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Dependence of magnetoelectric properties on the magnetostrictive content in 0–3 composites

Mohsin Rafique[a,*], Syed Qamar ul Hassan[a], M.S. Awan[b], Sadia Manzoor[a,b]

[a]*Magnetism Laboratory, Physics Department, COMSATS Institute of Information Technology, Park Road, 44000 Islamabad, Pakistan*
[b]*Center for Micro and Nano Devices (CMND), COMSATS Institute of Information Technology, 44000 Islamabad, Pakistan*

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Abstract

The magnetoelectric response in composites of barium titanate (BTO) and cobalt ferrite (CFO) has been determined by measuring the magnetoelectric susceptibility coefficient. This was done by two different methods: magnetocapacitance measurements and magnetoelectric voltage measurement using a lock-in technique. These composites were prepared by the sol–gel method. Four different compositions with different molar ratios of the magnetostrictive phase (CFO) embedded in a piezoelectric matrix of BTO were studied to investigate the effect of the magnetostrictive content and the number density of interfaces on the magnetoelectric response. It was found from both techniques that the magnetoelectric coupling effect increases with the increase of applied field and it had a non-linear dependence on the percentage of magnetostrictive content in the composites.

Keywords: A. Sol–gel processes; B. Composites; C. Piezoelectric properties

1. Introduction

Multiferroics are materials which simultaneously exhibit more than one ferroic order [1–4]. The most interesting ferroic orders for technological applications are ferromagnetism and ferroelectricity. Materials in which these orders occur simultaneously and are coupled to each other are called magnetoelectric (ME) multiferroics. These are the most promising materials in achieving an efficient mutual control of magnetism and electricity, i.e. modifying magnetization by using an electric field or controlling electric polarization by a magnetic field [5–9]. ME multiferroics have applications in novel multifunctional devices and a new generation of spin-based low-power-consumption electronics [9–12].

ME coupling is an intrinsic property of some single phase compounds e.g. $TbMnO_3$, $BiFeO_3$ etc. However in these intrinsic multiferroics, the coupling is very weak at device operating temperatures, which hinders their practical applications [13,14]. However, in composites made of piezoelectric and magnetostrictive materials, the two phases mechanically couple to produce a strain mediated ME effect at room temperature, several times higher than that of single phase multiferroics [10–14]. When a composite ME multiferroic is placed in a magnetic field, the magnetostrictive phase gets strained. This strain is transferred to the piezoelectric phase inducing polarization in it. (The converse happens in an electric field.) This polarization can be detected in terms of the electric field induced across the sample (dynamic method) or the change in the dielectric response of the sample (magnetocapacitance (MC) method).

Both the above methods can be used to find the magnetoelectric coupling coefficient α which quantifies the strength of the ME coupling. This is the ratio of the electric polarization P induced in a sample when exposed to a magnetic field H (direct ME effect) or the ratio of the magnetization M induced by an electric field E (converse ME effect). Many candidates for ME composites are in fact poor insulators that cannot sustain the electric fields required to switch the polarization making it difficult to measure the ME coefficient directly.

In this paper we report a comparison of the results obtained from the dynamic method and the MC method. Both methods give somewhat different values of α but there is a similarity in these results. Both of these methods

*Corresponding author.
E-mail address: mmohsin8389@gmail.com (M. Rafique).

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show a non-linear dependence of the coupling coefficient on the ratio magnetostrictive content in the composites. Another similarity is the linear dependence of α on the applied magnetic field strength. We find that the two methods complement each other in different frequency ranges.

2. Experiment

2.1. Preparation of composites

The sol–gel method was used to prepare the cobalt ferrite–barium titanate nanocomposites. The gels of both constituents were prepared with equal molarities and mixed in four different molar ratios: 20–80, 30–70, 40–60 and 50–50. These were labeled as the 20–80, 30–70, 40–60, and 50–50 CFO–BTO composites respectively. The gels were dried at 120 °C to obtain the composite powders, which were calcined at 850 °C for 2 h in air. The powders were subsequently pressed into pellets using cold isostatic pressing and then sintered at 1000 °C for 12 h. Silver paste was used to paint electrodes onto the faces of the pellets. The densities of the samples are given in Table 1.

