

# Size Dependent Ferromagnetism in Bismuth Iron Oxide Nanoparticles for Magnetoelectric Applications

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## ABSTRACT

The class of materials that demonstrate the presence of ferroelectricity and ferromagnetism are known as multiferroic materials. Ferroelectricity is obtained by existence of transition metal ion that has outer empty shell of electrons. On the other side, ferromagnetic properties arise because of the exchange interaction of electrons present in partly filled "d" or "f" sub-shells. Due to lack of mutual existence of ferroelectricity and ferromagnetism at room temperature choice of material regarding practical applications is restricted. Among the limited choices, bismuth iron oxide (BiFeO<sub>3</sub>) is known as the prototype multiferroic material that shows room temperature ferroelectric and ferromagnetic properties along with magnetoelectric coupling at room temperature. Despite the advantages bismuth iron oxide offers, there are various matters that are to be taken into consideration. Biggest issue includes synthesis of phase pure BiFeO<sub>3</sub> at low temperature. Bismuth iron oxide nanoparticles have been synthesized using sol-gel method. Bi/Fe ratio is varied as 0.9, 1.0 and 1.10. X-ray diffraction patterns confirm formation of BiFeO<sub>3</sub> phase at Bi/Fe ratio of 1.10. Nanoparticles synthesized using Bi/Fe 0.9 and 1.0 ratio show weak ferromagnetic behavior. Transition to strong ferromagnetic behavior was observed at Bi/Fe ratio 1.10. This transition in magnetic properties arises due to conversion of helical spin structure to linear structure. Bismuth iron oxide nanoparticles prepared using Bi/Fe ratio 0.9 and 1.0 result in normal dispersion behavior in dielectric constant. While high dielectric constant and anomalous dispersion is observed for nanoparticles prepared using Bi/Fe ratio 1.10.

## 1. INTRODUCTION

Multiferroic materials are one of the most widely studied materials due to the increasing demands of compact and high efficiency devices. During the last few decades, drastic scaling of electronic components has taken place and the industry is expected to continue this approach (Wen et al. 2016, Sharif et al. 2016, Fu et al. 2016). Multiferroic materials exhibit at least two of the ferroic orders simultaneously i.e. ferroelectricity, ferromagnetism or ferroelasticity. Most interesting combination of ferroic

orders involves the mutual presence of ferromagnetism and ferroelectricity as it opens new pathways for various applications. But a comprehensible difference has to be made between the materials that demonstrate ferroelectric and ferromagnetic behavior and between those which exhibit magnetoelectric coupling between the two ferroic orders. Presence of magnetoelectric interaction between ferromagnetic and ferroelectric properties helps to control the magnetization with the help of electric field and vice versa (Riaz et al. 2014a,b, Majid et al. 2015). The main problem is to find such materials. One of the choices is to combine two ferroelectric and ferromagnetic materials. But magnetoelectric coupling between these two materials is carried out through strain that results in slow switching rates. So, the single phase materials exhibiting intrinsic ferromagnetic and ferroelectricity along with magnetoelectric coupling are highly desirable (Rogez et al. 2010, Shah et al. 2014a,b).

Bismuth iron oxide ( $\text{BiFeO}_3$ ) is a potential candidate among various multiferroic materials with both ferromagnetic and ferroelectric ordering at room temperature.  $\text{BiFeO}_3$  has perovskite structure with rhombohedral distortion in the unit cell. This results in lattice parameters of  $a = 5.5775 \text{ \AA}$  and  $c = 13.861 \text{ \AA}$ . Bismuth iron oxide exhibits ferroelectric Curie temperature of  $826^\circ\text{C}$ . Below its Curie temperature polarization in the direction of pseudo-cubic [111] axes can be detected. It undergoes a transition from rhombohedrally distorted structure to orthorhombic structure. In addition,  $\text{BiFeO}_3$  demonstrates G-type antiferromagnetic behavior. Magnetic behavior in  $\text{BiFeO}_3$  arises due to the presence of 3d electrons of iron. On the other hand ferroelectricity is due to structural instability that arises because of the hybridization between Bi unfilled 6p and oxygen 2p orbitals (Riaz et al. 2015, Riaz et al. 2014a,b).

In spite of the advantages  $\text{BiFeO}_3$  exhibits some drawbacks. The most important drawback to be addressed is the synthesis of phase pure  $\text{BiFeO}_3$  along with ferromagnetic behavior. For addressing / overcoming this difficulty bismuth iron oxide nanoparticles were synthesized using sol-gel method by varying Bi/Fe ratio as 0.9, 1.0 and 1.10. Changes in structural and magnetic properties have been correlated with changes in Bi/Fe ratio.

