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# Magnetic field induced polarization and magnetoelectric effect of $Ba_{0.8}Ca_{0.2}TiO_3$-$Ni_{0.2}Cu_{0.3}Zn_{0.5}Fe_2O_4$ nanomultiferroic

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The $xBa_{0.8}Ca_{0.2}TiO_3$-$(1 - x)$NiCuZn ferrite ($x = 0.1$, 0.3, 0.5, 0.7, and 0.9) nanocomposites were prepared by using sol-gel method. The densification of these composites was carried out using microwave sintering method. The magnetic field induced changes in the ferroelectric polarization loop may support the possible magnetoelectric coupling between $Ba_{0.8}Ca_{0.2}TiO_3$ and NiCuZn ferrite phases. The observed change in ferroelectric polarization with applied magnetic field proves the coupling between magnetic and ferroelectric order parameters. The loop change is observed with the composition and with magnetic field. The magnetoelectric coefficient of the nanocomposite with $x = 0.3$ shows a value of 280 mV/cm Oe is obtained. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4795820]

Recently, multiferroic materials have attracted a lot of attention due to its applications in actuators, transducers, magnetic sensors, storage media, and spintronics devices as they provide a novel approach to the magnetic/electric field conversion. The coupling between magnetic and ferroelectric phases enables electrical polarization to be controlled using a magnetic field and, conversely, the manipulation of magnetization by varying an electrical field.[1–5] Nevertheless, the disadvantages of a weak magnetoelectric (ME) response, low working temperatures, and the novel properties of the materials limit the range of application of single-phase compounds. A two phase multiferroic composites have been used extensively for magnetoelectric coupling as it provides a large ME coefficient[6–10] as compared to single phase materials. Suchtelen *et al.*[11] suggested the realization of composites of piezoelectric and magnetostrictive phases, which could be electromagnetically coupled via stress mediation. A large magnetoelectric output voltage has been observed in composites with lead based ferroelectrics. But recently owing to concerns regarding the environmental pollution and its toxicity to human beings,[12] lead based materials are prohibited. Therefore, extensive research is going on worldwide to find lead free ferroelectric-ferromagnetic composites with high value of magnetoelectric voltage. Zvezdin *et al.*[13] and Bohdan Kundys *et al.*[14] observed the magnetic field induced polarization behavior in single phase bulk $BiFeO_3$ and $Bi_{0.75}Sr_{0.25}FeO_{3-\delta}$, respectively, and so far this behavior is not observed for multiferroic composites in bulk form.

In the present investigation, $Ba_{0.8}Ca_{0.2}TiO_3$-$Ni_{0.2}Cu_{0.3}Zn_{0.5}Fe_2O_4$ nanocomposites have been synthesized by Sol-gel method and the coupling behavior between its constituent phases in ceramic samples were studied.

The composites of $xBa_{0.8}Ca_{0.2}TiO_3$ (BCT)-$(1 - x)$ $Ni_{0.2}Cu_{0.3}Zn_{0.5}Fe_2O_4$ (NiCuZn ferrite) ($x = 0.0$, 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0) were prepared by using sol-gel method. For the preparation of $Ba_{0.8}Ca_{0.2}TiO_{3,}$ high purity (99.9%) barium acetate, calcium acetate, and titanium *n*-butoxide were dissolved in acetic acid and 2-methoxyethanol, respectively. By controlling the hydrolysis condition of the complex solution, a gel was formed. The dry gel was calcined at 500 °C for 6 h in atmosphere and the powders were obtained. Similarly, $Ni_{0.2}Cu_{0.3}Zn_{0.5}Fe_2O_4$ was prepared using nickel nitrate, cupric nitrate, zinc nitrate, and ferric nitrate, respectively. The ferrite dry gel was calcined at 500 °C/4 h. The obtained powders were mixed with $Ba_{0.8}Ca_{0.2}TiO_3$ powders in different proportions ($x = 0$, 0.1, 0.3, 0.5, 0.7, 0.9, and 1) to obtain composite powder. All the powders were mixed with appropriate amount of polyvinyl alcohol (PVA) as binder and uniaxially pressed into pellets at 5 MPa. All the composite pellets were sintered at 1150 °C/90 min using microwave sintering method.[15]

The phase formation and morphology studies were carried out using X-ray diffraction (Brucker D8 Advance) method and field emission scanning electron microscopy (FE-SEM) (FEI).The magnetic field dependent polarization loops were carried out using ferroelectric loop tracer (Premier II, Radiant Technologies, USA) and physical property measurement system (PPMS, Quantum Design). For polarization measurements, the bulk composite samples with a thickness of ~2 mm and 3 mm dia were polished to obtain flat surfaces. The silver paint was applied on both the sides of the samples and then an electrical field of 1 kV/mm was

