

Theoretical and Experimental Evidence of Modified Structure, Magnetism and Optical Properties in Ba and Mn Co-Substituted BiFeO₃

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Abstract. To improve the vacancy related defects associated with pure BiFeO₃ (BFO) different Ba-Mn co-doped samples (Bi_{1-x}Ba_xFe_yMn_yO₃; x=0.1; y=0.0, 0.05, 0.1, 0.15) were prepared from sol-gel method. The influence of co-doping on structural, magnetic and optical properties of BiFeO₃ has been studied in different experimental conditions. Particle size and magnetic properties were measured from SEM and VSM analysis respectively. Again band gap was calculated from UV analysis. The co-doped samples showed reduced particles size as well as better surface morphology. M-H loops suggest that the presence of Mn²⁺ increased ferromagnetic quantity at some levels. Still room temperature occurrence of ferromagnetism obtained from M-H loops of all samples showed weak ferromagnetic behaviour. In addition the incorporation of Ba²⁺ at Bi³⁺ site and Mn²⁺ at Fe³⁺ site decreased the band gap which was evidenced by increased optical property.

Keywords: Multiferroics, BFO, Ferromagnetism, Band gap, Surface morphology

1. Introduction

Multiferroic materials are those which can exhibit more than one ferroic order simultaneously such as ferroelectricity, ferromagnetism and ferroelasticity. It is possible to control the degree of magnetism using electric field and vice versa. It is only possible due to their magnetoelectric coupling. In recent years these materials have achieved a great deal of attention due to their multidimensional applications such as data storage media, spintronics and multistate memories. Bismuth ferrite (BFO) is one of the most promising multiferroic materials that can exist in room temperature. It shows ferroelectric ordering below curie temperature (1103K) and space-disproportionate antiferromagnetic property below the neel temperature(643K) [1]. It also offers a coupling interaction between polarization and magnetization called magnetoelectric coupling. However BiFeO₃ shows weak ferromagnetic property at room temperature because of the combined action between exchanges and spin orbit interactions. For this reason a vanishing magnetization is obtained in BFO by spin canting away from perfect antiferromagnetic ordering and spiral spin arrangement. From the last decade's vigorous research documents, it can be inferred that, the properties of BFO can be tailored towards an ideal multiferroic material through suitable doping. Co-doping can be an effective way to tailor the multiferroic properties



of BFO [2]. In this research BFO is synthesized using modified sol-gel method technique and the influence of co-doping (Ba-Mn) on structural, ferroelectric, ferromagnetic and optical properties of BiFeO₃ have been studied in different experimental condition [3]. Recently a large number of investigations have already been conducted on BiFeO₃ co-doped with various element combinations in which Ba-Mn co-doping shows very promising result. In this paper, some surprising findings are revealed for Ba-Mn co-doped BFO.

2. Experimental

2.1. Materials and Method

Co-doped Bi_{1-x}Ba_xFe_{1-y}Mn_yO₃ [x=0.1; y=0, 0.5, 0.10, 0.15] samples were prepared by modified sol-gel method. Weighed amount of Bi(NO₃)₃·5H₂O (Merck®, India), Fe₂(NO₃)₂·9H₂O (Merck®, India), Ba(NO₃)₂·6H₂O (Merck®, India), Mn(NO₃)₂·4H₂O (Sigma Aldrich, USA) were dissolved in 250ml deionized water under continuous stirring at 70°-75°C. The reaction media was made acidic by using citric acid. In the next step 5ml Ethylene glycol was added as chelating agent. After turning the solution blackish-red ethylene glycol was again added as polymerization agent and stirring kept continuous until the formation of dried gel. The temperature of the dried gel was further slightly increased only to be ignited at any point of time. After ignition, the dried gel began to burn at a self-propagating combustion reaction with vigorous flames until the gel was completely burnt out to form ash like flakes. Then these flakes were dried out at 120°C for 24hr. After that these flakes were neatly collected and collapsed by using spatula or glass rod to obtain the fluffy fine loose powder of BBFO or BBFMO nanoparticles. After that samples were calcined at 600°C for 2hrs and annealed at 500°C with a heating and cooling rate 3°C/min to remove any impurity and improved crystallization.

