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# Observation of direct and indirect magnetoelectricity in lead free ferroelectric (Na$_{0.5}$Bi$_{0.5}$TiO$_3$)–magnetostrictive (CoFe$_2$O$_4$) particulate composite

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A particulate composite consisting of 65 mol. % Na$_{0.5}$Bi$_{0.5}$TiO$_3$ and 35 mol. % CoFe$_2$O$_4$ was synthesized, and it's structure, microstructure, ferroelectric, magnetostrictive, magnetic, and direct/indirect magnetoelectric properties were studied. The composite showed different magnetization behaviour under electrically poled and un-poled conditions. The percentage change in magnetization as a result of poling is approximately $-15\%$ at 500 Oe magnetic field. Magnetostriction measurements displayed a value of $\lambda_{11} = -57 \times 10^{-6}$ and piezomagnetic coefficient $\delta\lambda_{11}/\delta H = 0.022 \times 10^{-6}\,\text{kOe}^{-1}$ at 2.2 kOe for the composite. The maximum magnetoelectric output varied from 1350 mV/cm to 2000 mV/cm with change in the electrical poling conditions. © *2012 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4745840]

Magnetoelectric materials are a class of multiferroic materials that display simultaneous magnetic and electric ordering and have attracted tremendous interest due to their potential applications in electronic devices[1] such as multi-state memories, tunable filters, sensors, and electromechanical devices.[2] These materials are either in the form of single phase or composites containing two constituent materials exhibiting two different ordering. However, the magnetoelectric (ME) coupling coefficient in single-phase compounds at ambient conditions is typically too small to be useful in applications.[3] Hence, in recent years the focus has been on composite magnetoelectric materials.[4–6]

Several lead-free ferroelectric materials have been investigated as replacement for Lead Zirconate Titanate (PZT)-based ceramics in magnetoelectric composites because of the toxic nature of lead. One of the well-studied Pb free ferroelectrics is sodium bismuth titanate (Na$_{0.5}$Bi$_{0.5}$)TiO$_3$ (NBT). NBT possesses a Curie temperature $T_c$ of 320 °C, a relatively large remanent polarization $P_r$ of 38 $\mu$C/cm$^2$, and a coercive field $E_c$ of 73 kV/cm at room temperature.[7] Cobalt ferrite (CFO) has a much larger resistivity (of the order of M$\Omega$ cm) as compared to $R$-Fe compounds (of the order of m$\Omega$ cm) and are thus more compatible to be coupled with piezoelectric materials which have resistivity of the order of G$\Omega$ cm to form magnetoelectric composites especially for high frequency applications. Ferrites are also known to reach saturation in their magnetostriction at low bias magnetic fields due to their low magnetic anisotropy.[8] CFO has a much higher negative saturation magnetostriction ($-252 \times 10^{-6}$) as compared to Mg ferrite ($-8 \times 10^{-6}$) and Li ferrite ($-5 \times 10^{-6}$).[8]

The ME effect in composite materials is known as a product tensor property and can be attributed to the cross interaction between different orderings of the two phases in the composite. Thus the ME effect in these composites is a result of the product property of the magnetostrictive effect (magnetic/mechanical effect) in the magnetic phase and the piezoelectric effect (mechanical/electrical effect) in the ferro (piezo) electric phase.[9,10] When a magnetic field is applied to the composite, the magnetic phase changes its shape magnetostrictively. The produced strain is then transferred to the piezoelectric phase, resulting in an electric polarization (direct ME effect). On the other hand, when an electric field is applied, the ferro/piezoelectric phase changes its shape electrostrictively, and the produced strain is transferred to the magnetic phase which dynamically alters the magnetic anisotropy of the magnetic phase via their magnetostriction resulting in magnetization (converse or indirect ME effect).[11]

In our earlier studies, we have reported magnetoelectric coupling in single phase-bismuth layered structured ferroelectromagnetics (BLSFs) and composites of BaTiO$_3$–BaFe$_{12}$O$_{19}$ system.[12–16] The key observation from the BaTiO$_3$–BaFe$_{12}$O$_{19}$ composite system is that the magnetoelectric output does not improve beyond 5 mV/cm even up to a field of 10 kOe, irrespective of the processing route adopted. Hence, there is a need to investigate other composite systems with lead free (piezo) electric constituent. In light of the above, we have chosen NBT, which is ferroelectric/piezoelectric, and CFO, which is magnetostrictive/piezomagnetic, and prepared a particulate composite consisting of 65 mol. % NBT and 35 mol. % CFO, henceforth, designated as (65)NBT–(35)CFO. No report is available in literature on this particular lead free multiferroic composite. Its ferroelectric, magnetic, magnetostrictive, and direct/indirect magnetoelectric properties at room temperature were investigated.

