MICROSTRUCTURE AND OPTICAL PROPERTIES OF BiFe_{1-x}Mn_xO₃ THIN FILMS

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ABSTRACT

Thin films of Bi_{1-x}Mn_xFeO₃ (x=0–0.2) have been prepared on the quartz substrates via chemical solution deposition (CSD) with a spin coating technique. The goal of this study is to investigate the influence of Mn doping on BMFO thin film properties. The microstructure, morphology and cross-section, and optical properties of the thin films were examined by XRD, SEM, and UV-Vis spectrophotometer, respectively. The XRD patterns reveal a single phase of BFO on each BMFO thin film. The higher Mn number in BMFO results in smaller crystallite size and grain size, and higher crystallinity that enhances the optical properties of BMFO thin film by a decline in the band-gap values. The band-gap values of BFO, BMFO1, BMFO3, BMFO5, BMFO10 and BMFO20 are 2.5 eV, 2.40 eV, 2.39 eV, 2.34 eV, 2.29 eV, and 2.25 eV, respectively. Hence, the Mn doping in this study is beneficial and surely alters the structural and morphological properties that further improve the optical properties of the films.

Keywords: Mn-doped, Bismuth ferrite (BFO), Microstructure, Optical Properties

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INTRODUCTION

Multiferroic materials have become intensely studied materials for their multifunctional application. The materials have both ferroelectric and antiferromagnetic properties, which could deliver numerous characteristics by applying them in external electric or magnetic fields.¹⁻³ The multiferroic has various electronic device applications such as data storage media, multi-state memories, magnetoelectric sensors, photocatalyst, capacitors, and photovoltaic.⁴⁻¹⁰ Several ferroelectric materials are BaTiO₃, LiNbO₃, Pb (Zr, Ti)O₃, SrBi₄Ti₄O₁₅, BiFeO₃ and BiMnO₃.¹¹⁻¹⁵

BiFeO₃ or denoted as BFO is one of the multiferroic materials with a rhombohedral perovskite crystal structure (ABO₃) in which Bi³⁺ and Fe³⁺, respectively occupy the A-site and the B-site.^{7,13} It exhibits both ferroelectric at Curie Temperature (T_C) = 1103 K and antiferromagnetic at Neel Temperature (T_N) = 643K.^{4,13} BFO has been studied extensively for photocatalytic or photovoltaic material due to its narrow band gap (2.1 eV – 2.7 eV).^{8,10} The low band-gap materials can absorb more photons, so that produces a high electron excitation.¹² Ferroelectric materials with good photovoltaic characteristics must have a low leakage current as well so that the electric current resulted is maximized.

However, it has been reported that BiFeO₃ is known to have a large leakage current.^{2,11} Nonetheless, this matter could be overcome by doping with various compounds such as Co³⁺, Mn²⁺, Nd³⁺, Sm³⁺, and La³⁺ in the BFO crystal structure.^{7,16-21}

Among the existed doping constituents, Mn-doping has fascinated excessive consideration owing to its special role in BFO. Barman et al. have reported that Mn-doped BFO increased its ferroelectric properties of polarization and dielectric tunability.¹⁹ Sharma et al. have declared that Mn doping in BFO could enhance the ferroelectric (dielectric constant and loss tangent) and magnetic (AC conductivity) properties.²⁰ Yan et al. have studied that Nd/Mn doping could improve structural and magnetic properties in BFO.¹⁷ Nakashima et al. have researched that Mn addition could increase the photovoltage in BFO by improving the electronic structure.¹⁰ Thang et al. have demonstrated the influence of (Sm, Mn) co-doping on the structural, magnetic, electrical, and ferroelectric properties of BFO which were enhanced by the

doping.¹⁶ Of these, and many more, researches on Mn-doped BFO thin films have mainly focused on structural, ferroelectric and magnetic properties.^{2-6,11} However, few studies are concerned with the optical properties of Mn-doped BFO. Yan et al. reported Mn-doped BFO thin films prepared on Pt/Ti/SiO₂/Si(111) substrates by a chemical solution deposition method and analyzed by X-ray diffraction (XRD), and Raman scattering and ellipsometric spectroscopy.⁹ Xu et al. demonstrated that Mn (5%) doped BFO (BiFe_{0.95}Mn_{0.05}O₃) thin films could rise the optical and PEC properties.⁷ Yan et al. have reported that different Mn number dopant BFO films by the pulsed laser deposition method could improve the microstructure, optical, ferroelectric, and photovoltaic performance.⁸ It should be noted that Mn³⁺ dopants are worth being further studied. Hence, different from the mentioned researches, this study presents the work of fabricating Mn-doped BFO thin films by chemical solution deposition on quartz substrates and the influences of Mn concentration (0%, 1%, 3%, 5%, 10%, and 20%) on the structural, morphological, and optical properties.

