

LEAD BASED Vs LEAD FREE CERAMIC POLYMER COMPOSITES FOR ENERGY HARVESTING APPLICATIONS

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Abstract

Lead free ferroelectric ceramic polymer composites have been given utmost importance in comparison to lead based composites due to environment concerns. Lead free [(BZT-BCT)-(PVDF)]/[0.5[Ba(Zr_{0.2}Ti_{0.8})O₃]-0.5[(Ba_{0.7}Ca_{0.3})TiO₃]-PVDF] 0-3 composites have been synthesized by hot press method and characterized. The ϵ_r and d_{33} values can be comparable with the lead based counterparts.

Key words: ferroelectrics, ceramic polymer composites, lead free.

INTRODUCTION

Lead based ferroelectric ceramics like Lead Zirconate Titanate (PZT) has been used since decades due to its large dielectric and piezoelectric properties [1]. These lead based ceramics contain more than 60 wt% of lead oxide which causes many harmful diseases. Due to environmental concerns, WEEE (Waste Electrical and Electronic Equipment) and RoHS (Restriction of Hazardous Substances) have put ban on use of lead based materials [2]. Now-a-days, scientists have focus on lead free materials as an alternative to lead based materials. In the year 2009, Liu *et al.* first reported a lead free ferroelectric system $\{x[\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3]-(1-x)[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3]\}/(\text{BZT-BCT})$, which can replace lead based systems [3]. (BZT-BCT) 50/50 system shows highest ferroelectric, piezoelectric and electro-mechanical properties due to the presence of MPB (morphotropic phase boundary).

The major disadvantages of ferroelectric ceramics are brittleness and high processing temperature. On the other hand, polymers are flexible but possess low dielectric and piezoelectric properties. Recently, there has been a great interest in hybrid materials such as ceramic polymer composites which can have superior properties in comparison to their individual counterparts. Ceramic polymer composites possess electro-mechanical properties of ceramics and flexibility,

formability and low cost of polymers. The advantages of ceramic polymer composites are high dielectric constant, high electromechanical coupling co-efficient, low dielectric loss and low acoustic impedance. Recently, focus on the study of 0-3 ferroelectric polymer composites have been increased due to their ease in fabrication. Among the lead free ferroelectrics, BT, BNT, BST, etc are mostly exploited [4,5]. There have been limited studies on (BZT-BCT) polymer composites. Again, among different polymers, Polyvinylidene difluoride (PVDF) is a semicrystalline polymer with high values of ferroelectric and piezoelectric properties among different ferroelectric polymers [6]. Addition of PVDF polymer to (BZT-BCT) ceramics enhances the electrical properties of the composite materials.

In this paper, synthesis and characterization of (BZT-BCT)-PVDF 0-3 ceramic polymer composites with different volume fractions were discussed in details.

EXPERIMENTAL PROCEDURE

Lead free (BZT-BCT) ceramic samples were prepared by conventional solid state reaction route. Barium Carbonate (BaCO₃, 99% purity [Merck, India]), Zirconium Dioxide (ZrO₂, 99.5% purity [Merck, India]), Calcium Carbonate (CaCO₃, 98.5% purity [Merck, India]) and Titanium Dioxide (TiO₂, 99% purity [Merck]) were used as starting materials for synthesis of the (BZT-BCT) ceramics. Stoichiometric weights of all the powders were mixed and ball milled with acetone for 8h using zirconia balls as the grinding media. Then calcination of the samples was done at 1,300°C for 4h. This calcined powder was mixed then mixed with 2wt% poly vinyl alcohol (PVA) binder solution and pressed into disks of diameter ~10 mm and thickness ~1.5 mm at ~60 MPa pressure. The calcined samples were undergone sintering at 1,400°C for 6h at a heating rate of 5°C/min. After sintering, the pellets were again crushed into powder form using a mortar and pestle. Then 0-3 composite samples were prepared by the hot pressing technique. PVDF of average molecular weight of ~534,000 (Sigma-Aldrich) was

