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Electric field tunable magnetic properties of lead-free $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3/\text{CoFe}_2\text{O}_4$ multiferroic composites

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Lead-free multiferroic particulate composites of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) and CoFe_2O_4 (CFO) have been synthesized by solid-state sintering method. A systematic study of structural, magnetic and magnetoelectric (ME) properties is undertaken. Structural and morphology studies carried out by x-ray diffraction and field emission scanning electron microscopy indicate formation of single phase for parent phases and presence of both phases in the composites. Magnetic properties are investigated using vibrating sample magnetometer and ferromagnetic resonance (FMR) measurements at room temperature. Strong ME coupling is demonstrated in NBT-CFO 70-30 mol% composite by an electrostatically tunable FMR field shift up to 428 Oe (at $E = 3.9$ kV/cm), which increases to a large value of 640 Oe at $E = 6.8$ kV/cm. Furthermore, these lead-free multiferroic composites exhibiting electrostatically induced magnetic resonance field at microwave frequencies provide great opportunities for electric field tunable microwave devices. © 2011 American Institute of Physics. [doi:10.1063/1.3544500]

I. INTRODUCTION

Multiferroic materials have drawn constantly-increasing interest due to their multifunctionality, which can be used in devices such as signal processors that include tunable resonators, phase shifters, and filters.¹⁻⁴ Multiferroics exhibit an induced electric polarization by a magnetic field and vice versa, which is realized as magnetoelectric (ME) effect.^{5,6} The ME effect is observable in single-phase materials as well as composites. Low ME output of single-phase materials necessitates use of alternate materials to enhance ME properties, for example, a composite, comprising a ferri- or a ferromagnetic (FM) phase with a ferroelectric (FE) phase.⁷⁻¹⁰ ME composites can be stimulated in two ways: using magnetic field and measuring change of polarization or with electric field and measuring corresponding magnetization change, which is Converse ME effect.¹¹ Up to now, the emphasis has been on FM/FE composites and the tuning of electric response through the magnetic-field-induced stress on the FE phase. Nevertheless, electric-field tunable multiferroic composites can yield a better tuning of the magnetic response and provide an opportunity for various device applications.¹² Laminated composites of magnetic phases of yttrium iron garnet, $\text{Zn}_{0.1}\text{Fe}_{2.9}\text{O}_4$, Metglass (FeGaB) bonded to Pb-based piezoelectric ceramics are known to possess large ME effects as well as electric-field tunable magnetic properties.¹¹⁻¹⁴ Due to the concerns to the human health, lead-free materials are being preferred.^{15,16} Sodium bismuth titanate (NBT), is a perovskite ferroelectric material, which is attracting more attention as an alternative material in piezoelectric and pyroelectric applications.^{17,18} Cobalt ferrite (CFO) is a hard magnetic material characterized by high coercivity, moderate saturation magnetization, good chemi-

cal stability, significant hardness, and large magnetostriction.^{19,20} Hence, the lead-free particulate composite of NBT/CFO is a good candidate for the study of electric field tunable magnetic properties. However, there has been no experimental report, so far, on electrostatically tunable ferromagnetic resonance (FMR) field properties on multiferroic particulate composites. In this paper, we report electrostatically tunable FMR at room temperature in NBT-CFO multiferroic particulate composites. The results suggest that the electric field induced deformation in NBT plays an important role in the manipulation of FMR.

II. EXPERIMENTAL PROCEDURES

Multiferroic composites of $(1-x)\text{NBT}-(x)\text{CFO}$ (where $x = 0.15, 0.30, \text{ and } 0.45$) were synthesized by solid-state double sintering technique. All the starting materials were basic oxides of high purity (99.999%) from Alfa Aesar, USA. First, Co_3O_4 and Fe_2O_3 were chosen as starting materials to synthesize CFO, while for NBT the starting materials used were Na_2CO_3 , Bi_2O_3 and TiO_2 . All the starting materials were weighed in stoichiometric proportions and thoroughly mixed for 10 h in a ball mill. Mixed CFO powder was calcined at 1000 °C for 10 h, and again ground and sintered at 1150 °C for 15 h. NBT powders were presintered at 900 °C for 3 h and final sintering was carried out at 1100 °C for 3 h. To make the composite, NBT and CFO powders were mixed thoroughly in proportions of 85:15, 70:30, and 45:55 mol%, hereafter referred to as NBT-CFO 85-15, NBT-CFO 70-30, and NBT-CFO 55-45, and sintered at 1050 °C for 3 h after grinding them for 3 h. These sintered composite powders, after several hours of grinding were pressed into pellets of 6 mm diameter and 0.5-2 mm in thickness. The pressed pellets then were finally sintered at 1100 °C for 3 h.

