Anomalous Dielectric Behavior of Phase Pure BiFeO$_3$ Nanoparticles – High Frequency Effects

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ABSTRACT

The most desirable feature of multiferroics is the coexistence of ferroelectric and ferromagnetic order at the room temperature for device application. However, there are few single phase multiferroic materials which show ferroelectric and ferromagnetic coupling at room temperature. Among such materials bismuth iron oxide (BiFeO$_3$) is most commonly known multiferroic. Furthermore, high frequency effects on dielectric behavior of BiFeO$_3$ are rarely reported. For obtaining phase pure BiFeO$_3$ nanoparticles, we here report sol-gel synthesis with variation in synthesis temperature as 80–110°C (interval 10°C). BFO nanoparticles are characterized under as-synthesized conditions. X-ray diffraction results show amorphous behavior at synthesis temperature of 80°C. Transition to crystalline phase pure BiFeO$_3$ is observed at 90°C. Relatively higher synthesis temperature of 100°C and 110°C result in mixed BiFeO$_3$ and Bi$_2$Fe$_4$O$_9$ phases with reduced crystallinity. Nanoparticles synthesized at 80°C exhibit paramagnetic behavior. Ferromagnetic behavior is observed for temperature range of 90–110°C. Whereas, highest magnetization of 0.11304 emu is observed for BiFeO$_3$ nanoparticles synthesized at 90°C. High frequency based anomalous dielectric behavior is observed under all synthesis conditions. Highest dielectric constant of 78.88 (log f = 5.0) is obtained for nanoparticles synthesized at 90°C. Shift of maximum value of imaginary impedance and peak broadening with changes in synthesis temperature indicate that frequency based relaxation mechanism strongly depends on changes in phases of bismuth iron oxide that is governed by variation in synthesis conditions.

1. INTRODUCTION

Among various oxide materials multiferroics have gained much attention for its applications in spintronic and non-volatile memories (Yang et al. 2017; Romana et al. 2017; Kleemann 2017; Yan et. al 2017; Chiu et al. 2017). Multiferroics are class of materials that possess two or more ferroic orders simultaneously. The most important ferroic orders include ferromagnetism and ferroelectricity. In addition, magnetoelectric coupling between these ferroic orders allows control of electric polarization by magnetic
field and magnetic polarization by electric field. Such materials will lead to magnetic memories where the bits can be written using electric field (Park et al. 2007).

Among multiferroics, bismuth iron oxide (BiFeO$_3$; BFO) has gained much consideration owing to its high antiferromagnetic Neel temperature and high ferroelectric Curie temperature. First perovskite BFO was synthesized in late 1950s (Martin et al. 2010). Since then the main focus is on its magnetic and electronic properties and magnetoelectric coupling. Antiferromagnetic and ferroelectric character of BFO was studied in early 1960s (Martin et al. 2010; Teague et al. 1970). Nevertheless, exact ferroelectric nature of BFO was revealed in 1970 when ferroelectric measurements were carried out at 77K (Teague et al. 1970). These experiments showed polarization of $6.1\mu$C/cm$^2$ along direction [111]. Later ferroelectric properties were proved to be stable with in 4K to 1103K (Martin et al. 2010; Teague et al. 1970; Munos et al. 1985).

BFO is composed of two distorted perovskite cells that are linked along body diagonal to form rhombohedral unit cell. In this structure, oxygen octahedrons are rotated along [111] direction by $\pm 13.8^\circ$. Iron cations are shifted by 0.135Å along the same axis away from centre position. Ferroelectric properties are defined by disarticulation of bismuth ions with respect to FeO$_6$ octahedron (Martin et al. 2010; Moriya1960).

During 1980s magnetic nature of BFO was studied in detail and antiferromagnetic nature was observed (Martin et al. 2010; Sosnowska et al. 1982). It has cycloidal spin structure of 620Å with Neel temperature of about 673K that is disproportionate with the lattice. weak ferromagnetic behavior in BFO is the result of small canting of the magnetic moments (Shah et al. 2014; Majid et al. 2015).

Synthesis of BFO is extremely difficult both in single crystal and polycrystalline forms. One of the major problems is presence of Bi$_2$O$_3$, mullenite Bi$_2$Fe$_4$O$_9$ and sillenite Bi$_{25}$FeO$_{40}$ phases along with BiFeO$_3$. In addition, temperature reported for synthesis of phase pure BFO is $\sim$400-900°C. α-Bi$_2$O$_3$ an intermediate compound in BFO synthesis, and is volatile, thus, evaporates at high temperatures. As a result, its magnetic and dielectric properties strongly degrade. So, to minimize these problems it’s extremely crucial to control kinetic and thermodynamics conditions for BFO synthesis (Shah et al. 2014a; Majid et al. 2015; Shah et al. 2014b; Riaz et al. 2015; Riaz et al. 2014a).

