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Enhanced multiferroic properties in $(1-y)BiFeO_3-yNi_{0.50}Cu_{0.05}Zn_{0.45}Fe_2O_4$ composites

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ABSTRACT

Multiferroic composites $(1-y)BiFeO_3-yNi_{0.50}Cu_{0.05}Zn_{0.45}Fe_2O_4$ ($y=0.0$, 0.1, 0.2, 0.3 and 0.4) are synthesized by the standard solid state reaction method. The X-ray diffraction analysis affirms the formation of both the component phases and also reveals that there is no chemical reaction between them. From the energy-dispersive X-ray spectroscopy study it is observed that the percentage of the elements in the component phases is well consistent with the nominal composition of the composites. Field Emission Scanning Electron Microscopy analysis shows almost homogeneous mixture of the two phases. The real part of the initial permeability increases (up to 67%) and the loss decreases with the ferrite content in the composites which is important in application point of view. Dielectric constant (ε'), loss tangent and AC conductivity are measured as a function of frequency at room temperature. The highest ε' is obtained for $0.6BiFeO_3-0.4Ni_{0.50}Cu_{0.05}Zn_{0.45}Fe_2O_4$ composite. The dielectric dispersion at lower frequency ($<10^5$ Hz) is due to the interfacial polarization. The complex impedance spectroscopy is used to correlate between the electrical properties of the studied samples with their microstructures. Two semicircular arcs corresponding to both grain and grain boundary contribution to electrical properties have been observed in all the studied samples. The maximum magnetoelectric voltage coefficient is found to be ~38 mV cm^{-1} Oe^{-1} for the composite with 80% ferroelectric+20% ferrite phases. The present composite might be a promising candidate as multiferroic materials showing effective electric and magnetic properties.

1. Introduction

With the increasing demand of new technology, composite materials have been widely used for modern electronic devices where high performance, limited space and multifunction are required. Multiferroic materials, which simultaneously exhibit ferroelectricity and ferromagnetism, have recently stimulated expanding number of research activities for their scientific interest and significant technological promise in the novel multifunctional devices [1–4]. The magnetoelectric response of natural single-phase multiferroic compounds is either relatively weak or occurs at temperatures too low for practical applications. In contrast, multiferroic composites having ferroelectric and ferri-/ferromagnetic phases generally yield huge coupling between the two phases above room temperature and makes them ready for potential technological applications. Composite materials may show sum or product properties [5–7]. The weighted sum of the component phases, proportional to volume fraction of these phases gives rise to sum properties. The physical quantities such as density, magnetization, and dielectric properties come in category of sum properties. The product property is more remarkable which is absent in the individual phases but is present in the composite. The magnetoelectric effect is a product tensor property which was first proposed by Suchtelen [7]. Due to noteworthy applications of composite materials in switches, actuators, magnetic field sensors and memory devices in the past few years, the composite materials have attracted a great attention in the regime of magnetoelectric material studies in recent years [8]. Various magnetoelectric composite systems such as $CoFe_2O_4-BaTiO_3$ [9], $NiFe_2O_4-BaTiO_3$ [10], $Ni_{0.8}Zn_{0.2}Fe_2O_4-Ba_{0.6}Sr_{0.4}TiO_3$ [11], $(x)Co_{0.5}Zn_{0.5}Fe_2O_4-(1-x)$PLZT [12], $xNi_{0.5}Zn_{0.5}Fe_2O_4-$BPZT [13], $Ni_{0.75}Zn_{0.25}Fe_2O_4-BiFeO_3$ [14], $MnFe_2O_4-BiFeO_3$ [15] and $BiFe_{0.5}Cr_{0.5}FeO_3-NiFe_2O_4$ [16] have been reported in the literature.