2.2. Characterization of composites

Crystalline phase and structure of the CFO-BTO composites were studied by using an X-ray diffractometer (Xper Pro, Panalytical company) with Cu Kα radiation. Magnetic properties of the nanocomposites were measured by a vibrating sample magnetometer (Riken-Denshi). The magneto-capacitance of the composites was measured using a permanent magnet and a Wayne Kerr Precision Component Analyzer (6440B).

The experimental set-up to measure the ME effect using the lock-in technique consists of a Helmholtz coil driven by an AC current generated by an Escort EGC-2230 function generator at frequencies up to 20 kHz. The amplitude of the AC field is measured using a guassmeter (Lakeshore 475 DSP) in RMS mode. The transverse (voltage measured perpendicular to applied magnetic field) and longitudinal (voltage measured parallel to applied magnetic field) ME effect was studied as a function of the AC magnetic field frequency. The ME votlage was detected by using a lock-in amplifier (Standford Research System, SR 830) in differential mode.

Table 1
Densities of the prepared samples.

Sample name	20–80	30–70	40–60	50–50
Density (g cm^{-3})	3.404	3.284	3.102	3.024

3. Results and discussion

3.1. Crystallography

The X-ray diffraction confirmed the presence of the spinel and perovskite phases representing the CFO and BTO respectively in all samples. No peaks corresponding to impurity phases were found in the diffraction pattern of any sample.

Fig. 1 shows the XRD result for the 50–50 sample. The normalized intensities of the major peaks were also found to be in proportion to the content of the CFO or BTO phase.

3.2. Magnetic and ferroelectric properties

The M-H loops in Fig. 2 shows the magnetically ordered structure of CFO–BTO composites. The saturation and remnant magnetizations increase with the increase of CFO content.

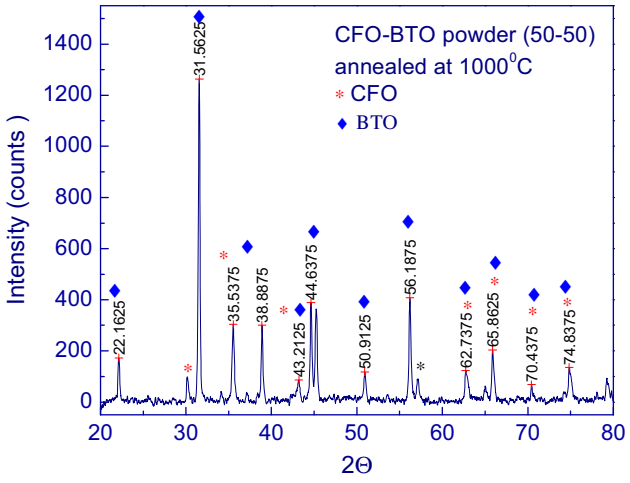

Fig. 1. X-ray diffraction pattern of the 50–50 $CoFe_2O_4$–$BaTiO_3$ composite.

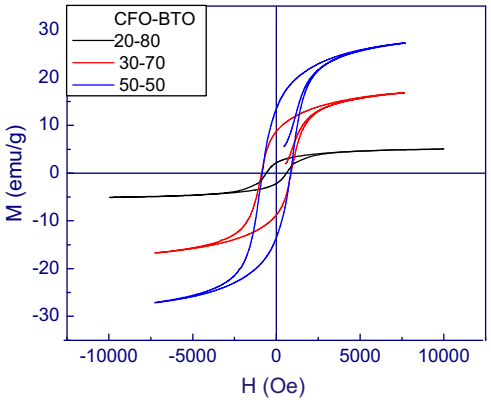

Fig. 2. Magnetization hysteresis loops of CFO–BTO composites.

