Electrical and magnetic properties of 0–3 Ba(Fe_{1/2}Nb_{1/2})O₃/PVDF composites

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Lead-free Ba(Fe_{1/2}Nb_{1/2})O₃/PVDF 0–3 composites were fabricated using melt-mixing technique. X-ray diffraction, scanning electron microscopy, dielectric, impedance, ac conductivity, magnetic force microscopy (MFM) and vibrating sample magnetometer studies were undertaken to characterize the samples. Average crystallite size of the Ba(Fe_{1/2}Nb_{1/2})O₃ powder, estimated using Williamson–Hall approach, was found to be ~42 nm. The filler particles of ~0.5–1 μm were found to disperse in the polymer matrix of all the composites. Filler concentration-dependent values of real and imaginary parts of complex permittivity showed increasing trend and were seen to follow Bruggeman and Furukawa equations. The data for ac conductivity exhibited negative temperature coefficient of resistance character of the test materials and were found to obey Jonscher's power law. The correlated barrier hopping model was found to explain satisfactorily the mechanism of charge transport occurring in the system. MFM confirmed the presence of magnetic phases in the composites. Typical magnetization versus applied field curves indicated the possibility of magnetoelectric coupling in the system. Hence, the present composites have shown themselves as potential multifunctional candidate materials for use in high density data storage applications.

Keywords: Random composite medium; dielectric properties; magnetic properties; effective permittivity; magnetic force microscopy.

1. Introduction

Studies on composites consisting of ceramic powder embedded in polymer matrix have attracted considerable global attentions in recent years in view of the growing demands of electronic and/or microelectronic industries for the development of suitable composites consisting of lead-free eco-friendly ceramics which are helpful in efforts toward miniaturization of multifunctional electronic devices. Polymer/ceramic composites have found their vast range of technological applications such as in embedded passive technology, high speed ICs, high charge storage capacitors, gate dielectrics, sensors, actuators, energy harvesting, artificial muscles, smart skins, etc.^{1–5} Besides, polymer-based materials have added advantages that they possess moderate dielectric constant, low dielectric loss and compatibility with printed circuit boards. Polymers are known to have high electric breakdown strength, light weight, excellent flexibility and low temperature processing requirement, albeit their low values of dielectric constant hindering their abundant use in practical applications. Therefore, ceramic powders having high dielectric constant are normally used as fillers to prepare

ceramic/polymer composites for improved performance. In addition, tailoring of their properties can be done as per the requirement by changing the proportions of the constituents. Recently, a large number of ceramic/polymer-based 0–3 composites have been fabricated and studied with different aims such as: BaTiO₃/PVDF,^{6–9} (Ba_{0.8}Sr_{0.2})(Ti_{0.9}Zr_{0.1})O₃/epoxy¹⁰ and (Bi_{0.5}Ba_{0.25}Sr_{0.25})(Fe_{0.5}Ti_{0.5})O₃/PVDF¹¹ for embedded capacitor applications and to understand the carrier transport mechanism; Ba_{0.5}Sr_{0.5}TiO₃/P(VDF–CTFE)¹² for energy storage applications; (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃/P(VDF–TrFE)¹³ to view the combined effect of segmental chain relaxation in polymer phase and dipole relaxation in ceramic phase; BCT–BZT/P(VDF–TrFE)¹⁴ and (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃/PVDF¹⁵ for piezoelectric, pyroelectric applications; Pb(Zr,Ti)O₃/PVDF¹⁶ toward utilization of dielectric, ferroelectric, piezoelectric, pyroelectric, electrooptic and superconducting properties in micro-devices; CaCu₃Ti₄O₁₂/PVDF¹⁷ and BCT–BZT/epoxy¹⁸ for flexible capacitors devices; BaZrO₃–BaTiO₃–Ba(Fe_{1/2}Ta_{1/2})O₃/epoxy resin¹⁹ and Ba(Fe_{0.5}Ta_{0.5})O₃/PVDF²⁰ to develop surface-mounted capacitor applications; 0.885Bi_{0.5}Na_{0.5}TiO₃–0.05Bi_{0.5}K_{0.5}TiO₃–0.015

$\text{Bi}_{0.5}\text{Li}_{0.5}\text{TiO}_3\text{--}0.05\text{BaTiO}_3/\text{terfenol-D}^{21}$ for magnetoelectric sensing applications, etc.

