International Review of Applied Engineering Research.
ISSN 2248-9967 Volume 4, Number 1 (2014), pp. 57-64

http://www.ripublication.com/iraer.htm

Core Shell Structured Multiferroic Nanocomposites for Smart Energy Harvesting: Electric Powering for Portable Electronic Devices

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Abstract

In this investigation, we highlight the advanced smart energy harvesters as sources for the portable electronic devices, medical applications, especially in remote zones where there is a scarcity of electric power supply. Core-shell structured $x[0.5Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.5(Ba_{0.7}Ca_{0.3})TiO_3]$-$(1-x)CoFe_{1.8}Cr_{0.2}O_4$, x ranging from 0.2, 0.4, 0.6, 0.8 multiferroic nanocomposites were synthesized by green co-precipitation method and were characterized for phase genesis, micro and nanostructural features, chemical stoichiometry, dielectric, relaxor, ferroelectric, piezoelectric, field induced strain, ferromagnetic and magnetoelectric properties. These nanocomposite core-shells ranged from 8 to 22 nm were dispersed in Polyvinylidene fluoride. These nanocomposite films were electroded and DC field poled samples were characterized for ferroelectric and piezoelectric characterizations. x = 0.6 nanocomposite prototype was found to be optimum for piezoelectric power conversion. Thus, this nanocomposite could be used as energy harvester for possible electronic devices.

Keywords: Core-shell, multiferroics, BZT-BCT, CFCO, energy harvesting, medical applications.

1. Introduction

Energy crisis is one of the most important problems to be resolved since the sources of energy are very limited. The solution for the energy crises is by means of energy harvesting from piezoelectric and multiferroic systems, which are green and most efficient process, and thus applicable as energizing portable electronics, medical diagnostic appliances and rural / remote areas applications. These emerging technologies of piezoelectric and multiferroic energy harvesters for energy conversion from naturally available mechanical and electromagnetic fields to electric charge, and then to dc electric power, which is quite suitable for portable electronics, and thus reduces electric power cost also. Magnetostrictive materials (used in actuators) exhibit a change in shape (strain or elongation) when an external magnetic field is applied. The reverse effect is called piezomagnetism (used in sensors), where a magnetic field is produced/altered upon application of a mechanical strain [**1**]. Materials, which are piezoelectric and magnetostrictive at the same time, are generally called "Magnetoelectric" or "Multiferroic" materials. Magnetoelectric (ME) materials show magnetically polarized when subjected to an electric field, and electrically polarized when subjected to a magnetic field. The ability to mutually switch control between magnetic and electric properties make the ME materials very smart for many applications e.g. multiple state memory elements, sensors, transducers, actuators, etc [**2**]. As compared to single phase multiferroic, piezoelectric-multiferroic composite materials exhibit larger magnetoelectric coefficients and therefore better suited for practical applications. Magnetoelectric (ME) materials become magnetized when placed in an electric field, and electrically polarized when placed in a magnetic field. The ability of mutual switching control between magnetic and electric properties make the ME materials very attractive for many applications. Multiferroic materials exists in single phase and bi-phase systems, however, bi-phase systems as composite formation can offer optimum functional properties for desires applications, i.e, these are multifunctional single or multifunctional-multicomponent composites showing applications on both sides of ferroelectric /piezoelectric and magnetic arena [**3**]. Among single phase non-Pb based piezoelectric systems, $Ba(Zr,Ti)O_3$-$Ba(Ca,Ti)O_3$ termed as BZT-BCT is superior piezoelectrics so far studied by several researchers and this system offers same rich functional properties as Pb-based PZT system. Several researchers have studied this BZT-BCT by solid state reaction method, sol-gel and several complex methods [**4-6**]. As far as authors knowledge and literature review, synthesis of BZT-BCT by green and inexpensive route of co-precipitation method is not reported so far in the literature. The magnetic properties of the spinal structured ferrites can be modified by substitutions or additions and also by controlling the processing parameters. Among which $CoFe_2O_4$ is well studied ferrite system with optimum magnetic properties. The tenability of magnetic properties towards hard and soft nature depends on substituting element and processing routes, and most of the ferrites have been studied by sol-gel, precipitation, and solid state reaction method and other thin film and nanomaterials [**7-12**]. Thus, in this investigation, we have considered multiferroic composite (piezoelectric BZT-BCT-Ferrite CFCO) system prepared by co-precipitation route to explore their optimum functionality for energy harvesting and medical applications. The conventional solid state reaction route involves lead volatilization, high temperature processing, time consumption, stoichiometric problems in end products the major issues. The main drawback in mechanical activation technique is the contamination. In order to over these constraints, it is indeed essential to have a process in which there is high purity and yield with low processing temperatures and agglomeration-free particles. Coprecipitation route is proposed as it plays a crucial role in preparing the fine end product by minimizing problems associated with diffusion, homogeneity, impurities, agglomeration, controlling of the particle surface state when compared to the conventional processes.

