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Structural and Optical Studies of Zinc doped BiFeO₃ on the Bi-site

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Abstract. Zinc-doped bismuth ferrite (Bi_{1-x}Zn_xFeO₃, $x = 0, 0.05, 0.1$) powdered were synthesized through sol-gel auto combustion methods to investigate the optical properties while maintaining the whole structure of BiFeO₃ (BFO). The Zn doped induced the reveal of Bi₂₅FeO₄₀ as a secondary phase and decreased the bond angle of Bi–O–Fe in the BFO phase structure which affect the electron density formation inside of the lattice. The presence of Zn content has also conducted the shifting of optical absorption in the UV-Vis region and increasing the dielectric constant value. This property is potent in visible light photonic applications.

1. Introduction

Multiferroic materials are materials that exhibit several ferroic behaviors, usually (anti)ferromagnetic and ferroelectric [1]. One of them is bismuth ferrite (BiFeO₃, BFO) which have ABO₃ perovskite type that mostly studied in recent years. Some of the important features of bismuth ferrite materials are optical behavior with a large ferroelectric polarization ($P \approx 90 - 100 \mu\text{C}/\text{cm}^2$) [2,3]. Strong coupling between those properties suggested in several studies makes it become a good candidate for advanced photonic application [3–5].

Structural engineering by doping BFO on Bi/Fe-site to improve its optical performance has been studied. Fatima *et al.* have reported that substitution of La and Mn on Bi/Fe-site in BFO were enhanced dye removal compared to pure BFO [8]. Meanwhile, Liu et al. were reported that Zn doped on Fe-site could improve the crystallinity and show a blue shift in the fundamental absorption edge [6]. Li-doped on Fe-site absorb in UV-Vis wavelength region with a red-shifted and blue – shifted were also being reported by Billah [7]. In the other hand, the presence of the oxygen vacancies in the lattice of the BFO doping sample could be determined by the frequency dependencies of the dielectric permittivity [9]. This vacancy could affect optical behavior, especially in the ability of light absorption [2].

In order to doped the BFO sample, we could use a sol-gel auto-combustion method. This method is a common technique to synthesized a perovskite – sample in many studies [1,10,11]. This method uses simple equipment, result in powder samples, and suitable for manufacturing an oxide material.

In this work, we have organized the study of structural and optical properties of Zn doped BFO in Bi_{1-x}Zn_xFeO₃ ($x = 0, 0.05, 0.1$). Whereare, doping Bi-sites with Zn is still rarely found in the previous studies. A destructive method was also used as an alternative technique to prepare Zn–metal as a



precursor in the sol–gel process. By this work, the effect of doping Zn in Bi-site of the BFO to the optical behavior expected could be identified.

2. Experimental procedures

Zinc doped bismuth ferrite ($\text{Bi}_{1-x}\text{Zn}_x\text{FeO}_3$; $x = 0, 0.05, 0.1$) powdered were synthesized by sol–gel auto–combustion methods. Bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), iron (III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) from Sigma–Aldrich, citric acid and aqua bidest were used as a precursor. A destructed zinc–metal in nitric acid were used as precursor to accompany a sol–gel methods. All the precursor in a proportional composition were converted to gel phase by stirring and heating at 80 °C till it became light brownish colour, then following with dried process at 110 °C for 24 h, afterwards ground and calcined at 600°C for 5 h.

The structure of obtained BFO powder samples was carried out by X-ray diffraction on an XRD PANalytical Diffractometer (Model: X'Pert Pro; Cu- $K\alpha_1$, $\lambda = 1.5405 \text{ \AA}$) at room temperature. This XRD data result was refined using the HighScore Plus. The 3D modeling base on Rietveld refinement result was developed by Vesta Ver. 3.3.9 software. The light absorption spectra of the sample were measured by Agilent Cary 100/300S UV–Vis spectrophotometer. The dielectric measurement was carried out by the four-point probe system on Agilent E4980A LCR meter over the frequency range from 50 kHz to 2 MHz at room temperatures.