EXPERIMENTAL

Material and Methods

Thin-films of Mn-doped BiFeO₃ or BiFe_{1-x}Mn_xO₃ (x=0%, 1%, 3%, 5%, 10%, and 20%) were fabricated via sol-gel method prepared with a spin coater. The raw materials were bismuth (III) nitrate pentahydrate [Bi(NO₃)₃.5H₂O] (Kojundo, 99.99%), iron nitrate monohydrate [Fe(NO₃)₃.9H₂O] (Kojundo, 99.99%), Manganese Nitrate [Mn(NO₃)₂] (Sigma Aldrich, ≥99.9%) as the Bi, Fe, and Mn sources. Additionally, Acetic Acid [CH₃COOH] (Sigma Aldrich, ≥99.9%) and 2-methoxyethanol (Sigma Aldrich, ≥ 99.9%) were solvents and Acetyl acetone (Sigma Aldrich, ≥99.9%) as a stabilizer.

General Procedure of the Thin Film Fabrication

Firstly, the raw materials of the BiFe_{1-x}Mn_xO₃ with various Mn concentrations were weighed as the stoichiometry. Bi(NO₃)₃.5H₂O, Fe(NO₃)₃.9H₂O, Mn(NO₃)₂, acetic acid, and 2-methoxyethanol were mixed using a magnetic stirrer for 60 min. Acetylacetone was added to the mixture solution and stirred with a magnetic stirrer forming the BiFe_{1-x}Mn_xO₃ solution. The solution was then let for 24 h. The solution was then deposited on quartz substrates with the spin coater at 3000 rpm for 30 s followed by pyrolysis on a hot plate at 150°C for 1 min. The deposition-pyrolysis cycle was repeated to get desired layer number. Finally, the samples were annealed at a temperature of 600°C for 1 h.

Materials Characterizations

The microstructure of BiFe_{1-x}Mn_xO₃ thin films was identified via used Philips PW 3710/40 kV X-Ray Diffraction (XRD) and the morphology used Scanning Electron Microscopy (SEM) instruments, respectively. Further, the optical properties measurement was done by a UV-Vis spectrophotometer. In this article, the thin films were named by BFO, BMFO1, BMFO3, BMFO5, BMFO10, and BMFO20 referred to BiFe_{1-x}Mn_xO₃ for x=0% (BFO), 1%, 3%, 5%, 10%, and 20%, respectively.

The crystallite size of the BFO and BMFO films was calculated using the Debye Scherrer equation as Eq.-1.²²

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

In which k is the Scherrer constant, λ is the x-ray source wavelength ($\lambda_{Cu}=1.546\text{\AA}$), β is FWHM (Full Width at half maximum), and θ is Bragg angle/ diffraction angles. Meanwhile, the crystallinity was estimated by Eq.-2.

$$\text{Crystallinity \%} = \frac{\text{Intensity}_{\max}}{\text{Intensity}_{\max} + \text{Intensity}_{\min}} \times 100\% \quad (2)$$

RESULTS AND DISCUSSION

Figure-1(a) presents the XRD patterns of BFO, BMFO1, BMFO3, BMFO5, BMFO10, and BMFO20. Each peak of the diffraction patterns represents one crystal plane with a particular plane orientation. The diffraction patterns match with ICDD database #861518 owned by BiFeO₃. The patterns demonstrate a

single phase of BFO rhombohedral crystal structure with $a = b \neq c$ and peaks of (010), (110), (111), (020), (120), and (112).

Figure-1(b) reveals that the BMFO films' peaks shift to the right as the substitution of Mn. However, the shift is not significant since the Mn concentration added is small. The Mn doping in the BFO samples acts as a substitute for Fe atoms in the perovskite structure of BiFeO_3 . The atomic radius of Fe is $0.645\text{\AA}$ while Mn is $0.64\text{\AA}$.¹³ The right shift is because the atomic radius of Mn is smaller than the Fe atomic radius. The more Mn gave leads to the more Fe replaced. It also induces the atomic distance changing so that the lattice parameter becomes smaller in this case. As a result, the cell unit volume of the crystal changes in a smaller size. Moreover, the Mn addition leads to a decrease in the crystallite size of the BMFO thin films which is considered due to the change of the cell unit volume of the crystal. Further, the lattice strain of the samples' crystal also alters as the modification of Mn concentration. The lattice strain of the BFO crystal is smaller than those of all BMFO samples indicating the Mn addition could raise the lattice strain value. However, for each BMFO sample, there is no tendency whether the values are getting increase or decrease with the variation of the Mn concentration. Nevertheless, the rising strain approves a decline in the structure stability.¹⁶ Table-1 summarizes the estimation of lattice parameter, crystallite size, and lattice strain of the BFO and BMFO films.