NBT, CFO, and (65)NBT–(35)CFO composite were synthesized using the solid state sintering method. Starting raw materials for the synthesis were high purity sodium carbonate (Na$_2$CO$_3$), barium carbonate (BaCO$_3$), titanium dioxide (TiO$_2$), cobalt oxide (Co$_3$O$_4$), and iron oxide (Fe$_2$O$_3$) of Sigma Aldrich (99.99% purity). Stoichiometric amounts of

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above oxides were mixed and ground. Final sintering of the pellets was performed at 1100 °C for 2 h. X-ray diffraction (XRD) studies were carried out using a PANlytical x'pert pro-powder x-ray diffractometer at $2\theta$ scan rate of 0.25°/min with Cu-K$_\alpha$ radiation. The microstructure and distribution of grains were determined using FESEM (ZEISS make). Ferroelectric hysteresis loops were measured using a ferroelectric hysteresis loop tracer (aixACCT Systems, GmbH, Achen, Germany). Magnetization measurements were performed using a vibrating sample magnetometer (Digital Measurement Systems, USA), up to a magnetic field of 2 T. Magnetostriction measurements were carried out using strain gauges and an electromagnet. Magnetoelectric measurements were carried out at room temperature up to a field of 0.8 T.

Fig. 1(a) shows the XRD patterns of NBT, (65)NBT–(35)CFO, and CFO. The XRD patterns of NBT and CFO sintered specimens indicate that they are pure and highly crystalline. NBT has a rhombohedral crystal structure with a lattice parameter of 3.87 Å, and CFO has a spinel cubic crystal structure with a lattice parameter of 8.39 Å. The XRD pattern of the composite shows peaks of both NBT (ferroelectric) and CFO (magnetostrictive) constituents. No intermediate or interfacial phases were detected. However, in the composite, all the XRD peaks are shifted to a lower angle by about 0.06° as shown in Fig. 1(b). This suggests that there is an increase in lattice parameters of the constituents in the composite.

Fig. 2 presents the microstructures of (a) NBT, (b) (65)NBT–(35)CFO, and (c) CFO sintered at 1100 °C. The grain sizes of NBT and CFO are in the range of 2–5 $\mu$m which is evident from the micrographs of NBT and CFO. Dense (5.42 g/cm$^3$) and homogeneous (65)NBT–(35)CFO composite was obtained on sintering at 1100 °C (Fig. 2(b)).



FIG. 2. FESEM images of (a) NBT, (b) (65)NBT–(35)CFO, (c) CFO.

The SEM image for the composite clearly shows the presence of two individual phases (as indicated in Fig. 2(b)) with smaller grains of NBT and larger grains of CFO. Also, the composite did not show any additional phases caused by chemical reaction or inter-diffusion between the two phases, as confirmed by the corresponding XRD patterns (Fig. 1). The composite shows an increase in grain sizes of both NBT and CFO phases when compared to their pure phases as evidenced from Fig. 2.

The ferroelectric hysteresis loops at different applied electric fields for NBT and (65)NBT–(35)CFO composites are shown in Figs. 3(a) and 3(b), respectively. The P-E loops of the NBT as well as the composite do not show saturation. It should be noted that recording well saturated loops in NBT is difficult because of the large coercive field and relatively large conducting nature of NBT.[17] The P$_s$ and P$_r$ values for NBT are 34.5 $\mu$C/cm$^2$ and 27 $\mu$C/cm$^2$, respectively. It can also be observed from Fig. 3(b) that the spontaneous polarization (14.02 $\mu$C/cm$^2$) and remanence (16.35 $\mu$C/cm$^2$) values of the composite are marginally lower when compared to NBT. This can be attributed to the lower resistivity of the CFO phase as compared to the NBT phase which offers a leakage path for the charges developed across the ferroelectric phase.

In order to measure the indirect magnetoelectric coupling between the ferroelectric and magnetostrictive constituents, the (65)NBT–(35)CFO composite was electrically poled at a field of 25 kV/cm at a temperature of 70 °C for 1 h. The electrically poled and un-poled samples were subjected to magnetization measurements at room temperature.