Barium iron niobate ($\text{Ba}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$, hereinafter abbreviated as BFN) ceramic is considered very attractive due to its giant dielectric constant ($\sim 10^5$) and magnetoelectric properties^{22–28} while polyvinylidene fluoride (PVDF) is one of the most effective low-cost polymers having low complex permittivity and low thermal conductivity. It would not be out of place to mention here that both the constituents of the above-referred ceramic/polymer composite are environment-friendly. Recent reports revealed that serious attentions have been paid on the syntheses of and studies on BFN/PVDF-based composites with an aim to get improved dielectric properties.^{29–33} In a study reported by the present authors' group, BFN showed magnetic properties^{27,34} in addition to its dominant dielectric properties. Further, it is worth mentioning that the information on the magnetic property and mechanism of carrier transport of BFN/PVDF composites has remained unexplored as yet and, hence, the system deserved further investigation. Accordingly, microstructure, dielectric properties, ac conductivity, vibrating sample magnetometer and magnetic force microscopic (MFM) studies on lead-free $x\text{BFN}/(1-x)\text{PVDF}$ 0–3 composites synthesized using the melt-mixing technique are reported in the present work. The applicability of different predictive dielectric mixture equations for effective complex relative permittivity in the present composite system was also seen by choosing suitable values of shape-dependent parameter as and where required.

2. Experimental

2.1. Preparation of BFN/PVDF composites

AR grade (99.9%+ pure, Merck) chemicals (BaCO_3 , Fe_2O_3 and Nb_2O_5) were used to synthesize BFN powder by solid state synthesis route in air atmosphere at 1200°C for 5 h. The completion of the formation of required compound was checked by X-ray diffraction (XRD) technique. Now, 0–3 type of $(1-x)\text{PVDF}/x\text{BFN}$ composites with $x = 0.025, 0.05, 0.10, 0.15$ were synthesized by melt-mixing technique using a conical twin-screw extruder (Micro 5, DSM Research, Netherlands) at 160°C for 5 min at 150 rpm. All the test samples were vacuum dried for 10 h at 80°C . Compression molded films of 0.5 mm thickness were used for dielectric, magnetic and MFM studies. Besides, the ceramic powder was cold pressed as thin cylindrical pellet (1.14 mm thick and 10 mm diameter) and was sintered at 1250°C for 4 h.

2.2. Characterizations

The XRD data of PVDF, BFN powders and their composites were collected with XPERT-PRO, Pan Analytical X-ray diffractometer using CuK_α -radiation ($\lambda = 1.5405 \text{ \AA}$) with

Bragg angle (2θ) between 10° and 80° at the scanning speed of $5.08^\circ \text{ min}^{-1}$. The dispersion of BFN powder in PVDF host was determined from the morphology of cryo-fractured surfaces of BFN/PVDF composites using scanning electron microscope (SEM) (JEOL JSM 5800LV). The composites were sputtered by gold using JEOL JEEE-400 in order to circumvent the difficulties encountered in overcharging. Both real and imaginary parts of complex relative permittivity of BFN ceramic and BFN/PVDF composites were measured as functions of frequency (1 Hz–1 MHz) and temperature (-60 – 130°C) using a computer-controlled Alpha high resolution dielectric analyzer (NOVOCONTROL Technologies, GmbH & Co. KG, Germany). Conductive silver paste was applied on opposite faces of the cylindrical pallet as well on the composite samples (area of electrode $\sim 78.5 \text{ mm}^2$). The temperature was varied at a rate of 1°C/min . MFM images of all the composites were taken in tapping mode at the ambient temperature using an atomic force microscope (AFM) (NT-MDT, NTEGRA having a resolution $\sim 1 \text{ nm}$). Studies of field-dependent magnetic characteristics of the test materials were undertaken using a vibrating sample magnetometer (model: 7410) of Lake Shore Cryotronics, Inc.