Fig-1: (a) XRD Patterns of BFO, BMFO1, BMFO3, BMFO5, BMFO10, and BMFO20 Thin Films; (b) Peak magnification of (110) Plane Orientation; and (c) Cross-sectional of BMFO1 and BMFO10 Layers

Table-1: Analysis of Diffraction Patterns of Mn-doped BFO Thin Films

Samples	Crystallite Size (nm)	Crystallinity	Lattice Parameter (nm)		Lattice Strain
			a=b	c	
BFO	12	86	5.566	13.855	0.0086
BMFO1	10.1	88	5.576	13.860	0.0109
BMFO3	10.9	87	5.580	13.862	0.0099
BMFO5	11.2	86	5.575	13.853	0.0087
BMFO10	10.8	87	5.574	13.846	0.0090
BMFO20	8.9	88	5.565	13.710	0.0110

Figure-1(c) displays the cross-sectional images of BMFO1 and BMFO10 thin films which represent all cross-sectional images of BFO and BMFO films. We want to show through these images that the layers' thicknesses deposited using a spin coater look flat and homogenous. There is an effect of Mn addition on the interface structure of the films, however, due to the limitation of the test equipment for a certain magnification, we were unable to show the interface structure between the films and substrates affected by doping. Though, in their results study, Huang et al. reported that from the cross-sectional images, it was obvious that the interface between films and substrates became more tenuous with increasing Mn doping (0%, 10%, and 20%).¹¹

Figure-2 displays the morphology image of the BFO and BMFO thin films. It can be seen that the number of Mn affects the grain size. The more Mn number tends to the smaller grain size except for BMFO10 that is very distinct as compared to the others. The micrograph image of BMFO10 exhibits a very large grain size (compared to other samples) and a long-grain shape. This result is similar to the study of Sharma et al. which mentioned the formation of different sized nanorods in the Mn (10%) doped BFO ceramic ($\text{BiFe}_{0.90}\text{Mn}_{0.10}\text{O}_3$) as compared to other Mn numbers (0 and 20%).²⁰ The reason is unclear, but Sharma et al stated that this designated the incorporation of Mn in the BFO lattice site.²⁰

Fig.-2: The Morphology of BFO, BMFO1, BMFO3, BMFO5, BMFO10, and BMFO20 Thin Films

Figure-3(a) exhibits the transmittance spectra of BFO and BMFO thin films at wavelengths of 200-700 nm. It shows that the addition of Mn causes a decrease in the transmittance value, which means an increase in the absorbance values. This indicates that more dopants could induce the material to absorb more photons. At the wavelength around 700 nm, the lowest transmittance is gained by the BMFO1. The transmittance values can be related to the surface morphology of the samples. The SEM image (Fig.-2) shows that the BFO1 surface looks denser with small pores found, in which this condition causes fewer photons to transmit. Meanwhile, the highest transmittance at the wavelength around 700 nm is obtained by BFMO3 because it has less density (Fig.-2). The pores in the surface morphology of materials can advance the transmittance. However, the transmittance value of the BMFO1 tends to be constant at the wavelengths around 550-700 nm while indeed the transmittance of the BMFO20 reduces at those wavelengths making the BMFO20 possess the lowest transmittance at the wavelength below 700 nm which may affect the band-gap value.

