

Article

Effect of Mn Concentration on the Structural, Ferroelectric, Optical, and Magnetic Properties of BiFeO₃ Nanoparticles

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Abstract: In the present work, Bi_{1.05}Fe_{1-x}Mn_xO₃, (x = 0, 0.01, 0.03, 0.05, 0.07, 0.10) NPs were synthesized successfully using the sol-gel technique followed by annealing at 550 °C. The synthesized NPs were investigated for their structural, ferroelectric, optical, and magnetic properties through X-ray diffraction, P-E (polarization vs. electric field) hysteresis loops, UV-vis absorption spectroscopy, Photoluminescence (PL) spectroscopy, and DC-magnetization. The analysis of XRD patterns revealed that the crystallite sizes, lattice parameters, and strain were found to be reduced with an increase in Mn concentration. The ferroelectric properties were studied from the P-E hysteresis loops, which revealed the maximum remnant polarization obtained for Bi_{1.05}Fe_{0.95}Mn_{0.05}O₃ NPs. The UV-vis and PL spectra revealed excellent optical properties indicating a reduction (1.91–1.36 eV) in the bandgap with an increase in Mn concentration. The magnetic properties were investigated through the magnetic field (H) dependent magnetization (M) hysteresis loops. The saturation magnetization was found to be maximum (~1.4 emu/g) for Bi_{1.05}Fe_{0.90}Mn_{0.10}O₃ NPs. The MH hysteresis loops narrow down near H = 0 forming a wasp waist shape that is maximum for Bi_{1.05}Fe_{0.90}Mn_{0.10}O₃ NPs and may be associated with the presence of the canted spins.

Keywords: multiferroics; XRD; P-E hysteresis loop; M-H hysteresis; UV-vis spectra



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1. Introduction

Bismuth ferrite, BiFeO₃ (BFO) is one of the most preferred multiferroic materials to investigate magnetoelectric (ME) coupling, which is utilized for the fabrication of next-generation devices such as memories, solar cells, sensors, spintronics based devices, etc. [1,2]. The preference given to BFO over other multiferroics is due to its high Curie (T_C = 1100 K) and Néel (T_N = 640 K) temperatures as well as a small bandgap range (2.2–2.8 eV) [3,4]. BFO possesses a rhombohedrally distorted structure (space group: R3c) of the type ABO₃ that exhibit the spin interactions between neighboring Fe³⁺ ions at the A-site in FeO₆ octahedra, producing antisymmetric exchange interactions (Dzyaloshinskii–Moriya interaction) and assigning it with a ferromagnetic character [5–7]. At the same time, the lone pairs of Bi 6s hybridize with O2p to create the dipolar moments at the B-site that give rise to the ferroelectric character. The resulting electric polarization in BFO has been observed as high as ~100 μC/cm² as per the literature [1]. Consequently, the significant amount of electrical polarization couples efficiently with the ferromagnetic spin interactions

giving rise to a magnetoelectric coupling, which is highly desirable in multiferroics for advanced applications [1]. The large electric polarization modulates the G-type antiferromagnetic arrangement in BFO that was earlier stabilized by the $\text{Fe}^{3+}\text{--O--Fe}^{3+}$ exchange interactions. If this modulation is cycloidal, then there is no magnetoelectric effect, however, if the interaction of electric polarization with antiferromagnetic arrangement causes canted spins resulting in non-cycloidal modulation, i.e., cone-type or spiral, then the ME effect can be observed. In this way, the magnetoelectric coupling can be well utilized to mutually control the existing multiferroic orders (ferromagnetism and ferroelectricity) [8]. However, BFO also exhibits some inherent drawbacks such as a small saturation magnetization caused by the non-cycloidal spin ordering, a poor ferroelectric display due to the low resistivity of BFO, a high leakage current, and secondary phases. The formation of secondary phases creating oxygen non-stoichiometry, and the presence of mixed oxidation states of Fe ($\text{Fe}^{2+}/\text{Fe}^{3+}$) are responsible for the low resistivity that hamper the ferroelectric properties and causes large leakage current.

Fortunately, these drawbacks can be overcome by controlling the ionic concentration at A-site and B-site. It is reported that the doping of transition metal (TM) ions at the B site in BFO can tailor the ferromagnetic, as well as the ferroelectric properties [9–12]. For instance, Cr doped BFO, investigated by Sinha et al. with various Cr-concentrations, has exhibited enhanced ferroelectric and ferromagnetic properties with substantially reduced leakage current [13]. Similarly, Khomchenko et al., have substituted Ca and Mn on the A-site and B-site of BFO, respectively, and found that the oxygen vacancies were filled, and magnetization was enhanced [8]. In conjunction with that, through the substitution of TM ions in place of Fe^{3+} ions, the cycloidal modulation was also suppressed by changing the contributing magnetic anisotropy without even influencing the $\text{Fe}^{3+}\text{--O--Fe}^{3+}$ exchange interactions, leading to the enhancement in the multiferroic orders [8]. Amongst the TM ions, Mn being the most soluble in BFO at ambient pressure, can be mixed in trivalent/tetravalent states in BFO giving rise to strong ferromagnetic interactions via $\text{Mn}^{3+}\text{--O--Mn}^{4+}$ interactions [8,14,15]. As an example, Yang et al. have reported that the Néel temperature was reduced to 420 K in Mn-doped BFO indicating amplified magnetoelectric coupling [16]. Therefore, in the present work, we have synthesized Mn-doped BFO by employing the sol-gel technique. Bi is taken with 5% excess in order to consider the volatile nature of the Bi in BFO [17]. The synthesized NPs were investigated for structural, electrical, optical, and magnetic properties through various characterization techniques.

2. Experimental Details

2.1. Materials

Bismuth nitrate pentahydrate [$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$]; iron nitrate nonahydrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$]; manganese nitrate tetrahydrate [$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$], citric acid ($\text{C}_6\text{H}_8\text{O}_7$), concentrated nitric acid (HNO_3), and ethylene glycol. All precursor salts and reagents were of high purity (>97%) and purchased from Central Drug House (CDH), New Delhi, India.

2.2. Method

$\text{Bi}_{1.05}\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$, ($x = 0, 0.01, 0.03, 0.05, 0.07, 0.10$) NPs were synthesized using sol-gel method. An appropriate amount of citric acid ($\text{C}_6\text{H}_8\text{O}_7$) was dissolved in 50 mL DI water to obtain a molar concentration of 0.1M. The ratio of metal nitrate and citric acid was kept at 1:1. The mixture was stirred at room temperature to make solvent for further reactions. Then, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was added to the solvent followed by an appropriate amount of concentrated HNO_3 to dissolve $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. Once, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved, then manganese nitrate tetrahydrate [$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$] and iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were added as per their pre-decided ratio. These precursor salts were mixed well at room temperature. Finally, ethylene glycol was added to the mixture under vigorous stirring at 90 °C to form a gel and allowed to dry completely. The obtained product was grinded well and calcined at 550 °C for 2 h. The $\text{Bi}_{1.05}\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$, ($x = 0, 1, 3, 5, 7, 10$) NPs are labelled as BFO, BMFO1, BMFO3, BMFO5, BMFO7, and BMFO10.

