Enhanced dielectric and magnetic properties in multiferroic $Bi_{0.99}Y_{0.01}Fe_{0.99}Ni_{0.01}O_3$ ceramic

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ABSTRACT

An enhanced low-frequency dielectric constant, ($\varepsilon' \sim 10^4$), and ferromagnetic behavior at room temperature were observed in $Bi_{0.99}Y_{0.01}Fe_{0.99}Ni_{0.01}O_3$ (BYFNO) ceramic sintered by a modified solid state reaction method. The anti-ferromagnetic (AFM) nature of $BiFeO_3$ (BFO) changed to ferromagnetic (FM) with saturation magnetization, M_s, and coercivity H_c values of $\sim 0.03 \mu_B/f. u.$ and ~ 250 Oe, respectively at room temperature. The XRD patterns revealed that the co-doping of Y^{3+} and Ni^{2+} ions at the $A–$ and $B–$ sites of $BiFeO_3$ (BFO) resulted in a rhombohedrally distorted perovskite structure. This result was discussed in terms of the modification of the cycloidal spin structure, presence of Ni^{2+} carriers and preservation of oxygen vacancy during the sintering process. This enhanced properties entitle the $Bi_{0.99}Y_{0.01}Fe_{0.99}Ni_{0.01}O_3$ one of the few multiferroic materials that exhibits both significant ferromagnetic and dielectric behaviors at room temperature.

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Bismuth Ferrite ($BiFeO_3$) is one of the most widely studied multiferroic materials in electric ceramics category. It has rhombohedrally distorted perovskite structure with $R3c$ space group of symmetry. These materials are attracting significant attention because of the co-existence of the ferroelectricity and anti-ferromagnetism above room temperature [1]. The ferroelectricity in BiFeO3 (BFO) is originated from the $6s^2$ lone pair electrons of Bi^{3+} ions structural distortion while the anti-ferromagnetism comes from the Fe^{3+} site through anti-ferromagnetic coupling of two adjacent crystal planes [2]. However, BFO has a major problem in this kind of application. Particularly, $R3c$ symmetry allows the existence of weak ferromagnetic moment but the cycloidal spin structure prevents net magnetization which leads to net zero magnetization. Room temperature spontaneous polarization along the $[111]_C$ direction is also found to be less than the theoretical values [3].

Various alternative strategies have been proposed to overcome these difficulties. Among them, doping with rare earth ions in Bi site and transition metal ions in the Fe site is reported to be one of the most effective ways to improve the overall properties [4]. Recently, A Mukherjee at el [5] presented reduction in bismuth volatilization and oxygen vacancies due to 1% doping of Y ions in the bismuth site. Y.R. Dai et al [6] revealed in an enhancement of magnetization due to doping of Ni^{2+} in the Fe^{3+} site due to the suppression of the cycloidal spin structure. In this letter, we report the effect of co-doping with Y^{3+} and Ni^{2+} ions on the crystalline structure, dielectric and magnetic properties of polycrystalline bismuth ferrite systems. In addition, the possible origins for the enhanced dielectric and magnetic characteristics will be presented.

Thus, $BiFeO_3$ (BFO) and co-doped with Y^{3+} and Ni^{2+}, $Bi_{0.99}Y_{0.01}Fe_{0.99}Ni_{0.01}O_3$ (BYFNO) ceramics were sintered by a modified solid state reaction method. The detail of the sintering process is fully discussed in our earlier work [7]. In summary, a mixture of powders in stoichiometric composition were placed directly into a 880 °C pre-heated muffle furnace only for 20 min. Then, the calcined powders were rinsed off in dilute nitric acid to eliminate possible impurity phase of $Bi_2Fe_4O_9$ and dried at 80 °C for 12 h. Disc-shaped pellets of 10 mm diameter and 2 mm thickness were pressed uni-axially and followed by cold isostatic pressing (CIP) at 300 MPa for 15 min. Then, the green pellet samples were directly placed into a 800 °C pre-heated muffle furnace dwelt 1 h before been quickly removed from the furnace. This rapid quenching preserved the point defect formed during the high temperature sintering process [8].