3. Results and Discussion

Figure 1 depicts the indexed XRD patterns of PVDF, BFN ceramic and BFN/PVDF composites. The presence of mixed phases (α and γ) of PVDF, which are semi-crystalline in nature, is easily seen and is found to be consistent with the previous report.²⁵ The XRD analyses indicated that BFN ($x = 1.0$) has a cubic unit cell ($a = 4.079 \text{ \AA}$) with $Pm\bar{3}m(221)$ space group, which is in consistence with the literature report (JCPDS-ICDD#: 81-3122). Also, positions of all the peaks of BFN/PVDF composites were found to match with the peaks of BFN and hence could be indexed similar to BFN. The average crystallite size as estimated to be 42 nm using a linear least squares fitting of $\beta \cos \theta - \sin \theta$ data according to Williamson–Hall equation is

Fig. 1. XRD patterns of BFN/PVDF composites for $x = 0, 0.025, 0.05, 0.10, 0.15, 1.0$.

Fig. 2. SEM micrographs of BFN/PVDF composites for $x = 0.025, 0.05, 0.10, 0.15$; filler (BFN powder) and BFN ceramic ($x = 1.0$).

$\beta \cos \theta = (K\lambda/D) + 2(\Delta\xi/\xi) \sin \theta$, where β is diffraction peak width at half intensity and $\Delta\xi/\xi$ is the lattice strain and K is the Scherrer constant ($= 0.89$). The term $K\lambda/D$ is representative of the distribution of Scherrer particle size in the test specimen.

Figure 2 shows the SEM-micrographs of BFN ($x = 1.0$) ceramic and cryo-fractured surfaces of x BFN-($1 - x$)PVDF composites ($x = 0.025, 0.05, 0.10, 0.15$) along with BFN powder (filler). The filler particles of unequal sizes (~ 0.25 – $0.5 \mu\text{m}$) appear to be distributed homogeneously in the polymer congregation of all the composites. Also, the shapes of grains are clearly seen in the SEM micrograph of fractured surface of sintered BFN ceramic, indicating the existence of polycrystalline microstructure. Along with the grains of unequal sizes (~ 8 – $15 \mu\text{m}$), few agglomeration of grains could also be noted. The absence of large pores was indicative of highly dense nature of BFN ceramic.

The variation of dielectric permittivity (ϵ') and loss tangent ($\tan\delta$) of BFN/PVDF composites with frequency at different temperatures have been plotted in Figs. 3 and 4, respectively. It is seen that with the increase of frequency both ϵ' and $\tan\delta$ decrease, a common behavior generally followed by most of the dielectric/ferroelectric materials. In the lower frequency region of ϵ' - f graph, relatively higher dielectric constants along with dispersion are observed and the dielectric constant is seen to drop at high frequencies. The complex permittivity of a dielectric material in an alternating field is given by $\epsilon^* = \epsilon' - i\epsilon'' = \epsilon_\infty + (\epsilon_s - \epsilon_\infty)/[1 + (i\omega\tau)^{1-\alpha}]$, where ϵ_s and ϵ_∞ are the low and high frequency values of ϵ' , respectively, $\omega = 2\pi f$ (f = frequency

of measurement); τ is the relaxation time and α represents the spread of relaxation time. At very low frequencies ($\omega \ll 1/\tau$), dipoles successfully follow the field and thus $\epsilon' \approx \epsilon_s$ (static dielectric constant). At higher frequencies (when $\omega < 1/\tau$), dipoles are lagging behind the field and ϵ' slightly decreases. At the characteristic frequency ($\omega = 1/\tau$), the dielectric constant drops, thereby representing the relaxation process and dipoles are unable to follow the field at very high frequencies ($\omega \gg 1/\tau$), leading to $\epsilon' \approx \epsilon_\infty$. The aforesaid behavior has been observed to be followed qualitatively in BFN/PVDF. Further, the value of $\tan\delta$ decreases with rise in frequency in the low temperature region, while at higher temperatures; it finds a maximum, which shifts toward higher frequency side, thereby indicating the increasing loss in the sample. It is evident from Fig. 4 that the values of $\tan\delta$ are higher at low frequencies and with the rise in temperature, relaxation part (referred to as polarization loss) dominates. It consists of two components: the conductivity response of free charges and the frequency-dependent polarization loss response of dipoles which follows the expression $\epsilon^* = \epsilon' - i(\epsilon'' + \sigma/\omega\epsilon_0)$, where the electrical conductivity might contribute significantly to ϵ^* at higher temperatures. Insets of Figs. 3 and 4, respectively, illustrate the variation of ϵ' and $\tan\delta$ with temperature for BFN/PVDF composites at different frequencies. All the plots show broad maxima (T_m) which shift toward higher frequency side showing relaxor behavior of BFN/PVDF. Besides, it is found that the value of ϵ' at room temperature increases with increasing BFN content in the composite while no such trend has been observed in the $\tan\delta$ variation (Fig. 5 and its inset). However, addition of BFN