2.3. Sample Characterizations

The synthesized products were characterized using X-ray diffraction, Field emission scanning electron microscopy (FESEM), PE loop, dielectric spectroscopy, UV–vis absorption spectroscopy, Photoluminescence (PL), and DC-magnetization. Bruker AXS D8 X-ray diffractometer (MPD 3040, EA Almelo, The Netherlands) with Cu K α radiation ($\lambda = 1.54178$ Å; 2θ range: 10 – 90°), at a scanning rate of $0.02^\circ/\text{s}$ was used to study the phase purity of the samples. The FESEM micrographs were obtained by a field emission electron microscope (FESEM, JSM-7500, JEOL, Tokyo, Japan). The ferroelectric properties were measured using P-E loops at MARINE PE—01 PE Loop Tracer System (Marine, New Delhi, India). The optical properties were studied using UV–vis absorption spectroscopy performed using a photo-spectrometer (S-4100) of SINCO Instrument Co. Seoul, Korea. The PL spectra were obtained at Model LAMBDA 35, PerkinElmer (Waltham, MA, USA). The M-H hysteresis loop measurements were carried out using Quantum Design physical properties measurement setup (PPMS-6000, Quantum Design, San Diego, CA, USA).

3. Results and Discussion

3.1. XRD Analysis

The XRD patterns of $\text{Bi}_{1.05}\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$, ($x = 0, 0.01, 0.03, 0.05, 0.07, 0.10$) NPs are displayed in Figure 1a in the 2θ range 20 – 80° . The peak positions and intensities are assigned to the rhombohedral crystal structure with space group R3c corresponding to the JCPDS number 86-1518 except for a small peak with negligible intensity observed at $\sim 28^\circ$. All the samples exhibit the primary phase with space group R3c along with a small impurity peak corresponding to a secondary phase $\text{Bi}_2\text{Fe}_4\text{O}_9$ (Orthorhombic: Pbam) agreeable with JCPDS number 72-1832 [18]. The XRD patterns indicate the successful incorporation of Mn-ions in place of Fe-ions. Figure 1b shows the XRD patterns in a narrow 2θ range (27 – 34°) in which the closely positioned most intense (104) and (110) peaks, as well as the secondary peaks, are distinctly visible. The traces of the Pbam phase along with the R3c phase have also previously been detected as reported in the literature [7,12,19]. Further, the Rietveld refinement was performed using FullProf Suite software to confirm the phases and to determine the lattice parameters [18]. The R3c and Pbam phases were identified as the primary and secondary phases, respectively. The refined XRD patterns for the NPs are displayed in Figure 2, where the observed data points are represented in black, the overlapping red line indicates the calculated pattern, the difference between the two is displayed in blue, while the Bragg's positions of both phases are displayed by green vertical lines. The most intense main peak corresponds to the R3c phase, and a small peak corresponds to Pbam. The quality of the refinement has been corroborated by the values of the reliability factors (*R-factors*) and χ^2 (χ^2), which have been displayed in Table 1. The refinement reveals that no structural transformation takes place with the increase in Mn content in the BFO matrix in which Mn^{2+} ions substitute the Fe^{3+} ions. However, the intensity of the secondary peaks is reduced with the increase in the Mn content. Also, the phase fraction of secondary phases is found to be reduced with the increasing amount of Mn in the samples accompanied with the reduction in the density of the material. Alongside this, a trivial peak shift has also been observed towards a higher 2θ with the increase in Mn content, which indicates a decrease in lattice parameters leading to the reduction in the cell volume. Nonetheless, this change in the position and intensity of the peaks is so small that it does not lead to any structural transformation unlike that reported by Camayo et al. [3]. They reported significant changes in the structural parameters that resulted in the phase transition from R3c to Pbnm along with the coexistence of both phases. The values of the lattice parameters (*a/c*) and the corresponding cell volume have been represented in Figure 3a,b, respectively. Both the lattice parameters show a decrease with an increase in Mn content, leading to the correspondingly decreasing cell volume. The possible reason for the decrease in the lattice parameters may be the fact that the substitution of Mn^{2+} in place of Fe^{3+} creates the oxygen vacancies that entrap the neighboring electrons. These electrons may undergo exchange interactions with the surrounding cations causing them to come

closer, resulting in the reduction in lattice parameters. Nonetheless, the decrease in lattice parameters is small, which can be associated with the small shifting in the peak positions. In addition, the tetragonality ratio (c/a) has also been estimated and has been found to decrease from 2.486 (BFO) to 2.483 (BFMO5), however, it shows an increase to 2.487 for BFMO10. The values of the c/a ratio suggests that the change in tetragonality as small as this does not cause the phase transition.

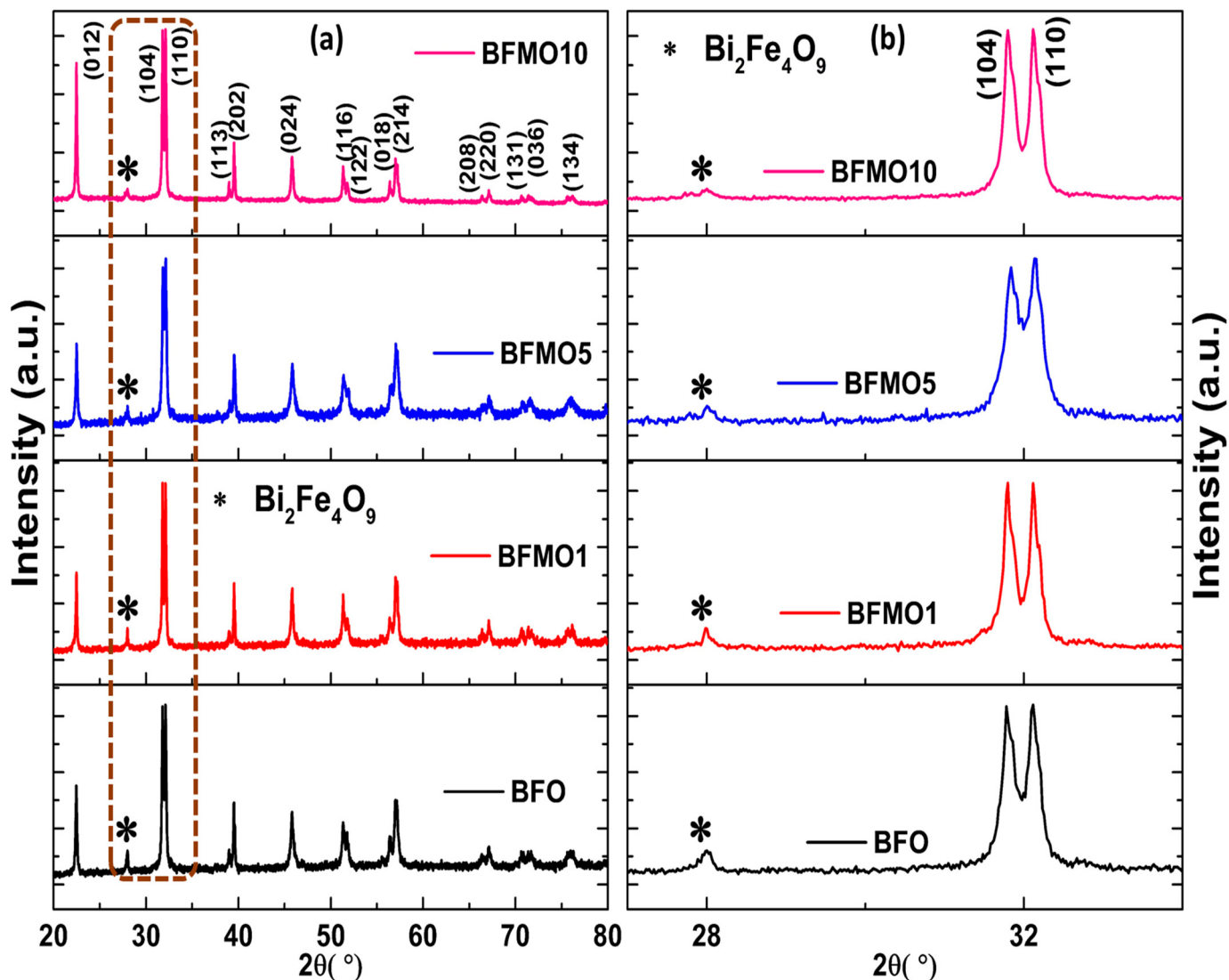


Figure 1. XRD patterns of BFO, BFMO1, BFMO5, and BFMO10 in the 2θ range (a) $20\text{--}80^\circ$; (b) $27\text{--}33^\circ$.