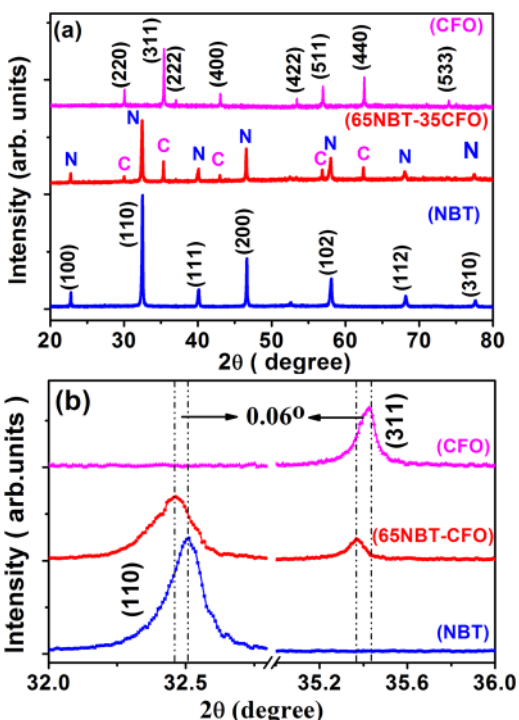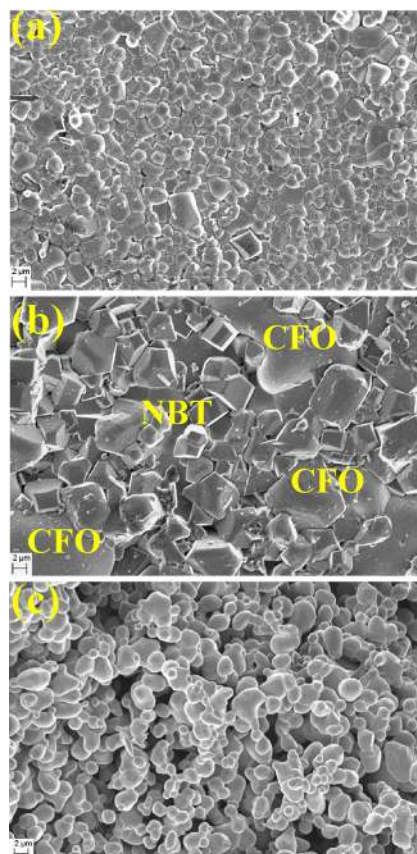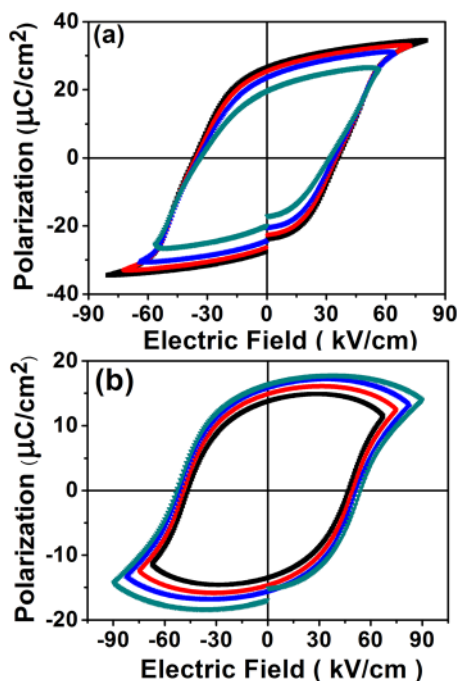
FIG. 1. (a) X ray diffraction of sintered NBT, CFO, and (65)NBT–(35)CFO. (b) The shift in parent peaks towards lower angle for (65)NBT–(35)CFO.

FIG. 3. (a) PE Hysteresis loops for NBT at different fields (b). PE hysteresis loops for (65)NBT–(35)CFO at different fields.



FIG. 4. Magnetization verses magnetic field plot of electrically poled and un-poled composite. (a) Magnified image from −0.7 to 0.7 kOe. (b) Percentage change of magnetization with bias magnetic field for electrically poled composite.

Fig. 4(a) displays the plot of magnetization versus magnetic field for electrically poled as well as un-poled (65)NBT–(35)CFO composite at room temperature.