2.2. Characterization

To observe the morphology of the synthesized powder, field emission scanning electron microscope, FESEM (JEOL JSM 7600F) was used. Powder samples were adhered with carbon tape that was attached to a Copper Stub. Samples were made conductive, coated with platinum by ion sputtering method. Then sample holder was mounted on a holder and inserted in FESEM. The micrographs obtained from FESEM analysis were used for microstructural study. Energy dispersive X-ray spectroscopy (EDS) and SEM were simultaneously allowed for targeted analysis of sample surfaces. X-ray diffraction analysis was conducted using the XRD (3040-X'Pert PRO, Philips) facility in order to determine the phases present in the synthesized powders. The high intensity Cu K- α radiation was focused on the sample in the scanning from 10° to 90° [4]. The magnetization response of the samples with changing magnetic field i.e. the M-H loop was determined using a vibrating sample magnetometer (VSM: Model EV-9, Microsense LLC, USA). A small piece of the sample (15-20mg) was broken off and put in the instrument after weighing. VSM was used to determine the magnetic property of the synthesized powders up to applied field of 21 kOe. The band gap refers to the energy difference between the top of the valance band to the conduction band [5]. Band gap was determined from UV-Vis absorption value where energy and wavelength were calculated.

3. Results and discussion

3.1. XRD Analysis

Figure 1 showed the XRD patterns of 10 mol% Ba and 0, 5, 10, 15 mol% Mn Co-doped BFO samples. All the prominent peaks in the XRD patterns confirmed single phase formation in all the Mn doped BBFO nanoparticles without any trace of impurity phase. From the XRD peaks it was observed that, co substitution of both A and B site atom didn't change the parent structure of the BFO samples. Some peaks near 25°-30° represented γ - Bi₂O₃ phase in 0 mol% Mn doped sample while the others were in good agreement with the BFO reference profile. It was very difficult to obtain pure BFO nanoparticles.

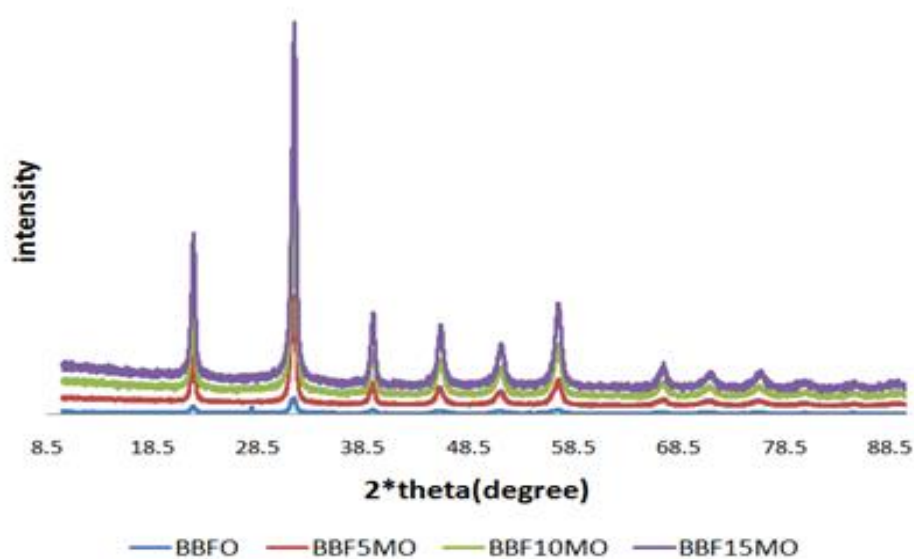


Figure 1 XRD pattern of Ba and Mn doped BFO

due to kinetics of formation. However, it could be seen from Figure 1 that the highest peaks of [104] and [110] at around 30° appeared overlapped, which was a common phenomenon in BFO nanoparticles. The A-site substitution by barium ion (Ba^{2+}) has been attempted by many authors in recent years to enhance the multiferroic properties of $BiFeO_3$. Ba^{2+} having a large ionic radius than Bi^{3+} distorted the original structure of $BiFeO_3$ and changes its cycloidal spin structure to a canted spin structure resulting in net magnetization at room temperature [6]. Moreover, addition of Ba also significantly reduced the oxygen vacancy related defects (leakage current) by occupying evaporated Bi sites and increased the electrical resistivity of BFO by controlling grain size. Further incorporation of Mn in the Fe site in BFO had been marked by a slight decrease in the impurity phase peaks near 27° , 32° or 35° due to reduce chances of bismuth evaporation.[7]

3.2 Microstructural analysis:

Figure 2 showed the FESEM image of BBM-4 samples with EDS analysis sintered at 600°C . It revealed the dense and uniform distribution of particles having grain size near 100nm had been obtained by sol-gel method. EDS analysis proved the successful doping of Ba and Mn from the composition of the product. In the doped sample the amount of Ba and Mn detected by EDS analysis was a little less (table 1) than those actually added during the synthesis of the sample but an approximate idea can be developed from these values. Increase of Mn as well as decrease of Fe content told that co-doping took place for the samples [8].