Fig. 3. Frequency dependence of real part of the dielectric constant of BFN/PVDF composites (a) $x = 0$, (b) $x = 0.025$, (c) $x = 0.05$, (d) $x = 0.10$, (e) $x = 0.15$ and (f) $x = 1.0$ at different temperatures. Inset: Temperature dependence of real part of the dielectric constant at different frequencies.

to PVDF could reduce the loss value (inset Fig. 5). Further, $\epsilon''-f$ plots for BFN find maxima after 200°C, which shift towards lower frequency side with increasing temperature, assumably due to the resonance effect.²⁴

The precise prediction of the filler concentration-dependent effective relative permittivity (ϵ'_{eff}) as well as dielectric loss factor (ϵ''_{eff}) of composite materials is very important from the viewpoint of design of packaging

Fig. 4. Frequency dependence of loss tangent of BFN/PVDF composites (a) $x = 0$, (b) $x = 0.025$, (c) $x = 0.05$, (d) $x = 0.10$, (e) $x = 0.15$ and (f) $x = 1.0$ at different temperatures. Inset: Temperature dependence of loss tangent at different frequencies.

materials and substrates. Several equations and/or models given by Knott, Cuming, modified Rother-Lichtenecker, Furukawa, Hashin-Shtrikman, Maxwell-Wagner, Skipe-trov, modified Cule-Torquato, Taylor, Lewin, Sillars,

Wiener, Bruggeman, Jayasundere-Smith, Poon-Shin, etc.^{35,36} were proposed to estimate effective ϵ'_{eff} . The volume fraction (f_c) required in the following equations was derived from the corresponding weight fractions (x).

Fig. 5. Variation of real part of dielectric constant and loss tangent of BFN/PVDF 0–3 composite as a function of weight fraction (x) of BFN in the composite. Inset: Frequency dependence of dielectric constant and loss tangent BFN/PVDF composite at room temperature.

The formulae used in the present investigation are as follows:

(a) Bruggeman equation:

$$\varepsilon'_{\text{eff}} = \varepsilon'_p \left[1 + \frac{f_c(\varepsilon'_c - \varepsilon'_p)}{\varepsilon'_p + n(1 - f_c)(\varepsilon'_c - \varepsilon'_p)} \right], \quad (1)$$

where the subscripts “c” and “p” represent “ceramic” and “polymer”, respectively.

(b) Furukawa equation:

$$\varepsilon'_{\text{eff}} = \varepsilon'_p \frac{1 + 2f_c\{(\varepsilon'_c - \varepsilon'_p)/(\varepsilon'_c + 2\varepsilon'_p)\}}{1 - f_c\{(\varepsilon'_c - \varepsilon'_p)/(\varepsilon'_c + 2\varepsilon'_p)\}}. \quad (2)$$

(b) Only one equation given by Bruggeman as given below is available for the prediction of effective dielectric loss factor for composites:

$$\varepsilon''_{\text{eff}} = \varepsilon'' = \frac{\varepsilon''_p[(\varepsilon'_c - \varepsilon')(\varepsilon'_c + 2\varepsilon'_p)\varepsilon']}{[(\varepsilon'_c - \varepsilon'_p)(\varepsilon'_c + 2\varepsilon'_p)\varepsilon'_p]} + \varepsilon''_c \frac{3(\varepsilon' - \varepsilon'_p)\varepsilon'}{(\varepsilon'_c - \varepsilon'_p)(\varepsilon'_c + 2\varepsilon')}, \quad (3)$$

