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Magnetodielectric Properties of Multiferroic Composite Films

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ABSTRACT

In this work we report the magnetic and magnetodielectric properties of two types of composite films, namely, (i) $CuFe_2O_4$- Poly (vinylidene-fluoride)-$BiFeO_3$ (CBO) and (ii) $CuFe_2O_4$-Poly (vinylidene-fluoride)-$PbTiO_3$ (CPO) at room temperature. These films were synthesized by solid state reaction of ceramics followed by hot press method. Distinct ferroelectric domains observed by using piezoelectric force microscopy and the hysteresis loops observed in magnetization measurements; show the multiferroic nature of both the films. The coercive fields, H_c were observed to be ~ 0.835 kOe and ~0.7305 kOe for CBO and CPO films, respectively, whereas the values of remnant magnetization, M_r were found ~ 4.3 emu/g and ~ 4.9 emu/g, respectively. Moreover, we observe a systematic enhancement (more than 7 %) of dielectric constant with increase in strength of magnetic field for both of these films. Although $BiFeO_3$ is multiferroic material but due to good magnetodielectric behaviour in this composite film represents a sign of strong effective mechanical interaction between $CuFe_2O_4$ and $BiFeO_3$ through the polymer matrix. This type of study may lead to innovative solution for various technological application such as memory devices, magnetic sensors, spin based devices (spintronics)etc.

Keywords: Multiferroics material, Magnetocapacitance, Magnetic field, Ferroelectric domains

1. INTRODUCTION

Multiferroics are the materials which simultaneously show ferromagnetism in which magnetic polarization can be changed with magnetic field as well as ferroelectricity where electric polarization can be changed with applied electric field. Recently peoples have great interest in multiferroics due to discovery of many new compounds with a strong multiferroic coupling and its potential for replacement in various electronic devices. The discovery of these type of materials came from charge control with applied magnetic field as well as spin control with applied voltages which results into multifunctional devices. The coupling between electric polarization and intrinsic magnetization of these materials give rise to magnetodielectric effect. In presence of external electric field the magnetic dipoles will reorient, which results in a net shift in magnetization direction of the material. This type of magnetic control would allow for magnetic switching using an applied electric field, this could be applied towards improvement of memory devices, electronic systems, innovative solution for application in spintronics devices transducers, sensors, data storage, switching devices, etc [1, 2]. Apart from applications in magnetoelectric devices multiferroics might find applications as microwave absorption materials due to magnetoelectric coupling in these materials [3]. Some multiferroics material found in nature such as Cr2O3, Ti2O3, GaFeO3, PbFe0.5Nb0.5O3, and many others have been widely investigated [4, 5, 6, 7]. Since these materials exhibit the magnetoelectric effect but the changes are not significant enough to allow for large-scale applications [8]. The solution to this problem is fabrication of synthetic multiferroics which results to artificial multiferroic devices. The coupling in these artificial devices is higher as compared to naturally occurring multiferroics. Perovskite-type $BiFeO_3$ is

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well known room temperature multiferroics with simultaneous ferroelectric (T_c=1103 K) and G-type antiferromagnetic (T_N = 643 K) nature [9-12]. In $BiFeO_3$, Bi–O orbital hybridization (or covalency) due to Bi $6s^2$ lone pair is responsible for the ferroelectric instability while Fe–O–Fe antisymmetric Dzyaloshinskii–Moriya exchange gives rise to a complicated magnetic order [13]. Lead Titanate ($PbTiO_3$) is a ferroelectric ceramic but has not been proved to be a technologically important material by itself. It is a significant component material in electronics such as capacitors, ultrasonic transducers, thermistors, and optoelectronics. Till date, researchers have synthesized composites of ferrites ($CoFe_2O_4$, $CuFe_2O_4$, and $ZnFe_2O_4$) with PZT/$BaTiO_3$/$BiFeO_3$ both in bulk and thin films in order to enhance the multiferroic properties [14]. Recently, a large ME output has been reported in nanocomposites of Co and Cu ferrites with ferroelectric $BiFeO_3$ as piezoelectric phase [15]. In spite of these, literature survey indicates that not much detailed work has been done on the magnetoelectric in composite thick film.