Table 1. Structural parameters and secondary phase fraction obtained from Rietveld refinement of XRD patterns.

Samples	Density of the Compound (g/cm^3)	R_p	R_{wp}	R_{exp}	χ^2	Secondary Phase Fraction (%)
BFO	8.813	8.1	11.2	5.4	4.4	13.1
BFMO1	8.788	10.7	13.4	9.3	2.1	12.2
BFMO5	8.630	9.3	11.9	8.6	1.9	8.7
BFMO10	5.214	10.7	13.5	9.1	1.9	3.2

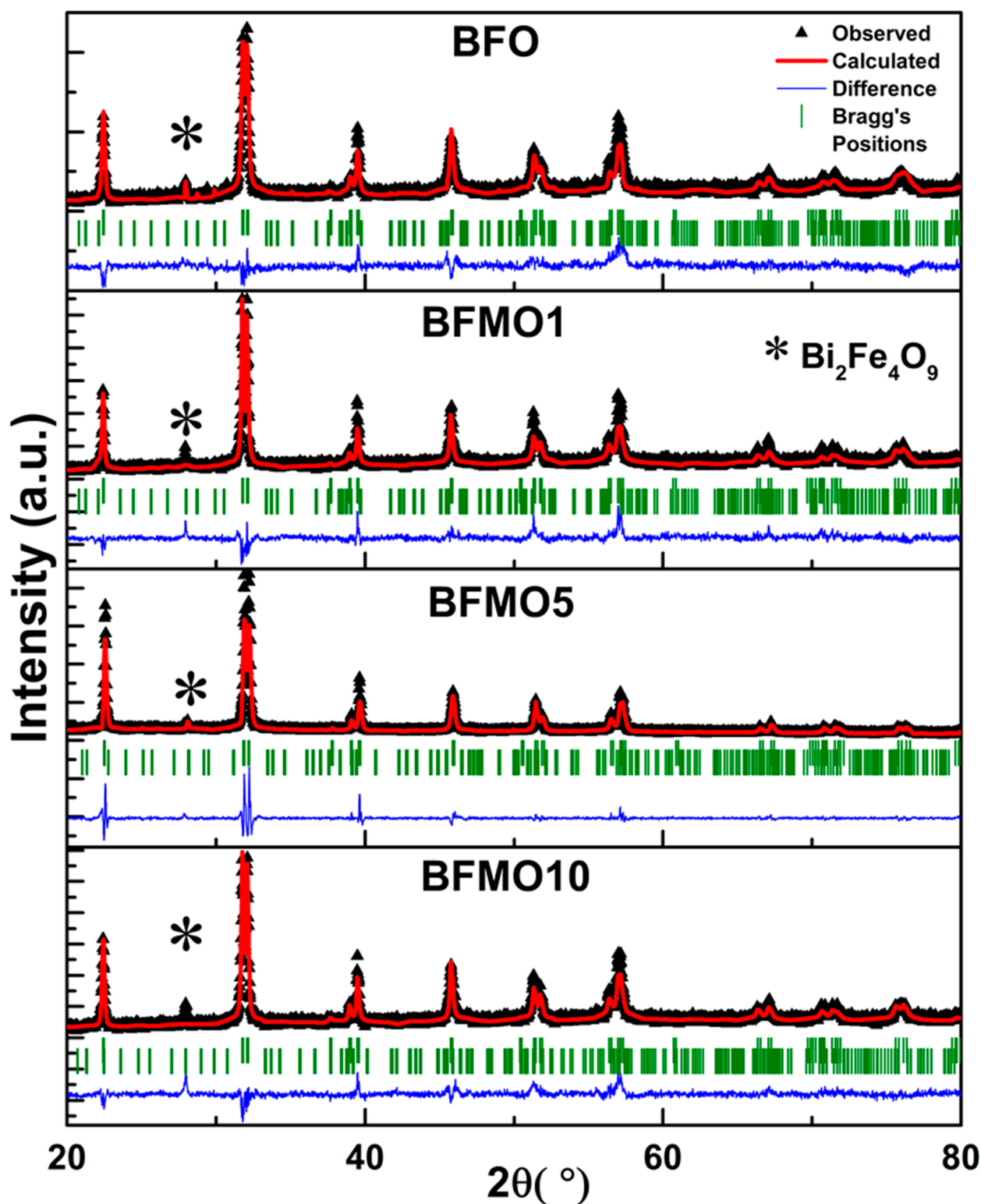


Figure 2. Rietveld refinement of BFO, BFM01, and BFM05 indicating BiFeO_3 as the primary and $\text{Bi}_2\text{Fe}_4\text{O}_9$ as the secondary phase.

Furthermore, the crystallite size has been calculated using the Scherrer's formula [20]: $K\lambda/\beta \cos\theta$, where K is the shape factor (0.89), λ is the wavelength (0.15418 nm), β is the FWHM (full width at half maximum) and 2θ is the Bragg's angle. The strain (ϵ) has been calculated using the $\beta = 4\epsilon \tan\theta$. The decrease in crystallite sizes and the strain with

increasing Mn content are displayed in Figure 3c,d, respectively. It is worth mentioning here that the ionic radius of Fe^{3+} is 0.063 nm, while that of Mn^{2+} is 0.080 nm. The reason behind the decreasing crystallite size of the NPs despite the higher ionic radii of Mn^{2+} than Fe^{3+} may be attributed to the decreasing lattice parameter.