As per literature survey no work has been reported on $(1-y)BiFeO_3-yNi_{0.5}Cu_{0.05}Zn_{0.45}Fe_2O_4$ ($y=0.0$, 0.1, 0.2, 0.3 and 0.4) multiferroic composites. A suitable combination of ferrite and

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ferroelectric materials is very important to obtain enhanced ME effect. For this, the magnetostriction coefficient of ferrite phase and piezoelectric coefficient of ferroelectric phase must be high [17,18]. In the present study, the preparation and characterization of $(1-y)BiFeO_3$–$yNi_{0.5}Cu_{0.05}Zn_{0.45}Fe_2O_4$ composites containing $BiFeO_3$ (BFO) as the ferroelectric component and $Ni_{0.50}Cu_{0.05}Zn_{0.45}Fe_2O_4$ (NCZFO) as the ferrite one have been the prime focus. The selection of these two components has been made on the basis of above mentioned criteria. The nickel ferrite doped with Zn^{2+} and Cu^{2+} is expected to have high magnetostriction coefficient since a Jahn–Teller ion such as Zn^{2+}, Cu^{2+} has high coupling coefficient [18,19]. BFO is a good ferroelectric and piezoelectric material [20]. The coexistence of ferromagnetism and ferroelectricity at room temperature makes this material a significant one. Moreover, BFO exhibits certain attractive features such as G-type antiferromagnetism, high Curie temperature (T_c = 1103 K) and high Neel temperature (T_N = 643 K) [14]. Therefore, it is quite interesting to find out possible changes in the various physical properties of a class of BFO–NCZFO composites. In this paper, we report the structural, magnetic, dielectric and magnetoelectric properties of $(1-y)$BFO–yNCZFO composites.

2. Experimental

2.1. Sample preparation

Various $(1-y)$BFO–yNCZFO composites were prepared by the standard solid state reaction technique. To synthesize BFO, stoichiometric amounts of high purity Bi_2O_3 (99.9%) and Fe_2O_3 (99.9%) were weighed and mixed thoroughly in acetone media for 5–6 h. The well mixed powder was then calcined in a closed alumina crucible at 780 °C for 4 h. Stoichiometric amounts of high purity NiO (99.9%), CuO (99.9%), ZnO (99.9%) and Fe_2O_3 (99.9%) were mixed to synthesize NCZFO by the same method as BFO. The mixed powder was then dried and pre-sintered at 1100 °C for 4 h in air. After pre-sintering, powders were again grinded to get a homogeneous fine powder of the desired compound. The obtained powders of the two phases were mixed in weight proportions in acetone media for 3–4 h to obtain $(1-y)$BFO–yNCZFO composites for various values of y. The composite powders were mixed with polyvinyl alcohol (PVA) and then uniaxially pressed to prepare pellet- and toroid-shaped samples from each composite. The prepared samples were sintered at 810, 830 and 850 °C for 4 h in air for various characterizations.

