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Magnetoelectric 0.2(CoFe₂O₄)-0.8(Ba_{0.85}Ca_{0.15} Zr_{0.1}Ti_{0.9}O₃) lead free composite for spintronic applications

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Abstract. Lead free (0.2) $CoFe_2O_4$ (CFO) – (0.8) $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ (BCZT) composite is prepared by mechanical mixing of CFO and BCZT phases. The constituent phases, CFO and BCZT are prepared by sol-gel technique. XRD data shows characteristic peaks of both magnetic and piezoelectric phases without any secondary phases confirming the formation of the composite. Polarization (P) versus Electric field (E) measurements show a proper ferroelectric loop for BCZT with $P_{\text{max}} \sim 4.3 \ \mu\text{C/cm}^2$ whereas composite shows a leaky behaviour. Room temperature *M*-*H* loops show a decrease of magnetization from ~ 80 emu/g for pure CFO to 17 emu/g for composite. Thus, 0.2 CFO- 0.8 BCZT composite shows both electric and magnetic properties at room temperature.

1. Introduction

Magnetoelectric multiferroics are materials which show simultaneous ferromagnetic and ferroelectric orders. Such materials have magnetoelectric (ME) effect, which is characterized by a coupling between a magnetostrictive and piezoelectric phase. They are of great interest due to its promising applications in the development of actuators, sensors, spintronic devices, bio-medical applications etc. [1-4]. Compared to the single phase ME based materials, composites show a high ME coupling coefficient at room temperature, which is very essential for realizing the applications [2]. However, the choice of suitable magnetostrictive and piezoelectric compounds dictates the ME coupling in the composites. Moreover, the individual phases of the composite can be tuned as per the requirements, increasing the degrees of freedom in designing the device as to meet the necessities.

CoFe₂O₄ (CFO) is a well-known hard magnetic material with high magnetostrictive nature and high strain sensitivity. For CFO, the magnetostriction and strain values are reported to be 230 ppm and $1.3*10^{-9}$ A⁻¹m respectively [1, 3]. Also, CFO has the advantage of showing a high mechanical stability, low thermal conductivity and excellent corrosion resistance [1]. Hence, CFO is a suitable magnetostrictive material to make ME composite. On the other hand, $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ (BCZT) is a very good lead free- piezoelectric material with a high piezoelectric coefficient, d₃₃ ~ 620 pC/N [4-9]. The high piezoelectric coefficient in this material is governed by the existence of morphotropic phase boundary (MPB) at room temperature, causing a low energy barrier for polarization rotation and hence lattice distortion [4-6]. To obtain the high ME coupling, we have taken CFO as the magnetic phase and Ba_{0.85}Ca_{0.15} Zr_{0.1}Ti_{0.9}O₃ (BCZT) as the piezo-electric phase. In this study, CFO and BCZT have been synthesized successfully by sol-gel technique. The particulate composite has been prepared by mixing mechanically 20% of CFO and 80% of BCZT powders. Praveen P J et. al [2, 7] studied



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magnetoelectric response from CFO-BCZT composites in the laminated and particulate form. They have reported a high magnetoelectric coupling coefficient value (α_{ME}) ~ 803 mV/cm Oe⁻¹ [2] for the trilayer laminate composite and 6.85 mV/cm Oe⁻¹ for the 0.5CFO-0.5BCZT particulate composite at 1 kHz [7]. In this respect, it is interesting to investigate the compositional dependence of the α_{ME} in bulk and film forms. In the present study, we have systematically investigated the structural, magnetic and ferroelectric properties of the 0.2CFO-0.8BCZT bulk particulate composite. We report the detailed structural analysis and the observation of room temperature multiferroic characteristics in the composite.

2. Experimental Details

2.1. Preparation of Composite

Ferrimagnetic CFO and ferroelectric BCZT ceramics were synthesized using sol-gel method. Both the compounds were synthesized using analytical reagent (AR) grade chemicals. CFO was synthesized using cobalt acetate and ferric nitrate as precursors. These precursors were dissolved in deionized water and citric acid was added. After the solution becomes clear, it was kept at 250 °C under constant stirring. At this stage, nitrates and other organics get evaporated and a black powder formed at the end of the reaction. This powder is collected and calcined for the phase formation.