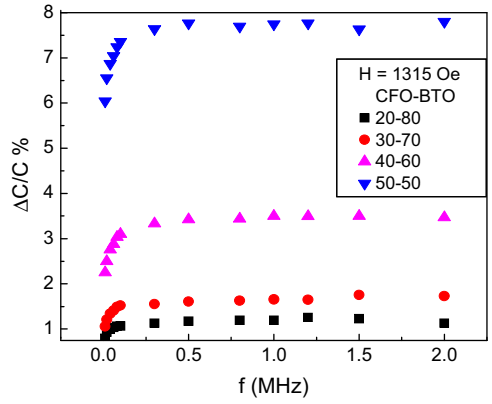

Fig. 3. Frequency dependence of magnetocapacitance for different samples.

3.3. Magnetocapacitance

Magnetocapacitance is defined as the change in capacitance in the presence of a magnetic field normalized by the zero-field capacitance, i.e.

$$MC = \frac{C(H) - C(H=0)}{C(H=0)} = \frac{\Delta C}{C} \quad (1)$$

The magnetocapacitance as a function of the frequency of the AC voltage (1 V) applied to the sample capacitor is shown in Fig. 3.

All samples display a positive magnetocapacitance. This is in agreement with similar results obtained on CFO–PZT composite films [15,16] and CFO–BTO core-shell nanocomposites. MC increases from about 1% in the 20–80 composite to 7.8% in the 50–50 composite. The above data were used to extract the magnetic field dependence of the magnetocapacitance at a fixed frequency of 0.5 MHz. The results are shown in Fig. 4(a). The MC is quite small and increases linearly at low fields for all samples. After about 1100 Oe, there is a sharp increase in the MC for all samples and this was verified several times in experiment. This effect is the largest for the 50–50 composite. Higher DC fields could not be used due to experimental limitations, but this will be done in the future. The reason for this sharp increase is not entirely clear but we believe that this is due to the sudden sharp increase in the magnetostriction of CFO at about the same values of the DC field [17,18].

Fig. 4 shows the variation of MC with CFO concentration for a fixed field $H=1315$ Oe and different frequencies. We find a strong nonlinear dependence of MC on the CFO content. This is due to the compound effect of an increase in the magnetostrictive phase as well as an increase in the number density of CFO–BTO interfaces. There is an ongoing controversy in the literature that the MC effect in composite multiferroics may not be a measure of the magnetoelectric coupling [19]. It has been argued that magnetoresistive samples with Maxwell–Wagner behavior could show magnetocapacitance; this cannot be taken as evidence of magnetoelectric coupling. In order to confirm