2.2. Characterization

X-ray diffraction (XRD) analysis was carried out using X-ray diffractometer (Philips PANalytical X'PERT-PRO) equipped with CuKα radiation (λ = 1.5418 Å). Surface morphology and microstructural analysis were performed by Field Emission Scanning Electron Microscopy (FESEM, model no. JEOL JSM 7600F). The energy-dispersive X-ray spectroscopy (EDS) analysis was performed using the FESEM for the compositional study. The bulk density, ρ_B, of each composite was calculated using the relation: $\rho_B = m/(\pi r^2 t)$, where m is the mass, r is the radius and t is the thickness of the pellet. The X-ray density of the composite was calculated using the relation: $\rho_x(\text{composite}) = (M_1 + M_2)/(V_1 + V_2)$, where M_1 is '(1-y)' times molecular weight of BFO, M_2 is y times molecular weight of NCZFO, $V_1 = M_1/\rho_x(\text{Ferroelectric})$, $V_2 = M_2/\rho_x(\text{Ferrite})$ and y is the weight fraction of NCZFO in the composites [12]. The ρ_x(Ferrite) and ρ_x (Ferroelectric) are determined by the general formula, $\rho_x = nM/N_AV$, where n is the number of atoms in a unit cell, M is the molar mass of the sample, N_A is the Avogadro's number and V is the volume of the unit cell. The porosity of the samples were calculated using the formula, $P(\%) = [(\rho_x - \rho_B)/\rho_x] \times 100\%$. The dielectric and magnetic properties were carried out at room temperature with the variation of frequency using an Impedance Analyzer (WAYNE KERR 6500B). The real part of the complex initial permeability (μ_i') was calculated using the relation: $\mu_i' = L_s/L_0$, where L_s is the self-inductance of the sample core and $L_0 = \mu_0 N^2 S/\pi\, \bar{d}$ is derived geometrically. Here L_0 is the inductance of the winding coil without the sample core, N is the number of turns of the coil (N=4), S is the area of cross section and $\bar{d} = (d_1 + d_2)/2$ is the mean diameter, where d_1 and d_2 are the inner and outer diameter of the toroidal sample, respectively [21]. For dielectric measurements samples were painted with conducting silver paste on both sides to ensure good electrical contacts. The dielectric constant, ε', was calculated using the formula: $\varepsilon' = Ct/\varepsilon_0 A$, where C is the capacitance of pellet, A is the cross-sectional area of the electrode and ε_0 is the permittivity in free space. The AC conductivity, σ_{AC}, of the samples was calculated using the relation: $\sigma_{AC} = \omega\varepsilon_0\varepsilon' tan\delta$, where ω is the angular frequency and $tan\delta$ is the dielectric loss. The ME effect was obtained by applying an ac magnetic field superimposed on a dc magnetic field on the sample, and then measuring the output signal with applied dc magnetic field. An electromagnet was used to provide a dc magnetic field of up to 0.7 T. A signal generator operating at a frequency of 50 Hz was used to drive the Helmholtz coil to generate an ac magnetic field. The output voltage generated from the composite was measured using a Keithley multimeter (Model 2000) as a function of dc magnetic field. ME voltage coefficient, α_{ME}, was calculated using relation, $\alpha_{ME} = (dE/dH)_{H_{ac}} = V_o/h_o t$, where V_o is the ME voltage across the sample surface and h_o is the amplitude of the ac magnetic field [22].

3. Results and discussion

3.1. Lattice parameters, density and porosity of the samples

The XRD patterns of BFO and various $(1-y)$BFO–(y)NCZFO composites sintered at 850 °C are shown in Fig. 1. The peaks in the XRD patterns have been identified with their corresponding Miller indices. A phase pure BFO is difficult to obtain due to the kinematics of formation and the present composite also contains some impurity peaks (e.g. $Bi_2Fe_2O_9$ and $Bi_{36}Fe_{24}O_{57}$) in the XRD patterns. The BFO sample forms rhombohedral distorted perovskite structure. It is observed from XRD that the composites exhibit both the ferrite and ferroelectric phases and the peaks of the ferrite phase indicates cubic spinel structure. No third phase has been observed in the XRD confirmed that there is no chemical reaction between the two phases. The intensity of most of the ferrite peaks increases while that of perovskite peaks decreases with the increase of ferrite content in the composites. The intensity of XRD peaks and number of peaks depend on the amount of corresponding phases in the composites. The values of lattice parameter obtained for each plane are plotted against the Nelson–Riley function, $F(\theta)$ [$F(\theta) = (1/2)[\cos^2\theta/\sin\theta + \cos^2\theta/\theta]$, where θ is the Bragg's angle] [23]. A straight line fit has been obtained and the accurate value or the true lattice parameter determined from the extrapolation of these lines to $F(\theta) = 0$. The true values of the lattice constants (Table 1) for both the ferrite and ferroelectric phases are found to be in good agreement with the earlier reports [14,24]. It is observed that in case of composites there is an insignificant change in the lattice parameter of ferroelectric and ferrite phase that may be due to stress exerted on each other by the two phases [25] and also due the diffusion of a small amount unreacted elements into the two phases. Fig. 2(a) shows the variation of ρ_B of various $(1-y)$