## 2. EXPERIMENTAL DETAILS

Bismuth iron oxide nanoparticles were synthesized with sol-gel method. Iron nitrate and bismuth nitrate were used as precursors. Iron nitrate was mixed in ethylene glycol and stirred at room temperature. Bismuth nitrate was also mixed in ethylene glycol at room temperature. Two solutions were mixed together and stirred for 30 minutes. The solution was heated at  $80^\circ\text{C}$  and resultant precipitates were centrifuged at 4000rpm for 60 seconds. Detailed sol-gel synthesis is reported elsewhere (Riaz et al. 2015). During sol-gel synthesis Bi/Fe ratio was kept as 0.9, 1.0 and 1.10.

Bismuth iron oxide nanoparticles were characterized under as-synthesized conditions. Bruker D8 Advance X-ray diffractometer (XRD) and Lakeshore's 7407 Vibrating Sample Magnetometer (VSM) were used to study structural and magnetic behavior whereas dielectric properties were studied using 6500B Precision Impedance Analyzer.

## 3. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns for bismuth iron oxide nanoparticles prepared with variation in Bi/Fe ratio as 0.9, 1.0 and 1.10. XRD patterns show amorphous behavior for Bi/Fe ratio 0.9 and 1.0. As Bi/Fe ratio was increased to 1.10 transition from amorphous to crystalline behavior was observed. Presence and splitting of diffraction peaks corresponding to (104) and (110) planes indicated the formation of phase pure bismuth iron oxide. It can be seen that no peaks corresponding to non-perovskite phases of bismuth iron oxide were observed. These results indicate that ratio of Bi/Fe cations plays a crucial role for synthesis of phase pure bismuth iron oxide with crystalline order under as-synthesized conditions. In sol-gel method, synthesis of crystalline nanoparticles strongly depends on nucleation and growth stages. Larger numbers of small crystallites are formed as the result of high nucleation rate while larger crystallites are formed due to slow nucleation rates. With increase in Bi/Fe ratio to 1.10 number of  $\text{Bi}^{3+}$  cations that diffuses in the sol and react with  $\text{Fe}^{3+}$  cations increases. This leads to increase in nucleation rate and thus formation of smaller crystallites (Yoo et al. 2013). Formation of small crystallites leads to increase in long range order (Yoo et al. 2013) in bismuth iron oxide nanoparticles thus inducing crystallinity in bismuth iron oxide nanoparticles.

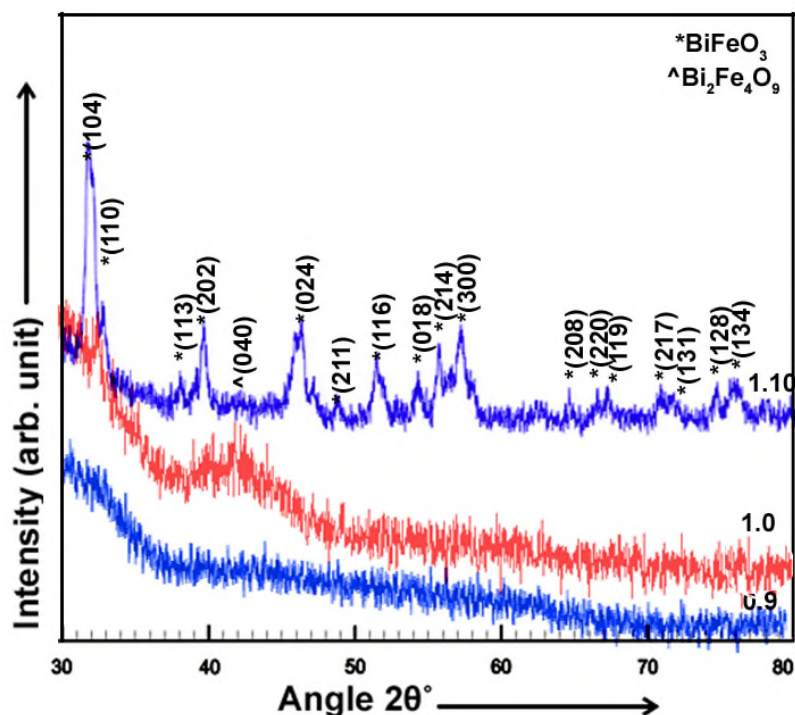


Fig. 1 XRD patterns for bismuth iron oxide nanoparticles

Crystallite size ( $t$ ) (Cullity 1956), dislocation density ( $\delta$ ) (Kumar et al. 2011) and lattice parameters (Cullity 1956) were calculated using Eqs. 1-3

$$t = \frac{0.9\lambda}{B \cos \theta} \quad (1)$$

$$\delta = \frac{1}{t^2} \quad (2)$$

$$\sin^2 \theta = \frac{\lambda^2}{3a^2} (h^2 + k^2 + hk) + \frac{\lambda^2 l^2}{4c^2} \quad (3)$$