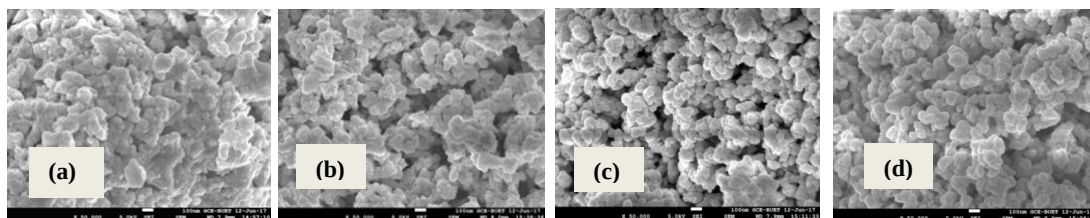


Figure 2: SEM images of (a) 0% (b) 5% (c) 10% and (d) 15% Mn doped BBFO.

The introduction of dopants had a little effect on the morphology of the particles [6, 7]. The particles after sintering became porous due to the decomposition of citric acid, and the diameter shrank to about

100 nm. From the FESEM micrographs of the sintered pellets, it was clear that the average grain size of pure BFO was relatively large; whereas comparatively smaller sizes of grains were observed in the co-doped samples [9]. It had been observed that grain growth was depended on the concentration of oxygen vacancies and diffusion rate of the ions. In pure BFO, evaporation of Bi (highly volatile) generated large amount of vacancies; which made it easy for the ions to diffuse and thus resulted in larger sized grains [10]. Microstructure of the pellets was overall dense; but few scattered pores were observed. The different Ba-Mn content had pronounced effect on average grain size, density and homogeneity of the grains with increasing Ba-Mn content, the grain size of the doped samples had a tendency of decreasing, which was due to the inhibition of grain growth brought by Ba-Mn codoping. From the SEM analysis it is observed that the minimum grain size was observed for Mn content 10% but with the increase of Mn content oxygen vacancies were formed for charge compensation and grain size increased at 15% Mn content [11].

Table 1. EDS observed components quantity

Element	Wt% (0%Mn)	Wt% (5%Mn)	Wt % (10%Mn)	Wt % (15%Mn)
O	4.28	3.10	3.76	4.20
Mn	0	1.89	2.23	3.56
Fe	28.41	17.53	16.28	15.54
Ba	6.55	5.85	4.03	5.07
Bi	60.77	71.63	73.71	71.63

3.3 Magnetic property

The magnetic hysteresis (M-H) loops of Ba and Mn doped BFO nanoparticles measured at room temperature were shown in Figure 3 which indicated soft ferromagnetic behavior of the samples. The magnetization increased with increasing the Mn content in BBFO samples. Remnant magnetization (2Mr) of 0.124, 0.217, 0.259, 1.203 emu/gm were observed for 0, 5, 10, 15% Mn doped BBFO samples respectively. The coercive field (2Hc) and saturation magnetization (Ms) were shown in the table 2. With the increase of Mn content, larger magnetization at room temperature was observed. The origin of spontaneous magnetization was due to crystal structure of BFO sample [12]. With the decrease of particle size, the helical order in the spin can be suppressed. It had been already been theoretically proven that suppression of helical order with a periodicity about 62nm or canted antiferromagnetic order between successive (III) ferromagnetic planes, might have resulted higher magnetization. In this way, with the increase of Mn content, distortion was created in the rhombohedral structure and magnetization was increased [13]. Nevertheless, an enhancement in ferromagnetic properties of BFO with increasing Ba concentration may be expected due to increasing structural distortion. However, the substitution of Ba^{2+} for Bi^{3+} may cause two parallel phenomena with respect to concentration of oxygen vacancies, one was decrease in concentration of oxygen vacancies by filling the probable vacant volatilized Bi^{3+} sites and the second was the creation of oxygen vacancies to neutralize the charge produced by substituting Ba^{2+} for Bi^{3+} [14]. Hence, leakage current of BFO decreased up to an optimum Ba doping and then again increased on further doping. It had been reported that, above 0.2 mole fraction Ba^{2+} addition ($x=0.2$) the leakage current effect became prominent again for this reason Ba^{2+} content remained fixed ($x=0.1$) in this research while percentages of Mn^{2+} content were changed ($y=0, 0.05, 0.1, 0.15$). Generally BFO showed weak ferromagnetic property due to distorted rhombohedral perovskite structure. With the Mn doping, distortion was increased in the BFO lattice which was confirmed by morphology analysis. However addition of Mn^{2+} ion to the BFO required charge compensation which may be achieved by the formation of Fe^{4+} or oxygen vacancies. If Fe^{4+} exists, the statistical distribution of Fe^{3+} and Fe^{4+} ions in octahedral may also lead to the net magnetization and ferromagnetism [15]. The increased magnetization in BBM samples may be attributed to the structural phase transition from rhombohedral to orthorhombic

