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Structural, non-volatile magnetization, and dielectric studies on zinc-doped BiFeO₃

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Abstract. We investigate the structure, non-volatile magnetization, and dielectric properties of zinc doped bismuth ferrite (Bi₁₋ₓZnxFeO₃; z = 0, 0.05, and 0.15) powder synthesized via sol-gel auto-combustion method. We have found that the doping of Zn induced the presence of Bi₂₅FeO₄₀ as a secondary phase and decreased the lattice parameter of bismuth ferrite (BFO) phase structure. Furthermore, the doping decreases the dielectric constant and increases the slope of magnetization and magnetic coercivity. The increase of magnetic coercivity value implies the increase of non-volatile magnetization properties.

1. Introduction

Bismuth ferrite (BiFeO₃, BFO) displays a broad range of interesting properties, including ferroelectric, magnetic, ferroelastic and electro-optical properties [1, 2]. Because of these phenomena, BFO is widely studied since its discovery. In recent years, a considerable interest has arisen in studying multiferroic properties of BFO [3]. BFO possesses a ferroelectric–antiferromagnetic property observed around room temperature (300 K) which has a ferroelectric transition temperature of 1100 K and an antiferromagnetic Néel temperature up to 640 K [4].

The increase of ferromagnetic properties arises as one of the main issues in developing BFO materials. It offers a new class of applications such as multi-stage data storage devices [1, 5]. Recently, low-dimensional BFO multiferroic nanostructures combined with site engineering capabilities present an improved ferromagnetic property compared to that of the bulk ones [6, 7]. It is also reported that the values of the dielectric constant of nanoparticle-doped BFO are much higher than those of the ceramics and thin films, [7–9]. In the case of the integration of doped BFO into its functional structures, it is crucial to investigate the stability of BFO and the possible parasitic phases on the magnetic properties [6]. For non-volatile memory devices applications, the presence of small magnetic coercivity may affect in the stability of magnetism. Consequently, the magnetic poles can easily change.

The effect of Zn doped BFO into Bi-site in the magnetic properties is rarely reported. Meanwhile, Liu et al. [10] found that Zn substitution on Fe-site had improved the magnetic saturation. In contrast, Xu et al. [11] found that Zn substitution on Fe-site made ferromagnetism in BFO vanished at room
temperature, where Zn-doping was responsible for the oxygen vacancies and the intervening in the Fe atom chains. However, doping Zn into Bi-site is also expected to improve its ferromagnetic properties and could change their dielectric properties.

Based on those facts, this research attempts to investigate the influence of Zn doped BFO on the enhancement of magnetic coercivity and the dielectric constant of BFO nano-powder for non-volatile magnetization while maintaining the entire structure of BFO. Following procedure of previous researches in producing nano-sized particle samples, sol-gel is chosen as the preparation method [4, 6, 10, 11].

2. Experimental Methods
Zinc doped bismuth ferrite ($\text{Bi}_{1-z}\text{Zn}_{z}\text{FeO}_3$; $z = 0, 0.05, 0.15$) powder were synthesized via low temperature sol–gel auto-combustion methods. In this method, bismuth nitrate ($\text{Bi(NO}_3\text{)}_3\cdot6\text{H}_2\text{O}$) and iron (III) nitrate ($\text{Fe(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}$) from Sigma–Aldrich, and zinc metal dissolved in nitric acid were used as precursor. All the precursors were prepared in a proportional composition according to the wt% fraction of $\text{BiFeO}_3$. The Citric acid as a chelating agent was added in 3:1 molar ratio with the metal ions. The mixture solution was stirring and heating at 80°C until it became viscous light brownish gel, followed by dried at 120°C for 24 h till become xerogel. Then, the xerogel was further ground and calcined at 600°C for 5 h.

The study of BFO phase structure were carried out by XRD with PANanalytical Diffractometer (X’Pert Pro, Cu-Kα, $\lambda = 1.5405$ Å) at room temperature. The crystal structure and the lattice parameters were refined using the HighScore Plus, based on the XRD results. The magnetic measurements were carried out using a vibrating sample magnetometer (VSM) over a magnetic field range from 0 – 14 kOe at room temperature ~27°C. 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 phases and the crystalline structures of the samples within the range of 20 = 20 – 70° were investigated by x-ray diffraction (XRD). The peak patterns of $\text{Bi}_{1-z}\text{Zn}_{z}\text{FeO}_3$ ($z = 0, 0.05, 0.15$) for the powdered samples were displayed in figure 1, and the parameter result of both phase structures were obtained in Table 1. It is clearly seen that the XRD patterns of the samples matches that of the BFO phase structure. The characteristic of $hkl$ peaks at (104) and (110) in between 20 = 31 – 32° were confirmed as the presence of rhombohedral (hexagonal) structure with space group (s.g.) $R\overline{3}c$ (ICSD 98-018-0501) [1, 6, 12]. The small amount of $\text{Bi}_3\text{FeO}_9$ with a cubic structure and s.g. $I23$ (ICSD 98-004-1937) have also been detected at $z = 0.05, 0.15$ as a secondary phases [13].