In this work, we have done a systematic study on local ferroelectricity, magnetic and magnetoelectric properties of $CuFe_2O_4$- Poly (vinylidene-fluoride)-$BiFeO_3$ and $CuFe_2O_4$-Poly (vinylidene-fluoride)-$PbTiO_3$ composite films. Here, poly (vinylidene-fluoride) (PVDF) works as a matrix to enhance the magnetoelectric properties in composite ceramics or in other words to bind the two different types of materials strongly. A similar study were also carried by K L Yadav in his research paper in research material express but with different material that is Nickel ferric oxide and barium titanate[16].

2. EXPERIMENTAL DETAILS

$CuFe_2O_4$, $PbTiO_3$ and $BiFeO_3$ ceramics were prepared using high purity grade chemicals (99.99% purity) Cu_2O, Fe_2O_3, PbO, TiO_2 and Bi_2O_3 powders. The components were weighted as per their stoichiometric ratios and wet mixed for approximately 3 h in acetone medium. After getting a well mixed powders, we calcined the so obtained powder at 1000 ºC (820 ºC, $BiFeO_3$) for 2 h in alumina crucible in glass furnace. Then the obtained mixtures of $CuFe_2O_4$: $PbTiO_3$ and a-PVDF were grinded nearly for ~ 3 h with 2:1 weight ratio of ceramics to the polymers. Similarly, mixtures of $CuFe_2O_4$: $BiFeO_3$ and a-PVDF were grinded for ~ 3 h with 2:1 weight ratio of ceramics and polymers. Finally obtained powders (ceramics and PVDF) were hot pressed for about 20 minutes at 180 ºC in a hot polymer press with a pressure of approximately 5 MPa and then cooled to room temperature slowly. We get a film of the order of millimeter and for precise measurement we utilize AFM technique for measuring the thickness of obtained films and we have found that the thickness of $CuFe_2O_4$–poly (vinylidene-fluoride) (a-PVDF) – $PbTiO_3$ (CPO) composite film ~ 0.3 mm and thickness of $CuFe_2O_4$- Poly (vinylidene-fluoride)-$BiFeO_3$ composite film ~ 0.25 mm. In order to find its magnetodielectric properties we put a conductive coating on cross section 10×10×0.3 mm and 10×10×0.25 mm of both the films. This conductive layer is important in order to ground the sample during the measurement of the magnetodielectric properties. Magnetic properties were measured by vibrating sample magnetometer (VSM) by varying the applied magnetic field. Local ferroelectricity was observed by PFM (Piezoelectric Force Microscopy) by applying the voltage to the tip and analyzing the small deformation in the sample.

3. RESULTS AND DISCUSSION

In this work we have done ferroelectric measurement of both the films using an atomic force microscopy (AFM, make asylum research) by operating it in the contact-resonance enhanced mode of piezo response microscopy (PFM). A conductive tip coated with Pt/Ir has been used for all PFM studies so that we can ground the sample. In PFM, the ac voltage $V=V_{ac}\cos\omega t$ with a dc voltage (V_{dc}) is applied between the tip and sample, and if our sample has the piezoelectric properties, then the area below the tip will be deformed (attract or repel) due the applied external electric field and can be figure out easily by monitoring the amplitude value. Amplitude of the tip can be written as $A= A_0 +A\omega \cos (\omega t+\varphi)$. Here, φ (Phase change) gives the information about electric polarization under the tip. When a graph is plotted between $A\omega$ and V_{dc}, then the resultant graph so obtained is called ‘butterfly loop’, which is considered as a sign of piezoelectricity in the sample. Moreover switching in phase is directly related to the switching of ferroelectric domains. The phase image shows regions with high (bright) and low (dark) values of φ. From the bright to the dark region the phase φ shifts by 180° indicating that the bright and dark regions are respectively ‘up’ polarized and down polarized ferroelectric domains [17]

Here, in Figure 1 (a) represents topographic image of 2μm×2μm area on the CPO film using DART PFM [18] and (b) phase image on the same region of the CPO film as in (a) indicating domains at 300 K. Similarly, Figure 2 (a) topographic image of 2μm×2μm area on the CBO film using DART PFM and (b) phase image on the same region of the CBO film as in (a) showing domains at 300 K. Similarly, Figure 2(a) shows topographic image of on a 2μm×2μm area on the CBO film using DART PFM and (b) phase image on the same region of the CBO film as in (a) showing domains at 300 K.