used. For the preparation of (BZT-BCT)-PVDF composite samples, the sintered (BZT-BCT) and PVDF powders were mixed thoroughly on a magnetic stirrer for 1h. The mixture was then subjected to ultrasonic agitation to evenly disperse the powder and then hot-pressed at 150°C to obtain a sheet of area 180 mm² and 0.4 mm thickness. A series of (BZT-BCT)-PVDF composites with different ceramic volume fractions ranging from 5 to 25 % were fabricated. The samples were cut into rectangular shapes for characterization. XRD analysis of the composites were performed with a Philips X-ray diffractometer X'PertMPD using Cu K α ($\lambda = 0.15405$ nm) radiation to examine the phases present. The microstructures were observed using scanning electron microscope (SEM, JEOL JSM-6480LV). The bulk densities of the samples were measured by the Archimedes method. Silver paste was applied on both sides of the samples for electrical measurements. Values of ϵ_r and $\tan\delta$ were measured as a function of both temperature and frequency with a computer-interfaced HIOKI 3532-50 LCR HITESTER. Poling of the composite samples was done by the corona discharge method by applying a high voltage of 5 kV for 20 min. d_{33} values of the composite samples were measured using piezometer.

RESULTS & DISCUSSION

Figure 1 shows the XRD patterns of $\Phi\{0.50[\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3]-0.50[(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3]\}-(1-\Phi)\text{PVDF}/[(\text{BZT-BCT})-\text{PVDF}]$ (where $\Phi = 0.05, 0.10, 0.15, 0.20$ & 0.25 volume fractions) ceramic polymer composites with 0-3 connectivity. XRD pattern of the composite samples shows the presence of both (BZT-BCT) ceramic and PVDF polymer peaks showing good connectivity between the ceramic phase and polymer phase. Again with the increase in ceramic volume fraction, the XRD pattern of the composites shows peaks more resemblance with (BZT-BCT) ceramic.

Figure 2 shows SEM micrographs of (BZT-BCT)-PVDF composite samples with different volume fractions. SEM figure shows even distribution of ceramic particles in PVDF matrix which is well agreement with 0-3 connectivity pattern [7]. Again, the composite samples show the increase in the distribution of (BZT-BCT) ceramic phase with the increase in the volume fraction.

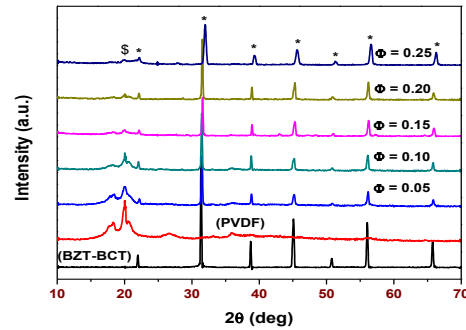


Fig. 1 XRD patterns of $\Phi(\text{BZT-BCT})-(1-\Phi)\text{PVDF}$ composites, where \$, and * represent PVDF, and (BZT-BCT) phases, respectively.

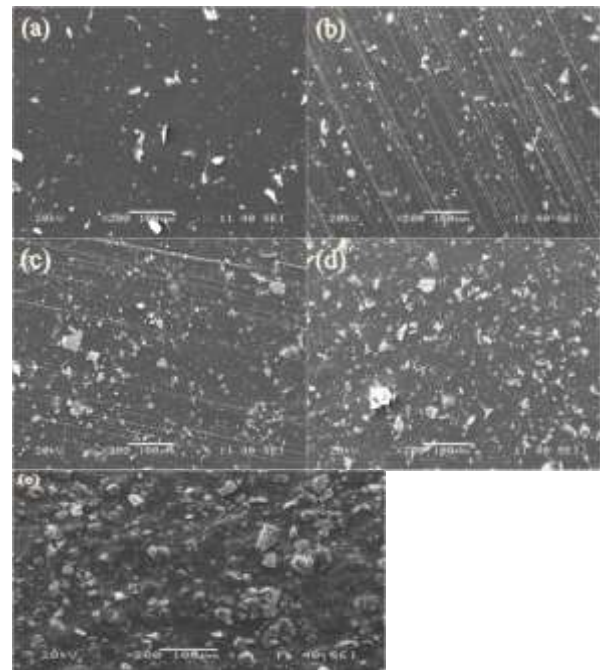


Fig. 2 SEM images of $\Phi(\text{BZT-BCT})-(1-\Phi)\text{PVDF}$ composites with (a) $\Phi = 0.05$, (b) $\Phi = 0.10$, (c) $\Phi = 0.15$, (d) $\Phi = 0.20$ & (e) $\Phi = 0.25$, respectively.

