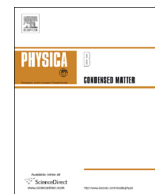




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# Enhanced magnetic and electrical properties of Y and Mn co-doped BiFeO<sub>3</sub> nanoparticles

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## ABSTRACT

Multiferroic (Y, Mn) substituted BiFeO<sub>3</sub> had been synthesized by a facial sol-gel method. The single phase polycrystalline nature of samples was confirmed from X-ray diffraction pattern. The average particle size was estimated to be around 30–32 nm from transmission electron microscopy. The magnetic properties of codoped nanoparticles had been studied using Bloch equation and the estimated value of the Bloch constant was found to be much larger than usual ferromagnetic materials. Coercivity values for different temperature is used to calculate the blocking temperature and found to lie above room temperature. The dc electrical transport properties were studied in the temperature range 298–523 K and explained using a Mott's 3D variable range hopping model and the density of states was estimated near the Fermi level. The ac electrical data were found to follow the correlated barrier hopping model. Well-developed *PE* hysteresis loops were observed in codoped nanoparticles, which were attributed to a decrease in oxygen vacancies, bismuth volatilisation due to doping and an increase of the effective potential barrier height for charge carriers.

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## 1. Introduction

Bismuth ferrite (BFO) is one of the promising room temperature multiferroic materials which show ferroelectric ordering below Curie temperature (1103 K) and space-incommensurate antiferromagnetism below the Néel temperature (643 K) and enable a coupling interaction between ferroelectric and antiferromagnetic order. This kind of coupling interaction also called the magnetoelectric coupling produces mutual control and detection of electrical polarization and magnetism [1,2]. Upon extensive research in the past few years, it was confirmed that multiferroic properties of BFO can be greatly tailored toward an ideal multiferroic material through suitable doping [3–6] and/or forming solid-state-solution with other perovskite type oxides [7]. Several groups tried to improve the magnetic properties of BFO by suitably doping with rare earth elements like La<sup>3+</sup>, Nd<sup>3+</sup>, Gd<sup>3+</sup>, Sm<sup>3+</sup>, Pr<sup>4+</sup> [8–11] where the dopants produce magnetization by suppressing the spiral spin structure of BFO. Several groups also tried to improve the ferroelectrical, electrical and optical properties of BFO by doping strategies [12–15]. However co-doping is a much more efficient way to tailor the magnetoelectric properties of BFO.

Local ferrimagnetic/ferromagnetic structure for improving the magnetic moment in bismuth ferrite has been proposed in transition metal doped Bi<sub>0.8</sub>La<sub>0.2</sub>Nb<sub>0.01</sub>Fe<sub>0.94</sub>TR<sub>0.05</sub>O<sub>3</sub> [16]. Several groups have attempted to ameliorate the electrical and magnetic properties of BFO by virtue of codoping [17–19]. In this paper we report the detailed magnetic and electrical properties of Y–Mn codoped BFO explaining some theoretical models which are useful in device applications.

## 2. Experimental

### 2.1. Material and methods

Codoped BiFeO<sub>3</sub> (Bi<sub>1-x</sub>Y<sub>x</sub>Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>3</sub>) ( $x=0.01$ ,  $y=0.01$ ,  $0.05$ ) nanoparticles designated as BiFeO<sub>3</sub> (Pure), Bi<sub>0.99</sub>Y<sub>0.01</sub>FeO<sub>3</sub> (1Y), BiY-Fe<sub>0.99</sub>Mn<sub>0.01</sub>O<sub>3</sub> (1Mn), Bi<sub>0.99</sub>Y<sub>0.01</sub>Fe<sub>0.99</sub>Mn<sub>0.01</sub>O<sub>3</sub> (1Y–1Mn), Bi<sub>0.99</sub>Y<sub>0.01</sub>-Fe<sub>0.95</sub>Mn<sub>0.05</sub>O<sub>3</sub> (1Y–5Mn) were prepared by a simple sol-gel route. Weighted amounts of Bi (NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (Sigma-Aldrich, 99.99%), Fe (NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Sigma-Aldrich, 98%+), Y (NO<sub>3</sub>)<sub>3</sub>·10H<sub>2</sub>O (Sigma Aldrich, 99.99%) and Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (Alfa Aesar, 99.9%) were dissolved in 20 ml distilled water under continuous stirring. The reaction medium was made acidic by using HNO<sub>3</sub> and pH of the solution was maintained at 2. In the next step, 0.03 mol of malic acid was dissolved in 30 ml distilled water in a separate beaker.