The optical band-gap is the energy gap between the valence band and the conduction band. Here, it can be correlated with the absorption coefficient explained by the Tauc equation as follows.²³

$$(\alpha h\nu)^2 = A(h\nu - E_g)^{1/2} \quad (3)$$

In which h is Planck's constant, $h\nu$ is the photon energy, E_g is the optical band-gap, and α is an absorption coefficient. The plot between $(\alpha h\nu)^2$ and $h\nu$ is displayed in Fig.-3(b). E_g can be achieved by taking the intersection of the extrapolated line on the X-axis. The band-gap values (E_g) of BFO, BMFO1, BMFO3, BMFO5, BMFO10, and BMFO20 are 2.5 eV, 2.40 eV, 2.39 eV, 2.34 eV, 2.29 eV, and 2.25 eV, respectively. It means that the increasing mole number of Mn results in lower band-gap values. This result is similar to the reported results.⁷ The band-gap is getting lower through doping because dopants fill the state between the valence band and the conduction band. The narrow band-gap in this research can be

used to develop in the photocatalytic and photovoltaic fields. The lowest band-gap obtained by the BMFO20 is deliberated because it has the highest absorption coefficient denoted by its lowest transmittance spectra at the wavelengths of 200-700 nm affected by the change in the crystal structure and morphology due to doping. Moreover, it also exhibits that this doping level of $x=0.2$ could produce the best thin film with a low band-gap in this research.

Fig.-3: (a) Optical Transmittance Spectra of BFO, BMFO1, BMFO3, BMFO5, BMFO10, and BMFO20 Films (the inset: Photos of Samples); (b) the Plot of $(\alpha h\nu)^2$ against $h\nu$ for BMFO Films.

The transmittance data can be employed to determine the refractive index, extinction coefficient, and $1/(n^2 - 1)$ vs E^2 of the samples using the equations as follows:²³

$$n = \left[N_1 + (N_1^2 - s^2)^{\frac{1}{2}} \right]^{\frac{1}{2}} \quad (4)$$

In which N_1 and s are defined as $N_1 = \frac{2s}{T_m} + \frac{s^2+1}{2}$ and $s = \frac{1}{T_s} + \sqrt{\frac{1}{T_s^2} - 1}$. s is the transmission spectrum of the film substrate. N_1 is the spectral region of transparent. T_s is the substrate transmittance. n is the refractive index and T_m is the sample transmittance.

Fig.-4(a) displays the refractive index at the wavelengths of 200-700 nm. It shows that the more Mn number results in the higher refractive index in the particular wavelengths. The extinction coefficient is an overview of how much incident light is reduced or lost compared to the light energy on the surface. The reduction of the light energy is due to the absorption and scattering processes.¹⁴ The extinction coefficient (k) of the samples can be determined by using Eq.-5. Where α is the absorption coefficient, k is the extinction coefficient, λ is the wavelength.¹⁸

$$k = \frac{\alpha \lambda}{4\pi} \quad (5)$$

Figure-4(b) presents the extinction coefficient (k) values of the BMFO thin films as a function of the wavelengths of 400-600 nm. It demonstrates that the more Mn number results in the higher k value at a certain wavelength. The highest k value is found in the BMFO10 thin film.

Fig.-4: (a) Refractive Index (n); (b) Extinction Coefficient (k); and (c) Plot of $1/(n^2-1)$ vs E^2 of BFO, BMFO1, BMFO3, BMFO5, BMFO10, and BMFO20 Films

The equation for determining the relationship between the refractive index and the photon energy is written as follows:²³

$$n^2(E) = 1 + \frac{E_m E_d}{E_m^2 - E^2} \quad (6)$$

$$E_m = E_o \quad (7)$$

$$\frac{1}{n^2 - 1} = \frac{E_o}{E_d} - \left(\frac{1}{E_o E_d} \right) E^2 \quad (8)$$

$$E^2 = (h\nu)^2, h\nu = \hbar\omega = \frac{hc}{\lambda} \quad (9)$$

It is obtained the plot of the relationship $(n^2 - 1)^{-1}$ vs E^2 as Fig.-4(c). Where E_o is the single oscillator energy, E_d is the dispersed energy, and E^2 is the photons' energy. The figure displays that the addition of Mn causes an increase in the energy of the dispersion in the thin film.

CONCLUSION

Thin films of $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ have been deposited on the quartz substrates using the sol-gel technique. The XRD patterns of the BMFO thin films exhibit a single-phase BFO rhombohedral crystal structure. The results present that the more Mn amount results in the smaller crystallite size, higher crystallinity, and smaller grain size. This improves the optical properties by a decrease in the band-gap values. The band-gap values of BFO, BMFO1, BMFO3, BMFO5, BMFO10, and BMFO20 films are 2.5 eV, 2.40 eV, 2.39 eV, 2.34 eV, 2.29 eV, and 2.25 eV, respectively. The narrow bandgap in this research indicates that the films can be used as a solution for developments in the photocatalytic and photovoltaic fields. Therefore, the Mn doping in this study is advantageous and surely modifies the structural and morphological properties that further enhance the optical properties, particularly the band-gap of the materials based on the reduced band-gap.

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