Figure 3 (a) represents the hysteresis curve between phase and dc bias of 35 V and (b) represents the butterfly like curve for CPO film at room temperature (300 K). Similarly, figure 4 (a) represents the hysteresis curve between phase and dc bias of 30 V and (b) butterfly like curve for CBO film at room temperature. Figure 5 (a) represents the change in magnetization of CPO film. From the image we can determine that the coercive field (±2H_c) and remnant magnetization (M_r) were found to be ~ 1.45 kOe and ~ 4.9 emu/g respectively.

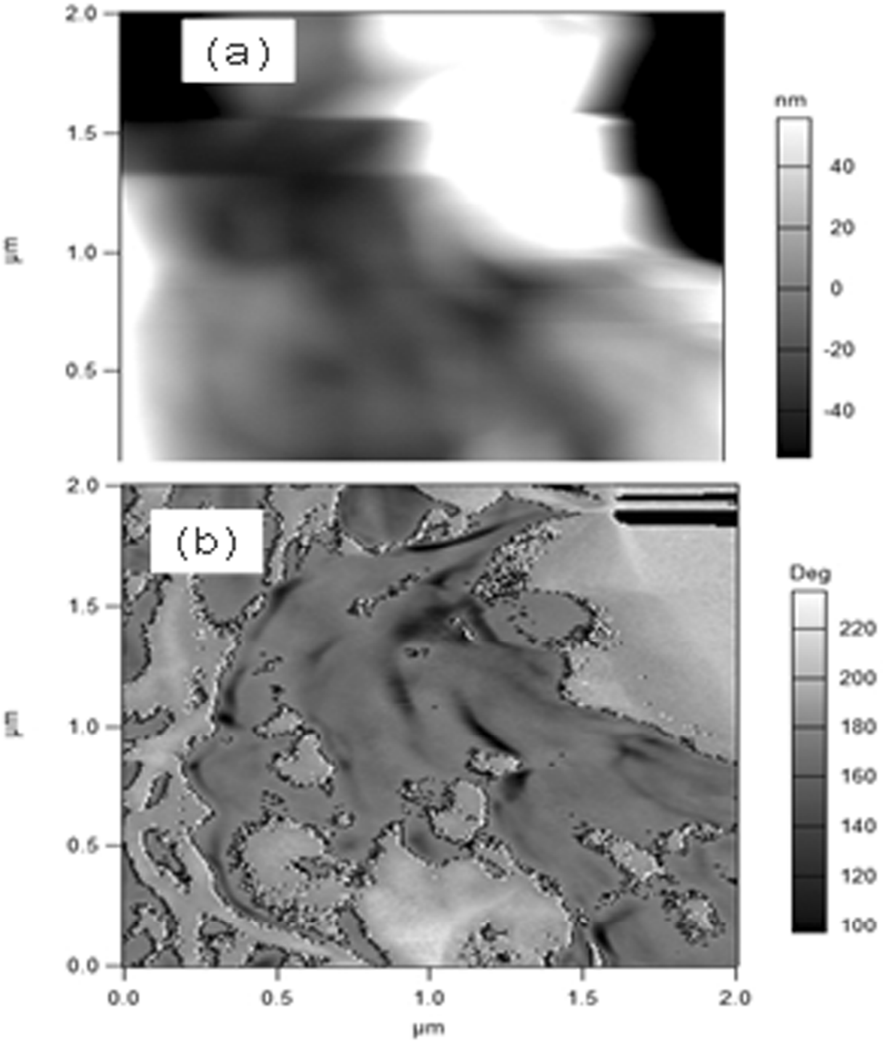

Figure 1: (a) Topographic image on 2μm×2μm area on the CPO film using DART PFM. (b) Phase image on the same region of the CPO film as in (a) showing domains at 300 K.

