

Strong magnetoelectric coupling in ferrite/ferroelectric multiferroic heterostructures derived by low temperature spin-spray deposition

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Abstract

Strong magnetoelectric (ME) interaction was demonstrated at both dc and microwave frequencies in a novel $\text{Zn}_{0.1}\text{Fe}_{2.9}\text{O}_4/\text{PMN-PT}$ (lead magnesium niobate–lead titanate) multiferroic heterostructure, which was prepared by spin-spray depositing a $\text{Zn}_{0.1}\text{Fe}_{2.9}\text{O}_4$ film on a single-crystal PMN–PT substrate at a low temperature of 90 °C. A large electric-field induced ferromagnetic resonance field shift up to 140 Oe was observed, corresponding to an ME coefficient of 23 Oe cm kV⁻¹. In addition, a large electrostatic field tuning of the magnetic hysteresis loops was observed with a large squareness ratio change of 18%. The spin-spray deposited ferrite/piezoelectric multiferroic heterostructures exhibiting strong ME interactions at both dc and microwave frequencies provide great opportunities for novel electrostatically tunable microwave magnetic devices synthesized at a low temperature.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Magnetization tuning in many microwave magnetic devices is performed by external magnetic fields generated by electromagnets, which is slow, bulky, noisy and energy consuming [1]. Recently, multiferroic composite materials with two constituent phases of ferro/ferrimagnetic phase and ferroelectric phase have attracted an increasing amount of interest due to their potential applications in many multifunctional devices [2–12]. Such materials can display a large stress/strain mediated magnetoelectric (ME) effect, i.e. a dielectric polarization variation as a response to an applied magnetic field or an induced magnetization by an external electric field. To achieve a large stress mediated ME coupling, strong adhesion between two constituent multiferroic phases and a small clamping effect from the substrate are essential. For a nano-multiferroic composite, core–shell nanowires or nanotube structures are good candidates for realization of

large ME coupling due to their large interface area and their small clamping effect by removing the support core [13, 14]; for a laminate multiferroic heterostructure, strong adhesion and a large volume ratio are necessary to guarantee 100% deformation transmission and achieve large ME coupling which could enable many device applications, such as picotesla magnetometers, filters, resonators and phase shifters [12, 15–17]. More recently, we have reported a new class of metallic FeGaB films derived by magnetron sputtering, which showed a record high tunable ferromagnetic resonance (FMR) frequency of 900 MHz or 58% in FeGaB/Si/PMN–PT multiferroic composites [18, 19]. However, the corresponding electrostatically induced effective magnetic field is still relatively low of ~30 Oe in the FeGaB film, which is also comparable to what has been reported by other groups [15–17]. New multiferroic composite materials are needed in order to achieve higher electrostatically induced effective magnetic fields which are critical for many microwave devices.

The spin-spray deposition process is a wet chemical synthesis technique involving several chemical reactions for

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generating high crystalline quality spinel ferrite films with different compositions directly from an aqueous solution [20–22]. One unique feature of spin-spray processing is the low growth temperature in the range 25–90 °C, which is much lower than the conventional ferrite film preparation methods requiring high temperatures of 600 °C or above, such as sputtering, MBE and PLD. In addition, ferrites can be easily deposited onto various substrates, such as ceramic, glass, metal, making these ferrite films readily integrated onto different integrated circuits. More recently, we have reported a multiferroic heterostructure with spin-spray deposited nickel ferrite on lead zirconium titanate (NFO/PZT) [23]. Strong interface adhesion between ferrite and ferroelectric phases was verified by high resolution transmission electron microscopy, which led to a strong dc ME coupling demonstrated by an electric-field induced remnant magnetization change of 10%.