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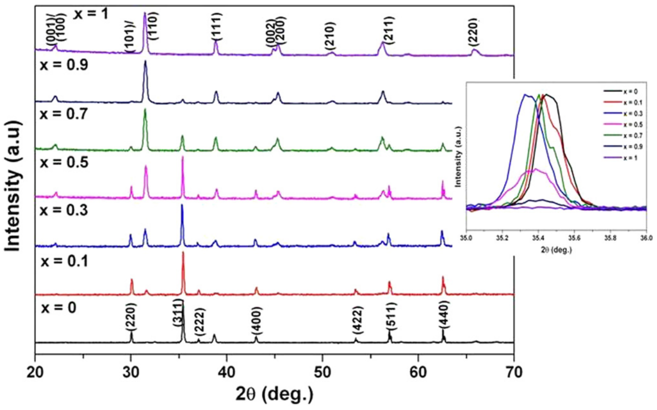

FIG. 1. XRD patterns of xBCT-(1 − x)NiCuZn ferrite composites (x = 0-1). The inset: XRD of (3 1 1) plane for all compositions.

applied in plane for electric polarization. The M-E effect is determined by measuring the polarization developed across the sample when a dc magnetic field is applied to it. The coupling is studied directly as the polarization response of the sample to an applied dc bias field.

Figure 1 shows the XRD patterns of $xBa_{0.8}Ca_{0.2}TiO_3$-$(1-x)Ni_{0.2}Cu_{0.3}Zn_{0.5}Fe_2O_4$ (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1) composites at room temperature. The co-existence of both ferroelectric and ferromagnetic phases can be seen from the (1 1 0) and (3 1 1) planes, respectively, in x = 0.1, 0.3, 0.5, 0.7, and 0.9 samples. No other phases were detected indicating that there was no apparent reaction between the two phases. The intensities of the peaks were increased with its constituent phase and vice verse. The lattice parameters calculated for tetragonal $Ba_{0.8}Ca_{0.2}TiO_3$ are a = 4.018 Å; c = 3.982 Å and cubic NiCuZn ferrite is a = 8.323 Å. It can also be observed from the inset of Fig. 1 that the (3 1 1) peak shifted towards the low angle side as x increased up to 0.3, with further increase of x, the peak shifted to higher angle side. It shows that with an increase of x up to 0.3, the composite is under stress produced by piezoelectric BCT and it is effectively transferred to the ferrite phase and then it is under strain but for higher concentration, x > 0.3, the strain is gradually decreased because as the percentage of x increased, the ferroelectric grains become larger/agglomerated and the larger grains are less effective in inducing strain than the smaller grains.[16]

Figure 2 shows the magnetization loops of BCT-NiCuZn ferrite nanocomposite at room temperature. The variation of saturation magnetization ($M_S$) and coercive field ($H_c$) for all composites is shown in Figure 2(b). It is noted that the Ms is 61 emu/g for pure ferrite is comparable with the microwave sintered $Ni_{0.6}Cu_{0.2}Zn_{0.2}Fe_{1.98}O_{4-\delta}$.[17] It is observed that as the percentage of x increases the Ms decreased due to the presence of nonmagnetic phase and interface effects, which changes the distribution of magnetic ions and their spin orientation which affects the magnetic interactions.[18]

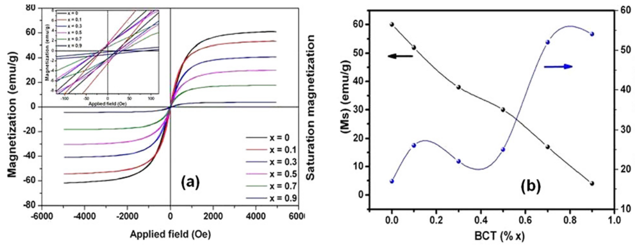

FIG. 2. (a) M-H loops of BCT-NiCuZn ferrite nanocomposites at room temperature. (b) Ms and Hc variation with BCT (%x) percentage.

According to the site occupancy,[19] $Ba^{2+}$ and $Ca^{2+}$ occupy the A site and $Cu^{2+}$ and $Ti^{4+}$ occupy the B sites of the spinel. The larger radius ions $Ba^{2+}$ (1.34 Å) and $Ti^{4+}$ (1.34 Å) substitute the $Fe^{3+}$ ion (0.64 Å) at A and B sites of the spinel ferrite structure, thereby decreases the amount of $Fe^{3+}$ ions and $M_S$. The coercive field, $H_c$, is increased with x up to 0.3 and then decreased for 0.5 and again $H_c$ is increased with further increase of x, which could be attributed to the domain wall pinning due to the ferrite phase. The decrease of $H_c$ for x = 0.5 may be due to the percolation limit of the composites.