phase resulting in destruction of spiral spin structure which in turn led to release of latent magnetization. The helical order in nanocrystals can be well suppressed through decreasing the particle size which actually caused higher magnetization. The remnant magnetization increased with the increase in the substitution concentration and reached a maximum at $y=0.05$, which indicated almost all broken spin cycloid structure. The further increase in substitution concentration resulted in the reduction of remnant magnetization due to the appearance of complete antiferromagnetic ordering in the orthorhombic structure because of the significant contribution from the crystallographic phase of Pbnm space group. The substitution and other effects can break the cycloid in BFO, which had been reported to affect the magnetic properties of the ceramics but presence of magnetic impurities (Fe_2O_3 or Fe_3O_4) may be the cause for the same. In our case, the presence of Fe_2O_3 magnetic impurity had not been detected from XRD patterns. Moreover, we had not observed ferromagnetic hysteresis loop for BFO which had largest amount of impurity phase among all ceramics. Also, the area of ferromagnetic hysteresis loop and coercivity increased with the increase in substitution percentage up to 5% and then decreased due to appearance of complete antiferromagnetic ordering in the orthorhombic structure.

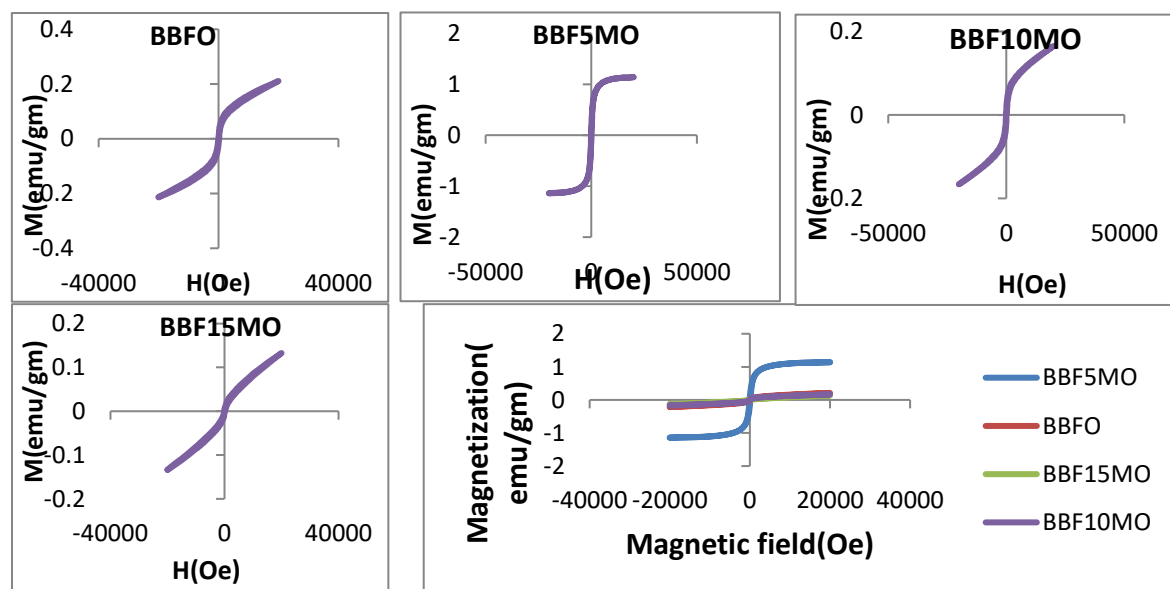


Figure 3: Magnetic property of different amount of Ba and Mn on magnetization of BFO samples.