For this purpose, we synthesized BFO nanoparticles with variation in reaction temperature in the range of 80°C to 110°C. BFO nanoparticles are characterized for their structural, magnetic and dielectric properties.

2. EXPERIMENTAL DETAILS

For synthesis of BFO nanoparticles, bismuth nitrate and iron nitrate were used as precursors. Ethylene glycol was employed as solvent in sol-gel synthesis. In the first step of sol synthesis, iron nitrate was dissolved in ethylene glycol and stirring was done at room temperature. In second step of sol synthesis bismuth nitrate was dissolved in ethylene glycol under stirring at room temperature. In the third step, the two solutions prepared in step one and two were mixed together. Solutions were heated at 80°C, 90°C, 100°C and 110°C to obtain BFO nanoparticles. These nanoparticles were then characterized without further heat treatment.
For structural characterization of BFO based nanoparticles Bruker D8 Advance X-ray Diffractometer (XRD) was used. Magnetic analysis was performed with Lakeshore’s 7407 Vibrating Sample Magnetometer (VSM). For dielectric analysis, 6500B Precision Impedance Analyzer with parallel plate configuration was used.

3. Results and discussion

Fig. 1 shows XRD patterns for as-synthesized BFO nanoparticles. BFO nanoparticles prepared with synthesis temperature of 80˚C (Fig. 1(a)) resulted in amorphous behavior. This indicates that synthesis temperature of 80˚C is not enough for the formation of BFO phases. As synthesis temperature was increased to 90˚C (Fig. 1(b)) transition to crystalline behavior was observed. The peaks are indexed with JCPDS card 86-1518. All peaks present in the diffraction pattern are well matched with JCPDS card 86-1518 indicating formation of phase pure BiFeO$_3$. With increase in temperature during synthesis to 100˚C and 110˚C (Fig. 1(c,d)) destruction of crystalline order was observed along with presence of mixed BiFeO$_3$ (marked by *) and Bi$_2$Fe$_4$O$_9$ (marked by ^; JCPDS card 74-1098) phases.

Based on above results it can be suggested that the time required for nucleation is increased at low synthesis temperature. In this case, two effects occur: 1) Ionic depletion regions around nucleus does not take place; 2) Supersaturation state is not disturbed. These factors lead to increase in mobility as well as diffusion. Thus, defects are decreased with improved crystal quality. As synthesis temperature is raised to 100˚C and 110˚C the rate of nucleation increases. Fast nucleation might result in large number of crystals. This results in reduced concentration of local reactants. Thus, defects start to appear in crystal and affect the crystalline quality. These defects also aid the formation of secondary phases (Manzoor et al. 2015).

![XRD patterns for BFO nanoparticles with synthesis temperature](image_url)

**Fig. 1.** XRD patterns for BFO nanoparticles with synthesis temperature (a) 80˚C; (b) 90˚C; (c) 100˚C; (d) 110˚C.

Crystallite size (t) (Cullity 1956), dislocation density (δ) lattice parameters (a, c) and unit cell volume (Cullity 1956) for BFO nanoparticles was calculated with Equations (1)-(4)
\[
t = \frac{0.9 \lambda}{B \cos \theta} \\
\delta = \frac{1}{t^2} \\
\frac{1}{d^2} = 4\left(\frac{h^2 + k^2 + h k}{a^2} + \frac{l^2}{c^2}\right) \\
V = 0.866a^2c
\]

Where, \( \lambda \) is wavelength 1.5406Å, \( B \) is full width at half maximum, \( \theta \) is diffraction angle and \((hkl)\) are miller indices. Crystallite size (Table 1) of 20.59nm was calculated for BFO nanoparticles synthesized at 90˚C. For BFO nanoparticles synthesized at 100˚C and 110˚C crystallite size was 14.72nm and 13.97nm, respectively. In synthesis of nanoparticles, supersaturated solution has high Gibb’s free energy. Difference between free energy related to supersaturated phase and new developing phase is the main force behind crystallization. If temperature and pressure are kept constant, any change during synthesis results in transition from higher Gibb’s free energy to lower Gibb’s free energy. Gibb’s free energy is strongly affected by changes in supersaturation state of solution/sol. The two important factors that are affected by changes in synthesis temperature are: 1) State of supersaturation; 2) Rate of hydrolysis. As temperature increases from 90˚C to 100˚C and 110˚C solubility increases and supersaturation decreases. Due to this, small nuclei are no more stable and can easily dissolve back in the solution. These dissolved nuclei then deposit on the surface of already formed larger particles (Kohli et al. 2012; Cao et al. 2004). Thus, the dissolution-growth process continues resulting in increase in crystallite size with increase in synthesis temperature.