The crystal structure of all samples was characterized by X-ray diffraction (XRD) using a Shimadzu diffractometer (model 6000) with CuKα radiation ($\lambda = 1.5418$ Å) for a wide range of Bragg angles ($20° \leq 2\theta \leq 80°$) with a scanning rate of 2^O/min at room temperature. The crystalline phases were identified using Fullprof software and the crystallographic data were obtained by using the NIMS material database (MatNavi). Structural parameters obtained from XRD pattern shown in Fig. 1 for $Bi_{0.99}Y_{0.01}Fe_{0.99}Ni_{0.01}O_3$ is in good agreement with reported values [9]. Lattice parameters a and
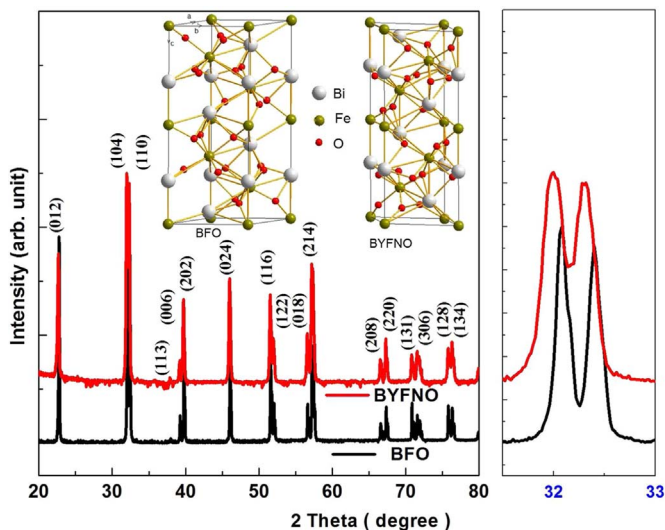
Fig. 1. XRD pattern for BFO and BYFNO. Inset shows the unit cell structure from the data obtained from Rietveld refinement. Enlarged area shows the XRD at $2\theta = 32°$.

Table 1
Bond angle and length values for both undoped $BiFeO_3$ and $Bi_{0.99}Y_{0.01}Fe_{0.99}Ni_{0.01}O_3$ (BYFNO) ceramic samples from the Rietveld refinement data.

	Bond type	Sample composition	
		BFO	BYFNO
Angle (degree)	Fe–O–Fe	135.1	139.6
	Bi–O–Bi	119.4	119.5
Length (Å)	O–Fe (1)	2.043	2.016
	O–Fe (2)	2.176	2.206
	O–Bi	2.125	2.189

c decreases with doping shown in the inset of Fig. 1 because of the fact that the ionic radii of Bi^{3+} and Y^{3+} ions are 1.03 Å and 0.9 Å, respectively. The smaller ionic radius of Y^{3+} compared to Bi^{3+} may lead to distortion of octahedron. This result suggests that the rhombohedral structure is distorted by Y^{3+} substitution of Bi^{3+} ions [10,11]. The calculated values of the Fe–O bond lengths (Table 1) increase by Ni^{2+} (0.690 Å) substitution in Fe^{3+} (0.645 Å) site. The tolerance factor obtained from the Goldschmidt formula [12] shows that doping substitution results in decrease of tolerance factor up to 0.937 from the tolerance factor of 0.939 for the pure BFO. The polar $R3c$ structure is stabilized in pure BFO matrix due to the lone pair of the Bi^{3+} ions that results ordered displacement of ions along [111] direction which is responsible for spontaneous polarization in $R3c$ perovskite. The smaller Y^{3+} ions on the Bi^{3+} site

suppress the Bi–O bond length which reduces the long range ferroelectric ordering in $Bi_{0.99}Y_{0.01}Fe_{0.99}Ni_{0.01}O_3$ ceramic. Indeed, the calculated values of the Bi–O bond lengths obtained from Rietveld refinement data show an upward trend with doping (Table 1). That is why doping substitution results in decrease of tolerance factor. In addition, the structural distortion due to rotation of Fe–O octahedra also helps to stabilize the $R3c$ structure. This is because of the fact that by Ni substitution two oxygen octahedra rotate in the opposite direction along the $[111]_C$ axis [13] hence increases the Fe–O–Fe angle. Furthermore, the effect of the decrease in particle size can be further observed in Fig. 2 from scanning electron microscope (SEM) images of fracture surface of BFO and BYFNO samples. Incorporation of Y ion in Bi site and Ni ions in Fe site resulted different type of grain growth in BYFNO samples when compared to grain growth of BFO. The smaller grains with aggregated grain cluster were due to the heterogeneous nucleation centers in the perovskite structure for the presence of the Y and Ni ions in BYFNO sample.