In this investigation, we have considered Cr modified CFO ferrite system as magnetic component and BZT-BCT as electric component. Accordingly, we have synthesized $CoFe_{1.8}Cr_{0.2}O_4$ nano-powder by co-precipitation route, which is dispersed during the synthesis of $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.5(Ba_{0.7}Ca_{0.3})TiO_3$ by co-precipitation route to cover CFCO particles to form BZT-BCT-CFCO core-shell structured nanocomposite powders, by varying x from 0.2, 0.4, 0.6, 0.8 in $x[0.5Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.5(Ba_{0.7}Ca_{0.3})TiO_3]$-$(1\text{-}x)CoFe_{1.8}Cr_{0.2}O_4$.

2. Experimental

Initially CFCO nanopowders are synthesized and optimized and then dispersed during the synthesis of BZT-BCT to cover CFCO core particles with BZT-BCT shells, as stated in the following section:

2.1 Synthesis and characterization of CFCO nanopowders

Aqueous solutions of Cobalt Sulphate, Chromium Chloride and Ferrous Ammonium Sulphate by using NaOH solvent were mixed in stoichiometric ratios (all these reactives are high pure 99.99% and from Sigma Aldrich, USA). This mixture was kept in a water bath at 70°C and subsequently, pure oxygen was bubbled into it. After attaining the temperature in mixture, freshly prepared 5 M NaOH was added drop wise with constant stirring till the pH of the medium reached 11.0. The whole content of the solution was kept at 70°C. The dark brown precipitate was filtered and washed with DI water until it shows pH as 7. The obtained precipitate was dried at 100°C for 24 h. Dried power was characterized for phase formation by powder X-ray diffraction technique and nanostructure analysis by Transmission Electron Microscopy, and magnetic properties by Vibrating Sample Magnetometer (VSM) studies.

2.2 Synthesis and characterization of core-shell x(BZT-BCT)-(1-x)CFCO, x=0.2, 0.4, 0.6 and 0.8 nanocomposites

All the reactives and solvents used in this study are high pure (99.999) and obtained from Sigma Aldrich, USA. Initially, TiOCl2 stock solution was prepared by dropping TiCl4 into ice-cooled de-ionized water slowly with constant stirring, since TiCl4 is very hygroscopic and easily precipitates with water at room temperature. This stock solution is used through out series synthesis for different compositions synthesis. According to stiochiometric calculations stated below for CS-1, CS-2, CS-3 and CS-4, respective concentrated solutions of BaCl2, CaCl2 and ZrOCl2 were mixed with TiOCl2 stock solution thoroughly for 1 h. The molar ratio of Ba/(Zr+Ti) were fixed at 1.1 and the (Zr+Ti) concentration was 0.2 M. The mixed solution was mixed quickly with above prepared CFCO powder and NaOH solution (15 M) which was heated in an oil bath at 85°C. The gelatinous precipitate formed was stirred for 1 h and then the precipitation was filtered, washed with DI water, and dried at 80°C. These dried core-shell powders were characterized for phase formation by powder X-ray diffraction technique and nanostructure analysis by Transmission Electron Microscopy, and magnetic properties by Vibrating Sample Magnetometer (VSM) studies.

Core-shell structured nanocomposites prepared were:

x = 0.2: CS-1: $0.2[0.5Ba(Zr_{0.2}Ti_{0.8})O_3\text{-}0.5(Ba_{0.7}Ca_{0.3})TiO_3]\text{-}0.8CoFe_{1.8}Cr_{0.2}O_4$
x = 0.4: CS-2: $0.4[0.5Ba(Zr_{0.2}Ti_{0.8})O_3\text{-}0.5(Ba_{0.7}Ca_{0.3})TiO_3]\text{-}0.6CoFe_{1.8}Cr_{0.2}O_4$
x = 0.6: CS-3: $0.6[0.5Ba(Zr_{0.2}Ti_{0.8})O_3\text{-}0.5(Ba_{0.7}Ca_{0.3})TiO_3]\text{-}0.4CoFe_{1.8}Cr_{0.2}O_4$
x = 0.8: CS-4: $0.8[0.5Ba(Zr_{0.2}Ti_{0.8})O_3\text{-}0.5(Ba_{0.7}Ca_{0.3})TiO_3]\text{-}0.2CoFe_{1.8}Cr_{0.2}O_4$