Figure 3 shows the density and porosity of the (BZT-BCT)-PVDF composites as a function of volume fractions of (BZT-BCT). The experimental densities of the composite samples are found to increase from 2.01 to 2.43 g/cm³ with an increase in volume fraction of (BZT-BCT) ceramics.

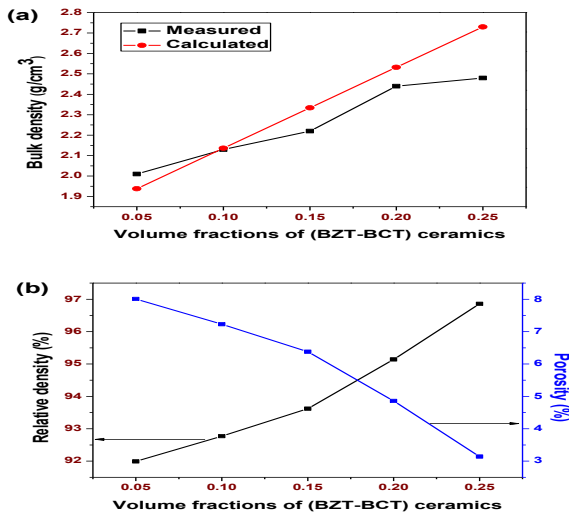


Fig. 3 (a) Bulk density, and (b) Porosity of (BZT-BCT)-PVDF composites as a function of volume fractions of (BZT-BCT).

Figure 4 (a) shows room temperature (RT) variation of ϵ_r with frequency for the composite samples. ϵ_r values for all the compositions are found to be higher than the ϵ_r value of PVDF polymer and lower than the ϵ_r value of (BZT-BCT) ceramics. Again ϵ_r values increase with the increase in volume fraction of the composite samples and a highest $\epsilon_r \sim 41$ at 1 kHz frequency is found for 25 vol% of (BZT-BCT) ceramics.

Figure 4 (b) shows frequency dependence of dielectric loss of (BZT-BCT)-PVDF composite samples. Figure shows a decrease in $\tan\delta$ value in 100 Hz-10 kHz frequency range and then increase in loss values ~ 1 MHz. The decrease in loss values at lower frequency range may be due to addition of ceramics. This may be due to interfacial polarization due to the heterogeneous nature of the composite system. Again the increase in loss values at higher frequency ranges may be due to the onset of ohmic conductivity of ceramic particles and also due to relaxation processes of polymer [8,9].

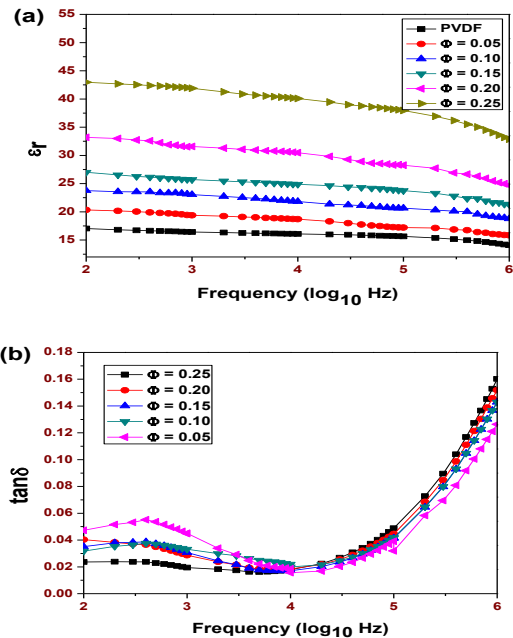
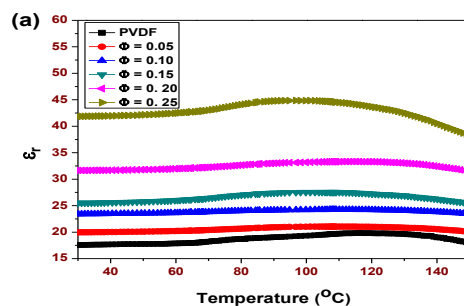


Fig. 4 Frequency dependence of (a) ϵ_r and (b) $\tan\delta$ of PVDF, and Φ (BZT-BCT)-(1- Φ)PVDF composites with $\Phi = 0.05, 0.10, 0.15, 0.20,$ and $0.25,$ respectively.

