Journal of Magnetism and Magnetic Materials 418 (2016) 294–299

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
Available online 22 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/

magnetoelectric devices, whose potential is seldom been investigated.

Magnetoelectric effect in composite materials is a product property often mediated via strain. So a magnetic material with high magnetostriction is essential to get an enhanced ME coupling in composites. Cobalt ferrite (CFO) possesses a very high magnetostriction, the highest among all known ferrites. A very high value of magnetostriction ~200–345 ppm has been reported for polycrystalline samples of cobalt ferrite [18–20]. Also, the high saturation magnetization (~80 emu/g) [21] and the coupling coefficient of CFO [20] in bulk makes it an ideal candidate for developing an ME composite for sensor and actuator applications.

The leakage current in the ferrite phase can adversely affect the ME coupling of the composite. A core–shell structure is ideal for separating ferrite particles and thereby reducing leakage current [22]. Also, the possibility of epitaxial growth of a ferroelectric shell over the ferrite core can increase the surface area between the ferrite-ferroelectric interface, and this will significantly enhance the ME coupling [23,24]. Hence, in the present work, we propose a core–shell magnetoelectric composite based on lead-free piezoelectric fabricated by employing BCZT as piezoelectric and CFO as the magnetostrictive component to combine their functionalities and tailor the ME coupling.

2. Experimental details

2.1. Synthesis and preparation of composite

The $80\%Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3 - 20\%CoFe_2O_4$ core–shell nanocomposites were synthesized by sol–gel method. Here the composite was prepared by taking 80 mol% BCZT and 20 mol% CFO as the piezoelectric and magnetic component in order to obtain well dispersed magnetic nanoparticles in a ferroelectric matrix. Stoichiometric amounts of Barium Acetate ($Ba(CH_3COO)_2$) and Calcium Acetate ($Ca(CH_3COO)_2$) were dissolved in preheated glacial acetic acid. Zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) and Titanium (IV) isopropoxide ($TiC_{12}H_{28}O_4$) dissolved in methanol were mixed with the above solution and stirred well. The stability and viscosity of the sol were optimized before making composite sol. Cobalt Nitrate ($Co(NO_3)_2 \cdot 6H_2O$) and Ferric Nitrate ($Fe(NO_3)_2 \cdot 9H_2O$) were used as the precursors and ethylene glycol as the solvent for the synthesis of CFO sol. The stabilized sols of both CFO and BCZT were mixed in the molar ratio 1:4 and stirred well. The obtained composite sol was heated at 60 °C to get a gel followed by a heat treatment at 200 °C to burn out the organic solvent. The as-synthesized powder was ground well and annealed at 850 °C. The pure phase CFO and BCZT were also synthesized for comparative studies. For electrical measurements, the powder was pressed into a pellet using a uniaxial hydraulic pellet press at an applied pressure of 2.5 t. The pellets were sintered at 850 °C for densification, crystallization and grain growth. Electrical contacts were soldered after depositing a thin layer of silver paste on either side of the pellet.

2.2. Characterization techniques

The structural characterization of the sample was carried out using Rigaku Miniflex-600 X-Ray diffractometer, with Cu-Kα radiation ($\lambda = 1.54$ Å) in the $\theta - 2\theta$ mode in horizontal sample loading mode. Microstructural images were obtained employing a High Resolution Transmission Electron Microscope, HR-TEM (JEOL, JEM-2100). The magnetization characteristics were obtained from the VSM module of multifunctional VSM (Versa lab, Quantum Design). The dielectric studies were performed using an LCR meter (Wayne-Kerr 6500B) in which the pellets were used as a sandwiched parallel plate capacitor structure and a thin layer of deposited silver paste served as the conducting layers. An electromagnet which can go up to 4 kOe was employed along with this setup to measure the magnetic field response of the dielectric characteristics (magnetocapacitance). PE loops traced at different applied magnetic fields using a setup consists of a PE loop tracer (Marine India) and a DC electromagnet which can go up to 3 kOe. Magnetoelectric coupling measurements were done with an automated system (Marine India).

3. Results and discussion

3.1. Structural and Microstructural characterization

Fig. 1 shows the X-Ray diffractograms of pure BCZT, CFO, and core–shell BCZT–CFO powders. The diffraction peaks of composite powder are indicative of both inverse spinel CFO and perovskite BCZT without any impurity (ICDD no: 00-001-1121 and 00-063-0610 respectively). Thus, the structures of both ferrite and ferroelectric are not modified and no other phases are formed by the intermixing of sols.

Fig. 2(a) and (b) shows the TEM micrographs of the BCZT–CFO core–shell particulate composite. The microstructure analysis indicates that the majority of particles formed are having the core–shell structure. The crystallographic phases are clearly identified as CFO core with (220) orientation and BCZT shell with (110) orientation. The average particle size of CFO core and BCZT shell as seen from the micrograph are ~9 and ~20 nm respectively. The formation of the core–shell structure is due to the difference in the crystallization temperature for CFO and BCZT. The low crystallization temperature of CFO enables it to act as the seeding site and BCZT forms as a shell later.

3.2. Magnetic properties

The magnetic field dependence of magnetization of the CFO and BCZT–CFO core–shell particulate composite at room temperature is presented in Fig. 3.

The observed saturation magnetization ($M_s = 65.31$ emu/g) of CFO is less than the bulk value of ~80 emu/g. This reduction is due the incomplete crystallization of the sample at the nano-regime.

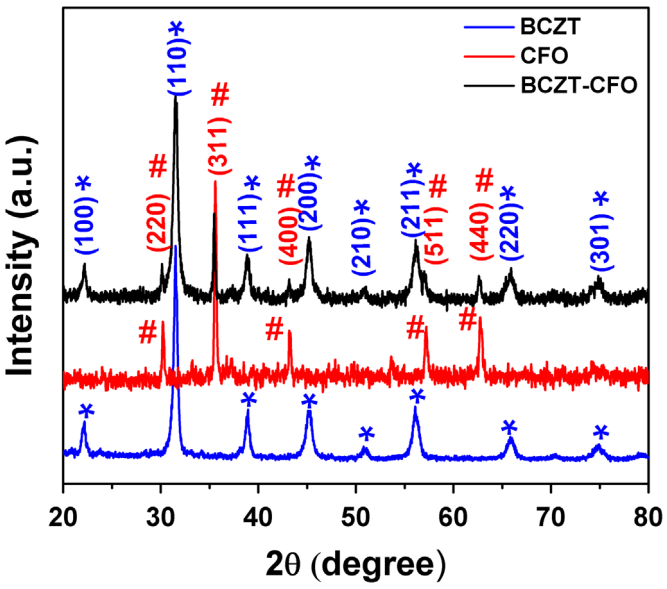

Fig. 1. X-Ray diffraction patterns of BCZT, CFO, and core–shell BCZT–CFO powders.