In this work, a single-crystal PMN–PT with large anisotropic piezoelectric coefficients was involved to prepare a $\text{Zn}_{0.1}\text{Fe}_{2.9}\text{O}_4$ /PMN–PT (ZFO/PMN–PT) multiferroic composite by low temperature spin-spray deposition. Static and microwave ME interactions were demonstrated. A large electrostatically induced effective magnetic field was observed at microwave frequencies, which resulted in an FMR field shift up to 140 Oe. This is much higher than most published values [6, 11, 15, 17]. Strong ME coupling at dc was also demonstrated by a large electric-field induced squareness ratio change of 18%. This ZFO/PMN–PT multiferroic heterostructure with strong ME coupling at microwave frequencies shows great promise in electrostatically tunable microwave devices.

2. Experimental

A multiferroic composite of ZFO/PMN–PT was synthesized by spin-spray deposition of a ZFO ferrite film with a thickness of $\sim 1 \mu\text{m}$ onto a commercially available (0 1 1) cut ferroelectric PMN–PT single-crystal substrate with a thickness of 0.5 mm. The (0 1 1) cut and (0 1 1) poled single-crystal PMN–PT have anisotropic in-plane piezoelectric coefficients of d_{31} and d_{32} , with a negative d_{31} of -1750 pC N^{-1} and a positive d_{32} of 900 pC N^{-1} , which is much larger than the piezoelectric coefficient of PZT and provides an exceptional opportunity for achieving a large change in the in-plane uniaxial anisotropy in the ferrite film and therefore a large FMR frequency tunability via inverse magnetoelastic coupling. In this work, 10 mmol L^{-1} iron (II) chloride and 0.3 mmol L^{-1} zinc chloride solutions were used as ferrite precursors; 2 mM NaNO_2 and 140 mM CH_3COONa were used as oxidization solutions. Through separate nozzles, these two solutions were sprayed onto a spinning hot PZT substrate at 90 °C with a flow rate of 40 ml min^{-1} . N_2 gas was blown into the chamber to mitigate the oxidization effects from oxygen in air. After thirty minutes of plating, a uniform Zn ferrite film on PMN–PT with strong adhesion and a thickness of $1 \mu\text{m}$ was obtained with a growth rate of $\sim 30 \text{ nm min}^{-1}$.

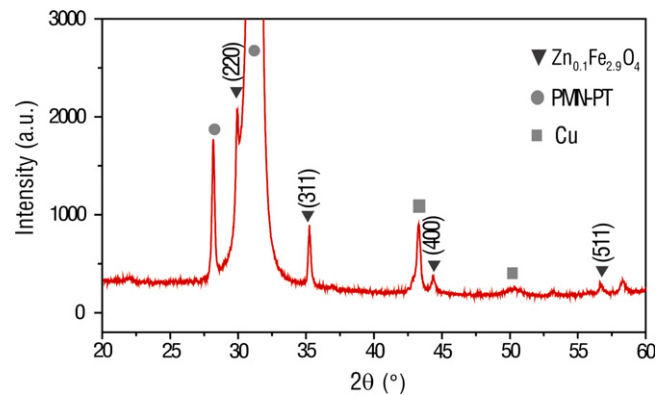


Figure 1. X-ray diffraction pattern of the spin-spray deposited ZFO/PMN–PT multiferroic composite.