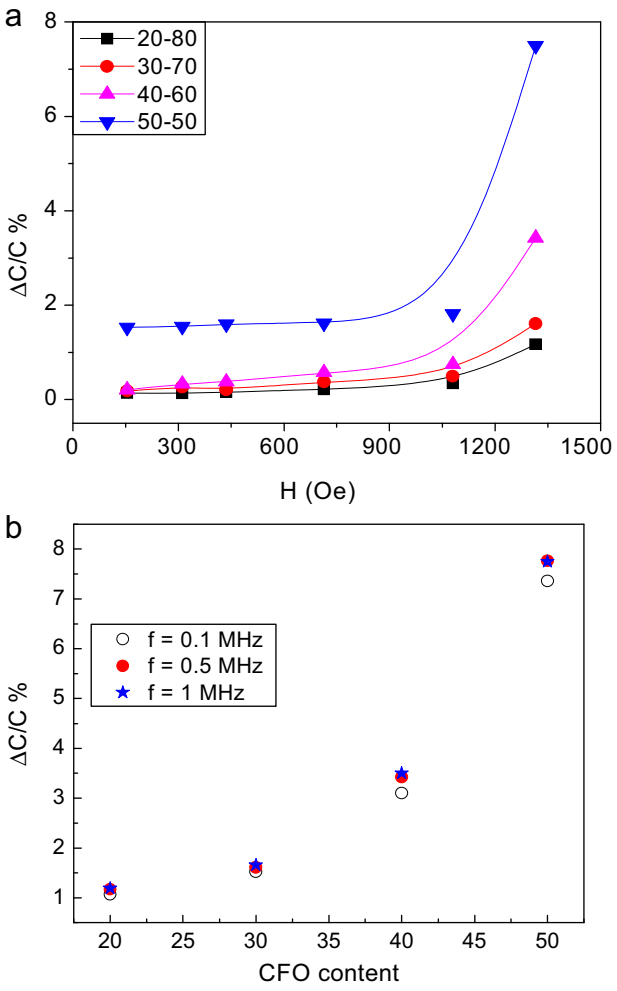

Fig. 4. Percentage magnetocapacitance vs. (a) H for different compositions of the CFO–BTO composite, and (b) CFO content in CFO–BTO composites at a fixed field of $H=1315$ Oe.

the existence of ME coupling we have measured the magnetoelectric voltage coefficient α_E in the following section. This is related to the ME coupling coefficient by $\alpha = \varepsilon_o \varepsilon_r \alpha_E$.

3.4. Magnetoelectric voltage coefficient

The dependence of the output voltage on the amplitude of the applied AC magnetic field measured for different samples is shown in Fig. 5. This voltage was measured transverse to the applied AC field using a lock-in amplifier at a frequency of 1 kHz.

All samples show a linear dependence of the transverse voltage on AC field amplitude. These data were used to calculate the magnetoelectric voltage coefficient according to the following relation:

$$\alpha_V = \frac{V_{out}}{tH_{AC}} \quad (2)$$

where V_{out} is the output voltage t is the thickness of the pellet and H_{AC} is amplitude of the AC magnetic field. The

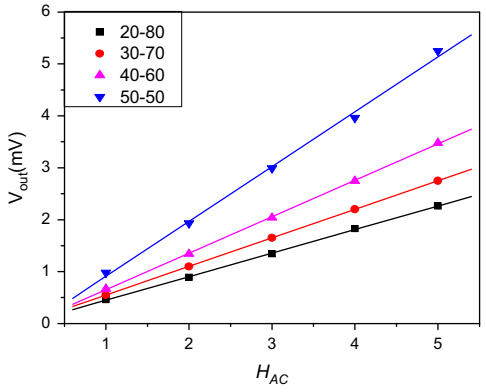

Fig. 5. Dependence of transverse output voltage on amplitude of AC magnetic field measured for different samples at f=1 kHz.

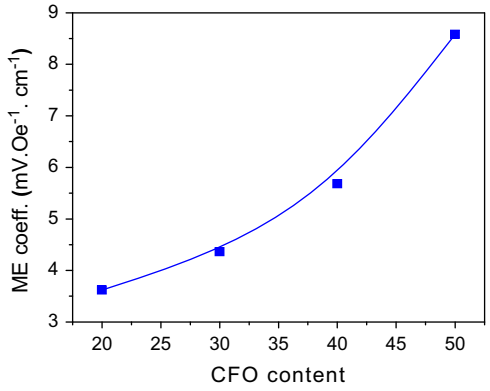

Fig. 6. Dependence of ME voltage coefficient on CFO content in the composites.

dependence of ME voltage coefficient on the CFO content is shown in Fig. 6. This clearly nonlinear behavior is similar to that obtained in Fig. 4(b).

4. Conclusions

We have measured the magnetocapacitance and ME voltage coefficient of CFO–BTO composites and found that it depends in a similar manner on the applied magnetic field and the CFO content. Both measurements imply a strain mediated magnetoelectric coupling in these materials.

Acknowledgments

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