3. Results and discussion

3.1. X-ray diffraction analysis

The crystalline structure and the phases present in the sample were investigated by XRD within the range of $2\theta = 10^\circ - 70^\circ$. Figure 1 shows the peak pattern of $\text{Bi}_{1-x}\text{Zn}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1$) powdered samples. The peak pattern affirms the presence of high (112), (104), (110), (024), (214), (202), (116) peaks for the existence of BFO phase. This phase recognized as the rhombohedral structure with space groups (s.g) $R3c$. The reveal of $\text{Bi}_{25}\text{FeO}_{40}$ as a second phase has also occurred with the presence of high (013), (022), (222), (123) peaks ($x = 0.05, 0.1$). This phase has recognized with a cubic structure and s.g. $I23$.

Table 1 were obtained a parameter result of both phase present. There is a good agreement between calculated and observed XRD pattern with a low value of Goodness of Fit (χ^2). We can see from the table, a small amount of Zn in BFO structure had reduced the lattice volume which causes an increase the lattice density. This condition indicated that some Zn with smaller atomic radii and smaller valence than Bi had replaced on its site and let a formation of $\text{Bi}_{25}\text{FeO}_{40}$ phase [7].

The 3D–imaging of the BFO modeling base on refinement result using Vesta Ver. 3.3.9 are shown in figure 2. The shifting of the atomic position as a caused of Zn doped was observed in the gray circle area (figure 2i). A change of tilt angle between Bi/Zn–O–Fe (figure 2ii) and O–O–O (figure 2iii) which correlated with the Bi/Zn–Fe (figure 2iv) distance position could be determined this shifting.

Table 2 had shown that Zn doped were decreasing the tilt angle of Bi/Zn1–O1–Fe1 bond and O1–O1–O1 bond followed by decreases of Bi/Zn–Fe distance position. In between $x = 0.05$ and $x = 0.1$ of the doping sample, we can see that the tilt angle of O1–O1–O1 bond has the same value, but the tilt angle of Bi/Zn1–O1–Fe1 bond becomes shrink with $\Delta\theta = 0.0008^\circ$. This condition was correlated with the increase of the BFO phase portion ration in the sample.

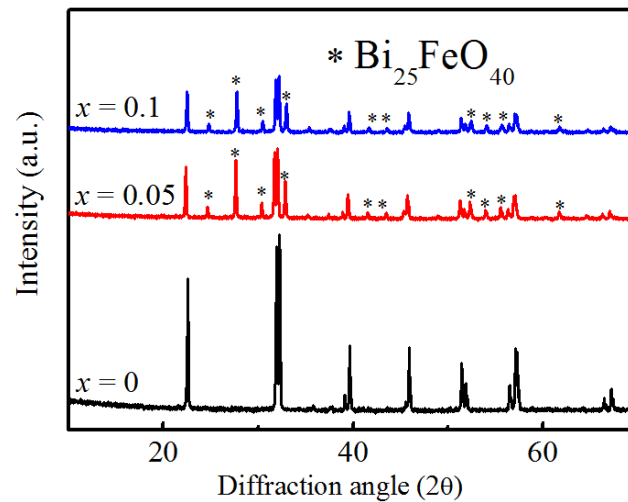


Figure 1. XRD pattern of $\text{Bi}_{1-x}\text{Zn}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1$) respectively prepared by sol-gel auto-combustion method. The Peak pattern shows BiFeO_3 phase at $x = 0$. When $x = 0.05$ and $x = 0.1$, the pattern of $\text{Bi}_{25}\text{FeO}_{40}$ phase clearly revealed.

Table 1. Rietveld refinement result of $\text{Bi}_{1-x}\text{Zn}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1$)

x	Parameter of BiFeO_3 s.g. R3c				Phase		Micro strain (%)	R_{wp} (%)	GOF (χ^2)
	$a=b$ (Å)	c (Å)	V (Å ³)	ρ (g cm ⁻³)	BiFeO_3 (%)	$\text{Bi}_{25}\text{FeO}_{40}$ (%)			
0	5.580	13.874	374.157	8.33	100	0	0.012	4.88	1.60
0.05	5.576	13.863	373.318	8.35	63.5	36.5	0.038	6.53	1.38
0.1	5.578	13.868	373.805	8.34	63.55	36.45	0.055	6.08	1.04
Cell parameters of $\text{Bi}_{25}\text{FeO}_{40}$ s.g. I23									
0.05	10.183		1055.758	9.31					
0.1	10.192		1058.661	9.28					