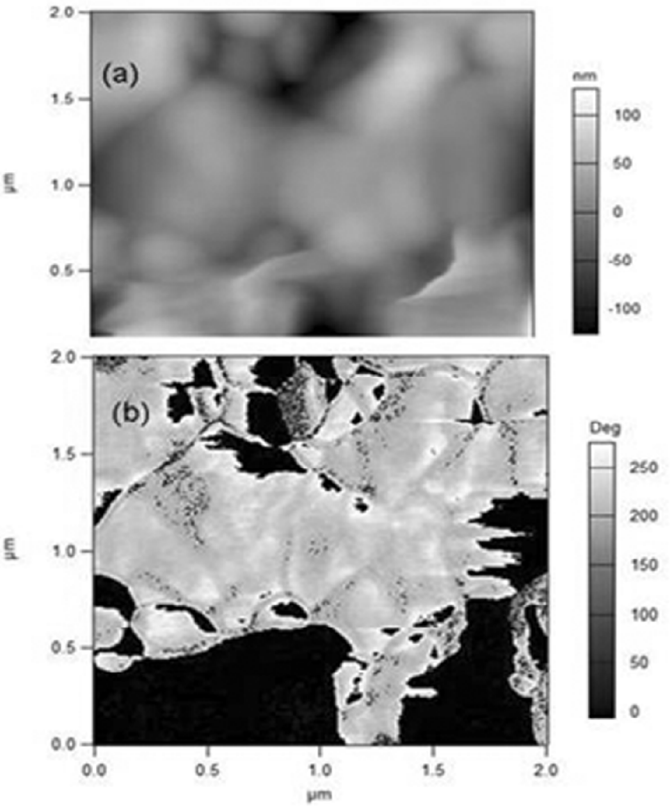

Figure 2: (a) Topographic image on $2\mu m\times 2\mu m$ area on the CBO film using DART PFM. (b) Phase image on the same region of the CBO film as in (a) indicating domains at 300 K

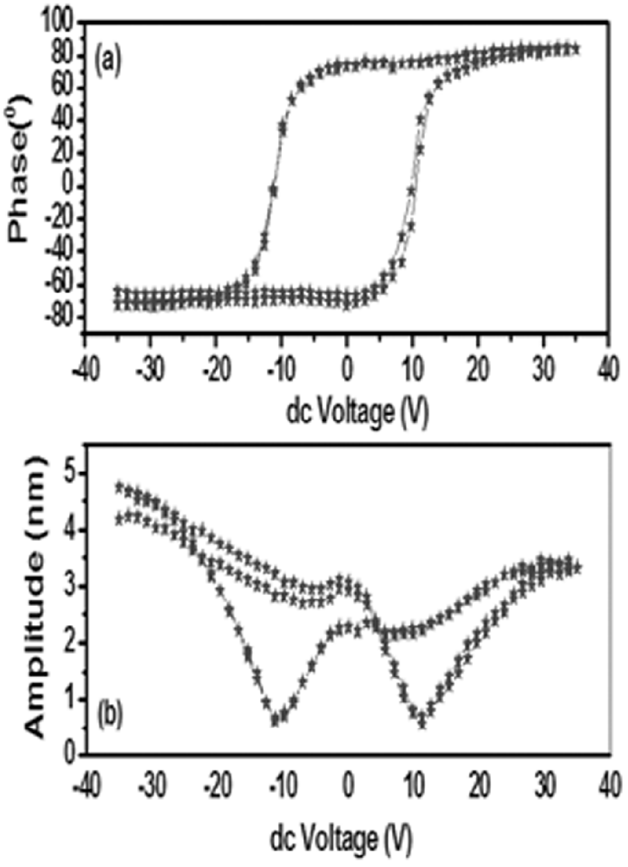

Figure 3: (a) Hysteresis curve between phase and dc bias of 35 V (b) butterfly like curve for CPO at room temperature