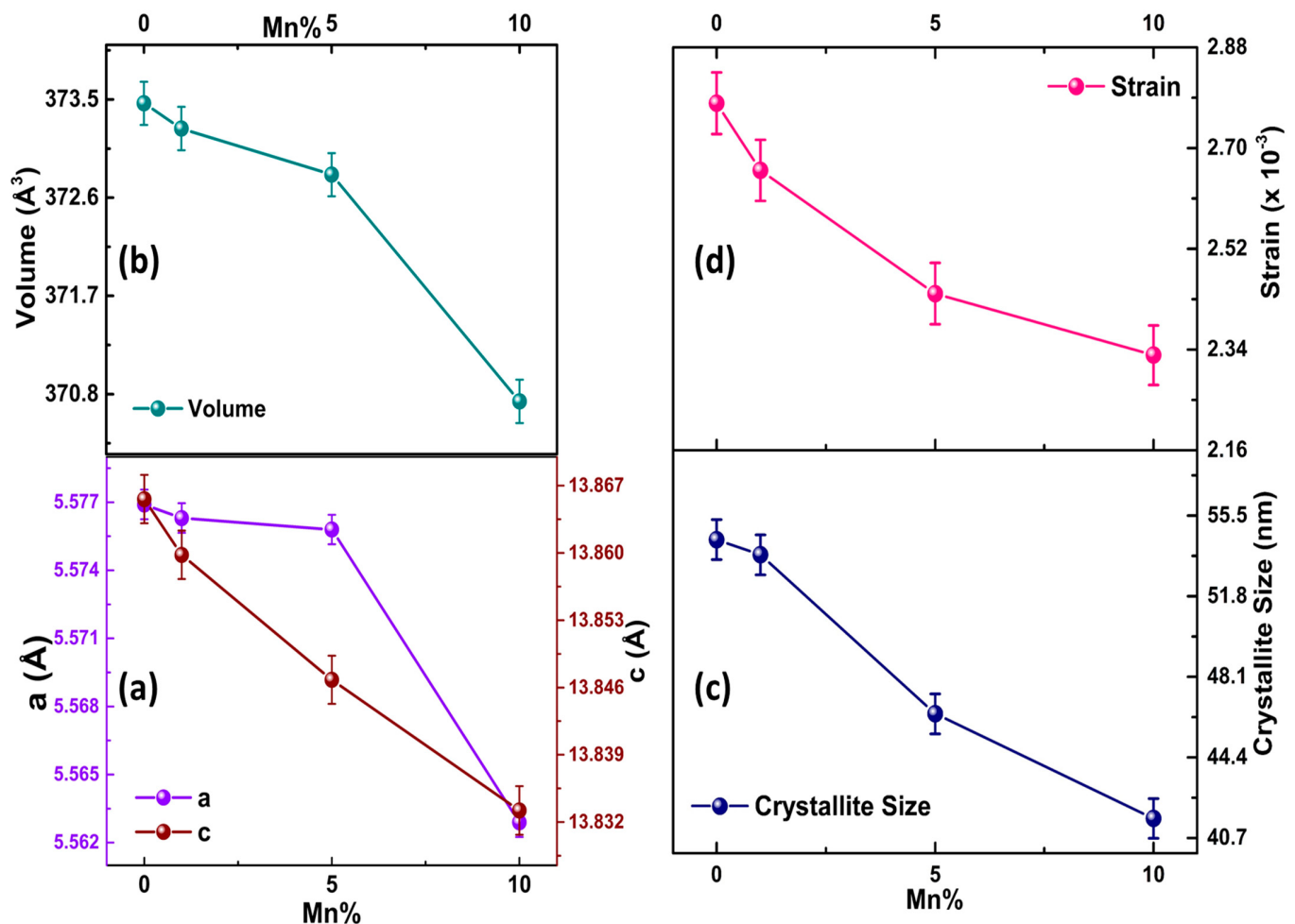


Figure 3. The values of the structural parameters; (a) lattice parameters ($a = b$)/ c ; (b) cell volume; (c) crystallite sizes; and (d) strain plotted as a function of Mn concentration.

3.2. Morphological Analysis

The FESEM micrographs of $\text{Bi}_{1.05}\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0, 0.01, 0.03, 0.05, 0.07, 0.10$) NPs are displayed in Figure 4a–d. The micrographs demonstrate smooth spherical shape morphology and the average particle size is detected by a broad particle size distribution histogram as indicated in the inset of each respective Figure 4a–d. The particles size calculated by fitting the size distribution histograms is found to decrease with an increase in Mn content with a small amount of amalgamation. The decreasing trend of particle sizes follows a similar trend as obtained for the crystallite sizes in XRD analysis. Further, the elemental analysis of the NPs has been carried out through EDX spectroscopy. The EDX spectra of the samples are displayed in Figure 4a'–d'. The major elements found in the spectra are Bi, Fe, O, and Mn. Although EDX does not give an accurate estimate of the atomic percentages, an approximate idea of composition can however be determined. It is evident from the tables indicated in Figure 4a'–d' that the at% of Mn increases in the samples indicating that Mn is well substituted in the BFO lattice.

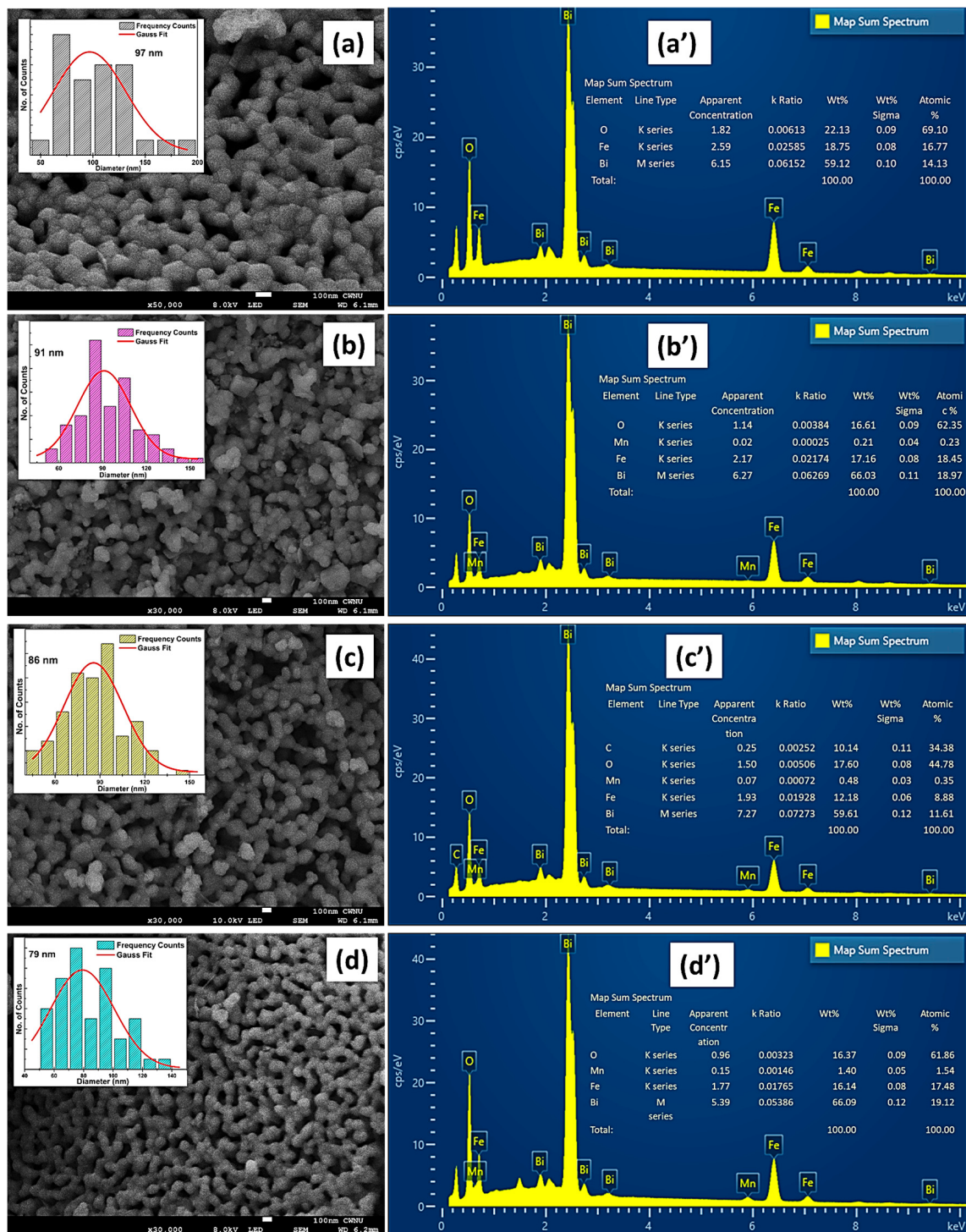


Figure 4. (a–d) FESEM micrographs of BFO, BFMO1, BFMO5, and BFMO10, respectively; inset shows the fitted histograms of size distribution; (a'–d') EDX spectra of corresponding BFO, BFMO1, BFMO5, and BFMO10.