Barium nitrate, calcium nitrate, zirconium oxynitrate and titanium iso-propoxide were used as the precursors for the preparation of BCZT. The precursors were weighed carefully in stoichiometric ratios using the sensitive balance. Barium nitrate, calcium nitrate and zirconium oxynitrate were separately stirred and dissolved in deionized water till a clear solution was formed. Titanium iso-propoxide was taken in ethylene glycol under the inert atmosphere to avoid the formation of TiO_2 precipitate. Later, all the solutions were mixed together and citric acid was added as a chelating agent under constant stirring for 10 hr. The solution was then heated at 250 °C to remove all the organics. At the end, a gel was formed and dried. The dried xerogel powders were collected and calcined to form the required BCZT phase.

CFO-BCZT composites were synthesized by mechanical mixing of the individual powders of CFO and BCZT (prepared as mentioned above) with weighted fraction. The weight fractions of ferrite (CFO) and ferroelectric (BCZT) phases were taken in the 1:4 ratio to form 0.2 (CoFe₂O₄)-0.8 (Ba_{0.85}Ca_{0.15} Zr_{0.1}Ti_{0.9}O₃) (0.2CFO-0.8BCZT). The particulate composite was made into pellets and sintered at 1000 °C for 24 hr. Further characterizations were carried out on these pellets.

2.2. Characterization Techniques

The crystalline structure of the particulate composite was investigated using a Rigaku X-ray diffractometer with Cu K_a wave length (1.5406 Å). For the electrical measurements, silver electrodes were applied in the capacitor geometry and heated at 200 °C. *P-E* loop measurements were performed using Radiant Premier Ferroelectric Tester. Magnetic measurements were carried out using Lake Shore VSM in the presence of an external magnetic field of ± 1.7 kOe.

3. Results and Discussion

The room temperature X-ray Diffraction pattern (XRD) of 0.2CFO-0.8BCZT composite sintered at 1000 °C for 24 hr is shown in figure 1. The XRD of composite is compared with the standard data of pure CFO (ICSD # 109045) and BCZT (ICSD # 187675). From the figure, the composite show the Bragg reflections of both magnetic and piezoelectric phases, at their respective angles. It is also observed that no additional peaks present in the XRD, which is a clear indication that the composite is free from the secondary phases, which might arise due to the intermixing of the individual phases, after sintering of the composite. The relative intensity of the BCZT peaks are higher than the CFO, signifying the less scattering centres of CFO due to small weight fraction of the composite.

Further, the XRD data is refined using the Rietveld method. In general, CFO exists in the cubic spinel structure with Fd-3m space group and BCZT exists in the mixed phase of tetragonal and

orthorhombic structures. Therefore, to find the structure solution, the experimental data is refined with mixed phases of cubic, tetragonal and orthorhombic. A best fit is obtained for this structure model, confirmed by the refinement agreement values. The refined diffraction pattern of the particulate composite is shown in figure 2. The resulting structural information with lattice parameters, unit cell volume is summarized in table 1. From the refinement it is found that, lattice parameters and the volume of the unit cell is larger for cubic phase followed by orthorhombic when compared to tetragonal phase.



Figure 1. X-ray diffraction of 0.2CFO-0.8BCZT in comparison to standard data of CFO and BCZT.



Figure 2. Rietveld refinement plot for 0.2CFO-0.8BCZT. The observed and calculated patterns are shown by circles (black) and lines (red), respectively. The difference between the observed and calculated patterns is shown by the blue line at the bottom of each panel. The vertical bars (green) represent the Bragg peak positions.

Phase	a (Å)	b (Å)	c (Å)	$V(\text{\AA}^3)$
Cubic	8.3854(6)	8.3854(6)	8.3854(3)	589.61
Tetragonal	3.9932(7)	3.9932(7)	4.0148(2)	64.02
Orthorhombic	4.0089(2)	5.6683(5)	5.7082(6)	129.71

Table 1. Refined structural parameters for 0.2CFO-0.8BCZT sample.

