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High performance Mn doping in BCZT ceramic material for piezoelectric Generator

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Abstract : In this article, we report the synthesis and characterization of material used for self-poled and flexible piezoelectric generator using lead free ceramics BCZT and BCZT-Mn3% nanoparticles embedded in PVDF polymer matrix. The result presented in this article shows that the piezoelectric generator containing BCZT doped with 3% Mn shows excellent electrical and piezoelectric performance on comparing with pure PVDF and BCZT-PVDF. It can generate 4.5V under gentle finger tapping. With the integration of Mn in BCZT nanoparticles incorporated with PVDF it enhances the electrical and mechanical properties, leading its enhanced piezoelectric performance.

Keywords- *Polyvinylidene fluoride (PVDF), BCZT_PVDF, BCZT-Mn3%_PVDF, solution casting, Dielectric, Flexible device, Piezoelectric energy generator (PEG).*

Introduction

Recently, portable electronic devices have become increasingly fashionable in health monitoring, wireless sensor networks, artificial intelligence, human machine interface, smart homes, and the Internet of Things. Additionally, a variety of small electronic devices and sensors require low power in remote location, brings a whole new challenge. Piezoelectric materials are the good option to tackle this issue [1,2]. Already piezoelectric materials have been widely used in various devices such as sensor, actuator, and high energy density capacitor due to their excellent dielectric, piezoelectric and ferroelectric properties. However, ceramics forms high dielectric constant but those materials are less exploited in related devices due to their brittle nature, low elasticity, and small dielectric breakdown strength which limits its applications. In contradiction to that polymer shows better mechanical strength, good flexibility. By combining ceramic with polymer, to form ceramic polymer composite it is expected to show higher breakdown strength, flexible as compared to ceramic and high dielectric constant as compared to PVDF [3]. Therefore, recently researchers have more focused on ceramic polymer composite and have explored in various practical applications.

Among all polymers and co-polymers PVDF has an electroactive polymer with semicrystalline in nature, which shows dielectric, piezoelectric, pyroelectric and ferroelectric properties. PVDF has exists in α, β, γ, δ phases depending upon (CH_2-CF_2) arrangement in polymer matrix. α-phases are non-polar whereas β and γ phases are polar phase (electroactive phase) which is responsible for ferroelectric and piezoelectric properties. To enhance electroactive phase in PVDF there are different mechanisms such as stretching, electro poling, hot pressing and electrospinning have been successfully investigated. Recently, addition of various piezoelectric nanoparticles such as PZT, PMN, etc based filler have been used in polymer matrix to enhance β-phase. As lead based materials are highly toxic in nature, lead-free barium titanate (BT) in morphotropic phase boundary region is an ideal replacement [4].

In this work we developed perovskite based lead-free BT ceramic with Ca^{2+}, Zr^{2+}, Mn^{4+} doping at defined ratio using solid state reaction route (SSR) route and BCZT-PVDF ceramic polymer composite by solution casting and hot-pressing technique. It achieved better piezoelectric coefficient and consisting phase transition considered as morphotropic phase boundary. No detail studies have been reported w.r.t enhanced electro active phase and to enhance piezoelectric performance of wearable flexible piezoelectric energy harvester. So, our work is on those aspects.

Experimental

Synthesis procedure

Solid state reaction route was used for the synthesis of ceramic using stoichiometric amount of BaO_2 (99.9%), $CaCO_3$ (99.9%), ZrO_2 (99.9%), TiO_2 (99.9%), and MnO_2 (99.9%). Detailed synthesis and analysis of BCZT & BCZT-Mn3% of ceramic preparation in solid state reaction route were reported in literature [5].

In order to prepare the piezoelectric ceramic polymer composite by solution casting technique. N, N-dimethylformamide (DMF) and PVDF were mixed in desired ratio. The solution was stirred till PVDF completely dissolved in DMF, then 10wt% of BCZT and BCZT-Mn added to the solution under stirring. Sonication was also done several times for homogeneous dispersion. Dispersed polar solvent were tape casted and dried in an oven at 80^0c for 4hr. After drying the free-standing polymer film were hot-pressed to improve the electroactive phase in polymer matrix as well as to get homogeneous film thickness. Free standing film in desired size were taken to fabricate piezoelectric harvester.

Characterization.

The structural analysis of the composite was carried out by using XRD technique (PANalytical, model Xpert Pro), with Cu Kα1 radiation. FTIR spectroscopy analysis carried out by using Alpha II, Bruker in the wavenumber range of 700 to 1400 cm^{-1}. The electrical properties were studied by HIOKI IM3570 Impedance Analysed in the frequency range from 4Hz to 5MHz at room temperature. Fabricated piezoelectric performance of polymer composite film were carried out by using digital oscilloscope DSM01002(scientific).

