Room temperature Magnetic Studies of phase pure (BiFeO₃-NaNbO₃)-(P(VDF-TrFE)) Nanocomposite films prepared by spin coating

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Abstract

(BiFeO₃-NaNbO₃)-(P(VDF-TrFE)) co-polymer thin films ($\approx$ 0.6 μm thickness) were fabricated by spin coating technique and their room temperature magnetic properties were investigated. In order to get the crystallization 'β' phase, the films have been annealed at 138° C. The structural analysis of the films have been carried out using XRD, SEM, AFM and FTIR spectroscopy which confirm the presence of BiFeO₃ and NaNbO₃ phases along with P(VDF-TrFE) crystalline phase. The magnetoelectric coupling measurements at room temperature confirm the multiferroic nature of the composite film with significant magnetoelectric coupling between BiFeO₃, NaNbO₃ and P(VDF-TrFE). The hysteresis loop observed at room temperature confirms the ferromagnetic property of the composite. The good magneto electric coupling and ferromagnetic property at room temperature of these innovative nanocomposites make them particularly attractive for technological applications as storage energy materials.

Introduction

ME composites fabricated by combining piezoelectric and magnetostrictive materials have drawn significant recent interest due to their multifunctionality, in which the coupling interaction between the piezoelectric and magnetostrictive phases produce a large ME response.[1] The ME coefficients obtained in these ceramic particulate or laminated composites are typically three orders of magnitude higher than in single phase materials. Polyvinylidene fluoride (PVDF) and it's copolymers have the best electroactive performance in the small class of polymers displaying piezo, pyro and ferroelectricity. The PVDF polymer can be characterized as a light, compliant material which exhibits considerable

dielectric strength, high sensitivity to mechanical loads and stable piezoelectric properties in diverse chemical environments.[2,3] Due to these qualities, PVDF and P(VDF-TrFE) have been increasingly used in a variety of applications particularly in such devices as sensors and transducers. [4-13]

Even if most of the pure polymers show low dielectric constant, PVDF and its co-polymer P(VDF-TrFE) have high dielectric constant which leads to good magnetoelectric coupling property. [6-11] It makes them more attractive in electronic and electrical industry due to their inherent advantages in flexibility, easy processing, low coast and high breakdown strength. Therefore a great deal of effort has gone into the development of ceramic–polymer composites, which are formed by suspending ceramic powders into a polymer matrix.

2. Experimental procedure

Stoichiometric powders of $(0.9)BiFeO_3$-$(0.1)NaNbO_3$ ceramics were synthesized from analytical grade (Aldrich) $BiNO_3$, $FeNO_3$, $NaNO_3$, $C_4H_4NNbO_9$ using pechini method.[25] The precursors were dissolved in double distilled water and citric acid was added to the solution with nitrates to citric acid molar ratio 1:1 and heated at 80-90°C for the gelation process. The obtained gel was heated at 500°C for 1 hour and final sintering was done at 850°C.

Then the copolymer P(VDF-TrFE) is dissolved in MEK (Methyl Ethyl Ketone) at a concentration of 14 wt %. The $(0.9)BiFeO_3$-$(0.1)NaNbO_3$ ceramic powder is dissolved in the polymer solution in different concentration. All the solutions were ultrasonicated in different steps and spin coated in to a glass substrate by ultrasonication. The crystal structures of the samples were examined by Phillips X'Pert Pro XRD with Cu-Kα radiation (1.54056Å). Step scanned powder XRD data was collected in the 2θ range 10°-80° at room temperature. Detailed structural analysis was performed using SEM (JEOL JSM 6390), Transmission Electron Microscope (JEOL JEM 2100) and FTIR spectroscopy. A conventional ME measurement has been carried out using the lock in amplifier method. The magnetization measurements were performed using Vibrating Sample Magnetometer.