These nanocomposites were dispersed in Polyvinylidene fluoride (PVDF) dissolved in Dimethylformamide (DMF) solvent, and deposited on micro-glass slide and dried at 80ºC for 4 hours. Dried samples were separated from glass plate and electroded as honey comb structured on both surfaces. DC field poled samples were characterized for piezoelectric charge coupling coefficients to optimize electric charge development across two electrodes against mechanical vibrations, and to know the out put power. The final prototypes were optimized depending on optimum piezoelectric charge coefficient as well magnetic properties.

3. Results and Discussion

3.1 X-ray diffraction results

Fig. 1 shows XRD patterns of core-shell xBZT-BXT-(1-x)CFCO multiferroic nanocomposites revealed the presence of both the spinel ferrite CFCO and tetragonal BZT-BCT perovskite phases [**4,8**], respectively. As the amount of x increased from 0.2 to 0.8, the coexistence of both tetragonality and spinal nature are evidenced in the XRD patters. Thus, the cations in the adjacent crystallites of both tetragonal perovskite and cubic spinal can interact each to enhance the electric and magnetic properties.

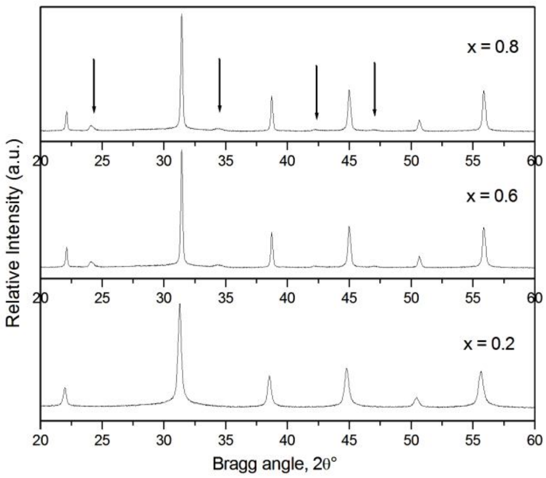

Fig. 1: X-ray diffraction patterns of core-shell xBZT-BXT-(1-x)CFCO nanocomposites

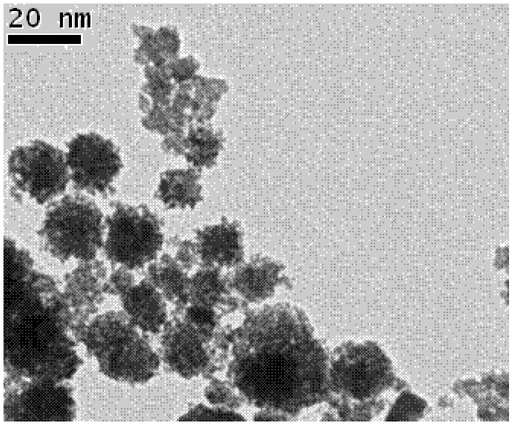

Fig. 2: Transmission micrograph of core-shell 0.6[0.5Ba(Zr0.2Ti0.8)O3-0.5(Ba0.7Ca0.3)TiO3]-0.4CoFe1.8Cr0.2O4nanocomposite

3.2 Transmission Electron Microscopy results

Fig. 2 shows TEM micrograph of core-shell $0.6[0.5Ba(Zr_{0.2}Ti_{0.8})O_3$-0.5 $(Ba_{0.7}Ca_{0.3})TiO_3]$-$0.4CoFe_{1.8}Cr_{0.2}O_4$ nanocomposite. These nanocomposite core-shells ranged from 8 to 22 nm. Cr modification in CFO with a cubic spinal structure resulted in spherical nature and further modification of tetragonal perovskite BZT-BCT (x) in the multiferroic nanocomposite resulted in spherical core-shell structured multiferroic nanocomposites as can be seen in Fig. 2. This could be attributed to both coexistence of spinel ferrite and tetragonal perovskite cations in the multiferroic nanocomposite system. These results are in agreement with literature [**7**].