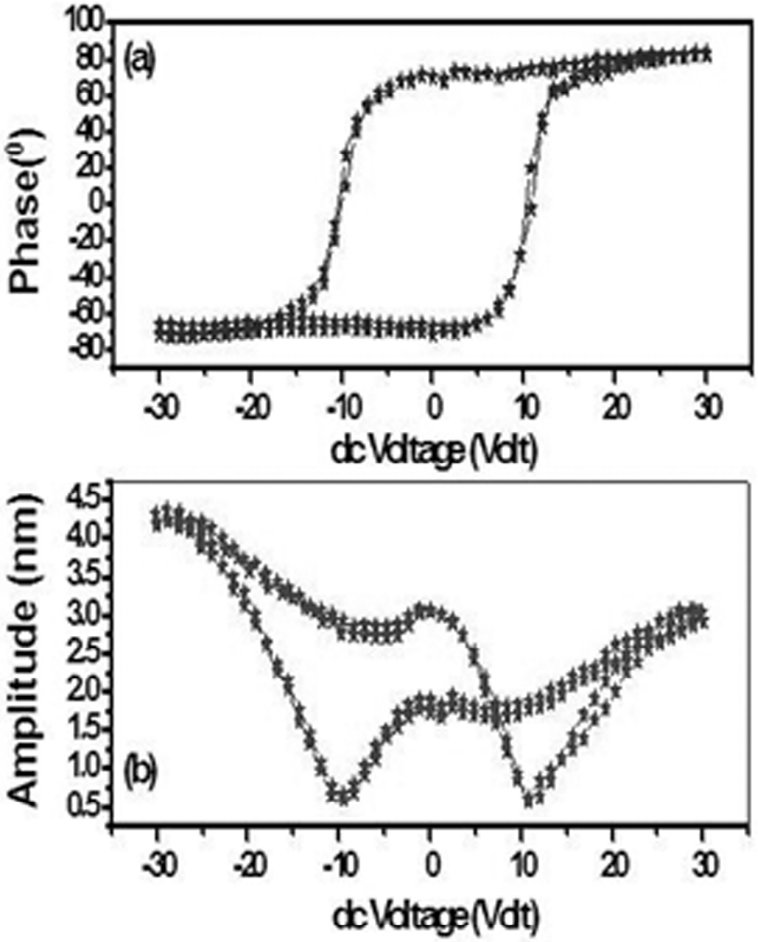

Figure 4: (a) Represents the hysteresis loops between phase and dc bias of 30 V (b) Represents butterfly-like loops for CBO film at room temperature

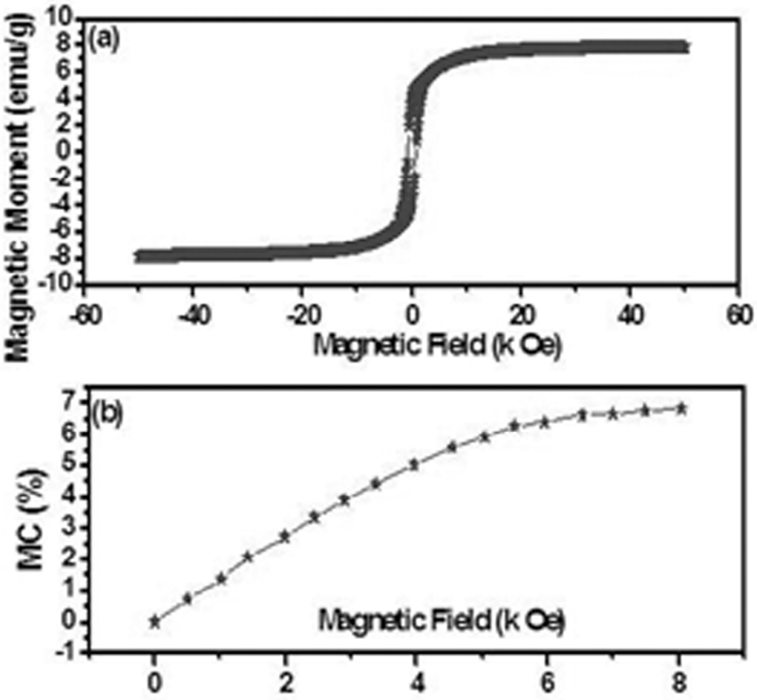

Figure 5: (a) Represents the change in magnetization with magnetic field of CPO film at room temperature. (b) Change in magnetocapacitance with magnetic field of the composite film at room temperature.