3.3. Ferroelectric Properties

The varying electric polarization (P) as a function of the applied electric field (E) has been investigated to study the ferroelectric properties of the NPs. The P - E hysteresis loops are obtained when the electric dipole moments in the material react to the applied electric field. The hysteresis loop signifies the resistance offered by the dielectric nature of the material. The P - E hysteresis loops of $\text{Bi}_{1.05}\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0, 0.01, 0.03, 0.05, 0.07, 0.10$)

NPs obtained at a frequency of 50Hz and at room temperature are displayed in Figure 5. The electric fields were applied in the range of ± 2 to ± 40 kV/cm. The shape of the hysteresis is found to be affected by the Mn content in the NPs. Interestingly, the hysteresis loss first decreases up to 3% Mn and then increases with the increasing concentration of Mn. The values of the maximum polarization ($P_{\max}$), the remnant polarization (P_r), and the electric coercivity (E_c) are indicated in Table 2. The highest values of the maximum polarization and remnant polarization are obtained for BFM07 and BFM05, respectively. This may be because the increasing Mn content suppresses the ferroelectric properties of the material.

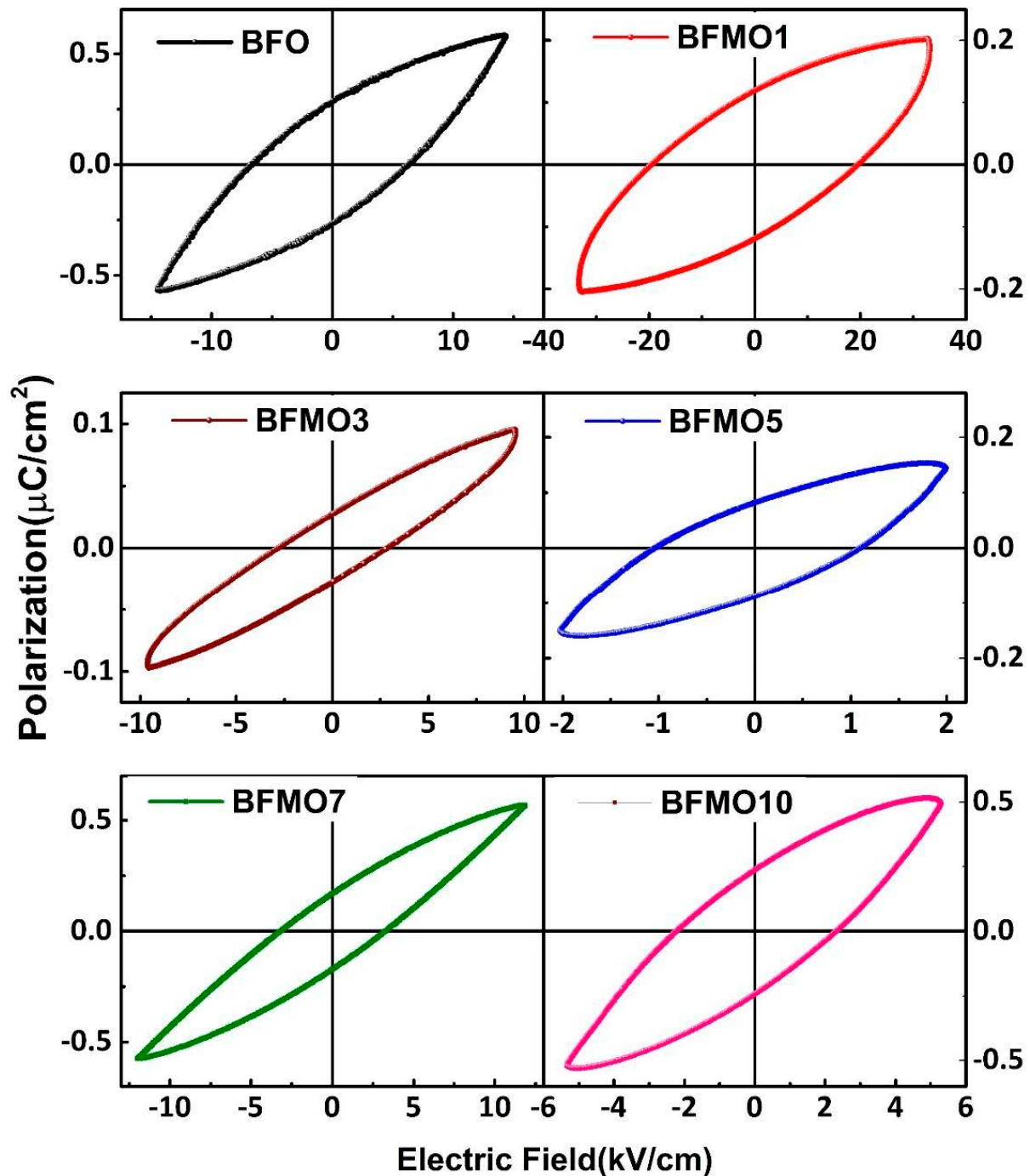


Figure 5. P-E hysteresis loops of BFO, BFM01, BFM03, BFM05, BFM07, and BFM10.

Table 2. Maximum polarization (P_{max}), remnant polarization (P_r), and electrical coercivity obtained from the P-E hysteresis loops.

Samples	P _{max} (μC/cm ²)	P _r (μC/cm ²)	Ec (kV/cm)
BFO	0.58	0.21	34.28
BMFO1	0.20	0.12	19.55
BMFO3	0.12	0.04	02.46
BMFO5	0.50	0.28	02.97
BMFO7	0.64	0.17	04.81
BMFO10	0.57	0.24	04.70

3.4. UV-Vis Spectroscopy

The optical properties of Bi_{1.05}Fe_{1-x}Mn_xO₃ ($x = 0, 0.01, 0.03, 0.05, 0.07, 0.10$) NPs are analyzed through the investigation of the absorption spectra as shown in Figure 6a in the range of 400–800 nm. The spectra exhibit strong bands in the wavelength range of 400–600 nm and a broad band around 700 nm. In BFO, the absorption bands typically arise due to the $d-d$ transitions of Fe³⁺ ions and the charge transfer excitations near the bandgap [21]. These strong bands correspond to the direct electronic transitions occurring due to bandgap absorption, whereas the broad band around 700 nm may be due to defect states such as oxygen vacancies or due to the on-site spin forbidden $d-d$ crystal field excitations [21]. Moreover, the bands demonstrate a decrease in the absorption and a slight shift towards a higher wavelength (redshift) indicating a decrease in the bandgap. The bandgap energy (E_g) has been calculated using the Tauc's plot [7]: $(\alpha h\nu)^2 = B(h\nu - E_g)$, α being the absorption coefficient, h is the Planck's constant, $h\nu$ is the absorbed photon energy, and B is the constant. The Tauc's plots of all the samples are shown in Figure 6b–g. Two regions can be observed in Tauc's plots: one is the higher energy region with an extending continuous linear portion and the other is a small shoulder in the low energy region. This small shoulder may be attributed to the defect states. The bandgap has been calculated by extrapolating the fitted portion of the continuous linear region. The point of intersection of the extrapolated line on the x -axis at zero absorption gives the value of the bandgap energy. These values are represented in Figure 6h for all the samples. The maximum value of the bandgap energy obtained is 1.91 eV, corresponding to BFO that decreases with increasing Mn content in the BFO matrix. The minimum value is obtained for BMFO10 with the maximum Mn concentration. It can be interpreted that the doping of Mn in the BFO matrix increases the density of states in the valence band and reduces the energy gap from 1.91 eV to 1.36 eV with increasing Mn content. This is due to the fact that in BFO, Fe is generally in an Fe³⁺ oxidation state, which is substituted by Mn²⁺ and may release oxygen leading to the formation of oxygen vacancies [22]. These oxygen vacancies can trap the delocalized electrons that contribute to the electronic density of states of the valence band and reduce the bandgap energy. Moreover, the obtained values in the present work are smaller than the values previously reported in the literature, for example, the bandgap energy obtained for Cr and Ho doped BFO was found to be in the range of 2.2–2.7 eV [22]. Thus, the increase in Mn concentration reduces the bandgap energy of Mn-doped BFO NPs.