3. Results and discussion

3.1 Structural analysis

 The phase structure of the film was examined using X-ray diffraction techniques. Fig. 1 shows X-ray diffractograms at room temperature of the P(VDF-TrFE)-$BiFeO_3$-$NaNbO_3$ composite films. For the as-cast film a sharp diffraction peak of (200) and (110) planes at 19.9^o and 38° (marked by 'P') attributed to ferroelectric ß phase of P(VDF-TrFE) and are

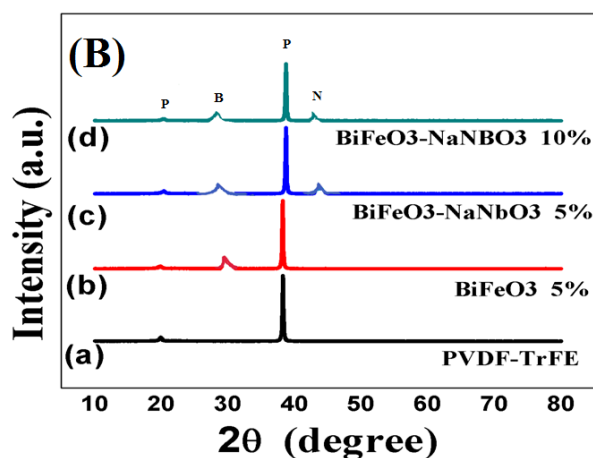consistent with previously reported results for P(VDF-TrFE) with other molar compositions.[8,12-14]

Fig 1. X-ray diffractogram of composite film samples for various nanoparticle concentrations in the polymer matrix
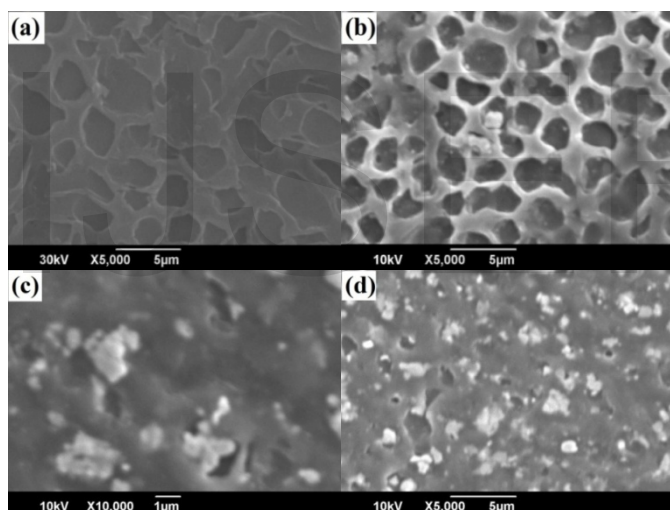

Fig. 2 SEM of $BiFeO_3$-$NaNbO_3$–P(VDF–TrFE) composite film samples for, (a) P(VDF-TrFE) alone, (b) 5% $BiFeO_3$ in the P(VDF-TrFE) matrix, (c) 5% $BiFeO_3$-$NaNbO_3$ in the P(VDF-TrFE) matrix, (d) 10% $BiFeO_3$-$NaNbO_3$ in the P(VDF-TrFE) matrix.

Fig. 2 shows the SEM images of the as-sintered surfaces of the film. From the SEM images we can observe the nanoparticle aggregates on the polymer matrices. Inorder to have more detailed interpretation of the structure of ceramic composite film samples, FTIR spectroscopy is used (fig. 3). Several vibrational bands for the co-polymer have been assigned to specific confirmations by previous reports[16-19] Characteristic absorption bands due to the electro active ß phase at 885 cm^{-1} (CH2 rocking, CF2 stretching and skeletal C-C stretching) have