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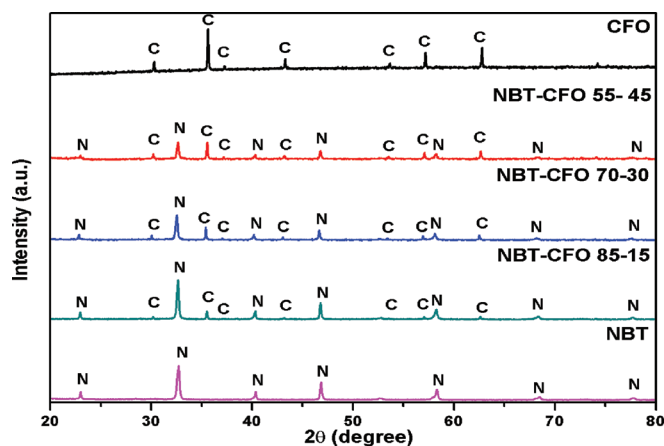


FIG. 1. (Color online) XRD patterns of NBT-CFO composites.

Structural and morphology studies were carried out by x-ray diffraction (XRD, PANalytical X'PERT PRO) and field emission scanning electron microscopy (FESEM, LEO 1530 VP). Magnetic properties were investigated using vibrating sample magnetometer (Princeton Measurement Corporation MicroMagTM 3900) and ferromagnetic resonance measurements [X-Band (9.8GHz) FMR Spectrometer, Bruker EMX 10/12] at room temperature. Tuning of FMR response was measured as a function of applied electric bias voltage.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction patterns of the sintered ceramic composite samples, which exhibit two-phase composition of the parent phases. The main peaks in the pattern could be attributed to the ferrite spinel and the lead-free ferroelectric perovskite NBT phase.^{18,20} The unit cell parameters calculated for the rhombohedral NBT are $a = 3.8762 \pm 0.0003 \text{ \AA}$; $\alpha = 89.9^\circ$ and for Cubic CFO are $a = 8.3615 \pm 0.0002 \text{ \AA}$. No other phase was detected. The two phases of the composite along with a uniform distribution of NBT and CFO grains is also confirmed by the FESEM images of the polished surfaces of the ceramic composite samples. The SEM micrographs are shown in Fig. 2, which illustrate fine-grained and dense microstructure of these ceramics. The images clearly show the presence of two individual phases, with the smaller grains of CFO and larger grains of NBT forming a matrix in 0–3 connectivity. Here, the CFO grains are surrounded by NBT grains and form a composite with 0–3 connectivity. The grain size of the ferrite is in the range 0.2–1 μm , while that of the ferroelectric is slightly larger ranging from 2–6 μm . It is well-known that the distribution of ferrite and ferroelectric phases in a composite plays

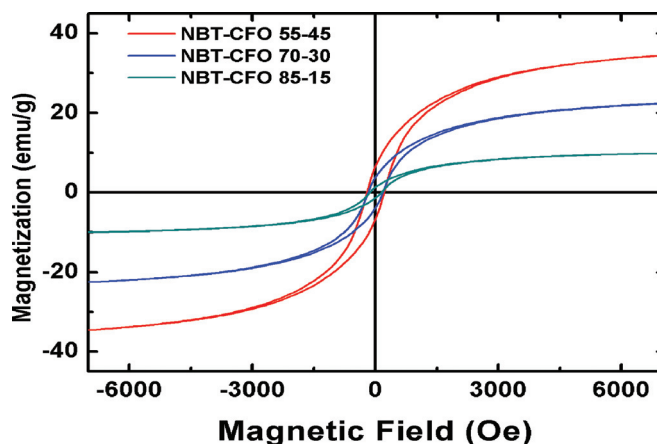


FIG. 3. (Color online) Magnetic hysteresis loops of NBT-CFO composites.

crucial role not only on the combination properties (magnetization, dielectric constant, resistivity, etc.), but also product properties viz. magnetoelectric coupling.²¹

Results of magnetization measurements performed at room temperature for all the composite samples are plotted in Fig. 3. The saturation and remnant magnetizations (M_s , M_r) of the (1-x)NBT-(x)CFO ($x = 0.15, 0.30$, and 0.45) composites are (9.82, 1.34), (22.39, 3.79), and (34.46, 6.58) in units of emu/g, respectively. Both M_s and M_r values are found to increase with increasing CFO content. The coercive field H_c of the composites is much lower than that of the pure CFO.¹⁹ This changed coercive field can be attributed to the change in the total magnetocrystalline anisotropy energy related to the ME coupling due to the compressive stress on the CFO phase caused by the lattice mismatch between the CFO and the NBT phases⁵ and the CFO particle size, particle distribution, etc. may be different from that of its bulk form, which can affect the coercive field.^{20,22}