Unit cell volume (Table 1) for BFO nanoparticles synthesized at 90˚C is close to that reported in literature. Decrease in lattice parameter at synthesis temperature 100˚C and 110˚C is due to presence of mix \( \text{BiFeO}_3 \) and \( \text{Bi}_2\text{Fe}_4\text{O}_9 \) phases observed in Fig. 1(c) and (d).

<table>
<thead>
<tr>
<th>Synthesis temperature (˚C)</th>
<th>Phase</th>
<th>Crystallite size (nm)</th>
<th>Dislocation density ( \left(10^{15}\text{ lines/m}^2\right) )</th>
<th>Lattice parameter (Å)</th>
<th>Unit cell volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>Amorphous</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>90</td>
<td>( \text{BiFeO}_3 )</td>
<td>20.5856</td>
<td>2.359788549</td>
<td>5.58</td>
<td>13.89</td>
</tr>
<tr>
<td>100</td>
<td>( \text{BiFeO}_3 + \text{Bi}_2\text{Fe}_4\text{O}_9 )</td>
<td>14.71809</td>
<td>4.616330226</td>
<td>5.50</td>
<td>13.83</td>
</tr>
<tr>
<td>110</td>
<td>( \text{BiFeO}_3 + \text{Bi}_2\text{Fe}_4\text{O}_4 )</td>
<td>13.97309</td>
<td>5.121710011</td>
<td>5.49</td>
<td>13.80</td>
</tr>
</tbody>
</table>

Room temperature magnetic-hysteresis (M-H) curves for BFO nanoparticles can be seen in Fig. 2 (a). Paramagnetic behavior was observed for nanoparticles
synthesized at 80°C. This paramagnetic behavior indicates that magnetic phases are not fully developed at this synthesis temperature. With increase in synthesis temperature to 90°C change in magnetic behavior from paramagnetic to ferromagnetic was observed with saturation magnetization of 0.11304emu (Fig. 2(b)). As synthesis temperature was further increased to 100°C and 110°C decrease in magnetization to 0.0373emu and 0.03544emu, respectively, was observed. This decrease in magnetization is due to presence of mix BiFeO$_3$ and Bi$_2$Fe$_4$O$_9$ phases as observed in Fig. 1(c) and (d).

In bulk form BFO is antiferromagnetic. An antiferromagnetic material is composed of two spin lattices. Two types of interactions arise in these sublattices: 1) Ferromagnetic interaction: arises between spins of same sublattice; 2) Antiferromagnetic interaction: arises with spins of neighboring sublattice. Based on Neel theory, magnetization in antiferromagnetic systems is due to uncompensated spins present in the sublattices and this magnetization becomes measurable only in particles with very small size. In nanoparticles, surface to volume ratio is very high and antiferromagnetic long-range order gets interrupted at the surface. This results in ferromagnetic behavior in antiferromagnetic material (Ahmed et al. 2013).

![Fig. 2. (a) M-H curves for BFO nanoparticles; (b) Saturation magnetization for BFO nanoparticles plotted for synthesis temperature.](image)

In addition, magnetic properties in a material change after its activation over an energy obstruction/barrier takes place. For each energy barrier, there is a related length scale. Three important length scales for magnetic materials are: 1) Applied field length scale ($l_H$); 2) magneto crystalline anisotropic length scale ($l_K$); 3) Magneto static length scale ($l_s$); where, $l_s$ and $l_K$ are both inversely proportional to $l_H$. These length scales basically govern the lowest length over which discrepancy in magnetic moments occurs. It also indicates size of domain wall width. Magnetization will not be able to keep track of randomly oriented easy axis if the crystallite size becomes slighter than this length scale. Thus, ferromagnetic behavior arises in this case. For BFO this length scale of 62nm is reported. As it was observed in Table 1 that crystallite size of BFO nanoparticles prepared with variation in synthesis temperature was less than 62nm.
thus, resulting in ferromagnetic behavior (Riaz et al. 2014; Riaz et al. 2015; Ahmed et al. 2013).

For studying dielectric properties of BFO nanoparticles, frequency based ($f$) capacitance ($C$) and resistance ($R$) was measured. Dielectric constant ($\varepsilon$) and tangent loss ($\tan\delta$) were calculated using Eq. (5) and (6) (Barsoukov and Macdonald 2005), respectively.

$$\varepsilon = \frac{Cd}{\varepsilon_0 A}$$  
$$\tan\delta = \frac{1}{2\pi f\varepsilon_0 \rho}$$  

(5)  
(6)

Where, $d$ is the thickness, $A$ area of device and $\varepsilon_0$ permittivity of free space and $\rho$ resistivity of nanoparticles.

