Figure 4(a), which suggests a lower magnetic response of (220)-oriented CFO pure film.

The magnetic anisotropy related with CFO phase has also been observed in other magnetic CFO nanopillar structures [1,28]. One source for the magnetic anisotropy could be the magnetostriction effect, which stems from the compressive strain of CFO. The stress

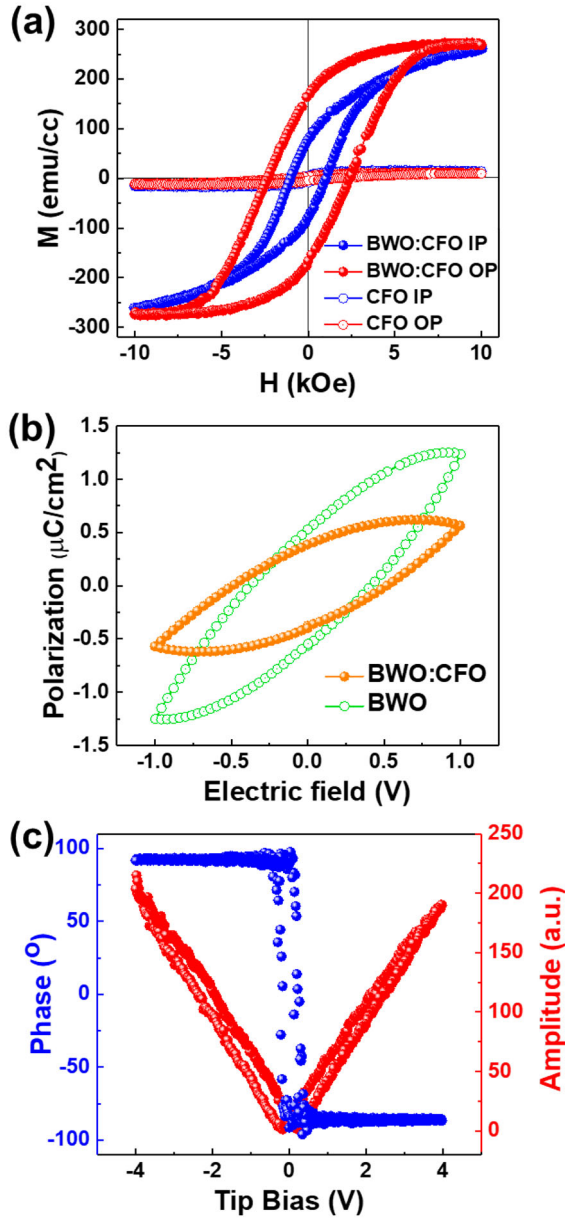


Figure 4. (a) In-plane (IP) and Out-plane (OP) magnetization hysteresis loops of BWO:CFO and pure CFO at 300 K. (b) Polarization hysteresis measurements for BWO:CFO and pure BWO. (c) Amplitude and phase switching behavior of BWO:CFO.

in CFO is given by the equation $\sigma = Y\varepsilon_{001}$, where Y is the Young's modulus (~ 141.6 GPa) [29] and ε_{001} is the strain along the [001] direction ($\sim -0.44\%$). The magnetoelectric energy (K_{me}) is calculated by $K_{me} = -3\lambda_{001}\sigma_{001}/2$, where λ_{001} is the magnetostrictive coefficient of CFO ($\sim -350 \times 10^{-6}$) [29]. Thus, the anisotropy energy for CFO in VAN is 3.27×10^6 erg/cm³. Another possible source for the magnetic anisotropy is the shape anisotropy of CFO. The anisotropy energy (K_s) is calculated based on a heterogeneous model $K_s = -2\pi M_s^2$ [30], which is -0.46×10^6 erg/cm³. The total anisotropy energy in BWO:CFO thin film is thus

2.81×10^6 erg/cm³. The anisotropy field is given by $H_{stress} = 2K/M_s = 20.8$ kOe, which is larger than the experimental observed value of 10 kOe. The difference could be due to other possible sources for the magnetic anisotropy such as interface exchange anisotropy and magnetocrystalline anisotropy. In addition, the model used for the calculation of shape anisotropy energy is only a two-dimensional model without consideration of CFO nanocone structures, which need to be modified in future work.

Ferroelectric measurements demonstrate a well-defined P-E hysteresis loop of BWO:CFO, as shown in Figure 4(b). It is compared with the loop of pure BWO. The remanent polarization (P_r) of BWO:CFO is $0.40 \mu\text{C}/\text{cm}^2$ which is slightly lower than that of pure BWO with $0.53 \mu\text{C}/\text{cm}^2$. It is probably due to the incorporation of non-ferroelectric phase CFO in the system. In addition, PFM measurement was performed on BWO:CFO VAN thin film. Figure 4(c) shows the out-of-plane phase and amplitude switching plots as a function of the bias applied. A 180° phase transition with the change of tip bias direction can be seen in the phase switching curve while a perfect butterfly-like shape is shown in the amplitude curve. This demonstrates the ferroelectric response of the BWO:CFO VAN thin film at room temperature.

The demonstration of multiferroic BWO:CFO paves a way to create new nanocomposites which combine a bismuth-based layered oxide with a spinel phase, beyond the conventional perovskite oxide systems. It also provides a practical approach for introducing magnetic components into the ferroelectric and piezoelectric layered oxides. BWO:CFO VAN exhibits a larger in-plane (M_r/M_s)_{||} anisotropy in magnetic property compared with the reported BFO:CFO VAN films [28,31]. The strong coupling effect between the layered BWO matrix and CFO could be the possible source. In addition, pure BWO thin films have been reported with directional polarization, which is highly dependent on the growth orientation [13]. Hence, the BWO:CFO VAN system is worthy of a systematic study on the influence of several experimental parameters, such as the molar ratios and deposition rate. It is promising to control directional multiferroic properties in 3D materials with build-in layered structure and to incorporate the new hybrid material platform for spintronic devices, nanoscale sensors and actuators.

Conclusion

In summary, BWO:CFO VAN thin films with layered oxide VAN structure have been grown on (001)-LAO substrates by PLD. The CFO phase forms inverted

cone-shaped nanopillars in BWO layered oxide matrix. The BWO:CFO VAN system shows robust multiferroic properties as a result of the vertical interface coupling between the ferroelectric BWO layered oxide matrix and the ferromagnetic CFO nanopillars, under room temperature. The BWO:CFO VAN thin films present a new hybrid layered oxide platform for room temperature multiferroics design towards nanoscale sensors and actuators.

Disclosure statement

No potential conflict of interest was reported by the authors.

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