Experimental investigation on multiferroic properties of Ti-doped BiFeO$_3$ bulk and nanoparticles

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Abstract. Bismuth ferrite (BiFeO$_3$), an inorganic chemical compound, has added a new dimension to the multiferroic materials research. We previously reported the synthesis routes and improved photocatalytic properties of 10\% Ti-doped BiFeO$_3$ (BiFe$_{0.9}$Ti$_{0.1}$O$_3$). In this study, we investigated the ferroelectric and ferromagnetism properties of BiFe$_{0.9}$Ti$_{0.1}$O$_3$ bulk and nanoparticles and compared them with those of undoped BiFeO$_3$ bulk ceramics. Elemental analysis was conducted to explore the chemical composition in the doped samples. The magnetic characterization and electrical measurements were performed in Vibrating Sample Magnetometer and Ferroelectric Loop Tracer respectively. Magnetization versus applied magnetic field, leakage current density, and polarization versus electric field measurements reveal improved multiferroic properties in Ti-doped bulk and nano samples compared to undoped BiFeO$_3$ bulk.

1. Introduction

The co-existence of (anti)ferroelectricity and (anti)ferromagnetism in the same phase of multiferroic materials has been of significant interest to researchers in the past few years [1,2]. Ferro-orders in multiferroics allow them to be electrically polarized by applying an external magnetic field and vice versa [3]. Thus, multiferroic materials may provide a wide range of opportunities for their potential applications in data storage, spintronics, and sensors [4]. Bismuth ferrite having the rhombohedrally distorted perovskite ABO$_3$ (A = Bi, B = Fe) structure is one of the most investigated and promising multiferroic materials. It possesses a ferroelectric Curie point ($T_C$) of 1103K and Néel temperature ($T_N$) of 653K approximately and thus exhibits multifunctional behavior at room temperature (RT) [5]. However, the application of BiFeO$_3$ (BFO) in the multifunctional context is being limited ascribed to the presence of impurity phases, free moving charges, and oxygen vacancy defects in the bulk ceramics [6,7].

Remarkable attempts, including synthesis method modification, foreign element doping, and solid solution formation with other perovskites have been undertaken to date aimed at eliminating the existing defects in BFO, thereby stabilizing the perovskite structure [8-10]. The selection of Ti as a dopant to
enhance the multiferroic features of the BFO ceramics has received special consideration owing to a closely similar ionic radius as that of Fe ion, partially filled 3d orbitals, and some other intriguing properties [11]. The behavior of Ti-doped BiFeO$_3$ (BFTO) materials largely depends on the synthesis parameters, which may lead to inconsistent outcomes among different researches conducted at variable process conditions [12]. In general, Ti doping results in improved magnetization along with reduced leakage current in BFO while literature exists revealing the opposite phenomena attributed to the structural defects originating from Ti$^{4+}$ substitution, thereby leaves a scope to contribute further in this arena [13,14]. Though BFO microstructures and thin films have received extensive attention, very few studies have been conducted to investigate the multiferroic properties of BFTO nanoparticles.

The synthesis process of Ti-doped BFO bulk and nano counterparts involving solid-state reaction technique and sol-gel method, respectively, were reported in our previous investigations [15,16]. Ti exhibits the characteristics of a potential dopant by reducing impurity phases, oxygen vacancies, and particle size and enhancing photocatalytic properties of BFO [15,16]. In this paper, efforts are aimed to investigate the magnetic and electrical behavior of BFO bulk, BFTO bulk, and BFTO nanoparticles at RT. Elemental analysis was performed to confirm Ti doping in BFTO bulk and nano counterparts. Magnetization versus applied magnetic field measurements were conducted to explore the magnetic properties while leakage current density and polarization versus electric field measurements were carried out for electrical characterization of the synthesized materials.