3.5. Photoluminescence (PL) Spectroscopy

To further investigate the band structure and presence of defect states, PL spectroscopy has been employed [4]. The PL emission response of Bi_{1.05}Fe_{1-x}Mn_xO₃ ($x = 0, 0.01, 0.03, 0.05, 0.07, 0.10$) NPs is displayed in Figure 7. The PL spectra illustrate three nearly spaced bands in the wavelength range of 400–500 nm that can be categorized as UV emission bands and visible emission bands. The bands, observed at 408 and 430 nm, lie in the UV region and can be called as UV emission bands, while the other two bands observed at 456 nm lie in the visible region and can be called visible emission bands [23]. The UV emission bands

arise due to the electronic transitions between the conduction band and the valence band and the visible emission bands are caused by the luminescent centres [23].

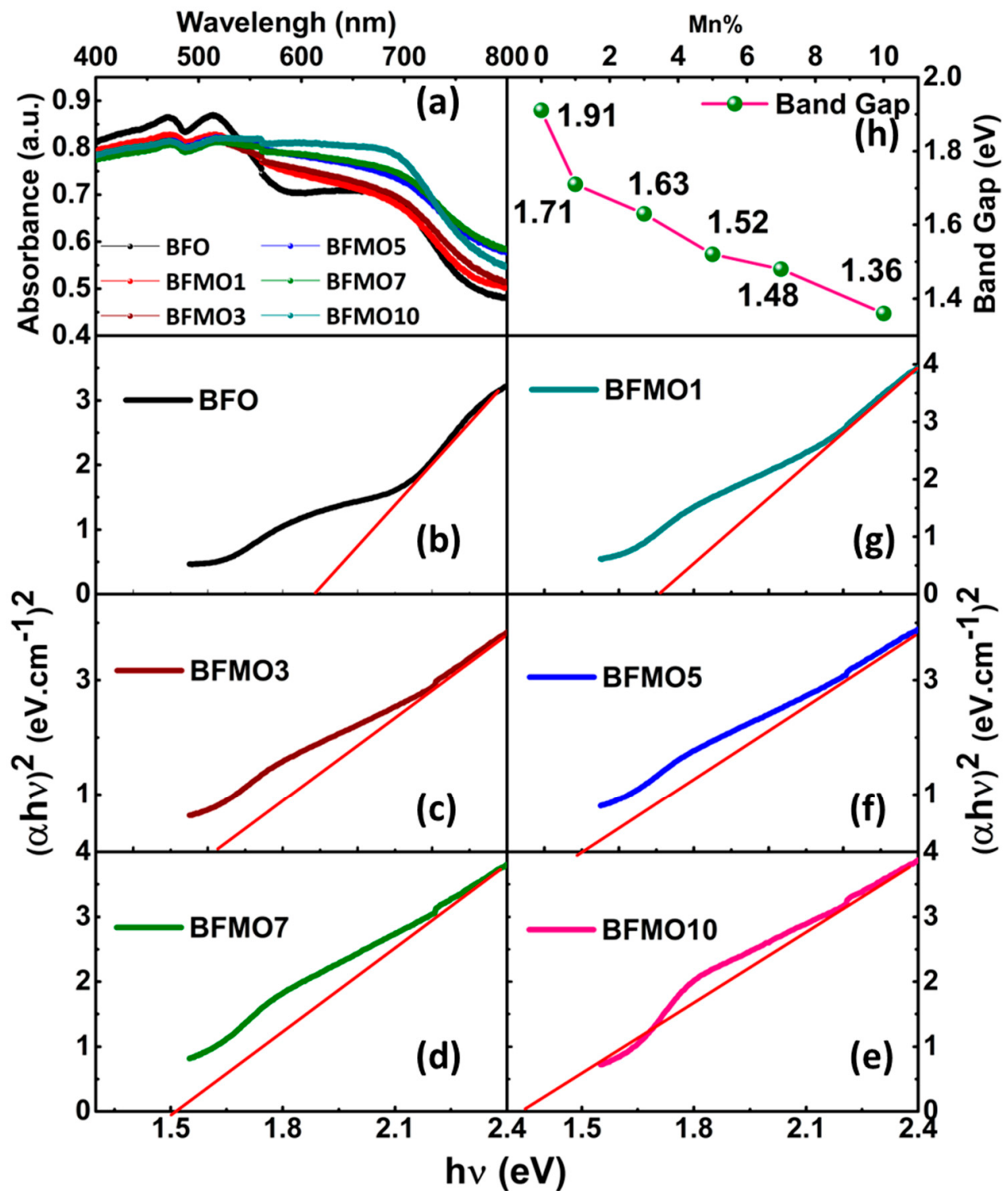


Figure 6. (a) UV-vis absorption spectra; (b–g) Tauc's plots indicating interpolated fitted linear region; and (h) band gaps as a function of Mn concentration.

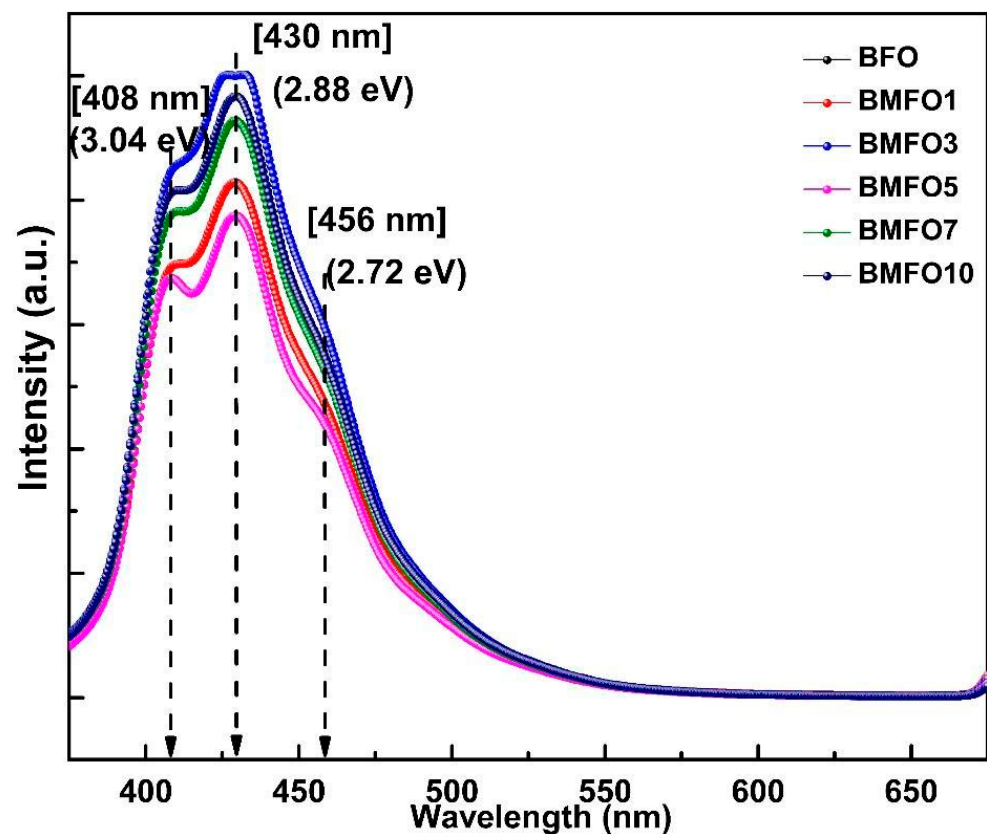


Figure 7. PL spectra of BFO, BMFO1, BMFO3, BMFO5, BFO7, and BMFO10.