still, the given equation paved the way for using all the equations available for $\varepsilon'_{\text{eff}}$ to substitute in Eq. (3) to get the respective values of $\varepsilon''_{\text{eff}}$ for their comparison with experimental results. Here, the quantity without a subscript refers to the composite. All the predicting equations were tried to obtain the values of $\varepsilon'_{\text{eff}}$ of 0–3 BFN/PVDF composites. It was observed that only Bruggeman equation fitted the concentration-dependent ε' data excellently well which could be owing to the fact that it contains adjustable shape-dependent parameter (n). For the present case, the most appropriate value of n was found to be 0.3. Figure 6 illustrates the filler concentration-dependent values of ε' and ε'' along with the

Fig. 6. Variation of effective relative permittivity and loss factor of BFN/PVDF 0–3 composite as a function of volume fraction of BFN in the composite. Inset: Suitably magnified curves at lower volume fractions.

fitted curves for $\varepsilon'_{\text{eff}}$ and $\varepsilon''_{\text{eff}}$ given by Bruggeman and Furukawa equations. The experimental points along with their fittings have been suitably magnified in order to see the variations in the lower volume content of the filler (insets of Fig. 6). The fitted curves using the data points yielded by Furukawa equation have been included as an example to show the deficiency of the equations in predicting the values of $\varepsilon'_{\text{eff}}$ as well as $\varepsilon''_{\text{eff}}$ at and near the extreme ends.

The ac conductivity data of BFN/PVDF composites were obtained using a relation: $\sigma_{ac} = \omega \varepsilon_o \varepsilon''(\omega)$. Owing to the presence of localized states existing in the dielectric materials, the ac conductivity is given by Jonscher’s power law: $\sigma_{ac} = \sigma_o + A\omega^s$, where σ_o is the dc part, s ($0 \leq s \leq 1$) is the index representing hopping parameter, ω is angular frequency of applied ac field and A is a constant. The above expression represents the displacement of charge carriers moving inside the sample via discrete hops between localized sites which are randomly distributed. The value of “ s ” can be estimated from the slope of $\log \sigma_{ac}$ versus $\log \omega$ plot. There are two different mechanisms guiding charge carrier transport inside the material namely, (i) quantum mechanical tunneling (QMT) and (ii) correlated barrier hopping (CBH). The applicability of a model out of the two depends on the value of “ s ” in $A\omega^s$. CBH model is applicable in cases where $s < 1$ while QMT model treated is suitable for the case in which $s > 1$. In these models, the exponent s is found to have two different trends of variation with temperature and frequency. The frequency dependence of σ_{ac} at various temperatures has been plotted in Fig. 7. The plots show dispersion in the entire frequency range of measurement. Moreover, with the rise in temperature, the plots get flattened, thereby indicating the dominance of dc conductivity

in the test materials. The transition from dc to ac part illustrates the onset of the conductivity relaxation, representing the switchover from long range to the short-range hopping. It was observed that the values of s are always

less than 1 and decrease with the rise in temperature which approaches zero at higher temperatures, thereby indicating that the dc conductivity dominates at higher temperatures in the low frequency region following Jonscher's

Fig. 7. Variation of ac conductivity of $\text{Ba}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3/\text{PVDF}$ composites with frequency at different temperatures (a) $x = 0$, (b) $x = 0.025$, (c) $x = 0.05$, (d) $x = 0.10$, (e) $x = 0.15$ and (f) $x = 1.0$.

power law in all the cases. According to the CBH model, the value of exponent “ s ” should decrease with rise in temperature. The experimental results corroborated the above proposition. It was further noted (Fig. 7(f)) that the values of σ_{ac} fall down at higher temperatures and higher frequencies, presumably due to the resonance effect occurring in BFN ceramic.