been found. The band at 1402 cm^{-1}, 1292 cm^{-1}, 1186 cm^{-1}, 885 cm^{-1}, 848 cm^{-1} are associated with crystalline phase (ß) of P(VDF–TrFE) co polymer which shows marginal increase in the absorption intensity irrespective of the nanoparticle addition   in the polymer film.   From previous reports, it was observed that the changes in the intensity at 1292 cm^{-1} bands is highly dependent on the amount of ferroelectric phase content and can be suitable candidate for monitoring the ferroelectric crystalline phase. The bands at 3439 cm^{-1},2928 cm^{-1}, 2335 cm^{-1} and 1385 cm^{-1} are due to the ceramic nano particle. The broad absorption band in the range of 3439 cm^{-1} is assigned to O-H stretching and the 2928 cm^{-1} band is due to C-H stretching vibrations.   A peak at 2335 cm^{-1} was representative of nitrile and the bands located at 1385 cm^{-1} indicate the existence of nitrate ions.[20-23]
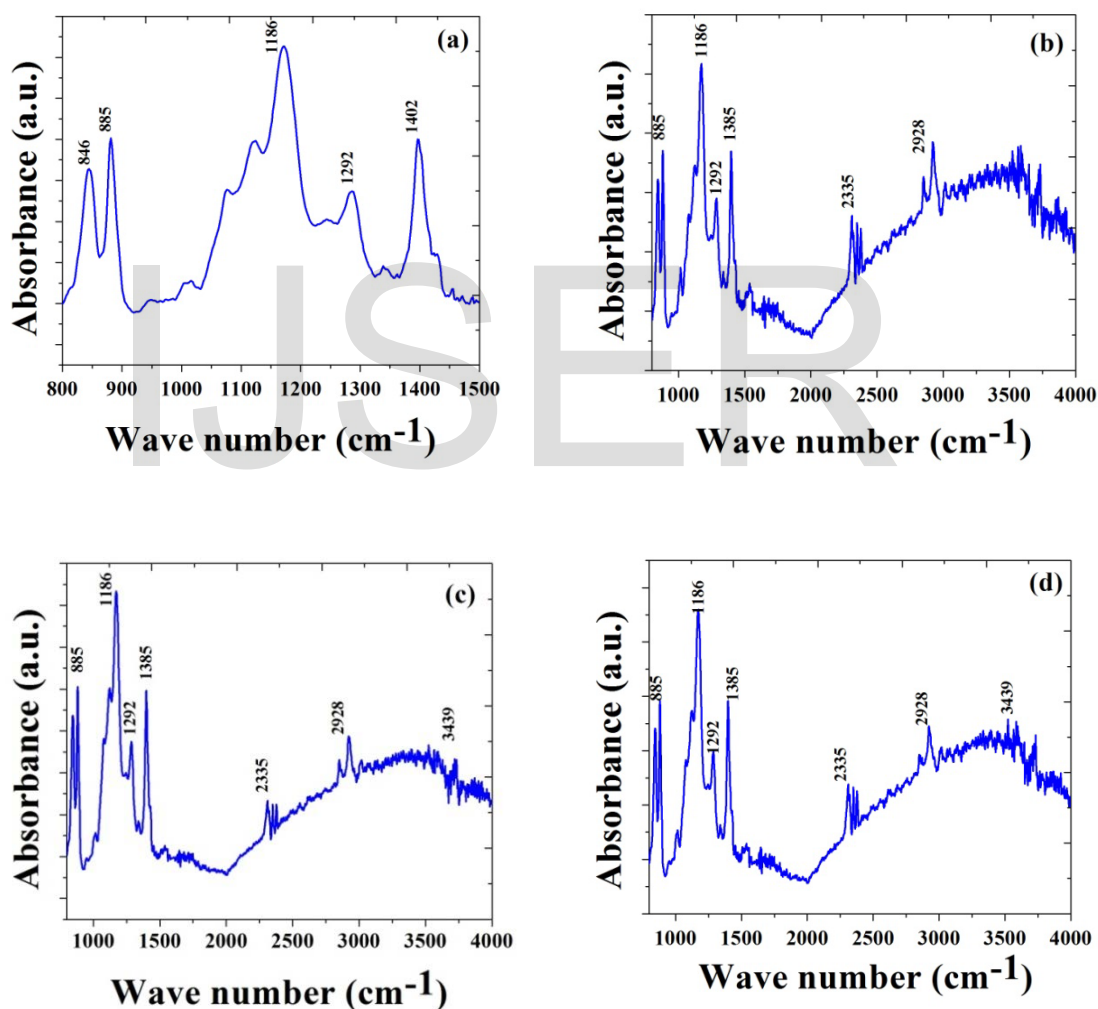