2. Experimental Details

The synthesis of BiFeO$_3$ (BFO) as well as Ti-doped BiFe$_{0.9}$Ti$_{0.1}$O$_3$ (BFTO) bulk polycrystalline powder was accomplished by conventional solid-state reaction technique [17]. The bottom-up synthesis process involved calcination of compact oxide mixture at 750°C succeeded by pressing the calcined powders into pellets and sintering at 850°C for five hours [15]. To prepare the BFTO nanoparticles, sol-gel method, a wet chemical technique was followed [18]. The individual solutions of Bi(NO$_3$)$_3$.5H$_2$O, Fe(NO$_3$)$_3$.9H$_2$O, and Ti Butoxide dissolved in 2-methoxy ethanol were mixed and stirred at 100-110°C for eight hours accompanied by drying and calcination at 650°C for one hour to get the desired nanoparticles [16]. The chemical compositions of BFTO bulk and nanoparticles were investigated in Energy Dispersive X-Ray Spectroscopy (EDS). The magnetization versus applied magnetic field ($M$-$H$) hysteresis loops of the synthesized materials were measured in Vibrating Sample Magnetometer (VSM). The ferroelectric measurements of the considered samples were conducted in Ferroelectric Loop Tracer (PE Loop Tracer).

3. Results and Discussion

3.1. Elemental analysis

EDS (Energy-dispersive X-ray spectroscopy) analysis was performed at three different positions of each BFTO bulk and nano samples to confirm successful Ti doping. The EDS spectra reveal that O, Ti, Fe, and Bi elements are homogeneously present throughout the prepared BFTO bulk and nano-materials, as shown in Figure 1. The absence of any foreign elements is also evident from total mass% (100%), as presented in Table 1. Calcination in the air at high temperature removed almost all other foreign components and eventually resulted in pure BFTO samples.
Figure 1. EDS images of the BiFe$_{0.9}$Ti$_{0.1}$O$_3$, (a) bulk material synthesized by solid-state reaction technique, (b) nanoparticles synthesized by sol-gel method

Table 1. Elemental mass percentage of BiFe$_{0.9}$Ti$_{0.1}$O$_3$ bulk and nanoparticle samples

| Samples                          | Elements | Mass% |
|----------------------------------|----------|-------|
| BFTO bulk prepared by solid-state reaction technique | O        | 2.44  |
|                                  | Ti       | 1.97  |
|                                  | Fe       | 16.83 |
|                                  | Bi       | 78.75 |
| **Total**                        |          | **100**|
| BFTO nanoparticles prepared by sol-gel method | O        | 2.58  |
|                                  | Ti       | 3.94  |
|                                  | Fe       | 19.66 |
|                                  | Bi       | 73.82 |
| **Total**                        |          | **100**|

3.2. Magnetic characterization

The field directed magnetic measurements were conducted to explore the magnetic behavior of undoped BiFeO$_3$, BiFe$_{0.9}$Ti$_{0.1}$O$_3$ ceramics, and BiFe$_{0.9}$Ti$_{0.1}$O$_3$ nanoparticles. Figure 2 presents the $M$-$H$ hysteresis loops of the synthesized samples investigated at room temperature (RT) with an applied magnetic field of up to ±10 kOe. The antiferromagnetic nature of undoped BFO is well demonstrated by the linear hysteresis loop having coercive field ($H_c$) and remanent magnetization ($M_r$) close to zero [19]. In contrast, 10% Ti-doped bulk and nanoparticle samples exhibited improved ferromagnetism with increased $H_c$ and $M_r$ values. The coercive field and remanent magnetization obtained in BFTO bulk were 58.97 Oe and 0.3041 emu/g, respectively, while those recorded in BFTO nanoparticles are 93.219 Oe and 0.0254 emu/g, respectively. Ti doping resulted in the demolition of spin cycloid structure within BFO associated with the release of latent magnetization inherently present inside the cycloid structure and eventually contributed to enhanced ferromagnetism in BFTO [20]. The $H_c$ and $M_r$ are calculated from the hysteresis loops adopting the following equations [21]

$$H_c = \frac{H_{c1} - H_{c2}}{2}$$  \hspace{1cm} (1)

where $H_{c1}$ and $H_{c2}$ represent the left and right coercive fields respectively

$$M_r = \frac{|M_{r1} - M_{r2}|}{2}$$  \hspace{1cm} (2)
Figure 2. M-H hysteresis loops of BFO bulk, BFTO bulk, and BFTO nanoparticles. The inset shows a magnified view of BFTO bulk.

where \( M_1 \) and \( M_2 \) denote the magnetization with positive and negative points of intersection respectively at \( H = 0 \).