Figure 8 depicts the variation of $\ln \sigma_{ac}$ versus $10^3/T$ at different frequencies. It is seen that the value of σ_{ac} increases with the increasing x (BFN content) which clearly indicated the negative temperature coefficient of resistance (NTCR) character of the samples. The apparent activation energy was obtained using the Arrhenius relationship:

$\sigma_{ac} = \sigma_o \exp(-E_a/k_B T)$. A linear least squares fitting of the ac conductivity data at 1 kHz to this equation give the values of the apparent activation energy, E_a to be 0.33, 0.324, 0.321, 0.32, 0.318 and 0.21 eV, respectively, for $x = 0, 0.025, 0.050, 0.10, 0.15$ and 1.0. Hence, the apparent activation energy value decreases with increasing BFN content in the BFN/PVDF composite. The low value of E_a supports the hopping type of charge carriers’ transport in the test materials between localized states in a random manner. The high value of conductivity in BFN may be considered due to the oxygen vacancies created during the sintering process (as per the reaction suggested by Kröger and Vink: $O_o \rightarrow \frac{1}{2}O_2 \uparrow + V_o^{\bullet\bullet} + 2e^{-1}$) that enhances the electrical conductivity,

Fig. 8. Variation of ac conductivity of $Ba(Fe_{1/2}Nb_{1/2})O_3/PVDF$ composites with temperature at different frequencies (a) $x = 0$, (b) $x = 0.025$, (c) $x = 0.05$, (d) $x = 0.10$, (e) $x = 0.15$ and (f) $x = 1.0$.

Fig. 9. MFM images of BFN/PVDF composites for $x = 0.025, 0.05, 0.10, 0.15$.

imaginary part of complex permittivity and accumulation of space charge at grain boundaries which are detrimental to the material's performance.

Figure 9 depicts the two-dimensional MFM images of BFN/PVDF composites which were obtained in order to ascertain the magnetic domain structures present in them. The image contrast observed in all the figures clearly indicated the presence of magnetic activity in BFN/PVDF composites. The contrasts as appeared at the dimensions of $2\mu\text{m} \times 2\mu\text{m}$ owe due to the force gradients between the AFM tip and the magnetic activity present on the samples' surface. The formation of domain structures found inside the magnetic materials reduces their magneto static energy at very small dimensions. The phase images were taken at different lift heights and the lift height was kept at 40 nm for MFM measurement after ensuring that the phase image does not have contribution from topographic features. The results obtained from MFM clearly show the acceptable coexistence of ferroelectric and magnetic orderings at room temperature both at macroscopic and microscopic levels. This reveals that BFN/PVDF composites have potential to be considered as multifunctional material candidates and may be useful for high density data storage applications.

Figure 10 shows the magnetization (M) versus applied field (H) curves for BFN/PVDF composites and BFN ceramic (inset: Fig. 10(b)) at room temperature. The $M-H$ data show typical ferromagnetic hysteresis curves for all the compounds. Inset of Fig. 10(a) shows variation of coercive

field (H_c), remanent magnetization (M_r) and saturation magnetization (M_s) with increasing BFN content. Low values of H_c are found in all the compounds and the value is found to be lowest (117.78 Oe) for $x = 0.10$, which may be considered as suitable for the recording applications. Further, the values of M_r and M_s increase with increasing BFN content. Thus, the present study clearly indicates that there is a possibility of existence of magnetoelectric coupling in the test system,

Fig. 10. Magnetization curves for BFN/PVDF composites at room temperature. Insets: (a) Compositional variation of H_c , M_r and M_s and (b) magnetization curve for BFN ceramic.

suggesting electric ordering controlling magnetic properties at the microscopic scale.

4. Conclusions

The cubic ($a = 4.079 \text{ \AA}$; space group: $Pm\bar{3}m$) BFN powder (average crystallite size $\sim 42 \text{ nm}$) was used to fabricate the ceramic/polymer (PVDF) 0–3 composites by melt-mixing method. The filler particles ($\sim 0.5\text{--}1 \mu\text{m}$) were found to be well dispersed in the polymer matrix of all the composites. The values of real and imaginary parts of dielectric constant increase with increasing filler concentration which followed Bruggeman and Furukawa equations. All the ceramics showed the NTCR character of the test materials and supported the hopping type of conduction. The frequency dependence of ac conductivity data obeyed Jonscher's power law. The existence of magnetic phases in the composites was confirmed using MFM. The possibility of magnetoelectric coupling in the system was undertaken using vibrating sample magnetometer. These results indicated that present composite system could be considered as potential multi-functional materials for their use in high density data storage applications.

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