Result and discussions

From fig.1 (a) shows the X-ray diffraction pattern of PVDF and PVDF-ceramic (BCZT, BCT-Mn) polymer composite consists of crystalline peak with broad background hump which suggests films are semicrystalline nature. At diffraction angle 18.3^0 and 20.12^0, suggests α and β phase in crystalline plane (020) and (110) respectively [6]. Here we observed, that BCZT and BCZT-Mn ceramic fillers are uniformly dispersed in PVDF matrix. These results were good agreement with FTIR analysis in fig.1 (b). The compositional band structure and electroactive phase of PVDF and PVDF ceramic composite have been evaluated. Here the phase transition of α to β and dipolar orientation were examined. The FTIR band at 764cm^{-1} and 794cm^{-1} represents CH_2 rocking which represents non-polar α-phase. Whereas band at 840cm^{-1} and 833cm^{-1} were referred to polar β & γ- phase respectively, responsible for dipolar orientation and energy harvesting application.

Structural and electrical analysis:

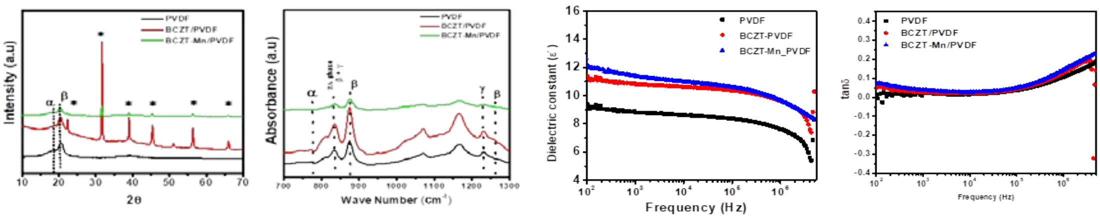

Fig. 1. *(a, b, c,d) are the, X-ray Diffraction, FTIR, Dielectric, and Dielectric Loss plots of Pure PVDF and PVDF- Ceramic polymer composite.*

In our study the electroactive phase of BCZT-Mn ceramic PVDF composite is 86.65% which is maximum as compared to BCZT-PVDF and pure PVDF are 83.74% and 73.89% respectively. Fig.1 (c, d) represents the dielectric constant and dielectric loss of polymer composite film carried out with respect to frequency at room temperature. Due to the addition of Mn3% in BCZT nano particles it increases conductivity and resistivity properties of the sample decreases. Due to the formation of additional charge and conducting network in ceramic polymer matrix the dielectric constant and dielectric loss value increases in BCZT-Mn3%_PVDF polymer composite [5].

Device fabrication and testing

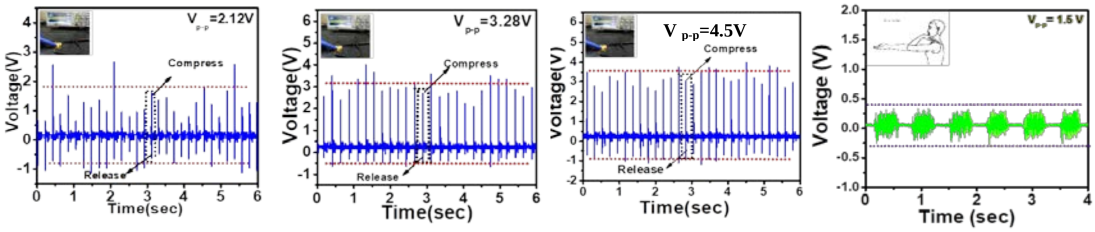

Fig. 2. *(a, b, c) & (d) are represents the output voltage of PVDF and PVDF-ceramic composite film obtained by gently human finger tapping and bending elbow of human body.*

Piezoelectric performance of PDVF and PVDF composite film with (2cm × 2cm) were taken. PVDF, BCZT-PVDF and BCZT-Mn3%_PVDF polymer composite film with (2cm × 2cm) were taken. Obtained films were sandwiched by two Al foil serving top and bottom electrodes, two copper wires were attached in both top and bottom electrode for output voltage measurement. The PEG additionally sandwiched by using Kapton Tape which provides a good protection, mechanical agitation, water and dust proof PEG. Here fig-2 (a, b, c) represents the piezo performance of human finger-tapping motion. In our work, BCZT-Mn/PVDF ceramic-polymer composite shows better piezo performance than the device prepared by BCZT-PVDF and PVDF piezoelectric generator. We have achieved 4.5V which is two times maximum than pure PVDF. Due to the presence of external charge carrier of Mn in BCZT ceramic it increases one time the output voltage. We have obtained 1.5V by bending PEG by human elbow.

Conclusion

Here we have successfully synthesised PVDF, 10wt% BCZT_PVDF, 10wt% BCZT-Mn3%_PVDF polymer composite by solution casting technique. XRD plot represents the β-phase at diffraction angle 20.6^0, which confirmed that the ceramic particles are well dispersed in PVDF matrix. In FTIR analysis the electroactive β-phase found to be 86.65% by Mn3% doped with BCZT nanoparticles which is maximum than other two films. The dielectric permittivity and piezoelectric performance of Mn doped sample has achieved maximum dielectric and output voltage i.e., 4.5V by human finger tapping. The output voltage obtained by Mn doped sample is two times and one times than pure PVDF and BCZT_PVDF composite PEG. Our work suggests a good potential in Mn doped in BCZT-PVDF composite film with certain modification to be used in wearable and flexible energy harvester.

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