Research Article

Ferroelectric and Magnetic Properties of Hot-Pressed BiFeO₃-PVDF Composite Films

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The ferroelectric and magnetic properties of hot-pressed BiFeO₃- (BFO) polyvinylidene fluoride (PVDF) composite films have been studied. The BiFeO₃ (BFO) ceramics have been synthesized by a rapid liquid phase sintering technique. The X-ray diffraction (XRD) studies revealed that the impure phase observed in pure BFO ceramics was significantly reduced in the composite films. The presence of both ferroelectric and magnetic hysteresis loops confirms the multiferroic nature of the composite films at room temperature. A well-saturated ferroelectric hysteresis loop with a remanent polarization (P_r) $\sim 4.8 \mu\text{C}\cdot\text{cm}^{-2}$ and coercive field (E_c) $\sim 1.55 \text{ kV/cm}$ has been observed in composite thin films at room temperature. The magnetic hysteresis loops were traced at room temperature with SQUID. The remanent magnetization (M_r) $\sim 3.0 \times 10^{-3} \text{ emu/gm}$ and coercive field (H_c) $\sim 0.99 \text{ kOe}$ was observed in the composite film. The magnetic polarization of the composite films has found to be enhanced as compared to pure BFO and correlated to reduction in BFO impure peak intensity.

1. Introduction

The coexistence of ferroelectric and magnetic nature in a single material, known as multiferroics, gives an additional degree of freedom to design various unconventional devices, such as multiple-state memory elements and electric-field controlled magnetic sensors [1, 2]. However, the simultaneous interaction of various electronic orders parameters in a given system also poses new challenges for fundamental physics. The key to device functionality is a multiferroic material with strong magnetoelectric (ME) coupling for making simple control of magnetization via polarization and vice versa. Unfortunately, very few materials have shown

coexistence of ferroelectricity and magnetism but their ME coupling remains weak at room temperature [3, 4].

BiFeO₃ (BFO) is one such material in which ferroelectricity and antiferromagnetism coexist at room temperature and it has a rhombohedrally distorted perovskite structure with the space group R3c. BFO exhibits two types of long-range ordering: G-type collinear antiferromagnetic ordering below a Neel temperature (T_N) of 643 K and the ferroelectric ordering at 1103 K [5]. Weak ferromagnetism is additionally expected in this compound due to Dzyaloshinskii-Moriya like interaction. However, as a result of a long-range cycloidal spin structure; there is no net magnetization [6, 7]. But, when this modulated spin structure becomes energetically

unfavorable (e.g., in a high magnetic field, in thin films by epitaxial strain, or by doping on the perovskite A-sites) the nonzero net magnetization may be induced.

Wang et al. [5] observed high value of remanent polarization ($P_r \approx 50 \mu\text{C}/\text{cm}^2$) and magnetization ($M_r \approx 6.88 \times 10^{-4} \text{ emu/gm}$) in (001) strained epitaxial 70 nm thin film of BFO on SrRuO_3 buffered SrTiO_3 substrate which is in good agreement with the density functional calculations. But, the polarization in case of bulk single crystal BFO were only 3.5 and $6.1 \mu\text{C}/\text{cm}^2$ along the (001) and (111) axes, respectively [8], and are expected in BFO due to the large distortion of the lattice and high T_c . However, there are still some great obstacles and further investigation is required in the preparation and characterization properties of BFO ceramic for technological applications and they include a high leakage current, wide difference in ferroic transition temperatures (T_c and T_N), weak magnetic characteristics, and lower magnetoelectric coupling coefficients. In order to overcome these problems, several researchers have attempted to modify the Bi or Fe sites of BFO by substitution with different transition metal ions or paramagnetic rare earth metal ions to get electric, magnetic, and electromagnetic properties [9–11].