Further, the Williamson Hall (W-H) Analysis is carried out to get the contribution of micro strain of the composite. The W-H equation is given by $\beta \cos\theta = K\lambda/D + 4\epsilon \sin\theta$, where K is the shape factor; β is the full width at half maximum for a particular θ ; D is the average crystallite size and ϵ is the lattice strain. The plot of $\beta \cos\theta$ versus $4 \sin\theta$ is shown in Figure 3. From this, the micro strain is found to be ~ 0.00103. Using Debye Scherer formula, D = $K\lambda/\beta \cos\theta$, where K ~ 0.99 (shape factor), $\lambda = 1.5406$ Å, β is the full width at half maximum for a particular θ ; D is the average crystallite size. The crystallite size is calculated, which is approximately ~ 32 nm.



Figure 3. W-H plot of 0.2CFO-0.8BCZT composite

3.2 Ferroelectric properties

The ferroelectric nature of the pure BCZT and composites are investigated at room temperature. Generally, ferroelectrics have large values of piezoelectricity. Moreover, the strain of most of the materials is proportional to the square of the polarization (not always true) [10]. Hence, it is important to know the ferroelectric behaviour of the composite. Figure 4. shows the Polarization (P) versus Electric field (E) loop for the 0.2CFO-0.8BCZT composite in comparison to BCZT.

From the figure 4, it is clear that the pure BCZT show a proper ferroelectric behaviour while the composite show the leaky behaviour. The 0.2CFO-0.8BCZT sample exhibit remnant polarization of $(P_r) \sim 3 \,\mu\text{C/cm}^2$ and a coercive field (E_c) of ~ 17.78 kV/cm compared to the $P_r \sim 1.32 \,\mu\text{C/cm}^2$ and $E_c \sim 4.33 \,\text{kV/cm}$ of pure BCZT. Though the values of P_r and E_c seems to be high, they do not represent real values as the *P*-*E* loop exhibited by the composite is more like a lossy dielectric loop, rather than actual ferroelectric hysteresis loop. The current conduction due to the oxygen vacancies results such lossy loops in the composite [11]. Also, as the CFO is centrosymmetric and have no spontaneous polarization, the polarization values of the composite are expected to low compared to the BCZT.



Figure 4. Polarization versus electric field for the 0.2CFO-0.8BCZT composite and pure BCZT ceramic.

3.3 Magnetic properties

The magnetization (*M*) behaviour of Cobalt ferrite (CFO) and 0.2CFO-0.8BCZT composite at a maximum applied field (*H*) of 17 kOe at room temperature is shown in Figure 5. The zoomed part of the graph near the origin is displayed in the inset of figure 5. The saturation magnetization (M_s), the remnant magnetization (M_r) and the coercivity (H_c) for pure CFO are found as follows 77.99 emu/g, 40.74 emu/g and 993.57 Oe, respectievely, whereas the composite show reduced values of $M_s \sim 15.9$ emu/g, $M_r \sim 4.4$ emu/g and $H_c \sim 315$ Oe. The decrease in the magnetization of 0.2CFO-0.8BCZT is due to the lower concentration of magnetic phase as BCZT phase is completely non-magnetic in nature.



Figure 5. The *M*-*H* loops of pure CFO and 0.2CFO-0.8BCZT composite. The inset show the zoomed part of the same near the origin.

4. Conclusions

Ferrimagnetic CFO and ferroelectric lead free BCZT polycrystalline samples are synthesized by using sol-gel method. The particulate composite, 0.2CFO-0.8BCZT is prepared by mechanical mixing of both the phases with 1:4 weight fraction. XRD and Rietveld refinement confirms the presence of both magnetic and piezo-electric phase in the composite and no secondary phases are observed due to the intermixing of the individual phases upon heating at high temperatures. The polarization measurements of the composite show a leaky *P*-*E* behaviour while BCZT shows a proper ferroelectric loop with $P_r \sim 1.32 \,\mu\text{C/cm}^2$. A reduction in magnetization values are observed for the composite sample compared to pure CFO due to lower concentration of magnetic phase. Thus, the 0.2CFO-0.8BCZT magnetoelectric coefficient of this sample is expected to be higher due to the strain mediated coupling. Hence, 0.2CFO-0.8BCZT composite is a promising candidate for the multiferroic applications.

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