Figure 4 shows room temperature ferromagnetic resonance (FMR) results obtained on the 70%NBT-30%CFO composite at 9.8 GHz frequency. The external magnetic field is applied parallel to the large surface of the composite samples, and is swept between 2000 Oe to 14000 Oe with superimposed electric field. It is seen in that 70-30 has a very wide and irregular absorption as reported.²³ The appearance of nonsymmetric broad absorption spectra in the composites may be due to the stresses developed during the sintering process and also changes in the total magnetocrystalline anisotropy due to the compressive stress in the CFO phase caused by the lattice mismatch between the CFO and the NBT phases. An applied electric field induces deformation in the piezo-/ferroelectric phase NBT, which leads to a strain in the magnetic phase, CFO, and therefore a change of the effective magnetic field which gives rise to a shift of the

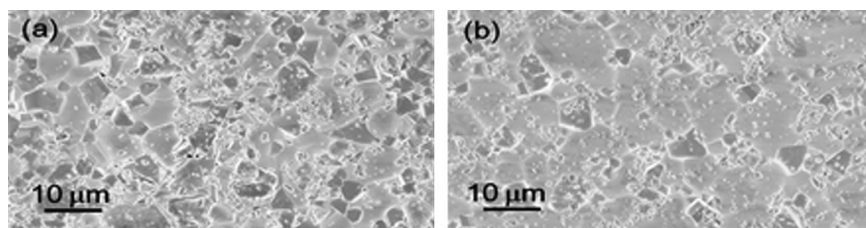


FIG. 2. SEM figures of (a) NBT-CFO 55-45 and (b) NBT-CFO 85-15 composites.

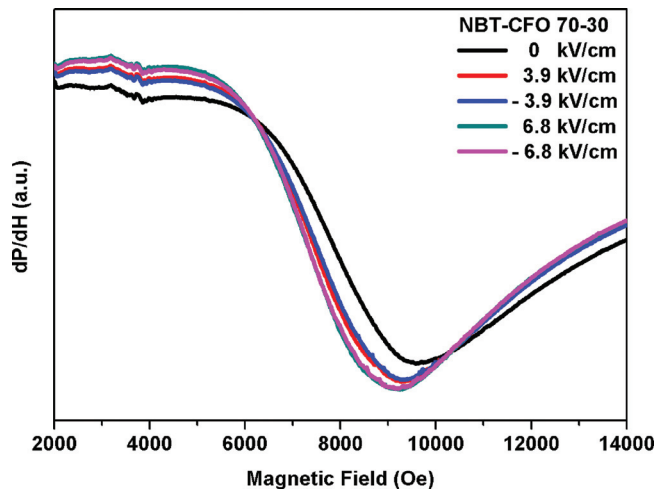


FIG. 4. (Color online) Ferromagnetic resonance (FMR) spectra of NBT-CFO 70-30 composite measured at 9.8 GHz. The profiles of absorption derivative vs static magnetic field (H) are shown for series of applied electric field.

ferromagnetic resonance frequencies. This indicates a giant ME coupling in NBT-CFO composites. The FMR field shifts from 7730 to 7090 Oe on changing an external electric field from 0 and ± 6.8 kV/cm in 70-30 composite. Initially, the composite showed a high electrostatically tuned ferromagnetic resonance field shift (δH_r) of 428 Oe for the applied external electric field of 3.9 kV/cm, and this value is further enhanced to a large value of 640 Oe, when the applied electric field is increased to 6.8 kV/cm. It is important to emphasize that the overall electric-field-induced FMR change of 640 Oe is the largest that has ever been reported in particulate composites. This FMR change is higher than the reported δH_r values of 202 (750 Oe) for FeGaB/PZN-PT single crystal multiferroic heterostructure under an applied external field of 5.8 (8 kV/cm).¹³ This is also higher than spin-spray deposited $Zn_{0.1}Fe_{2.9}O_4$ /PMN-PT single crystal, which showed FMR field shift of 140 Oe under 6 kV/cm external field.¹⁴ On the other hand, the composite with lower ferrite concentration, NBT-CFO 85-15, exhibited FMR field shift (δH_r) of 82 Oe for an applied electric bias field of 3.9 kV/cm, which is comparable with spin-spray deposited $Zn_{0.1}Fe_{2.9}O_4$ /PMN-PT single crystal multiferroic composite. We expect an improvement in the coupling in particulate composites due to enhancement in the interface area, strong adhesion and large stress transfer compared to the laminate type composite.²⁴⁻²⁶

IV. CONCLUSIONS

Novel lead-free multiferroic particulate composites of NBT and CFO produced large electric-field-induced FMR field shift of 640 Oe in the NBT-CFO 70-30 composite.

The giant electrostatically induced tunable magnetic resonance field at microwave frequencies makes them promising candidates for wide-band electrostatically tunable microwave devices.

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