In the present study, we intend to improve the multiferroic properties of BFO by embedding in the polymer matrix since the recent studies of ferroelectric ceramics (BaTiO_3 , PZT, KNO_3 , CsNO_3 , NaNO_2)-polymer composite films have shown the improved properties [12–14]. The presence of multiferroic nature of BFO-PVDF composite films was confirmed by measuring P-E and M-H hysteresis loops. The structural and morphological properties were also studied and correlated with multiferroic properties.

2. Experimental Technique

The BFO ceramics were prepared by conventional solid state reaction followed immediately by quenching process. The dried starting materials of Bi_2O_3 and Fe_2O_3 (purity > 99.0%) were carefully weighted in stoichiometric proportion and thoroughly mixed for about 36 h using acetone as a medium. The mixture was dried and then the dried mixture was pressed into rectangular-shaped pellets with dimensions $10 \times 5 \times 2 \text{ mm}^3$ by applying stain of $750 \text{ kg}\cdot\text{cm}^{-2}$. The BFO pressed pellets were sintered at temperature of 880°C for 8 min and rapidly cooled to room temperature.

The BFO: Polyvinylidene fluoride composite thin films were prepared by hot-press technique (M-15 KBR Press & Spectra Lab, India). A 1 : 1 mass ratio of BFO and PVDF were added successively and then mixed. The powder mixture was kept in a stainless steel die in the melt press machine. This mixture was heated up to a temperature of 220°C and then a stress of $250 \text{ Kg}\cdot\text{cm}^{-2}$ was applied for 420 sec. The temperature of the die was brought down to room temperature and then the stress was released. The thickness of composite films so obtained was 30–35 μm . The circular indium electrodes, having an area of 3.8 mm^2 on one side and complete metallization on the other side of the surface of composite films were deposited in a vacuum chamber at $2.1 \times 10^{-5} \text{ m}\cdot\text{bar}$ of pressure.

FIGURE 1: X-ray diffraction pattern of (a) sintered BiFeO_3 ceramics and (b) BiFeO_3 :PVDF composite films.

The structure of the BFO-sintered ceramics and composite films were characterized by X-ray diffraction (XRD) (Bruker AXS diffractometer) with Ni-filtered CuK radiation of wavelength of 0.154 nm. The surface morphology of the ceramics and composite films were carried out using FE-SEM (Quanta 200 FEG & FEI Netherlands). Ferroelectric measurements were performed using modified Sawyer-Tower circuit. The hysteresis loops were recorded with a storage oscilloscope connected to a computer with standard software (SP107E, Germany) while magnetic measurements were carried out using a superconducting quantum interference device (SQUID) magnetometer.

3. Results and Discussions

3.1. X-Ray Diffraction (XRD) Studies. Figure 1 shows X-ray spectra pattern of sintered pure BFO ceramics and hot-pressed BFO:PVDF composite films. The observed XRD patterns could be indexed to the rhombohedral structure with space group $R3c$ in BFO ceramics at room temperature according to the JCPDS card no. 71-2494 ($a = b = 5.577 \text{ \AA}$, $c = 13.86 \text{ \AA}$) [15, 16]. XRD patterns demonstrate that the synthesis reaction will easily take place in the Bi_2O_3 and Fe_2O_3 mixture. The $\text{Bi}_{36}\text{Fe}_2\text{O}_{57}$ impurity phase was still observed during the synthesis of BFO by conventional sintering process as reported by other authors [17–19]. The XRD pattern of BFO-PVDF composite film contains all the peaks of BFO in addition to the PVDF major peaks observed at 17.88° , 18.50° , and 20.05° . However, $\text{Bi}_{36}\text{Fe}_2\text{O}_{57}$ impurity phase observed in BFO ceramics has

FIGURE 2: FE-SEM images of (a) sintered pure BFO ceramics, (b) BFO-PVDF composite films, and (c) EDS spectra of composite film.

been significantly reduced in the composite films. Therefore, this study suggests that the interactions between polymer matrix and multiferroic ceramics have been helpful in reducing the impurity phase, which is mainly degrading the electrical properties.

