Journal of Magnetism and Magnetic Materials ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Multiferroic and magnetoelectric properties of $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$–$CoFe_2O_4$ core–shell nanocomposite

Ajith S Kumar [a], C.S. Chitra Lekha [a], S. Vivek [a], Venkata Saravanan [b], K. Nandakumar [c], Swapna S. Nair [a,*]

[a] Department of Physics, Central University of Kerala, Kasaragod 671314, India
[b] Department of Physics, Central University of Tamil Nadu, Thiruvarur 610101, India
[c] School of Pure and Applied Physics, Mahatma Gandhi University, Kottayam 686560, India

ARTICLE INFO

Article history:
Received 16 November 2015
Received in revised form
10 February 2016
Accepted 20 February 2016

Keywords:
Multiferroic magnetoelectrics
Sol–gel method
Magnetocapacitance
Magnetoelectric coupling
Magnetoelectric sensors

ABSTRACT

Lead-free magnetoelectric (ME) composites with remarkable ME coupling are required for the realization of eco-friendly multifunctional devices. This work demonstrates the ME properties of $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$–$CoFe_2O_4$ (BCZT–CFO) core–shell composites synthesized via co-sol–gel technique. Room temperature ferroelectric and ferromagnetic characterization have shown that the samples are magnetic and ferroelectric along with an adequate magnetoelectric coupling of 12.15 mV/(cm Oe). The strong dependence of electric parameters on applied magnetic DC bias fields demonstrated in ferroelectric and magnetoelectric measurements provide a framework for the development of potential magnetoelectric devices. Also, the high sensitivity of magnetoelectric coupling towards the applied AC magnetic field can be used for its application in magnetoelectric sensors.

1. Introduction

The possibility of miniaturization of devices by incorporating multitasking materials is the impetus behind the research of multiferroic materials recently [1]; even though it was discovered long ago [2]. These materials possess two or more ferroic orders such as ferromagnetic, ferroelectric or ferroelastic and there is often coupling between these, which is known as magnetoelectric (ME) effect. This unique coupling mechanism gives an additional control to input and store data such as electric field control of magnetization and vice versa. The observed weak ME coupling in single phase natural compounds brings more interest in composite multiferroics especially piezoelectric-magnetostrictive composites [3]. Lead-based $PbTiO_3$–$PbZrO_3$ (PZT)-ferrite systems and lead-free systems such as (K,Na)NbO_3-ferrite, (Bi,Na)TiO_3-ferrite and $BaTiO_3$-ferrite systems have been extensively studied over the past decade [4–9]. Lead-based ceramics have been in the forefront for years due to their outstanding piezoelectric behavior (d_{33}=500–600 pC/N) [10, 11]. The major reason for these enhanced piezoelectric properties is due to the existence of a morphotropic phase boundary (MPB), where three phases coexist. Such enhanced properties are being attributed to the reduction in energy barrier near MPB for polarization rotation. But the global restrictions on lead-based compounds due to Pb-toxicity, urges the research world to find a better alternative to PZT. However the existing lead-free systems such as (K,Na)NbO_3 ($d_{33}\sim$250 pC/N), (Bi,Na)TiO_3 ($d_{33}\sim$200 pC/N) and $BaTiO_3$ ($d_{33}\sim$150 pC/N) lacks an MPB similar to PZT and hence possesses much lower piezoelectricity [12–15]. Among these lead-free systems; $BaTiO_3$ is a perovskite oxide whose electrical properties can be altered by substituting in either "Ba" site or "Ti" site or both with Calcium, Zirconium etc. Calcium substitution in "Ba" site has shown a phase transition from rhombohedral to cubic while Zirconium substitution in "Ti" site leads to a tetragonal to cubic phase transition [16]. Liu and Ren have shown that an MPB can be achieved by combining $Ba(Z_{0.2}Ti_{0.8}O_3)$ and $(Ba_{0.7}Ca_{0.3})TiO_3$ systems $(50Ba(Z_{0.2}Ti_{0.8}O_3)-50(Ba_{0.7}Ca_{0.3})TiO_3$ or $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ (BCZT)) [17]. The high performance lead-free piezoelectric system, BCZT, was delivered a very high piezoelectric $d_{33}\sim$620 pC/N, and a high permittivity ~3060 at 2 MHz, comparable to the ever market dominated lead-based PZT. Bao et al. presented another variant of BCZT, with a slightly higher critical temperature of 114 °C at the expense of a lower d_{33} (450 pC/N) [16]. Thus, BCZT system is a better alternative to the conventional lead based PZT systems. This offers wide possibilities in piezoelectric as well as

* Corresponding author.
E-mail address: swapna.s.nair@gmail.com (S.S. Nair).

http://dx.doi.org/10.1016/j.jmmm.2016.02.065
0304-8853/