Table 2 The magnetic parameters for Ba and Mn doped BFO samples

Sample (BBFO)	Coercive field, $2H_c$ (Oe)	Remnant magnetization, $2M_r$ (emu/gm)	Spontaneous magnetization, M_s (emu/gm)
0 mol% Mn	2100	0.08	0.23
5 mol% Mn	2100	0.487	1.203
10 mol% Mn	2100	0.073	0.17
15 mol% Mn	2100	0.02	0.14

3.4 Photo catalytic behavior analysis

We studied the influence of grain and particle size on structural and optical properties of BiFeO_3 nanoparticles and resulting photo catalytic activity. The smaller particle size in most cases would give

rise to a larger surface area and stronger adsorption capacity, which was usually beneficial for photocatalytic activity. Unexpectedly, the photocatalytic activity was found to decrease while the expected surface reactions were decreased by increasing particle size [16]. Optical features, namely the Urbach energy and low energy bands, in the absorption spectra were substantially changed. We argued that these optical modifications related to defects and local distortions were mainly affected at the skin layer that was inherent to oxides like BFO. By reducing the particle size of BFO nanoparticles the skin layer thus altered, which in turns changed the photocatalytic properties. The optical absorption of the Ba and Mn doped BFO nanoparticle was characterized by measuring the UV–Vis diffuse reflectance absorption spectra of samples. Results were presented in samples doped with Ba and Mn have strongly enhanced absorption in visible light, especially 10 % Ba and 10%Mn doped sample, which may be attributed to the induced defects and phase structure changed. But for 15% Mn the effect was gradually decreased due to formation of excessive oxygen vacancy formation that was related to increase the size of BFO nanoparticle size [17].

3.5 Band gap analysis

The UV–vis absorption spectrum of as-synthesized BFO nanoparticles was shown in Figure 4. This was seen from the spectrum that BFO nanoparticles had strong absorption in UV–vis region 300–550 nm and slight absorption in 550–700 nm. This absorption characteristic can be used in the photo-catalytic activity in decomposition of organic compounds. The absorption curve gave an absorption edge at 510 nm. The inset of photocatalytic activity showed $(\alpha h\nu)^2 - h\nu$ plot for the direct band gap calculation. For any semiconductor, optical absorption near band edge obeys following equation,

$$(\alpha h\nu) \propto (h\nu - E_g)^n \dots\dots\dots (1)$$

where α , h , ν and E_g are the optical absorption coefficient, Plank's constant, light frequency and band gap energy, respectively. For the direct band gap, the variable ‘ n ’ in the equation is equal to 1/2. As BFO was a direct band gap semiconductor, the extrapolated line intercept at horizontal axis gave the value of direct energy band gap as 1.665 eV with the increase of Mn content. The band gap value was comparable with the earlier reported values. Also, the band gap of BFO at bulk level was reported to be 2.6 eV, which decreased to 1.665 eV for nanoparticles due to the size effect. To investigate the influence of Ba and Mn doping on the optical absorption of BFO, the UV-vis spectra of pure BBFO and Mn-doped BBFO samples were measured at room temperature, as shown in Figure 4. The absorption band edge of BBFO nanoparticles appeared, indicating that BBFO could respond to visible light for photocatalytic reaction. Compared to pure BFO, the Ba and Mn co-doped BFO samples exhibited enhanced absorption capability especially in the visible light region, and the absorption intensity became gradually stronger as increasing the Mn dopant content.[18] Moreover, the band gap could be calculated from the plot of the Kubelka-Munk function $((\alpha h\nu)^2$ vs photon energy ($h\nu$)) for the direct band gap semiconductor, as presented in the inset of Figure 4. The band gaps were estimated to be 1.725, 1.7, 1.665, 1.69 eV for the pure BBFO, Mn 5%-BFO, Mn 10%-BFO and Mn 15%-BBFO samples, respectively. With the increase of the Mn dopant content, the band gap of doped samples was gradually decreased, in turn leading to a higher absorption capability. Undoubtedly, the enhanced absorption property of Ba and Mn co-doped BFO would probably improve the photocatalytic activity of BFO, as shown in Figure 4.