Figure 3(a) shows the polarization vs electric field loops with different percentage of x at room temperature. It can be seen that all the BCT-NiCuZn ferrite nanocomposites exhibited ferroelectric properties. It can be seen that as x decreased, the polarization (+$P_s$) values decreased and coercive field (+$E_c$) is increased due to the leakage. The magnetic field induced polarization for x = 0.3, 0.5, and 0.7 is shown in Figures 3(b)–3(d), respectively. Even with the application of magnetic field, the ferroelectric loops did not show saturation but the leakage is found to be high. The reason could be the voltage drop across the ferrite which changes the impedance at BCT-NiCuZn ferrite interface. When the magnetic field is applied, the electronic phase separation takes place in the NiCuZn ferrite resulting in the voltage drop across the interface, which affects the ferroelectric switching behavior in BCT-NiCuZn ferrite nanocomposite. Similarly, the magnetic field induced change in ferroelectric hysteresis loop was reported in multiferroic $Bi_{0.6}Tb_{0.3}La_{0.1}FeO_3$ thin films, where the observed behavior was ascribed to the magnetic field induced disturbance created in the grain alignment.[20] Ortega *et al*. also reported that the polarization in multiferroic

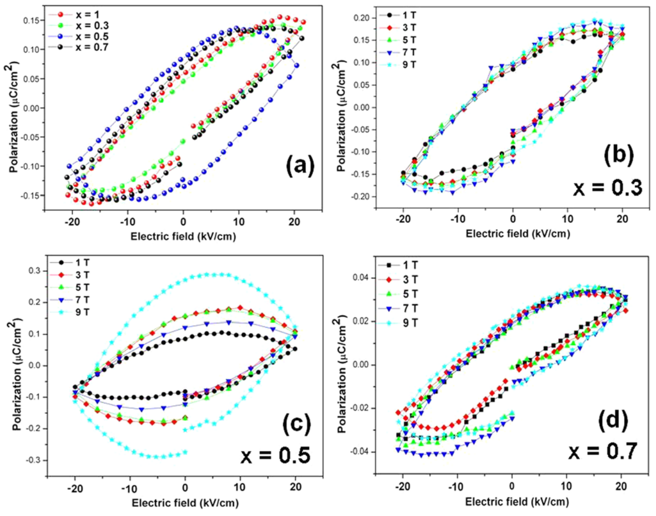

FIG. 3. (a) P-E loops for different compositions of x (%BCT) at room temperature. (b)–(d) Magnetic field induced polarization loops for x = 0.3, 0.5, and 0.7, respectively.

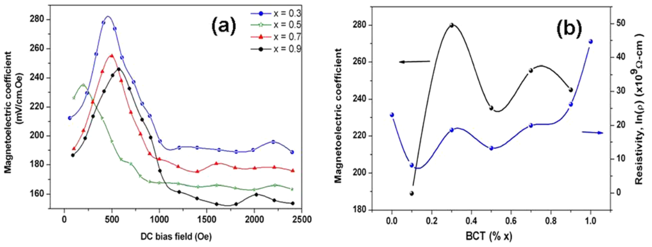

FIG. 4. (a) Variation of ME coefficient with dc magnetic field for BCT-NiCuZn ferrite composites. (b) Variation of ME coefficient and dc resistivity with different percent of BCT.

PZT/$CoFe_2O_4$ composite films was found to decrease with the increase of magnetic field.[21]

Figure 4(a) shows the variation of ME output with dc bias magnetic field for $x = 0.3$, 0.5, 0.7, and 0.9, respectively. It can be observed that ME output increased with bias field and reached maximum and with further increase of the field ME output decreased. It is known that magnetostriction gradually increases and reaches maximum with magnetic field poling and transfer the strain through interface to ferroelectric phase where it produces a voltage; therefore, at this point ME output shows a maximum value. The variation of ME output and resistivity for different concentration of BCT is shown in Fig. 4(b). The resistivity of the nanocomposite decreased with ferrite. In composites, the resistivity is different for BCT and ferrite and at higher percentage of ferrite, interfacial polarization results at grain boundaries. The value of resistivity for all the composites is in the range of $10^8\ \Omega$ cm.

It is also observed that with different mole percentages, the ME output is different, reasons could be due to the difference in resistivity, magnetostriction coefficient, piezoelectric coefficient, grain size, distribution, etc. It is also observed that the maximum value of ME output is 280 mV/cm Oe for $x = 0.3$, which is higher than the 538.59 micro V/cm, 692 $\mu$V/cm. Oe and ~13 mV/cm Oe for $0.3Ni_{0.02}Co_{0.03}Cu_{0.05}Fe_2O_4 + 0.7BaTiO_3$,[22] $0.15Ni_{0.3}Zn_{0.4}Cu_{0.3}Fe_2O_4 + 0.85(BaTiO_3 + PZT)$,[23] and $0.5Ni_{0.3}Zn_{0.62}Cu_{0.08}Fe_2O_4 + 0.5\ Pb(Fe_{0.5}Nb_{0.5})O_3$,[24] respectively. The differences in the output values compared to others might be because of the preparation method, i.e., sol-gel, microwave sintering, high density, small grain size, and high resistivity compared to solid state method with large grain size and low resistivity.

In summary, a lead free xBCT-(1 − x)NiCuZn ferrite nanocomposites were synthesized using sol-gel method and subsequently densified using microwave sintering method at 1150 °C/90 min. The composite with $x = 0.3$ shows a magnetoelectric coefficient of 280 mV/cm Oe at room temperature. We believe that a large ME voltage can be achieved at its transition temperature by a proper selection of composites with dopants (small ionic radii); a further research is going on to find the room temperature bi-phase composites.

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