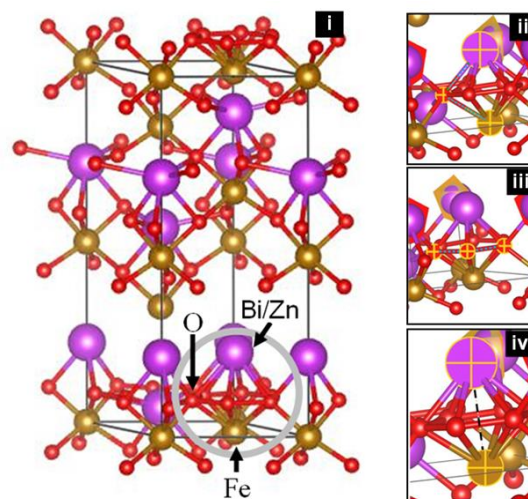


Figure 2. 3D modelling of BFO structure base on refinement result using Vesta Ver. 3.3.9 software. i) crystallite structure of BFO with a grey circle as an observed area, ii) Tilt angle of Bi/Zn-O-Fe , iii) Tilt angle of O-O-O , and iv) a distance of Bi/Zn-Fe displacement.

Table 2. Tilt angle (θ) of Bi/Zn–O–Fe bond, O–O–O bond and distance of Bi/Zn – Fe position

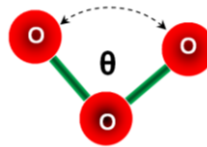
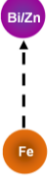
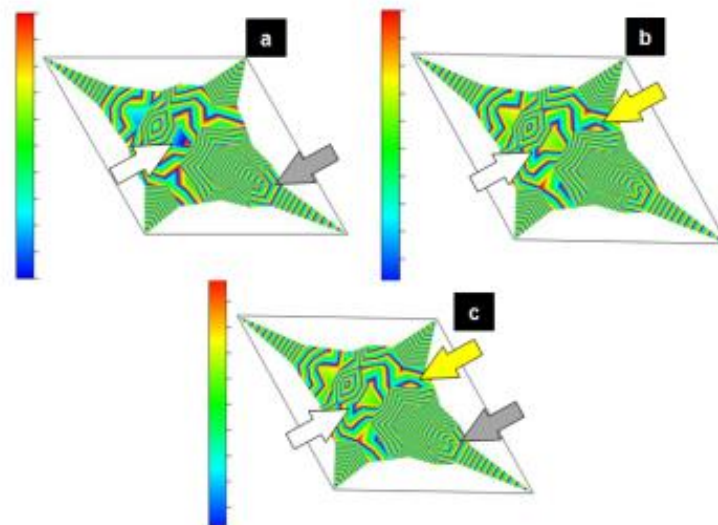
x	Tilt Angle ($^\circ$)		Distance ($\text{\AA}$)
			
	Bi1/Zn-O1-Fe1	O1-O1-O1	Bi1/Zn-Fe1
0	81.9961	132.8539	3.0588
0.05	82.7140	130.0406	3.0558
0.1	82.7132	130.0406	3.0573

Figure 3 shows electronic density of $\text{Bi}_{1-x}\text{Zn}_x\text{FeO}_3$ ($x=0, 0.05, 0.1$) on hkl -plane (0,0,0.2) at room temperature. When $x = 0$, we can see that the electron on the middle area (white arrow) was not too dense (figure 3a). The presence of Zn doped ($x = 0.05$) affected the increasing density on the middle area (white arrow) which followed by density alteration on the middle-right position (yellow arrow) (figure 3b). The increasing of Zn doped ($x = 0.1$) had caused a shifting density in the below corner position (grey arrow) (figure 3c). The change of electron density formation may govern its physical properties, especially in optical behavior.

**Figure 3.** An electronic density of $\text{Bi}_{1-x}\text{Zn}_x\text{FeO}_3$ for hkl -plane (0,0,0.2) at room temperature. a) $x=0$, b) $x=0.05$, c) $x=0.1$.