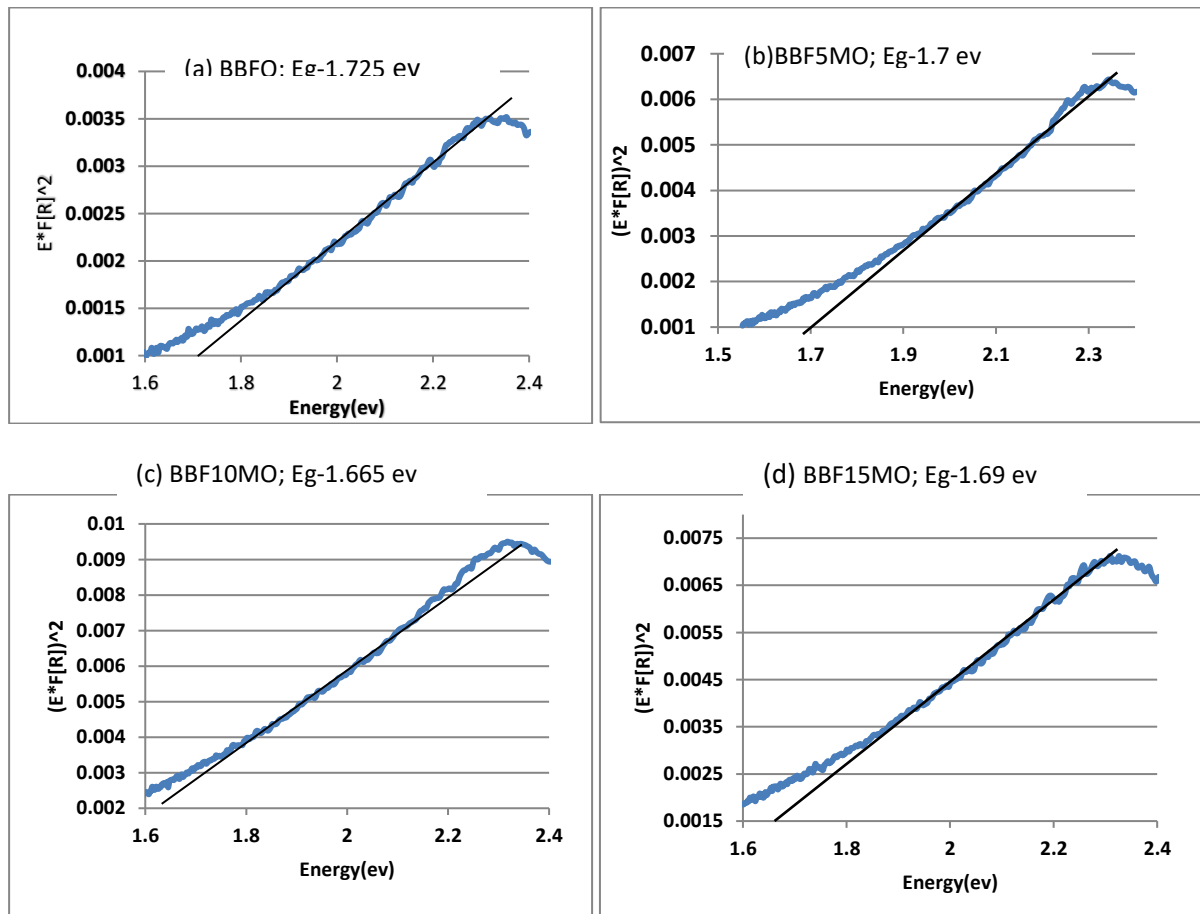


Figure 4: Photo-catalytic response of (a) 0%, (b) 5%, (c) 10% and (d) 15% Mn doped BBFO.

4. Conclusion

Ba-Mn co-doped BiFeO_3 nanoparticles were successfully synthesized by modified sol-gel method. The magnetic property value of pure BFO was greatly increased due to the size effects and (Ba, Mn) ions doping. Satisfying ferromagnetic performance was achieved due to the suppression of helical order at room temperature. The grain size decreased dramatically with increasing doping concentration for $\text{Bi}_{1-x}\text{Ba}_x\text{Fe}_{1-y}\text{Mn}_y\text{O}_3$ up to Mn content 10%. The grain size of the Ba-Mn doped BFO samples are found to be in the range of 100-120 nm. Absorption increased with the increases of Mn content up to 10% but decreased at 15% due to increase of the size of the particle. Band-gap analysis also agreed with the absorption phenomenon and it was minimum for $\text{Bi}_{0.9}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Mn}_{0.10}\text{O}_3$ sample and it increased further for increasing the Mn content due to increase of the grain size.

5. Reference

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