Fig. 3 FTIR spectra of BiFeO$_3$-NaNbO$_3$-PVDF TrFE composite film samples for (a) P(VDF-TrFE) alone, (b) 5% BiFeO$_3$ in the P(VDF-TrFE) matrix, (c) 5% BiFeO$_3$-NaNbO$_3$ in the P(VDF-TrFE) matrix, (d) 10% BiFeO$_3$-NaNbO$_3$ in the P(VDF-TrFE) matrix.
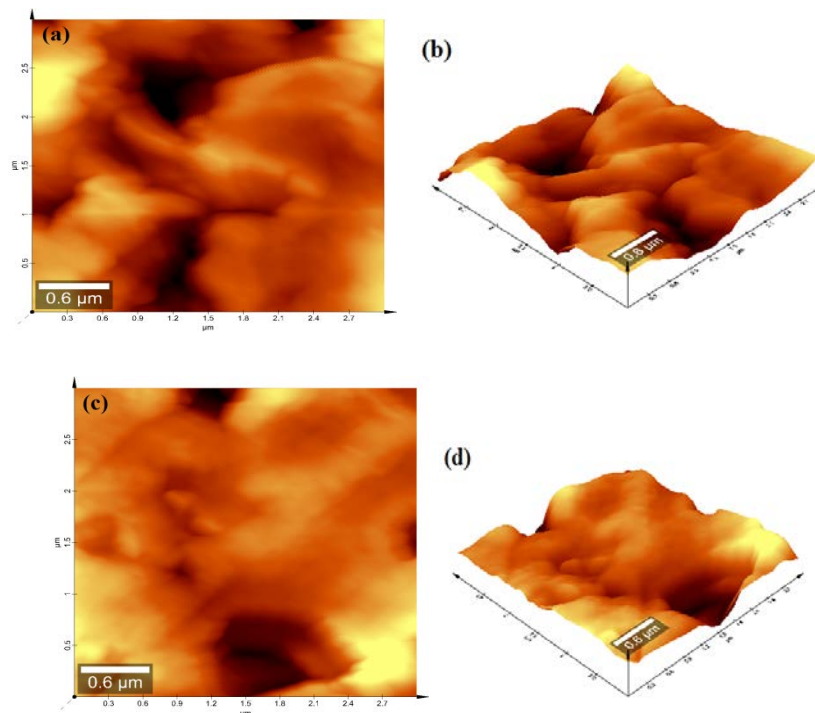
Fig. 4 (a) 2D AFM image of 5% $BiFeO_3$-$NaNbO_3$, (b) 3D AFM image of 5% BiFeO3-NaNbO3. (c) 2D AFM image of 10% $BiFeO_3$-$NaNbO_3$, (d) 3D AFM image of 5% $BiFeO_3$-$NaNbO_3$.