3.2. FE-SEM Study. The surface morphology of pure and composite films was studied by using FE-SEM. Figures 2(a) and 2(b) shows the FE-SEM image of pure BFO ceramics and composite films. The sintered BFO pellet exhibits rectangular shape grains with average length of 1–1.8 μm . The FE-SEM image of the composite film clearly revealed that BFO grains were homogenously embedded in polymer matrix, as a result, porosity will decrease. The interaction between the grains and polymers may be the responsible for suppression of secondary/impurity phase. The chemical composition of BFO-PVDF composite film was analyzed using elemental dispersive X-ray (EDS) analysis. The energy dispersive spectrum of the 50 wt.% BFO : PVDF composite shown in Figure 2(c) confirms the presence of Bi, Fe, C, F, and O elements. The present samples contain equal ratio in cation composition (Bi : Fe = 1 : 1).

3.3. Magnetic Properties. The evolution of magnetization as function of applied magnetic field for pure BFO and BFO-PVDF composite films were studied at room temperature. The measured M-H loop of pure BFO exhibits an antiferromagnetic behavior that appears as an almost linear contribution as shown in Figure 3. The similar magnetization was also reported by others in pure BFO-based thin films [17], whereas, the composite films exhibit a good magnetic hysteresis loop at room temperature as shown in Figure 3. The remanent magnetization (M_r) of the composite films was found to be enhanced as compared to that of pure BFO and correlated to the reduction in BFO impure peak intensity. The value of $M_r \approx 3.0 \times 10^{-3}$ emu/gm observed in present composite films is also found to be higher than that of potassium-doped bismuth ferrite as reported by Dhahri et al. [20], Gd-doped BFO reported by Chen et al. [21], BFO ceramics reported by Yuan et al. [17], and BFO single-crystal reported by Lu et al. [22].

3.4. Ferroelectric Properties. The ferroelectric properties of the composite films were also studied at room temperature. The BFO : PVDF composite film shows a well-saturated

FIGURE 3: Magnetic hysteresis loops of pure BFO ceramic and BFO-PVDF composite films.

FIGURE 4: P-E hysteresis loops of BiFeO₃ : PVDF composite films.

and square-shaped PE hysteresis loop with a remanent polarization ($2P_r$) $\approx 9.6 \mu\text{C}/\text{cm}^2$ and a coercive field ($2E_c$) $\approx 3.1 \text{ kV}\cdot\text{cm}^{-1}$ under the applied field of $10 \text{ kV}/\text{cm}$, as depicted in Figure 4. The obtained P_r value is less than that of epitaxial thin films, but comparable to the BFO thin films reported by Yang et al. on platonized silicon substrates (111)

FIGURE 5: Polarization current—electric field characteristics of BFO-PVDF composite films.

Pt/Ti/SiO₂/Si using a PLD technique [23] and it is larger than that of the bulk ceramics and single crystal [24–26].

The Ac field dependent-polarization current of BFO : PVDF composite film was also traced simultaneously with hysteresis loop and the corresponding I-E curve was shown in Figure 5. As the Ac electric field changes from the –ve maxima to +ve maxima, the peak value of the current appears on the positive side of the field and viceversa. The observed peak is due to the domains reversal from the –ve to +ve direction [27]. Hence, the observed current in the present composite films is dominated by the ferroelectric polarization current. The field corresponding to the peak current is taken as the coercive field, and this value is in good agreement with the E_c obtained from the hysteresis loop.

4. Conclusions

The hot-pressed BFO-PVDF composite films have shown the multiferroic nature at room temperature which was evidence by observing M-H and P-E hysteresis loops. The improved magnetization obtained in the composite films as compared to sintered pure BFO ceramics is correlated to the almost absence of impure phase as evidenced by X-ray studies. The FE-SEM study confirms the homogenous distribution of BFO grains in polymer matrix. The nonlinear behavior of Ac field dependent polarization current also supports the presence of ferroelectric nature.

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