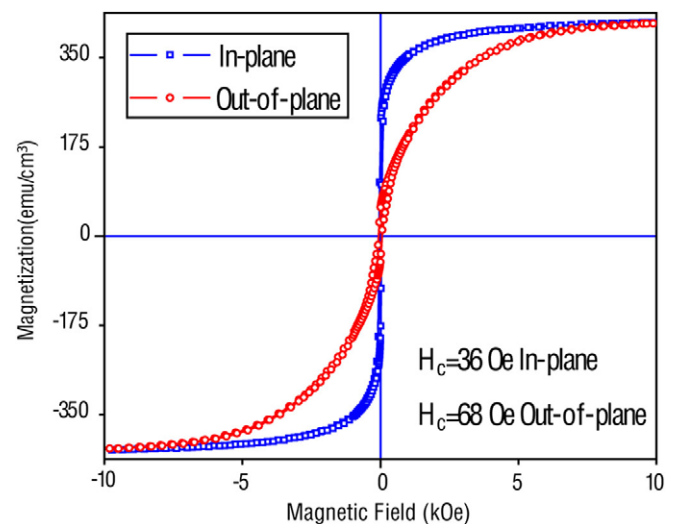


Figure 2. Typical magnetic hysteresis loops of a spin-spray deposited $\text{Zn}_{0.1}\text{Fe}_{2.9}\text{O}_4$ ferrite film on PMN–PT.

3. Results and discussion

3.1. Structural and magnetic properties of spin-spray derived $\text{Zn}_{0.1}\text{Fe}_{2.9}\text{O}_4$ ferrite film

The phase structure of the ZFO ferrite film on the PMN–PT composite was confirmed by x-ray diffraction. A pure spinel ferrite phase was clearly identified with no obvious preferential crystallographic orientation as shown in figure 1. Magnetic hysteresis behaviour of the spin-spray deposited ZFO/PMN–PT multiferroic composite was observed by a vibrating sample magnetometer (VSM) as shown in figure 2. Well-defined in-plane and out-of-plane magnetic hysteresis loops were observed when an external magnetic field was applied parallel and perpendicular to the film plane, respectively, showing an in-plane coercivity of 36 Oe and an out-of-plane coercivity of 68 Oe, respectively. The saturation magnetization of the ZFO film was determined to be 410 emu cm^{-3} .

3.2. Static ME coupling in ZFO/PMN–PT heterostructure

ME coupling of multiferroic heterostructures of ZFO/PMN–PT at dc was studied by electrostatically induced changes

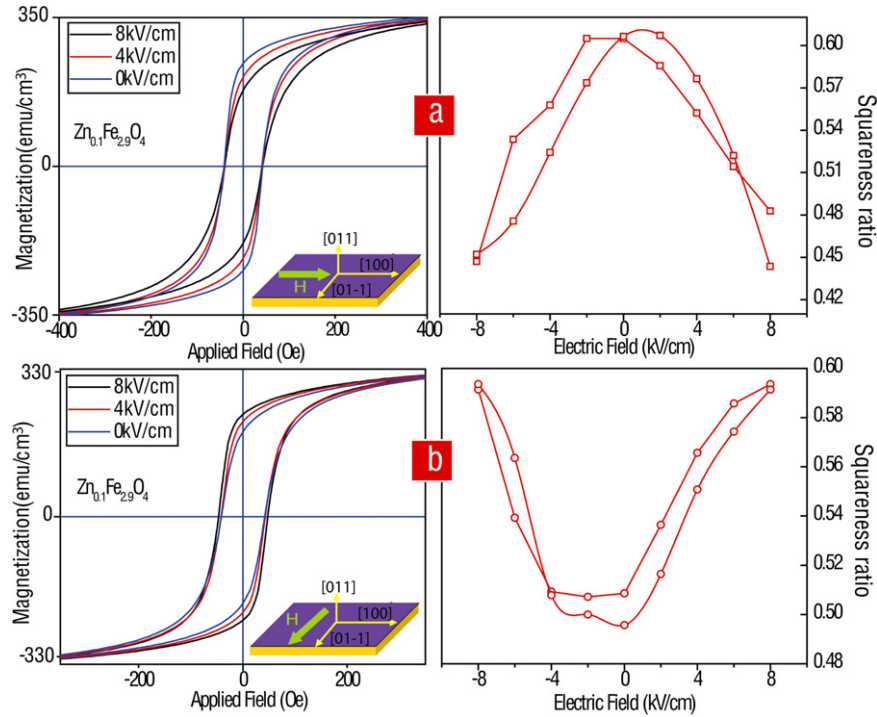


Figure 3. Magnetic hysteresis loops and remanence changes while external magnetic fields are along (a) the compressive stress direction [1 0 0] (d_{31}) of ZFO/PMN-PT and (b) the tensile stress direction [0 1 -1] (d_{32}) of ZMFO/PMN-PT.