Figure 5 (a) shows temperature dependence of ϵ_r of composite samples at 1 kHz frequency. Figure shows increase in ϵ_r value with the increase in (BZT-BCT) ceramic volume % upto a certain temperature range and then it starts decreasing. Figure 5 (b) shows the temperature dependence of dielectric loss of the (BZT-BCT)-PVDF 0-3 composites at an applied frequency of 1 kHz. The loss curves of the composite samples do not follow a particular trend. The dielectric loss values are almost constant in the 30 – 80 °C temperature range and then suddenly it starts increasing. This change in loss values can be attributed to the presence of different types of polarizations in the composites.



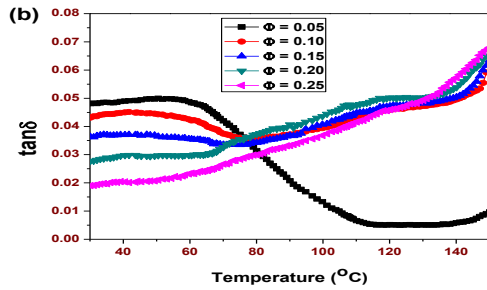


Fig. 5 Variation of (a) ϵ_r and (b) $\tan\delta$ with temperature at 1 kHz frequency of PVDF, and $\Phi(\text{BZT-BCT})-(1-\Phi)\text{PVDF}$ composites with $\Phi = 0.05, 0.10, 0.15, 0.20, \text{ and } 0.25$, respectively. A maximum d_{33} value ~ 31 pC/N is found in 25 vol% of (BZT-BCT)-PVDF composites. The performance of a piezoelectric material for energy harvesting applications can be expressed as the figure of merit (FOM) presented in the following Eqn FOM $\left(\frac{\text{pm}^2}{\text{N}}\right) = d_{33} * g_{33} = \frac{(d_{33})^2}{\epsilon}$ (1)

Figure 6 shows the FOM of (BZT-BCT)-PVDF composites as a function of (BZT-BCT) ceramic content for energy harvesting application. The FOM reaches maximum when the volume fraction of (BZT-BCT) ceramics is 0.25. g_{33} values are greatly affected by the volume fractions of ceramic filler. Therefore the maximum FOM for 0.25 volume fraction of ceramics can be attributed to the effect of g_{33} on the ceramic concentration. This phenomenon can also be explained by counteracting effects of density on the d_{33} [10].

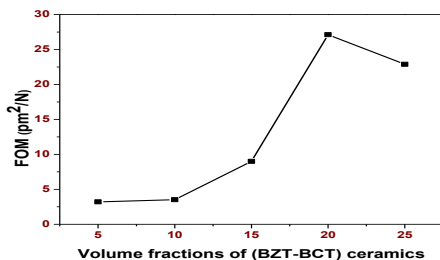


Fig. 6 FOM for energy harvesting application for (BZT-BCT)-PVDF composites as a function of the volume fractions of (BZT-BCT) ceramics.

CONCLUSION

The structural study of all the composite samples shows the presence of both ceramic and polymer phases. SEM studies confirm good connectivity of ceramic and polymer samples as desired in 0-3 composites. 0.25(BZT-BCT)-0.75(PVDF) composite

showed the highest relative permittivity (ϵ_r) ~ 42 with low temperature coefficient of capacitance and highest $d_{33} \sim 31$ pC/N. Hence, it can be concluded that 0.25(BZT-BCT)-0.75(PVDF) ceramic polymer composite is suitable for flexible capacitor devices and also for energy harvesting piezoelectric applications.

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