3.2. Optical characterizations

The optical property of Zn-doped BFO was studied by UV-Vis DRS absorption spectra. Figure 4 displays the UV-vis absorption results of $\text{Bi}_{1-x}\text{Zn}_x\text{FeO}_3$ ($x=0, 0.05, 0.1$). As seen in the figure, with the increasing concentration of Zn that the absorption slope is shifted toward the visible wavelength region as a green shift, in line with Liu et al. had reported [6]. This condition was also correlated with density change of electron inside of lattice structure. This matter indicated that the ability of BFO samples to absorb visible light increase with doping Zn. The result has shown that both samples have become a potential candidate for photonic applications.

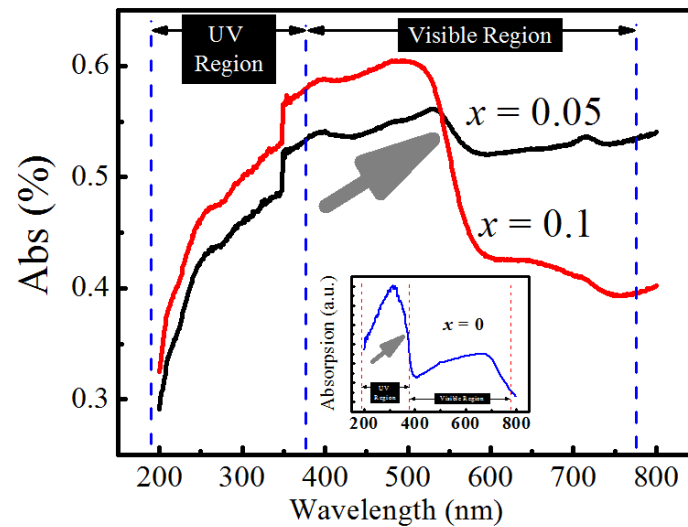


Figure 4. UV-Vis-DRS spectral of $\text{Bi}_{1-x}\text{Zn}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1$) at room temperature.

3.3. Dielectrical studies

The dielectric measurement of Zn – doped BFO was performed over frequency range 50 kHz – 2 MHz at room temperature. Figure 5 shows the frequency dependence of the relative permittivity or dielectric constant (ϵ_r) of $\text{Bi}_{1-x}\text{Zn}_x\text{FeO}_3$ at $x = 0, 0.05, 0.01$, respectively. Dielectric behavior was known as low frequency space–charge relaxation. As shown in the picture, the value of dielectric constant of $x = 0, 0.05$ have an identical value in frequency above 100 kHz, but splits below 100 kHz. Its correlated with the presence of some low electron density region in $x = 0$ [9]. The increasing of doping to $x = 0.1$ were raised the dielectric constant value which inline with the shifted of electron densities.

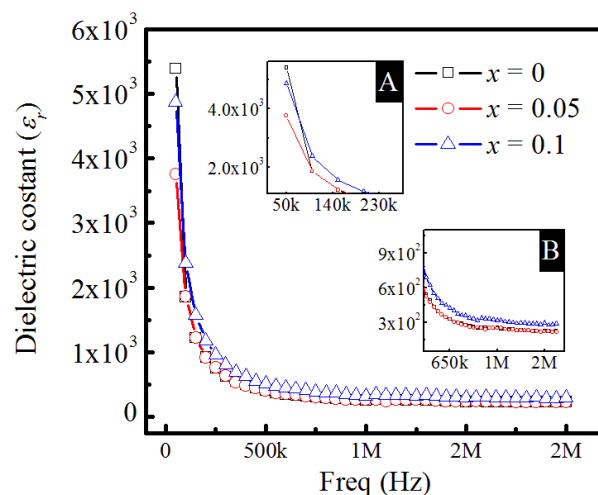


Figure 5. Dielectric constant as function of frequency for $\text{Bi}_{1-x}\text{Zn}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1$) at room temperature. inset: A) Freq. below 140 kHz, B) Freq. above 140 kHz.

4. Conclusion

The effect of Zn-doped BiFeO_3 for the Bi-site on the crystal structure, optical properties, and dielectric behavior has been studied. It has been found that the increasing value of Zn-doped had to change the structure and affected the electron densities formation. The optical absorption was shifted in line with the rising amount of dopant, as well as the dielectric constant which also increased. The

optical property of this material makes it becomes a potential candidate for visible light–photonic applications.

5. References

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