In the presence of magnetic field the magnetic domain induces strain in multiferroic material, since there is coupling between the magnetic and ferroelectric domains, the strain will induce stress in ferroelectric domains that will produce an electric field. Due to change in electric field the dielectric behavior of material will be changed with applied magnetic field. In this way we can indirectly change the electric behavior of material by applying magnetic field. The magnetocapacitance value can be evaluated using below mentioned formula:

$$MC\left(\%\right) = \frac{\varepsilon'(H) - \varepsilon'(0)}{\varepsilon'(0)} \times 100$$

Where ε′(H) and ε′(0) denote the values of ε′ in the presence and absence of magentic field (H) respectively. Figure 5 (b) and figure 6 (b) show the variation of magnetocapacitance with magnetic field for CPO and CBO thin films respectively. The absolute value of magnetocapacitance (MC ~ 7.12 % for CPO and 7.69 % for CBO) reveals the strong magnetoelectric coupling in these films. Strong magnetoelectric coupling in these composite films is a strong indication of higher mechanical interaction between piezoelectric phase and magnetic phase through the polymer matrix and may be helpful in various technological areas.

4. CONCLUSION

We successfully fabricate the muliteferroic material and also characterize it with various characterization techniques. We have successfully found ferroelectric properties and ferromagnetic properties in our composite films by using various experimental techniques such as PFM (Piezoresponse Force Microscopy), AFM (Atomic Force Microscopy), VSM (Vibrating Sample Magnetometer) etc. Piezoelectric Force Microscopy is good tool to find the local ferroelectricity in piezoelectric/ferroelectric materials. In this work we have done the imaging of ferroelectric domains in our composite films and successfully obtained the domain images at room temperature (300 K). The phase image represents regions with high (bright) and low (dark) values of φ. And there is shift in phase from the bright to the dark region 180° indicating the ‘up’ polarized and down polarized ferroelectric domains in the composite film. The magnetocapacitance (at frequency =

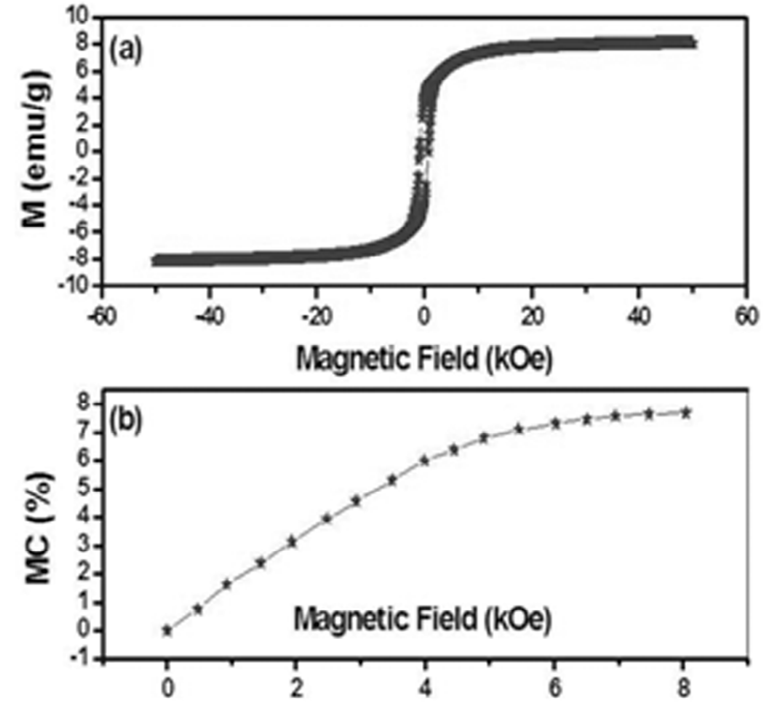

Figure 6: (a) Represents the change in magnetization with magnetic field of CBO film at room temperature. (b) Change in magnetocapacitance with magnetic field of the composite film at room temperature

1 kHz) was found to be ~ 7.12 % for CPO and 7.69% for CBO film at an applied dc magnetic field of 8 kOe, which is the strong indication of high magnetoelectric coupling in the material and due to this it may be useful in innovative solution in various application such as device application, Spin based devices (spintronics), magnetic sensors etc. Further study may be carried out in this area in order to find out interesting facts about multiferroics materials and also to enhance the magnetodielectric coupling between the materials such that these materials can be used in various technological applications in coming future. The realization of such type of composite material will give rise to an effective magnetic and electric switching and consequently it may give rise to large number of applications in electronics and communication and other related technological applications.

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