Chapter-4

Size effect on the magnetic properties of oleic acid stabilized substrate free BiFeO₃ nanocrystals

4. 1. Introduction

Due to the difficulty in fabricating phase pure BFO, the information available relating to the size dependent physical properties BFO nanocrystals are scarce to date. Though the size dependent magnetic properties of BFO nanocrystals have been investigated by park et al. [139] and other groups [166, 206], the observed magnetization is very less (1.55 emu/g) even for BFO nanocrystals of size ~ 14 nm, which possibly limits its applications in various electromagnetic devices. In this chapter, our main focus is to investigate the size dependent magnetic properties of our as synthesized phase pure BFO nanocrystals of different size and also to present detail structural characterization for clear understanding of structure-property correlations of this technically advanced material. Here we used different oleic acid concentration (0, 0.2, 0.4 and 0.6 ml) required in each case to obtain BFO nanocrystals of size ranging from ~ 10 nm to 100 nm. Observation of highly enhanced magnetic behaviour (0.27 emu/g to 8.17 emu/g) of such BFO nanocrystals makes our study prominent towards the development of advanced applications in electromagnetic devices.

4. 2. Experimental section

Synthesis of BFO nanocrystals of different size
The powder samples of BFO at different oleic acid concentrations such as 0 ml, 0.2 ml, 0.4 ml and 0.6 ml, so that to get different size distributions were prepared by chemical solution evaporation method in laboratory conditions. Same amounts of (1 m.mol) Bi(NO$_3$)$_3$.5H$_2$O and Fe(NO$_3$)$_3$.9H$_2$O were dissolved in 20% HNO$_3$ (30 ml) and stirred for 10 minutes to form transparent solution. After stirring for 10 minutes, oxalic acid (1:2 molar ratio with respect to the metal nitrates) was added to the above solution. Oleic acid was then added in a different concentration required each time as a capping agent. The solution was heated on a hot plate at 130°C under continuous vigorous stirring until all the liquid evaporated from the solution giving fluffy dark brown powder. This powder was dried on a hot plate at 130°C for 30 minutes and annealed at 420°C for 4 hours.

**Structural and magnetic measurements**

The crystallinity and phase purity are identified by powder x–ray diffraction (XRD) using PANalyticalX’Pert PRO X–ray diffractometer equipped with CuK$_\alpha$ radiation ($\lambda=0.154$ nm), over the scan range of 20–$70^\circ$ and scan speed of 5 degree/minute. The size and morphology are examined by field emission scanning electron microscope (FESEM, Quanta FEG 250) as well as transmission electron microscope (TEM, Technei G2 TF20ST) and selected area electron diffraction pattern (SAED) is taken simultaneously. Magnetic measurements are carried at room temperature by using vibrating sample magnetometer, VSM (LakeShore 7407 model).

**4.3. Results and Discussion**

To ascertain the crystal structure, phase purity and morphology of our as synthesized BFO nanocrystals, measurements were performed by using powder x-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM) as well. In Figure 4.1(a), we have shown the
larger area image of BFO nanocrystals demonstrating the distinct growth and the formation of well separated spherical shape like nanocrystals with size (d) ranging from \( \sim 10 \) nm to 100 nm. To further investigate the microstructure, we used HRTEM and SAED measurements on as synthesized BFO nanocrystals. In Figure 4.1(b), we have shown the high resolution TEM image where we can observe well pronounced lattice fringes with interplanar distance 0.279 ± 0.02 nm corresponding to (110) diffraction plane, indicating very good level of crystallinity. The selected area diffraction patterns (SAED) in Figure 4.1(d), shows a dot pattern that clearly exhibits the highly crystalline nature of BFO nanocrystals. XRD patterns of BFO nanocrystals shown in Figure 4.1(c). The prominent peaks in the plot are indexed to various (hkl) planes of \( \text{BiFeO}_3 \) belonging to the hexagonal crystal structure with space group \( \text{R}_{3\text{c}} \) (JCPDS card no: 86-1518).

**Figure 4.1:** Structural characterization of \( \text{BiFeO}_3 \) nanocrystals, (a) larger area FESEM image of BFO nanocrystals capped with oleic acid, showing well separated spherical shape like crystals, (b) high resolution TEM image shows interplanar lattice spacing of BFO nanocrystals, (c) XRD patterns of as synthesized BFO nanocrystals, (d) selected area diffraction patterns obtained for BFO nanocrystals.
To further confirm the phase purity of our BFO nanocrystals, we have taken XRD patterns of all the samples and shown in Figure 4.2, which is clearly demonstrating the phase purity of the samples without existing even small portion of impurity phases. As shown in Figure 4.3, sizeable reduction in the lattice parameter c has been observed while reducing the crystal size. This clearly indicates significant structural distortions in the lattice with increasing the oleic acid concentration. The oleic acid would attach to the surface of BFO nuclei to lower surface energy, which might noticeably decrease the growing speed of BFO nuclei and limit the size of BFO crystals.

![XRD patterns of BFO nanocrystals](image)

**Figure 4.2:** XRD patterns of BFO nanocrystals with different sizes (a) $d \sim 98$ nm (b) $d \sim 40$ nm (c) $d \sim 28$ nm and (d) $d \sim 12$ nm respectively, showing the phase purity of all the samples.
Figure 4.3: Variation in the lattice parameter \( c \) calculated from XRD data, as a function of particle size. Slight increase has been observed in lattice parameter \( a \), with reducing the particle size.