Three regions were observed in dielectric spectra of BFO nanoparticles (Fig. 3(a)): 1) $\log f < 4.5$: In this region dielectric constant decreases with increase in frequency (inset Fig. 3(a)); 2) $4.5 < \log f < 6.5$: In this region dielectric constant remains almost constant with increase in frequency; 3) $\log f > 6.5$: In this region dielectric constant rises with increase in frequency. This increase is sharp at $\log f > 7.0$. In first two regions, variation of dielectric constant can be described with respect to space charge polarization. This type of polarization is formed in dielectric material due to occurrence of high conductivity grains parted by low conductivity grain boundaries. This assembly of space charge carriers need some time to line up with field variations. At high frequencies, field reversal is rapid so space charge carriers don’t have sufficient time to follow modifications in field. This results in decrease in dielectric constant with frequency and then becomes constant at higher frequencies. According to Koop’s model electrons can respond to field changes only if the hopping time of electrons is less than half of the time the changes in field takes place (Anis and Asghar 2011). In region three, sharp increase in dielectric constant arises due to: 1) Matching of hopping frequency of electrons with the applied field. This increases polarization capability of electrons and hence dielectric constant; 2) Trapping of space charge carriers at low frequencies can occur at grain boundaries and lattice defects. At high frequencies these space charge carriers have enough energy to free themselves from these traps. Thus, they start to contribute to polarization and dielectric constant at high frequencies (Barsoukov and Macdonald 2005).

Tangent loss (Fig. 3(b)) decreases as frequency of applied field increases. Tangent loss is dependent on various factors including iron content, structural homogeneity and stoichiometry. At low frequencies, involvement of these defects to polarization leads the applied field. High tangent loss at low frequencies is observed as a result. At high frequencies changes in applied field lead the polarization arising from these defects. This results in decrease in tangent loss with frequency (Barsoukov and Macdonald 2005).

Dielectric constant rises from 69.70 to 78.88 ($\log f = 5.0$) (Fig. 4) with rise in synthesis temperature from 80°C to 90°C. This increase in dielectric constant indicated the phase purity of BFO nanoparticles as observed in Fig. 1(b). In addition, as pointed out by (Saravanan et al. 2009) polycrystalline dielectric material exhibits high
polarization capability and hence high dielectric constant as compared to amorphous dielectric material. Hence polycrystalline phase pure BiFeO$_3$ exhibit high dielectric constant at synthesis temperature 90˚C. At high synthesis temperature 100˚C and 110˚C reduction in dielectric constant and rise in tangent loss is due to: 1) Presence of mix BiFeO$_3$ phases (Fig. 1(c, d)); 2) Increased dislocations (Table 1).

![Fig. 3. (a) Dielectric constant and (b) tangent loss for BFO nanoparticles.](image)

![Fig. 4. Dielectric constant and tangent loss for BFO nanoparticles plotted for variation in synthesis temperature.](image)

Real ($Z'$) and imaginary ($Z''$) impedance for BFO nanoparticles can be seen in Fig. 5. Real impedance (Fig. 5(a)) remains almost constant in low frequency region and then decreases in mid frequency region. After this, real impedance remains constant at high frequencies. Imaginary impedance (Fig. 5(b)) grows with rise in frequency and achieves a maximum value. Imaginary impedance then declines and become frequency independent at high frequencies. Presence of maximum in imaginary impedance plots indicates presence of relaxation mechanism in BFO nanoparticles. With increase in synthesis temperature to 90˚C this maximum of imaginary $Z''$ shifts to low frequencies (Barsoukov and Macdonald 2005). Shifting of $Z''_{\text{max}}$ and changes in peak broadening indicate that the relaxation phenomena is strongly dependent on changes in synthesis temperature as can be seen in Table 2.
Fig. 5. (a) Real impedance and (b) Imaginary impedance for BFO nanoparticles.

Table 2. Relaxation frequency and time for BFO nanoparticles determined using impedance plots in Fig. 5.

<table>
<thead>
<tr>
<th>Synthesis temperature (°C)</th>
<th>Relaxation frequency ($f_{\text{max}}$) kHz</th>
<th>Relaxation time ($\tau_{\text{max}}$) µsec</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>6.309573</td>
<td>25.22438</td>
</tr>
<tr>
<td>90</td>
<td>3.981072</td>
<td>39.97795</td>
</tr>
<tr>
<td>100</td>
<td>63.09573</td>
<td>2.522438</td>
</tr>
<tr>
<td>110</td>
<td>31.62278</td>
<td>5.032925</td>
</tr>
</tbody>
</table>

REFERENCES


Yan, F., Han, K., Zhao, G., Shi, X., Song, N. and Jiao, Z. (2017), “Growth and magnetoelectric properties of (001)-oriented La$_{0.67}$Sr$_{0.33}$MnO$_3$/PbZrTi$_{0.48}$O$_3$ heterostructure films”, Mater. Charac., 124, 90–96.