Fig. 4 shows the AFM images of the film samples. Here, the particle distribution in the polymer matrix was studied with AFM by taking account of the composite surface. In the 3D AFM picture, we can clearly see the surface roughness. The coexistence of electric and magnetic phases in the samples which brings about the magnetoelectric (ME) coupling was measured using a Lock-in amplifier. The A.C. magnetic field dependence of ME voltage at room temperature is shown in Fig. 5. The magnetoelectric response for three different fixed DC field is measured. For every composition, it shows linear dependence on the applied field. The value of agnetoelectric coupling coefficient (α) is determined from the slope of the ME curve. The values of magnetoelectric coupling coefficient (α) are tabulated in Table 1. ME response of ceramic-polymer thin film shows very good result compared to the $BiFeO_3$-$NaNbO_3$ ceramic nano powder which we found in our previous experiments.[25] Here we can say that the piezoelectric polymer P(VDF-TrFE) enhances the ME response of the film samples.[26] For increasing vol % of ceramic nanoparticles in the composite the ME response is found to be increasing Even if BFO thin films show good magnetoelectric coupling at room temperature, they often show high leakage currents due to oxygen vacancies and mixed Fe valences. [27-29]
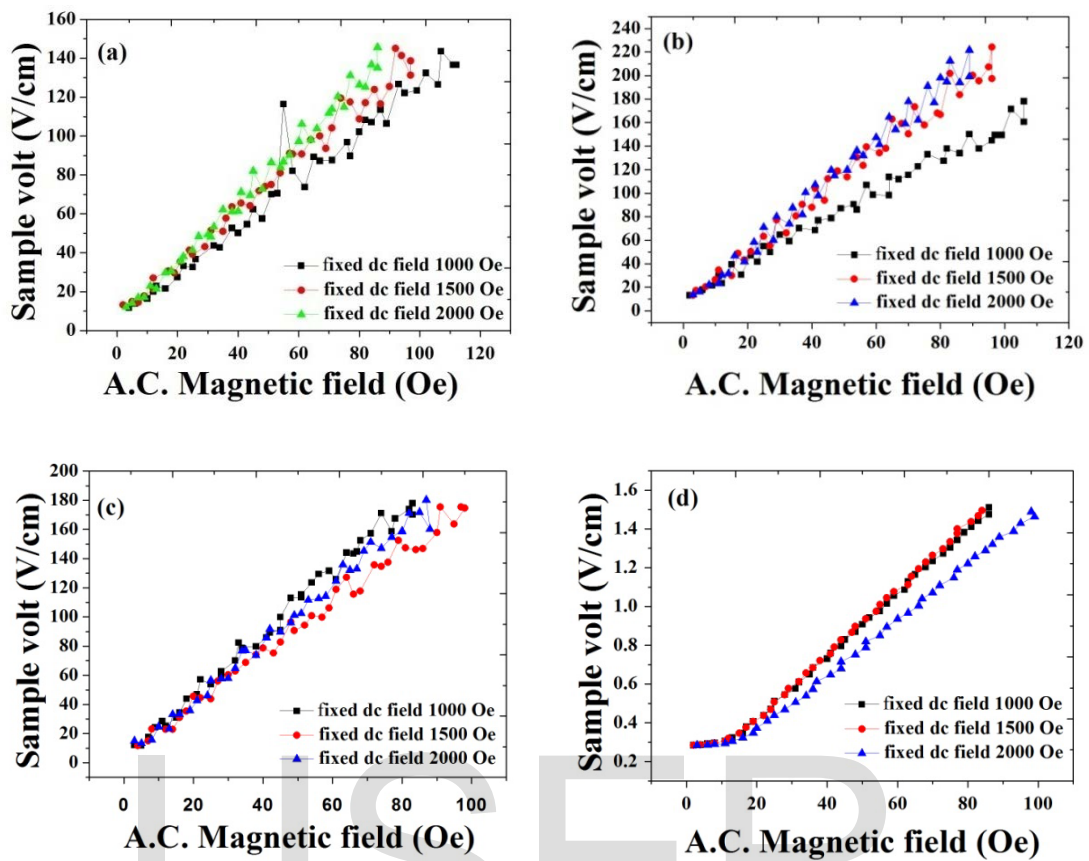
Fig. 5 ME voltage as a function of AC magnetic field at different fixed DC field for BiFeO$_3$-NaNbO$_3$ – P(VDF-TrFE) composite film samples for (a) P(VDF-TrFE) alone, (b) 5% BiFeO$_3$ in the P(VDF-TrFE) matrix, (c) 5% BiFeO$_3$-NaNbO$_3$ in the P(VDF-TrFE) matrix, (d) 10% BiFeO$_3$-NaNbO$_3$ in the P(VDF-TrFE) matrix.

Table 1 : Calculated values of magnetoelectric coupling coefficient (α)

Sl. No.	Sample Name	ME coefficient (α) (V/cmOe)	
		For fix dc 1000Oe	**For fix dc 2000Oe**
1	P(VDF-TrFE)	1.26	1.88
2	5% BiFeO$_3$	1.48	2.42
3	5% BiFeO$_3$-NaNbO$_3$	1.99	2.42
4	10% BiFeO$_3$-NaNbO$_3$	0.01	0.02