It can be clearly seen from Fig. 4(a) that there is a significant difference in the coercivity, remanence, and spontaneous magnetization values for the poled and un-poled composites. The electrically poled composite showed lower values of magnetization (15% lower at 500 Oe) when compared to un-poled sample. A similar kind of behaviour was also observed by other investigators.[18–20] This can be attributed to the fact that the ferroelectric dipoles align along the electric field direction (z-direction) when the sample is electrically poled at 70 °C and subsequently quenched from 70 °C to room temperature in the presence of electric field, and some of the electric dipoles will remain in the poled direction (remanent polarization). These aligned dipoles do not return to their original positions easily because of their stability. In addition, during the poling process the ferroelectric phase shows elongation in the field direction. This elongation produces compressive stress along z direction and tensile stress along magnetization direction (Y direction) in the magnetic phase. This stress can alter the magnetic domain structure and create a new source of magnetic anisotropy which changes the magnetization values. Materials which show positive magnetostriction elongate when they are magnetized. In such cases, the presence of tensile stress will result in an increase in magnetization whereas the presence of compressive stress will decrease it. On the contrary, in materials that show negative magnetostriction, the presence of compressive stress will result in increasing in magnetization whereas the presence of tensile stress will decrease it. These conclusions are valid whether or not a field is acting as long as M is not zero, because a stress applied to a demagnetized specimen will not produce any magnetization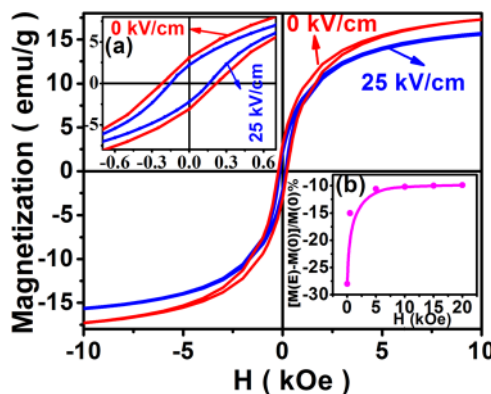.[21] In the present composite system, CFO exhibits negative magnetostriction. Hence the presence of tensile stress along magnetization direction due to elongation of NBT (ferroelectric) phase in the z direction results in a reduction in the magnetization values.

Fig. 4(b) shows the percentage change of magnetization values with increasing magnetic bias field (H) for the electrically poled composite sample. It is observed that the percentage change of magnetization $[M(E) − M(0)]/M(0) \times 100$ under various magnetic bias fields (H) also changes and its values decrease when bias field is increased upto 4 kOe. This is consistent with the observation that the magnetic anisotropy due to applied stress has more effect on low field magnetic properties such as permeability and remanence and less effect on high field properties.[21]

Magnetostriction measurements were performed on (65)NBT–(35)CFO and pure CFO for several times, and the average data is presented in Fig. 5. With the increase of magnetic field, the magnetostriction coefficient, $\lambda_{11}$, shows a decreasing trend and attains a saturation value of $−262 \times 10^{-6}$ at 6.2 kOe field. On the other hand, magnetostriction coefficient, $\lambda_{12}$, shows a increasing trend with increase in magnetic field and attains a saturation value of $95 \times 10^{-6}$ at 7.3 kOe field for CFO as shown in Fig. 5(a). Similar kind of behaviour is also observed for the composite but the saturation value for $\lambda_{11}$ is $−57 \times 10^{-6}$ at 6.7 kOe field and saturation value for $\lambda_{12}$ is $28 \times 10^{-6}$ at 5.5 kOe field. The variation in piezomagnetic coefficient (q) with dc magnetic field in CFO and (65)NBT–(35)CFO composite is shown in the inset of Fig. 5. The piezomagnetic coefficient is given by the equation $q_{ij} = (\delta\lambda_{ij}/\delta H)$. Hence, the transverse and longitudinal piezomagnetic coefficients are represented as $q_{11} = \delta\lambda_{11}/dH$ and $q_{12} = \delta\lambda_{12}/dH$, respectively. Initially $q_{11}$ increases with an increase in magnetic field and shows a maximum value of $0.16 \times 10^{-6}$ kOe$^{-1}$ field at 2.15 kOe for CFO and $0.022 \times 10^{-6}$ kOe$^{-1}$ at 2.2 kOe field for the composite and then subsequently decreases with further increase in magnetic field. On the other hand, $q_{12}$ does not vary significantly, with change in magnetic field for both CFO as well as (65)NBT–(35)CFO composite.