inmagnetic hysteresis loops. It is a well-known phenomenon that imposing a strain on a magnetic material by a mechanical stress alters the magnetization and changes the shape of the hysteresis loops. Therefore, through electric-field induced stress/strain by the piezoelectric effect, the electric-field manipulation of magnetization can be realized. As shown in figure 3, the ZFO/PMN-PT multiferroic composite displayed an obvious electric-field dependence of the magnetic hysteresis loops while applying the electric field across the thickness of PMN-PT. The remanence of the ZFO/PZT multiferroic composite exhibited a ‘butterfly’ curve dependence on the electric field. In addition, the (0 1 1) cut PMN-PT single-crystal slab has large anisotropic in-plane piezoelectric coefficients of d_{31} and d_{32} , which could generate in-plane compressive stress along [1 0 0] (d_{31}) and tensile stress along [0 1 -1] (d_{32}) while applying the electric field parallel to the [0 1 1] (d_{33}) direction. The ZFO ferrite on PMN-PT displayed a remarkably different magnetization process when it was magnetized along the two in-plane orthogonal directions [0 1 -1] and [1 0 0] of the PMN-PT slab, which was reflected by the opposite trend of the electric field dependence of the magnetic hysteresis loops and remanence versus electric-field ‘butterfly’ curves, as shown in figure 3. The remanence was reduced from ~62% at 0 kV cm⁻¹ to ~44% at the electric field of 8 kV cm⁻¹ when the external magnetic field was applied along the PMN-PT [1 0 0] (d_{31}) direction. However, when the external magnetic field was applied parallel to the PMN-PT [0 1 -1] (d_{32}) direction, the remanence was increased from 49% at 0 kV cm⁻¹ to 59% at an electric field of +8 kV cm⁻¹. It is notable that the electric-field induced remanence change for the ZFO/PMN-PT is much larger than that for Ni-ferrite/PZT [23].

3.3. Microwave ME coupling in ZFO/PMN-PT heterostructure

The ME interaction at microwave frequencies for the spin-spray derived ZFO/PMN-PT multiferroic heterostructure was demonstrated by an electrostatic induced in-plane magnetic anisotropy field H_{eff} which resulted in large changes in the FMR field at the X-band (9.5 GHz). Depending upon whether the H_{eff} is parallel or perpendicular to the applied external magnetic field, the FMR field could be tuned up or down by the electric field. The in-plane FMR frequency can be expressed by the well-known Kittel equation:

$$f = \gamma \sqrt{(H_r + H_k + H_{\text{eff}})(H_r + H_k + H_{\text{eff}} + 4\pi M_s)}, \quad (1)$$

where g is the gyromagnetic ratio, H_r is the FMR field that is supplied by an external electromagnet pair, H_k is the anisotropic field in plane, $4\pi M_s$ is the magnetization and H_{eff} is the effective in-plane magnetic anisotropy field due to ME coupling. The H_{eff} induced by the orthogonal in-plane compressive and tensile stresses could be positive or negative and can be expressed as

$$H_{\text{eff}} = \frac{3\lambda_s(\sigma_c - \sigma_t)}{M_s},$$

in which

$$\sigma_c = \frac{Y}{1 - \nu^2}(vd_{32} + d_{31})E$$

and

$$\sigma_t = \frac{Y}{1 - \nu^2}(d_{32} + vd_{31})E$$

are the compressive and tensile stresses generated by the electric field E and derived from Hooke’s law for the plane