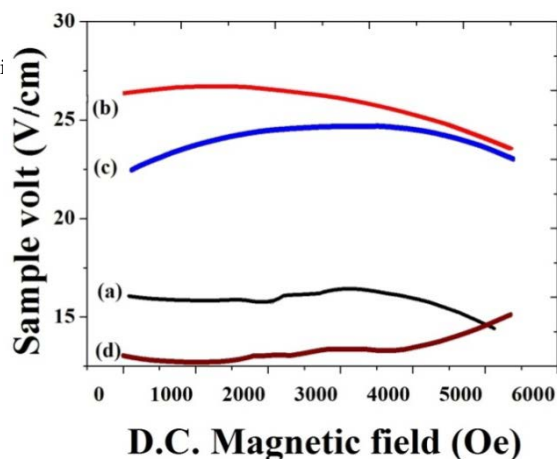**Fig. 6** ME voltage as a function of DC magnetic field for $BiFeO_3$-$NaNbO_3$-P(VDF-TrFE) composite film samples for (a) P(VDF-TrFE) alone, (b) 5 % $BiFeO_3$ in the P(VDF-TrFE) matrix, (c) 5% $BiFeO_3$-$NaNbO_3$ in the P(VDF-TrFE) matrix, (d) 10% $BiFeO_3$-$NaNbO_3$ in the P(VDF-TrFE) matrix.

However, multilayer heterostructures of $BiFeO_3$ show high magnetoelectric (ME) coefficients. $BiFeO_3$-$BaTiO_3$ composite film have a ME coefficient up to 2.4 V/cmOe at 300 K which is much higher than that of a single-phase $BiFeO_3$ reference film (4.2 V/cmOe). Fig. 6 shows the ME voltage variations of the film samples with DC magnetic field.
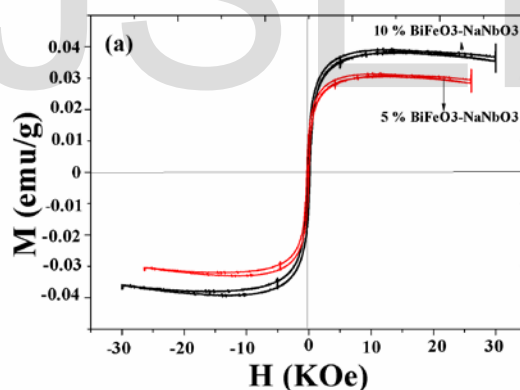

Fig. 7 Hysteresis loop of the 5% $BiFeO_3$-$NaNbO_3$ and 10 % $BiFeO_3$-$NaNbO_3$ in PVDF-TrFE matrix

Magnetic hystersis loop of 5% $BiFeO_3$ -$NaNbO_3$ and 10 % $BiFeO_3$-$NaNbO_3$ in PVDF-TrFE matrix at room temperature is shown in Figure 7. A good hysteresis behaviour which is saturated within the field of 30 KOe can be observed indicating a ferromagentic nature at room temperature. The ferromagnetism of these sample could be a result of several reasons. The main possibility is the the high piezoelectricity due to the presence of PVDF-TrFE co polymer and the other is due to the $NaNbO_3$ content which also has good electromechanical

property.[1] Since the XRD patterns have not detected any impurity phase, the properties which have been observed could be due to the contribution of the cermic part and co-polymer itself. The maximum magnetization attained is different for two compositions. The magnetization value is found to be increasing by increasing the amount of nanoparticle in the polymer matrix. While the coercivity (Hc) and remanant magnetization (Mr) are almost same for two compositions. The The remanant magnetization (Mr) observed is 0.04 emu/g and the coercive field (Hc) is 0.9 KOe for 10 $BiFeO_3$ -$NaNbO_3$.

4. Conclusion

Our findings lead to a novel way for preparing energy storing and transforming materials with ultrahigh dielectric constant and good magnetoelectric coupling which are required in embedded capacitors, microelectromechanical systems, ultrasonic resonators, high power transducers, actuators etc. A series of $BiFeO_3$-$NaNbO_3$-P(VDF-TrFE) composite films with various volume fraction of $BiFeO_3$-$NaNbO_3$ in the polymer matrix were prepared by using spin coating technique. The room temperature ferromagnetism and good magnetoelectric coupling promise tailored applications of current material in various fields. In the design of advanced multiferroic materials, multiphase $BiFeO_3$-$NaNbO_3$-P(VDF-TrFE) composite film is an attractive and successful approach to overcome the limitations of intrinsic single phase multiferroics.

Acknowledgement

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