3.6. Magnetization Analysis

The magnetic properties of $\text{Bi}_{1.05}\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0, 0.01, 0.03, 0.05, 0.07, 0.10$) NPs are studied through magnetic field (H) dependent magnetization (M). The MH hysteresis curves were measured at room temperature within the range ± 30 kOe, as displayed in Figure 8a. The hysteresis curves indicate the ferromagnetic behavior of the samples. However, the curves show an interesting behavior near $H = 0$. At a zero applied field, the curves narrow down, showing a deviation from the normal hysteresis behavior. Such a type of behavior may be observed due to the presence of the canted spins in the material. The canted spins may be related to the interaction of electrons trapped in the oxygen vacancies with the neighboring Fe^{3+} ions, resulting in the spin canting in the lattice. Thus, the Mn substitution alters the electronic structure via the formation of oxygen vacancies, which further alters the magnetic properties of the material [24]. Furthermore, the narrowing of the curve is most observed for BMFO5 NPs. Mn, being antiferromagnetic in nature, may be the possible cause of the spin canting in the system [25]. The remanent magnetization (M_r), saturation magnetization (M_s), and coercivity (H_c) have been represented in Figure 8b. The maximum value of the saturation of 1.4 emu/g is observed for BMFO10 NPs, which is quite significant for BFO. The values of M_r and M_s show a similar behavior. It is noteworthy that due to the narrowing of the curve, the coercivity should decrease, but the maximum coercivity is obtained for BMFO5 and minimum coercivity is obtained for BMFO10 NPs. Further, the curves show the increasing behavior at ± 30 kOe, which indicates that the strength of the applied magnetic field needs to be increased to attain the saturation of the curves.

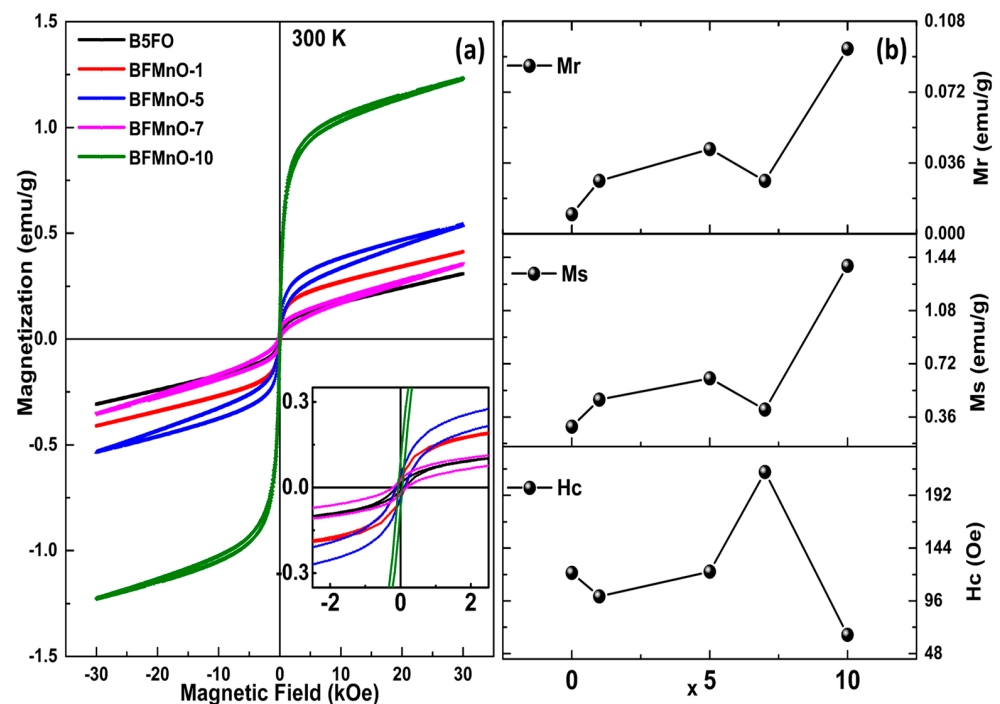


Figure 8. (a) M-H hysteresis curves of BFO, BFMnO1, BFMnO3, BFMnO5, BFMnO7, and BFMnO10; inset shows the behavior of the curves near $H = 0$, (b) Variation of M_r , M_s , and H_c as a function of Mn concentration.

4. Conclusions

The $\text{Bi}_{1.05}\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0, 0.01, 0.03, 0.05, 0.07, 0.10$) NPs were successfully prepared through the sol-gel technique and characterized using different techniques, viz. structural, ferroelectric, optical, and magnetic properties through X-ray diffraction, P-E (polarization vs. electric field) hysteresis loops, UV-vis absorption spectroscopy, Photoluminescence (PL) spectroscopy, and DC-magnetization. The Rietveld refinement indicates the rhombohedral (R3c) phase along with a minor secondary orthorhombic (Pbam) phase that is reduced with an increasing Mn concentration. The crystallite sizes, lattice parameters, and strain were found to be reduced with an increase in Mn concentration. The P-E hysteresis loops revealed the maximum remnant polarization obtained for $\text{Bi}_{1.05}\text{Fe}_{0.95}\text{Mn}_{0.05}\text{O}_3$ NPs. The UV-vis spectra revealed the reduction in the bandgap from 1.91 eV to 1.36 eV with an increase in Mn concentration. The PL spectra revealed an extra band that may be due to the transitions involving defect states, possibly oxygen vacancies. The magnetic field (H) vs. magnetization (M) hysteresis loops were investigated for their magnetic properties. The saturation magnetization was found to be maximum (~ 1.4 emu/g) for $\text{Bi}_{1.05}\text{Fe}_{0.90}\text{Mn}_{0.10}\text{O}_3$ NPs. The MH hysteresis loops showed the narrowing down behavior near $H = 0$, forming a wasp waist shape that was found to be maximum for $\text{Bi}_{1.05}\text{Fe}_{0.95}\text{Mn}_{0.05}\text{O}_3$ NPs. The narrowing down of the hysteresis loop may be attributed to the presence of the canted spins.