The observed change in all the magnetic parameters can be attributed to the change in the shape and stress induced magnetic anisotropy energy related to the inter coupling
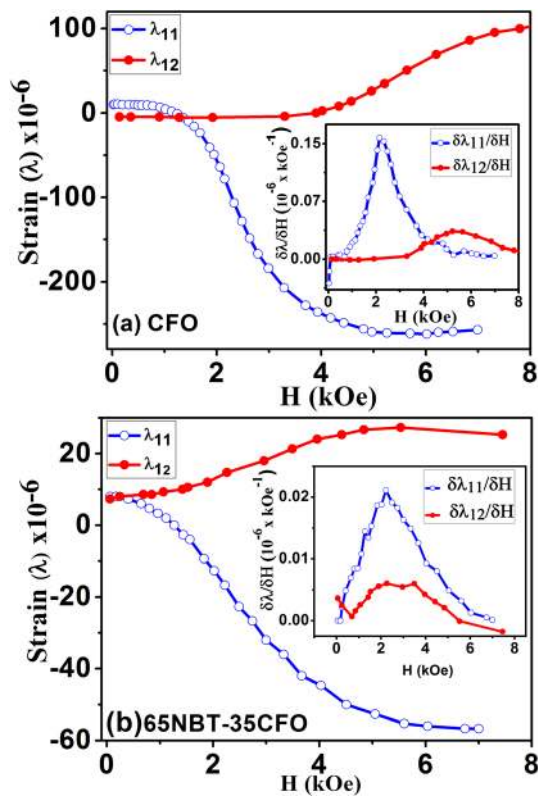
FIG. 5. Variation in magnetostriction coefficients $\lambda_{11}$ and $\lambda_{12}$ with magnetic field. Inset shows variation in piezomagnetic coefficient with magnetic field plot. (a) CFO, (b) composite.



FIG. 6. Magnetoelectric output verses magnetic field for (65)NBT–(35)CFO.

between the ferroelectric and magnetostrictive phases. In the composite, the individual ferrite grains act as centers of magnetization, and the saturation magnetization of the composite is its vector sum. The ferroelectric (non-magnetic) grains present in the composite act as pores in presence of magnetic field. The presence of the pores breaks the magnetic contacts between the magnetic grains.[22] Hence, increase in porosity (nonmagnetic phase) changes the magnetic anisotropy in the composite which reduces the net magnetization resulting in the reduction of magnetic properties for (65)NBT–(35)CFO composite as compared to CFO.

In order to demonstrate the direct coupling between ferroelectric and magnetostrictive sub-lattices in (65)NBT–(35)CFO, ME voltage was measured as a function of magnetic field at room temperature for two different poled conditions as illustrated in Fig. 6. For the composite which is poled at 25 kV/cm, ME voltage increases with increasing magnetic field reaches a maximum of 2000 mV/cm at 4 kOe field and then decreases to 250 mV/cm at a field of 7 kOe. On reversing the field from 7 kOe to 350 Oe the output voltage decreased to −1700 mV/cm and showed hysteresis. The composite sample which is poled at 15 kV/cm shows a maximum output value of 1250 mV/cm at 3.5 kOe field and minimum value of 150 mV/cm at 6.5 kOe field. On reversing the field from 6.5 kOe to 350 Oe, the output voltage decreased to −1150 mV/cm and exhibited half butterfly loops. This may be attributed to the strains generated in the composite which reverse magnetostrictively when magnetic field is reversed. Generally in piezoelectric materials, if an external force is applied to produce compressive or tensile strain in the mate-
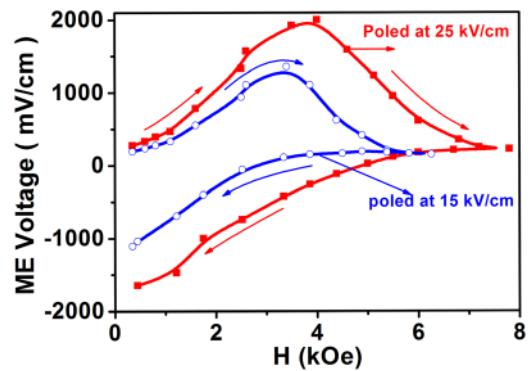
rial, the resulting deformation causes a change in dipole moment so that voltage appears across the sample. The measured voltage changes polarity when mechanical stress is changed from compression to tensile. The observation of a negative ME output when magnetic field is reversed is consistent with this behaviour. Similar kind of behaviour was also observed for PZT-LSMO and PZT-NFO composites.[23] The increased ME output exhibited in the magnetic field range of 1.5–4 kOe, maybe attributed to the fact that the domain wall mobility and domain alignment is much higher in this field range. This is confirmed by the observation of significant differences between electrically poled and un-poled specimens with change in magnetic field in the field range of 1.5–4 kOe. In addition, the magnetostrictive coefficient of CFO reaches saturation at 4 kOe, and hence further increase in field does not result in increase in magnetostriction.

Lead-free multiferroic particulate composite (65)NBT–(35)CFO were synthesized without any impurity phases. The composite exhibited M-H as well as P-E hysteresis loops. A variation in magnetization values and ME output values were observed by varying electric poling conditions. Direct and indirect ME measurements indicated that there was a strong intercoupling between ferroelectric/magnetic phases in the field range of 1.5–4 kOe. This particular composite has shown a much larger magnetoelectric output at room temperature as compared to any other NBT based composites reported in the literature.

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