Where,  $\theta$  is the diffraction angle,  $\lambda$  is the wavelength (1.5406Å) and  $B$  is Full Width at Half Maximum. Crystallite size, dislocation density and lattice parameters for Bi/Fe ratio 1.10 are listed in table 1. In case of bismuth iron oxide nanoparticles, crystallite size plays a crucial role. It has been reported earlier (Riaz et al. 2015, Fu et al. 2016) that bismuth iron oxide has cycloidal spin structure of 62nm. And as crystallite size falls below 62nm the changes in this spin structure leads to enhancement in magnetic properties as will be discussed later.

Table 1 Structural properties for bismuth iron oxide nanoparticles prepared with Bi/Fe ratio as 1.10

Crystallite size	12nm	
Dislocation density	$6.9 \times 10^{15}$ lines/m <sup>2</sup>	
Lattice parameters (Å)	a	5.51
	c	13.99
Unit cell volume	$367.82 \text{Å}^3$	

Figure 2 shows M-H curves for bismuth iron oxide nanoparticles prepared with variation in Bi/Fe ratio as 0.9, 1.0 and 1.10. Bulk bismuth iron oxide exhibits G-type antiferromagnetic behavior. According to Neel theory, integral multiple of spiral spin structure results in only presence of compensated magnetic moments. But if the grain size is above or below the spiral length uncompensated magnetic moments appear. Thus, each grain is composed of both ferromagnetic and antiferromagnetic component. Antiferromagnetic part is present within the grain itself while ferromagnetic component arises due to presence of grain boundaries. Uncompensated spins at the surface of grains is higher when the grain size is small. This leads to increase in magnetic moment with decrease in grain size (Sharma et al. 2016). It was observed in Table 2 that crystallite size of 12nm was observed for bismuth iron oxide nanoparticles with Bi/Fe ratio 1.10. This small crystallite size is effective in suppressing the spin structure of bismuth iron oxide. In addition, due to disturbance of Fe-O bond at the surface of particles antiferromagnetic long range order is disturbed at the surface of nanoparticles. This results in mixing of oxygen anions. These oxygen anions are the cause of presence of uncompensated spins from Fe<sup>3+</sup> cations. With decrease in size of nanoparticles due to large surface to volume ratio disorder at the surface increases thus resulting in uncompensated magnetic moments. These uncompensated magnetic

moments also contribute to overall magnetization of nanoparticles (Hasan et al. 2016). Another important factor that strongly influences the magnetic properties includes magneto crystalline anisotropy. Magneto crystalline anisotropy for bismuth iron oxide nanoparticles can be seen in Table 2. It can be seen that reduction in magneto crystalline anisotropy also leads to change in magnetic behavior of bismuth iron oxide nanoparticles.

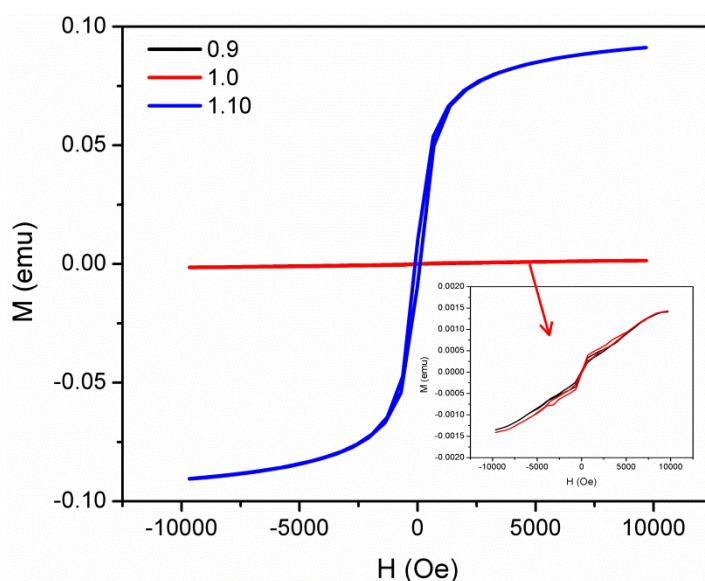


Fig. 2 M-H curves for bismuth iron oxide nanoparticles prepared using sol-gel method