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References

1. Carranza-Celis, D.; Cardona-Rodríguez, A.; Narváez, J.; Londoño, O.M.; Muraca, D.; Knobel, M.; Ornelas-Soto, N.; Reiber, A.; Ramírez, J.G. Control of Multiferroic properties in BiFeO₃ nanoparticles. *Sci. Rep.* **2019**, *9*, 3182. [CrossRef] [PubMed]
2. Meng, J.; Chen, K.; Mijiti, Y.; Chen, D.; Choueikani, F.; Zou, Z.; Wang, L.; Mu, G.; Geng, W.; Kong, Q.; et al. Charge-Transfer-Induced Interfacial Exchange Coupling at the Co/BiFeO₃ Interface. *Phys. Rev. Appl.* **2019**, *12*, 044010. [CrossRef]
3. Camayo, C.; J., S.G.; Raigoza, C. Effect of La and Pr substitution on structure and magnetic properties of Pechini synthesized BiFeO₃. *J. Magn. Magn. Mater.* **2021**, *527*, 167733. [CrossRef]
4. Pandey, D.K.; Modi, A.; Pandey, P.; Gaur, N.K. Variable excitation wavelength photoluminescence response and optical absorption in BiFeO₃ nanostructures. *J. Mater. Sci. Mater. Electron.* **2017**, *28*, 17245–17253. [CrossRef]
5. Rajeevan, N.E.; Pradyumn, P.P.; Kumar, R.; Shukla, D.K.; Kumar, S.; Singh, A.K.; Patnaik, S.; Arora, S.K.; Shvets, I.V. Magnetoelectric properties of Bi_xCo_{2-x}MnO₄ (0 ≤ x ≤ 0.3). *Appl. Phys. Lett.* **2008**, *92*, 102910. [CrossRef]
6. Pahwa, S.; Kumari, A.; Vij, A.; Alvi, P.A.; Kumar, S. Ferroelectric properties of Sm doped BaTiO₃ bulk ceramics. *AIP Conf. Proc.* **2020**, *2220*, 080049. [CrossRef]
7. Kumari, A.; Kumari, K.; Ahmed, F.; Alshoaibi, A.; Alvi, P.; Dalela, S.; Ahmad, M.M.; Aljawfi, R.N.; Dua, P.; Vij, A.; et al. Influence of Sm doping on structural, ferroelectric, electrical, optical and magnetic properties of BaTiO₃. *Vacuum* **2020**, *184*, 109872. [CrossRef]
8. Khomchenko, V.; Silibin, M.; Bushinsky, M.; Latushka, S.; Karpinsky, D. Magnetic structure and properties of Ca, Mn-doped bismuth ferrites near the polar/nonpolar phase boundary. *J. Phys. Chem. Solids* **2020**, *146*, 109612. [CrossRef]
9. Park, J.S.; Lee, M.H.; Kim, D.J.; Kim, M.-H.; Song, T.K.; Kim, S.W.; Kim, W.-J.; Kumar, S. Enhanced piezoelectric properties of BaZrO₃-substituted 0.67BiFeO₃-0.33BaTiO₃ lead-free ceramics. *J. Korean Phys. Soc.* **2015**, *66*, 1106–1109. [CrossRef]
10. Lee, M.H.; Kim, D.J.; Park, J.S.; Kim, M.-H.; Song, T.K.; Kumar, S.; Kim, W.-J.; Do, D.; Hwang, I.; Park, B.H.; et al. Lead-free piezoelectric BiFeO₃-BaTiO₃ thin film with high Curie temperature. *Curr. Appl. Phys.* **2016**, *16*, 1449–1452. [CrossRef]
11. Kumar, S.; Srivastava, G.; Almutairi, G.; Ahmed, F.; Shaalan, N.M.; Dalela, S.; Kumar, R.; Kumar, A.P.; Alvi, P.; Chae, K.; et al. Electronic structure and electrochemical properties of La-doped BiFeO₃ nanoparticles. *J. Electron Spectrosc. Relat. Phenom.* **2021**, *253*, 147138. [CrossRef]
12. Kumari, A.; Kumari, K.; Aljawfi, R.N.; Alvi, P.A.; Dalela, S.; Ahmad, M.M.; Chawla, A.K.; Kumar, R.; Vij, A.; Kumar, S. Role of La substitution on structural, optical, and multiferroic properties of BiFeO₃ nanoparticles. *Appl. Nanosci.* **2021**, 1–20. [CrossRef]
13. Sinha, A.; Bhushan, B.; Jagannath; Sharma, R.; Sen, S.; Mandal, B.; Meena, S.S.; Bhatt, P.; Prajapat, C.; Priyam, A.; et al. Enhanced dielectric, magnetic and optical properties of Cr-doped BiFeO₃ multiferroic nanoparticles synthesized by sol-gel route. *Results Phys.* **2019**, *13*, 102299. [CrossRef]
14. Kim, G.W.; Kumar, S.; Chang, J.; Lee, C.G.; Koo, B.H. Magnetic and electrical properties of La_{0.7}Ca_{0.3}Mn_{0.95}Co_{0.05}O₃ epitaxial layers by pulsed laser deposition. *Ceram. Int.* **2012**, *38*, S443–S446. [CrossRef]
15. Nisha; Shukla, D.K.; Kumar, S. Ferroelectric and Dielectric Properties of Mn Doped BiFeO₃ Bulk Ceramics. *AIP Conf. Proc.* **2018**, *2006*, 030037. [CrossRef]
16. Yang, C.-H.; Koo, T.; Jeong, Y. How to obtain magnetocapacitance effects at room temperature: The case of Mn-doped BiFeO₃. *Solid State Commun.* **2005**, *134*, 299–301. [CrossRef]
17. Kumari, A.; Kumari, K.; Ahmed, F.; Ahmad, M.M.; Sharma, J.; Vij, A.; Kumar, S. Role of Bi-excess on structural, electrical, optical, and magnetic properties BiFeO₃ nanoparticles. *J. Mater. Sci. Mater. Electron.* **2021**, *32*, 23968–23982. [CrossRef]
18. Kumar, A.; Varshney, D. Crystal structure refinement of Bi_{1-x}Nd_xFeO₃ multiferroic by the Rietveld method. *Ceram. Int.* **2012**, *38*, 3935–3942. [CrossRef]
19. Walker, J.; Mirjanic, A.; Prah, U.; Sadl, M.; Condurache, O.A.; Bencan, A.; Rojac, T.; Grigoros, M.; Ursic, H. Magnetic contributions in multiferroic gadolinium modified bismuth ferrite ceramics. *Scr. Mater.* **2020**, *188*, 233–237. [CrossRef]
20. Sharma, S.; Kumar, R.; Kumar, S.; Kumar, V.S.; Knobel, M.; Reddy, V.; Banerjee, A.; Singh, M. Magnetic study of Mg_{0.95}Mn_{0.05}Fe₂O₄ ferrite nanoparticles. *Solid State Commun.* **2007**, *141*, 203–208. [CrossRef]
21. Ramachandran, B.; Dixit, A.; Naik, R.; Lawes, G.; Rao, M.S.R. Charge transfer and electronic transitions in polycrystalline BiFeO₃. *Phys. Rev. B* **2010**, *82*, 012102. [CrossRef]
22. Puhan, A.; Nayak, A.; Bhushan, B.; Praharaj, S.; Meena, S.; Rout, D. Enhanced electrical, magnetic and optical behaviour of Cr doped Bi_{0.98}Ho_{0.02}FeO₃ nanoparticles. *J. Alloys Compd.* **2019**, *796*, 229–236. [CrossRef]
23. Kumari, K.; Aljawfi, R.N.; Chawla, A.; Kumar, R.; Alvi, P.; Alshoaibi, A.; Vij, A.; Ahmed, F.; Abusamak, M.; Kumar, S. Engineering the optical properties of Cu doped CeO₂ NCs for application in white LED. *Ceram. Int.* **2019**, *46*, 7482–7488. [CrossRef]
24. Sharma, S.K.; Thakur, P.K.; Kumar, S.; Shukla, D.K.; Brookes, N.; Lee, C.; Pirota, K.; Koo, B.; Knobel, M. Room temperature ferromagnetism in Fe-doped CeO₂ thin films grown on LaAlO₃ (001). *Thin Solid Films* **2010**, *519*, 410–413. [CrossRef]
25. Hashim, M.; Alimuddin; Kumar, S.; Shirsath, S.E.; Kotnala, R.; Chung, H.; Kumar, R. Structural properties and magnetic interactions in Ni_{0.5}Mg_{0.5}Fe_{2-x}Cr_xO₄ (0 ≤ x ≤ 1) ferrite nanoparticles. *Powder Technol.* **2012**, *229*, 37–44. [CrossRef]