The dielectric permittivity behavior of the ceramic samples was measured using a parallel-plate-capacitor using a computer controlled Agilent LCR Meter (model 4980 A) operating at a broad range of frequencies (20 Hz–2 MHz) applying an alternating 1.0 V to the opposite silver painted faces of the pellets. Fig. 3(a) shows the low frequency dependence of relative dielectric permittivity (ε') for both $BiFeO_3$ and $Bi_{0.99}Y_{0.01}Fe_{0.99}Ni_{0.01}O_3$ ceramics at room temperature. It is evident that low frequency dielectric permittivity value, $\varepsilon' \sim 7700$ for $Bi_{0.99}Y_{0.01}Fe_{0.99}Ni_{0.01}O_3$ ceramics at room temperature is higher than BFO. The origin of high ε' value may be linked with the deviation of oxygen stoichiometry due to the quick sintering method, presence of Ni^{2+} ions with doping concentration [14] and to the change in grain size of the ceramic samples (Fig. 2). According to the brick model, $\varepsilon' \propto \varepsilon_{gb}d/t$ [15], where, ε_{gb} is the dielectric constant of the grain boundary layer, d is the grains size and t is the barrier width. From this point of view, the applied voltage on the sample drops mainly across the thin grain boundary widths and space charge polarization is created which enhances the dielectric constant at the lower frequency.

Furthermore, when an alternating electric field was applied to the opposite side of the samples it may induce changes in the valences of Fe ions such as from Fe^{2+} to Fe^{3+} ($Fe^{2+} \leftrightarrow Fe^{3+}$) in the BFO and both $Fe^{2+} \leftrightarrow Fe^{3+}$, $Ni^{2+} \leftrightarrow Ni^{3+}$ dipoles in $Bi_{0.99}Y_{0.01}Fe_{0.99}Ni_{0.01}O_3$ ceramics and they align themselves in the direction of the field due to the orientational polarization. At lower frequency the hopping of electron between the $Fe^{2+} \leftrightarrow Fe^{3+}$ and $Ni^{2+} \leftrightarrow Ni^{3+}$ ions caused higher value of dielectric constant but with the increase of frequency due to the inertia of the charge movement in the relaxation time caused a sharp fall of permittivity and then finally reached a constant value at very high frequency when the dipoles failed to follow the switching of applied
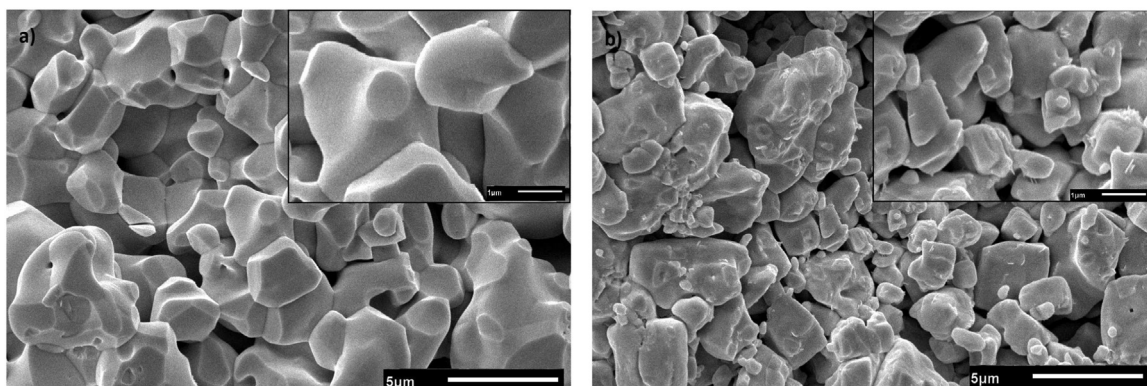
Fig. 2. Scanning electron microscope (SEM) images of fracture surface of (a) BFO and (b) $Bi_{0.99}Y_{0.01}Fe_{0.99}Ni_{0.01}O_3$ samples. Inset shows the magnified view of the images.