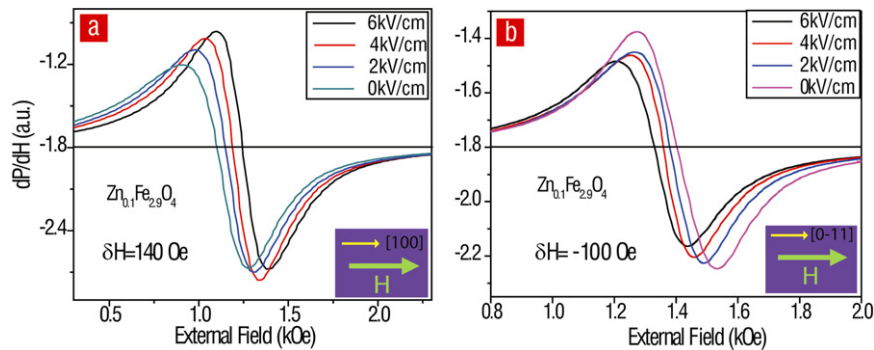


Figure 4. FMR absorption spectra of multiferroic composites ZFO/PMN–PT under different electric fields while applying an external magnetic field along (a) [1 0 0] and (b) [0 1 –1] directions.

stress, Y is Young's modulus of the zinc ferrite film, ν is the Poisson ratio, λ_s is the saturated magnetostriction constant and d_{31} and d_{32} the piezoelectric coefficients along the [1 0 0] direction and the [0 1 –1] direction for the (0 1 1) cut PMN–PT, respectively.

A TE_{102} mode microwave cavity operating at X-band (9.5 GHz) was used to perform the FMR measurements of the ferrite/ferroelectric multiferroic composites. The external bias magnetic field was applied in the ferrite film plane along the PMN–PT [1 0 0] or the PMN–PT [0 1 –1] direction, respectively, with the microwave RF field being in-plane and perpendicular to the dc bias field. As shown in figure 4(a), a large upward shift of the FMR field $\delta H_r = 140$ Oe was observed, corresponding to an ME coupling coefficient of 23 Oe cm kV $^{-1}$ when the external magnetic field was applied along the PMN–PT [1 0 0] (d_{31}) (compressive) direction and electric fields were applied across the PMN–PT thickness from 0 to 6 kV cm $^{-1}$. This upward shift of the FMR field can be explained by an electric field induced compressive stress which resulted in an induced magnetic anisotropy field along the [1 0 0] direction when $\lambda_s(\sigma_c - \sigma_t) < 0$ is valid. In contrast, a downward shift of the FMR field $\delta H_r = -100$ Oe was observed when the external magnetic fields were applied along the PMN–PT [0 1 –1] (d_{32}) (tensile) direction, with a corresponding microwave ME coefficient of 18 Oe cm kV $^{-1}$ as shown in figure 4(b). Both of them had a relatively narrow FMR linewidth of 270 Oe at zero electric field compared with 600 Oe of the spin-spray deposited Fe $_3$ O $_4$ film. These strong microwave ME interactions, which resulted in large tunable FMR fields at microwave frequencies, could lead to novel ME devices.

4. Conclusion

In summary, a ferrite/ferroelectric multiferroic heterostructure of Zn $_{0.1}$ Fe $_{2.9}$ O $_4$ /PMN–PT was synthesized by spin-spray deposition of Zn $_{0.1}$ Fe $_{2.9}$ O $_4$ ferrite films on PMN–PT substrates at a low temperature. Strong ME coupling was observed at dc and microwave frequencies with a tunable magnetic resonance field of 140 Oe. Compared with the reported microwave tunable YIG/PMN–PT laminate structure [6], spin-spray deposited ZFO/PMN–PT showed a large FMR tunability and a small ratio of tunable range over the FMR linewidth. This

small ratio could not be of benefit to microwave devices which highly rely on the FRM effect, but the large tunable range is of significant importance for devices which operate far from FMR frequency such as the phase shifter. So this large electrostatic tunable FMR field and low synthesis temperature make these multiferroic heterostructures great candidates for applications in electrostatically tunable microwave multiferroic devices.

Acknowledgment

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