The sol-gel method yielded nanoparticles in the nanometer range, while the sizes of the bulk ceramics prepared by the solid-state technique fell in the micrometer range as reported in our previous investigations [15,16]. The considerable size reduction may impart higher coercivity in BFTO nanoparticles than its bulk sample due to effective spin contribution to the magnetic moment of the particle at an increased surface-to-volume ratio [22,23]. On the other hand, higher remanent magnetization is evident in BFTO bulk compared to the nano counterpart. The low microstrain and leakage current (discussed in the later section) in BFTO bulk may play the preeminent role in augmented remanent magnetization [24]. Substantially higher maximum magnetization (\( M_r \)) was observed as well in BFTO bulk (3.599 emu/g) compared to its nano sample (0.3564 emu/g).

3.3. Electrical Measurements

To investigate leaky behavior in bulk polycrystalline and nanoparticle samples, leakage current density (\( I_d \)) versus electric field (\( E \)) measurements were performed, as shown in Figure 3. It is perceived from Figure 3 that Ti doping suppressed leakage current density in both bulk and nano counterparts. The higher leakage current in undoped BFO bulk was dominated by impurity phases and oxygen vacancies [25]. X-ray diffraction (XRD) results reported earlier revealed that those impurity peaks were prominent in undoped BFO samples [15]. In contrast, the elimination of impurity phases, to a considerable extent, was noticed in the Ti-doped bulk and nano samples [15,16]. Ti being a less volatile element, may hinder the volatile nature of Bi along with the formation of secondary phases. Though BFTO bulk and nano counterparts exhibit close \( I_d \) values, slightly better results are observed in bulk ceramics, presumably due to the presence of lower oxygen vacancies.

The polarization versus electric field (\( P-E \)) hysteresis loops of the considered samples generated at \( \pm 5 \) kV electric field and 50 Hz driving frequency are illustrated in Figure 4. The undoped BFO bulk ceramics produced a round-shaped hysteresis loop ascribed to freely movable charge and oxygen.
Figure 3. Leakage current density of undoped BFO bulk, BFTO bulk, and BFTO nanoparticles

Figure 4. P-E hysteresis loops of BFO bulk, BFTO bulk, and BFTO nanoparticles. The black, red, and blue Y-axes correspond to BFO bulk, BFTO bulk, and BFTO nanoparticles respectively.

vacancy defects [18]. The minor difference in leakage current densities of BFTO bulk and nano counterpart gave rise to a significant deviation in their hysteresis loops. The remanent polarization observed in BFTO bulk and nano counterpart were 0.005 μC/cm² and 0.373 μC/cm² respectively.

To explore further the ferroelectric polarization behavior in BFTO bulk and nano-materials P-E hysteresis loops measurements were conducted at variable electric fields and a constant driving frequency of 50 Hz. The obtained results depicted a gradual increase in remanent polarization with the electric field because the electric field of high magnitude imparts increased driving power to reverse the ferroelectric domains [26]. Ideal hysteresis loops are achieved in BFTO bulk owing to suppressed leakage current density, whereas the loops of BFTO nanoparticles are slightly distorted on account of
leaky behavior and space charge defect. Moreover, the agglomeration of particles during the Sol-gel synthesis process may cause deterioration of ferroelectric properties in nanoparticles [27].

4. Conclusion

Multiferroic properties of 10% Ti-doped BiFeO₃ bulk and nanoparticles synthesized by solid-state reaction technique and sol-gel method respectively have been reported. EDS analysis has confirmed the successful inclusion of the Ti dopant and the absence of any foreign elements in BiFe₀.₉Ti₀.₁O₃ samples. The M-H measurements reveal enhanced ferromagnetism in BFTO ceramics having increased coercive field, remanent magnetization, and maximum magnetization compared to undoped BFO bulk. Leaky behavior and rounder shape P-E hysteresis loops of BFO bulk have been ameliorated to a considerable extent in BFTO bulk and nano counterparts. Ti doping has resulted in the release of latent magnetization, reduced impurity phases as well as oxygen vacancy defects and thus yielded superior multiferroic materials. However, BFTO bulk ceramics exhibit improved magnetic and electrical properties compared to nano counterparts because of lower crystal microstrain and space charge defects. Hence, further research in the synthesis process of BFTO nanoparticles is being recommended to eliminate the existing defects, thereby enhancing the multiferroic aspects.

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