3.3 Magnetic Properties

Fig. 3 shows magnetic properties of core-shell xBZT-BXT-(1-x)CFCO multiferroic nanocomposites. It is clear from the picture that as x (BZT-BCT) concentration increased both remanent and spontaneous magnetic polarizations decreased while slightly influencing the coercive magnetic field. This can be explained as the tetragonal perovskite BZT-BCT can enhance the piezoelectric nature in the composites as x increased while diminishing net magnetic nature due to lower concentrations of CFCO and predominant shell which could influence the magnetic ordering in the multiferroic nanocomposites. These results are in agreement with literature [**8-11**]. This inversely proportional nature supports dielectric and piezoelectric trend in the following section.

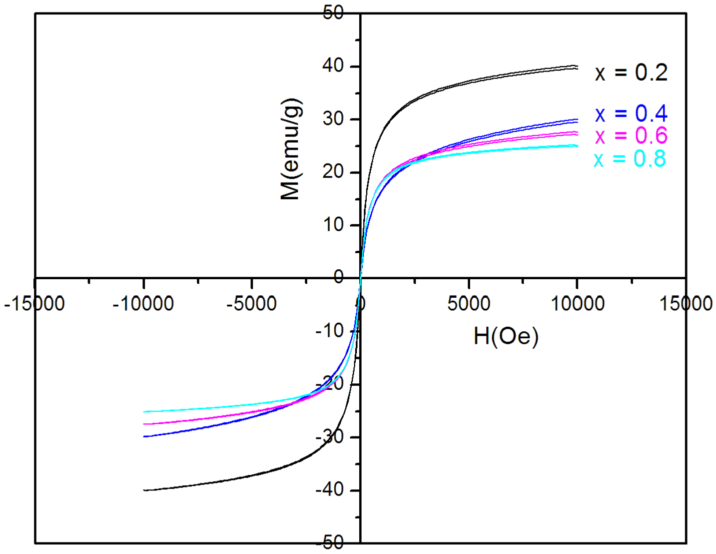

Fig. 3: Magnetic properties of core-shell xBZT-BXT-(1-x)CFCO nanocomposites

3.4 Dielectric and Piezoelectric properties

The following Table-1 shows the dielectric and piezoelectric data of core-shell xBZT-BXT-(1-x)CFCO multiferroic nanocomposites. As x increased in the multiferroic nanocomposites system, the electrical properties increased up to x = 0.6 and then decreased. In this series, x=0.6 is found to be optimum with relatively high dielectric constant, low dielectric loss and optimum piezoelectric charge and planar coupling coefficients since tetragonal BZT-BCT plays vital role along with spinal ferrite which influenced the electrical properties [**6**]. Further increase in x resulted in decresing trend in electrical properties due to interfacial effects between ferrite core (magnetic moments) to piezoelectric shell (electric dipoles) system. X = 0.6 has optimum electrical and magnetic properties that could be suitable for electrical and magnetic, and possible energy harvesting applications.

Table 1: Dielectric, piezoelectric properties of core-shell xBZT-BXT-(1-x)CFCO nanocomposites.

x = 0.2 (CS-1)	**2043**	**0.0682**	**294**	**0.304**
x = 0.2 (CS-1)	2043	0.0682	294	0.304
x = 0.4 (CS-2)	2286	0.0583	322	0.328
x = 0.6 (CS-3)	2489	0.0548	413	0.427
x = 0.8 (CS-4)	2381	0.0542	382	0.382

4. Conclusion

Core-shell xBZT-BXT-(1-x)CFCO multiferroic nanocomposites were successfully synthesized by green and inexpensive coprecipitation method. Powder x-ray diffraction results confirmed both coexistence of cubic spinal CFCO ferrite and tetragonal BZT-BCT perovskite, which influenced both magnetic and electrical properties in the series. Spherical core CFCO has supported to form spherical core-shell BZT-BCT-CFCO multiferroic nanocomposites and core-shells ranging from 8 to 22 nm. The interaction between ferrite core (magnetic moments) to piezoelectric shell (electric dipoles) and vice versa can be evidenced in this series. The optimum magnetic and electric features are found to be in x = 0.6 that could be suitable for possible energy harvesting applications.

5. Acknowledgements

This investigation had been funded by FONDECYT Project N°1110583, CONICYT, Chile. The author Koduri Ramam acknowledges funding authorities and University of Concepcion, Chile and Andhra University, India for extending their cooperation in carrying out this work.

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