Table 2 Magnetic and structural parameters for bismuth iron oxide nanoparticles

Bi/Fe ratio	Phase	Crystallite size	Saturation Magnetization (emu)	Magneto crystalline anisotropy ( $10^4 \text{erg/cm}^3$ )
0.9	Amorphous	----	Weak magnetic behavior	1.59
1.0	Amorphous	----		1.57
1.10	$\text{BiFeO}_3$	12nm	0.085	1.22

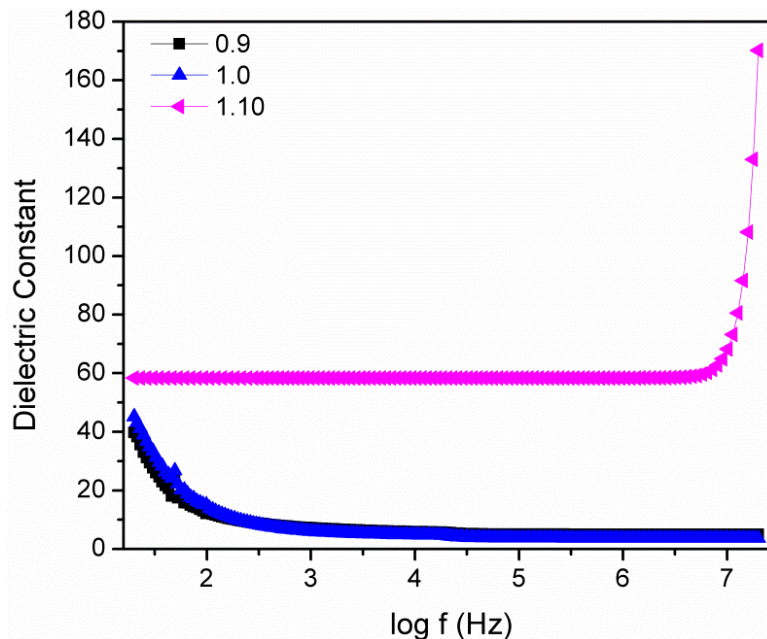
Figure 3 shows Dielectric constant and tangent loss for bismuth iron oxide nanoparticles. It can be seen that dielectric constant for  $\text{BiFeO}_3$  nanoparticles prepared using Bi/Fe ratio 0.9 and 1.0 resulted in normal dispersion behavior. While, transition to anomalous dispersion was observed with increase in Bi/Fe ratio to 1.10. On the other hand, tangent loss shows normal dispersion behavior. At low frequencies the space charge carriers follow the alteration in externally applied electric field thus producing large polarization. This results in high dielectric constant and tangent loss at low

frequencies. On the other hand, at high frequencies the space charge carriers have not moved before field changes (Riaz et al. 2015). This leads to reduction in polarization and hence dielectric constant decreases at high frequencies. The anomalous behavior observed for BiFeO<sub>3</sub> nanoparticles prepared using Bi/Fe ratio 1.10 arises from resonance effect. Resonance occurs when the jumping frequency of ions matches with that of the externally applied electric field. Relaxation peak observed in tangent loss data for bismuth iron oxide nanoparticles with Bi/Fe ratio as 0.9 and 1.0 can be explained on the basis of Rezlescu model. This model states that polarization for n-type and p-type charge carriers behave differently as frequency of applied field increases. If both types of charge carriers coexist then clear resonance peak is observed (Barsoukov and Macdonald 2005).

Dielectric constant and tangent loss are listed in table 2. Dielectric constant increases from 8 (log f = 5.0) to 59.9 as Bi/Fe ratio was increased to 1.10. This increase in dielectric constant is related to transition from crystalline to amorphous state. According to Clausius–Mosotti (C–M) relation (given in eq. 4) (Barsoukov and Macdonald 2005) intrinsic polarizability is associated with crystallinity of nanoparticles. This additional polarization thus leads to increase in dielectric constant.

$$\varepsilon = \frac{1 + 2b\alpha/V_m}{1 - b\alpha/V_m} \quad (4)$$

Where,  $V_m$  is the molar volume in Å<sup>3</sup>,  $\varepsilon$  is the dielectric constant,  $b$  is the constant and  $\alpha$  represents contribution from electronic and ionic polarization (Barsoukov and Macdonald 2005).