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Metal nitrate precursor solutions were added to malic acid under continuous ultrasonication. Polyethylene glycol (PEG) and malic acid in a molar ratio of 1:1 were subsequently added to the solution as a capping agent. The solution was dried to get precursor powder. Finally the ground powders were calcined in air at 873 K for 2 h.

## 2.2. Characterization

The single phase formation of  $(\text{Bi}_{1-x}\text{Y}_x\text{Fe}_{1-y}\text{Mn}_y\text{O}_3)$  ( $x=0.01, y=0.01, 0.05$ ) nanocrystals was confirmed by X-ray diffraction pattern. X-ray diffraction of these samples was recorded by an X'Pert Pro X-ray diffractometer (Panlytical, Almelo, Netherlands) fitted with nickel-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda=1.5414 \text{ \AA}$ ) in  $2\theta$  range from  $20^\circ$  to  $80^\circ$ . The transmission electron microscope (HRTEM, JEOL 2011) study confirmed the size and formation of BFO and co-doped BFO nanoparticles. The magnetic properties of the samples were measured by using a superconducting interface device (SQUID) magnetometer MPMS (Quantum Design, USA) fitted with a 7 T magnet. For electrical measurements the powder was taken in a steel mold of 1 cm diameter and compacted at a pressure of  $7 \text{ t/cm}^2$ . Silver paint electrodes (supplied by Acheson Colloiden, B.V. Holland) were applied on two opposite faces. Direct-current (dc) conductivity was measured by using Keithley 6514 electrometer. The temperature dependence of conductivity was measured in a furnace fitted with a Eurotherm temperature controller. The ac measurement was performed using an Agilent E4980A LCR meter. Room temperature ferroelectric loops were studied using a Radiant Technology precision premier II workstation (USA).

## 3. Result and discussions

XRD patterns of codoped BFO nanoparticles calcined at 873 K are presented in Fig. 1. All the prominent peaks in the plot are indexed to various  $(hkl)$  planes of  $\text{BiFeO}_3$  (JCPDS no. 86-1518), demonstrating the formation of single phase  $\text{BiFeO}_3$  nanoparticles. The transmission electron microscopy study was done to estimate the average particles size and is found to be in the range of 30–32 nm. Fig. 2(a) shows a typical TEM image of the 1Y–1Mn sample. Fig. 2(b) shows the high resolution TEM image of 1Y–1Mn sample taken from a portion of Fig. 2(a). The lattice planes  $(012)$  and  $(024)$  are clearly observed and match well with JCPDS no. 86-1518 confirming the good crystalline nature of BFO. Fig. 2(c) shows the SAED pattern taken from Fig. 2(a), which also reconfirmed the formation of BFO.

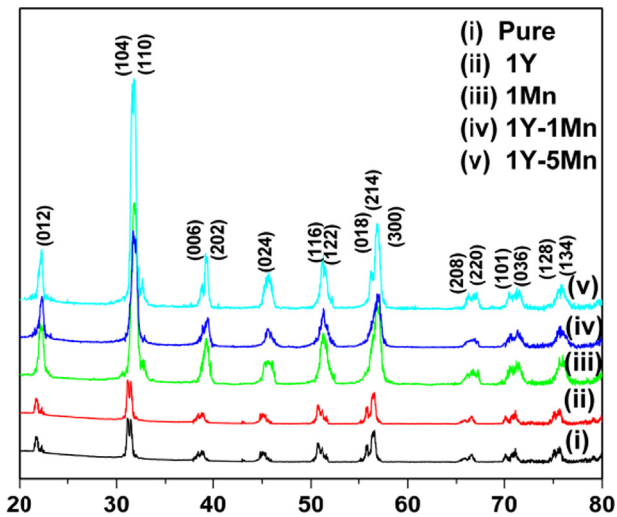


Fig. 1. X-ray diffraction pattern for all samples.