Apart from investigating the crystal structure and microstructural characterizations, to further realise the crystal size and distribution with different oleic acid concentration, we have taken FESEM images of our as prepared BFO nanocrystals. As shown in Figure 4.4(a-d), the sizes of our as prepared BFO nanocrystals with oleic acid concentrations 0 ml, 0.2 ml, 0.4 ml, 0.6 ml were noted to be ~98 nm, 40 nm, 28 nm and 12 nm respectively. The nanocrystal size distribution histograms as displayed in Figure 4.5(a-d) also confirm the average size of BFO nanocrystals. This remarkable effect of oleic acid as a stabilizing agent in obtaining various size BFO nanocrystals allows us to study its size dependent multiferroic properties.
Figure 4.4: FESEM images of BFO nanocrystals capped with, a) 0.6 ml oleic acid (d ~ 12 nm), b) 0.4 ml oleic acid (d ~ 28 nm), c) 0.2 ml oleic acid (d ~ 40 nm), d) 0 ml oleic acid (d ~ 98 nm), indicating the distinct growth of BFO nanocrystals with different oleic acid concentration.

Figure 4.5: Size distribution histograms of BFO nanocrystals of different size a) d ~ 12 nm b) d ~ 28 nm c) d ~ 40 nm and d) d ~ 98 nm.
We have shown earlier from optical absorption measurements, that our BFO nanocrystals exhibit a strong quantum confinement effect with a band gap $\sim 4.2$ eV [207]. The band gap is largely blue shifted from its bulk value $\sim 2.8$ eV at 300 K [197]. The degree of quantum confinement as revealed by the optical data is quite high compared to any previous reports so far [159]. The optical absorption data are therefore quite convincing to the strong quantum size effect in BFO nanocrystals. The effect of size confinement is further revealed by the observation of strong magnetization as discussed below.

**Magnetic Properties**

In Figure 4.6, we present the magnetic measurements of our BFO nanocrystals of different size to understand the magnetic behaviour as a function of particle size by using vibrating sample magnetometer (VSM). As shown in Figure 4.6(a), the data clearly illustrate the distinct spontaneous magnetization ($M_s$) as a function of particle size. Figure 4.6(b) is the zoomed view of the M-H hysteresis loops presented for clarity. In the absence of oleic acid, due to the wide distributions in size and shape of BFO nanocrystals, linear M-H hysteresis loop has been observed with very small coercive field $\sim 156$ Oe. We observe the spontaneous magnetization values $\sim 0.27$, $3.98$, $6.11$ and $8.17$ emu/g and coercive field ($H_c$) values $\sim 156$ Oe, $355$ Oe, $420$ Oe and $460$ Oe for BFO nanocrystals with sizes $\sim 98$ nm, $40$ nm, $28$ nm and $12$ nm respectively. The data shows that both magnetic moments as well as coercive field sharply increase with decreasing the crystal size as shown in Figure 4.6(c-d). The main sources of $H_c$ for magnetic materials are shape anisotropy and magnetoelastic anisotropy in addition to the magnetocrystalline anisotropy [208]. In our study, the crystallites are spherical in nature thus the contribution of shape anisotropy in $H_c$ can be neglected. Thus the observed $H_c$ in our BFO nanocrystals might be due to the magnetocrystalline anisotropy in addition to
the magnetoelastic anisotropy. The observation of such high coercivity in nanoscale region may help in finding the way for improving magnetization in BiFeO$_3$, in turn will lead to many applications.

**Figure 4.6:** (a) M-H hysteresis loops of our as synthesized BFO nanocrystals at 300 K with indicated sizes (crystal size is denoted by d). (b) Zoomed view of hysteresis loops shown in image (a) for clarity. (c) Magnetization ($M_s$) behaviour of BFO nanocrystals as a function of particle size. (d) Variation in the coercive field ($H_c$) with change in the particle size.

The observation of highly enhancement in the magnetic behaviour of our BFO nanocrystals is not ascribed to any impurity (like iron oxide (Fe$_2$O$_3$)) related issues as revealed by the phase purity of our as synthesized BFO nanocrystals. Observation of finite coercivity at low temperature, pointing out that design of particle size and shape may induce ferromagnetism in nanoscale BiFeO$_3$ [209]. Large amount of suitable
uncompensated spins at the surface in such small crystallites along with the suppression of intrinsic spiral spin structure below the critical nanoparticle size are primarily responsible for the observed high magnetic moments even at 300 K [139]. The Dzyaloshinskii–Moriya interaction which is believed to be responsible for spin-canting (away from perfect antiferromagnetic ordering) may instigate modification of the structural relaxation of the magnetically coupled cations and anions (Fe–O–Fe) [108] such a change in behavior of magnetic relaxation and exchange interactions are found to be observed in magnetic nanostructures [202, 210]. Therefore from our data, it is evident that the favourable magnetic properties of BFO nanocrystals with typical dimensions below 62 nm strongly correlate with the size of nanostructures themselves due to the particle size confinement, an effect which has been found to modify the long range spiral-modulated spin structures of BiFeO₃[211].

4. 4. Conclusion

In summary, we have prepared highly phase pure BFO nanocrystals of different size, ranging from ~ 10 nm to 100 nm and reported their size dependent magnetic properties along with the detailed structural characterizations. We find ever highest saturation magnetization ~8.17 emu/g for 12 nm particle along with finite coercive field 460 Oe at room temperature. This enhancement in the magnetic response (0.27 emu/g to 8.17 emu/g) of our BFO nanocrystals with reducing the crystal size is primarily due to the strong quantum confinement effect along with the structural distortion in the lattice, but not due to the any impurity phases. The observed enhancement in the coercive field while reducing the crystal size may be ascribed to magnetocrystalline anisotropy in addition to the magnetoelastic anisotropy. The observation of such high coercivity in nanoscale region may help in finding the way for improving magnetization in BiFeO₃, in turn, will lead to many applications.