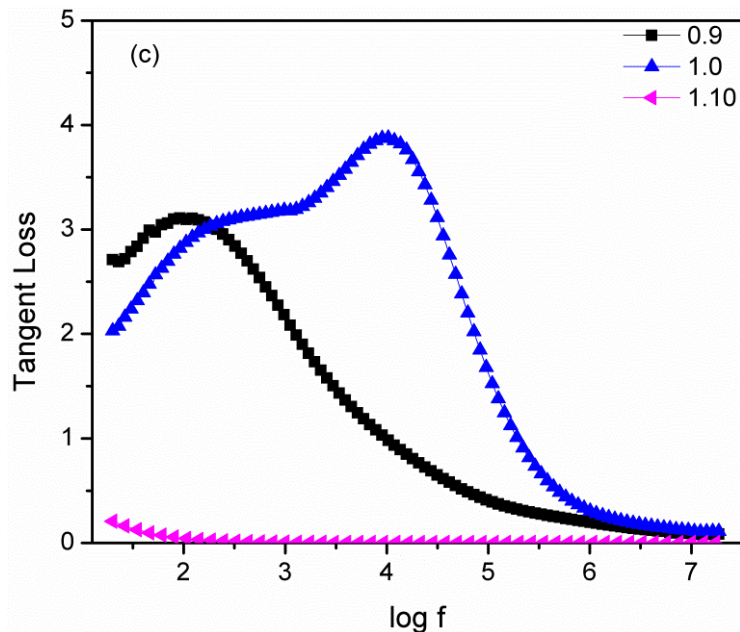


Fig. 3 Dielectric constant and tangent loss for bismuth iron oxide nanoparticles

An important factor that strongly influences the dielectric constant is the presence of oxygen vacancies. Oxygen vacancies lead to decrease in dielectric constant of the material. Activation energy is determined using straight line slope of  $\ln \sigma$  (conductivity) vs.  $1000/T$  ( $K^{-1}$ ) curve shown in Fig. 4. High activation energy of 1.56eV is indicative of less number of oxygen vacancies thus supporting the high dielectric constant observed in Fig. 3.

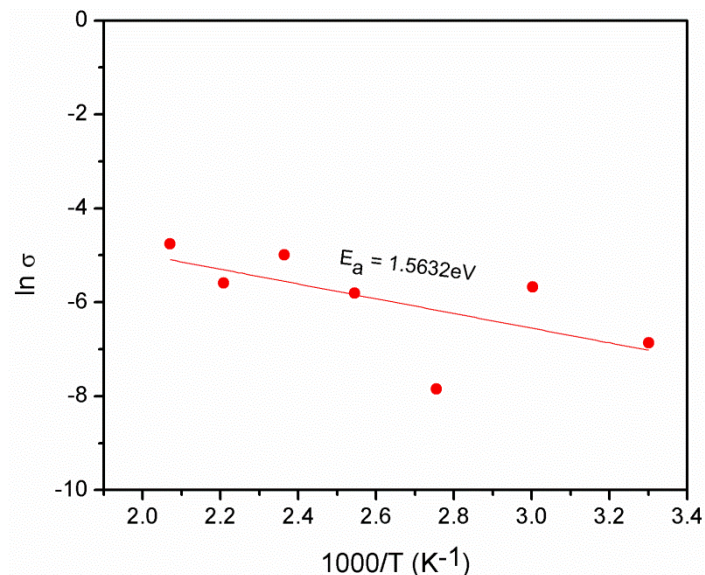


Fig. 4  $\ln \sigma$  (conductivity) vs.  $1000/T$  ( $K^{-1}$ ) curve for bismuth iron oxide nanoparticles prepared using Bi/Fe ratio 1.10

## 4. CONCLUSIONS

Bismuth iron oxide nanoparticles were prepared using sol-gel method with variation in Bi/Fe ratio as 0.9, 1.0 and 1.10. These nanoparticles were characterized under as-synthesized conditions. XRD results showed the formation of phase pure BiFeO<sub>3</sub> at Bi/Fe ratio 1.10 while Bi/Fe ratio 0.9 and 1.0 resulted in formation of amorphous structure. Nanoparticles prepared using Bi/Fe ratio resulted in weak magnetic behavior while transition to strong ferromagnetic behavior was observed with increase in Bi/Fe ratio to 1.10 due to suppression of spiral spin structure and decrease in magneto crystalline anisotropy. Dielectric constant for bismuth iron oxide nanoparticles prepared with Bi/Fe ratio 1.10 resulted in anomalous behavior while tangent loss exhibited normal dispersion behavior. Reduction in oxygen vacancies for bismuth iron oxide nanoparticles prepared with Bi/Fe ratio 1.10, indicated by high activation energy of 1.56eV, resulted in increase in dielectric constant.

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