Fig. 2(d) shows the EDS spectrum, taken from a portion of Fig. 2(a), which again confirms the presence of all the elements of 1Y–1Mn nanoparticles.

The hysteresis loop at 300 K for all the samples presented in Fig. 3(a and b) shows the enlarged view of Fig. 3(a) in the lower field region. Shapes of the curves confirm the ferro/ferrimagnetic nature of the samples. The magnetisation behavior of the samples had been analysed on the basis of Bloch function [20,21] given by

$$M_s(T) = M_s(0)[1 - BT^{3/2}] \quad (1)$$

where  $M_s(T)$  and  $M_s(0)$  are the saturation magnetizations at temperatures  $T$  K and 0 K, respectively, and  $B$  is the Bloch constant. Fig. 3(c) shows the variation of  $M_s(T)$  with  $T^{3/2}$ . It is clearly observed that saturation magnetization is increased with doping and it has taken maximum value in the case of 1Y–1Mn. We have fitted  $M_s(T)$  experimental data to Eq. (1) using  $M_s(0)$  and  $B$  as parameters. The value of Bloch constant is estimated to be  $4 \times 10^{-5} \text{ K}^{-3/2}$  which is much larger than ferromagnetic metals like  $\alpha\text{-Fe}$  [22] and  $\text{YFeO}_3$  [23]. Bulk perovskite BFO is antiferromagnetic ( $T_N \approx 643 \text{ K}$ ) in nature and exhibits very weak magnetization at room temperature due to a residual moment from a canted spin structure. BFO nanoparticles show ferromagnetic-like behavior due to the breakdown periodicity of the spin cycloid of iron. The potential causes for the increase in macroscopic magnetization were the suppressed inhomogeneous magnetic spin structure, increased canting angle due to co-doping and the formation of  $\text{Fe}^{+2}$  ions. However it is well established that during high temperature annealing process, coexistence of  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  is unavoidable [24]. The existence of  $\text{Fe}^{+2}$  ions would possibly cause a double exchange interaction between  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  ions through oxygen which may result in the enhancement of ferromagnetism [25,26]. When Mn is the only dopant, the magnetization increases due to the magnetic moment of Mn itself and the charge compensation effect. In case of 1Y–1Mn the pop-in of Y conflicted with Mn and pinned the Mn valance state. Y makes an impact on Fe and the moment of Mn can help strengthen the magnetization together with Fe valance state variation and  $\text{Fe}^{+2}\text{-O-Fe}^{+3}$  superexchange interaction caused by Y doping. However the potential cause for the decrease of magnetization in 1Y–5Mn is the structural distortion.

The variation of coercivity  $H_c$  with temperature for different samples is displayed in Fig. 3(d). The large value of coercivity observed indicates that the samples are not superparamagnetic below the room temperature. It is evident from Fig. 3(d) that the coercivity value increases as the temperature is lowered. This is to be expected in the case of ferro/ferrimagnetic particles [16]. The thermal dependence of  $H_c$  is expected to follow the equation

$$H_c = H_c(0)[1 - A(T)^k] \quad (2)$$

where  $H_c(0)$  is the coercive field at  $T=0 \text{ K}$ , and  $A$  and  $k$  are the parameters given by the following relation:

$$A = [\beta k_B / VK_{eff}]^k \quad (3)$$

where  $k_B$  is Boltzmann constant,  $\beta = \ln(\tau_m/\tau_0)$  depends on the typical measuring time  $\tau_m$  and characteristic time  $\tau_0$  and  $K_{eff} = K_V + (6/d)K_S$ , is the effective anisotropy constant, where  $K_V$  is the bulk anisotropy energy per unit volume,  $K_S$  is the surface density of anisotropy energy and  $d$  is the diameter of the particle [20]. It has been shown that a perfect spherical particle should have a zero net contribution from surface anisotropy and the exponent  $k$  has a value of 0.5 for an assembly of aligned particles [21] and  $k=0.77$  for randomly oriented particles [22]. Again from Arrhenius–Néel relation [23] the blocking temperature is given by

$$T_B = \frac{VK_{eff}}{\beta k_B} \quad (4)$$

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