The occurrence of Zn in the structure has reduced the lattice parameter of BFO. Zn with smaller atomic radii and valence than Bi was used to replace the atomic position of Bi. This condition affects the decrease in BFO cell volume, and the atomic density becomes denser. With these results, it is suspected that the smaller atomic radii of Zn had induced the secondary phase [14].

3.2. Magnetic characterizations

The magnetic measurements at room temperature were performed to investigate the magnetic ordering in the doped BFO powdered samples. It is already known that in the bulk form, BFO possesses a G-type antiferromagnetic order with a low magnetic saturation. However, an enhancement of the magnetization by site engineering was reported [5, 7, 8].

The room temperature of the magnetization hysteresis loops of $\text{Bi}_{1-z}\text{Zn}_{z}\text{FeO}_3$ ($z = 0, 0.05, 0.15$) were taken and shown in figure 2. From the picture, we can see the presence of magnetic order implied by the presence of a hysteresis loop. The remnant magnetization of the two samples shows an identical value ($M_r = 0.019$ and 0.021 emu/g for $z = 0$ and 0.05). Further, an increasing doping value of Zn into $z$
0.15 has made the remanence and saturation values rise dramatically to more than eleven times ($M_r = 0.257$ emu/g), compared to $z = 0.05$. The increase of remanence value is not linear with the amount of Zn added. The coercivity was also increased by the doping of Zn (from $H_c = 105.39$ Oe at $z = 0$ to $H_c = 152.18$ Oe at $z = 0.05$). However, the increases of coercivity value at $z = 0.15$ ($H_c = 180.21$ Oe) has shown a little increment from the previous value of $z = 0.05$. This increment has made its magnetic properties becomes more non-volatile.

According to the XRD results, the presence of the secondary phases in the last two samples ($z = 0.05, 0.15$) had increased its magnetic saturation slope [15]. This slope exhibits the presence of antiferromagnetic phase that appears in between the ferromagnetic phases [16]. Therefore, the

![Figure 1](image)

Figure 1. XRD pattern of Bi$_{1-x}$Zn$_x$FeO$_3$ ($z = 0, 0.05, 0.15$) prepared by sol-gel auto-combustion method. The peak pattern shows BiFeO$_3$ phase at $z = 0$. Meanwhile for $z = 0.05$ and $z = 0.15$, the peak pattern of Bi$_{25}$FeO$_{40}$ is clearly seen.

| $z$ | Cell parameters of BiFeO$_3$ | Present phases | R$_{wp}$ (%) | GOF |
|-----|-----------------------------|----------------|-------------|-----|
|     | $a=b$ (Å) | $c$ (Å) | $V$ (Å$^3$) | $\rho$ (g cm$^{-3}$) | BiFeO$_3$ (%) | Bi$_{25}$FeO$_{40}$ (%) |            |
| 0   | 5.580 | 13.874 | 374.157 | 8.33 | 100 | 0 | 4.88 | 1.60 |
| 0.05| 5.576 | 13.863 | 373.318 | 8.35 | 63.5 | 36.5 | 6.53 | 1.38 |
| 0.15| 5.578 | 13.862 | 373.547 | 8.340 | 56.8 | 43.2 | 7.28 | 1.54 |

Table 1. Cell parameters, and Rietveld refinement of BiFeO$_3$ (s.g. $R3c$) in Bi$_{1-x}$Zn$_x$FeO$_3$ ($z=0, 0.05, 0.15$) refined structure after X-Ray Diffraction (ICSD 98-018-0501). In addition, cell parameters of Bi$_{25}$FeO$_{40}$ phase structure are also presented.

| $z$ | s.g. | $a=b=c$ (Å) | $V$ (Å$^3$) | $\rho$ (g cm$^{-3}$) |
|-----|------|-------------|-------------|---------------------|
| 0.05| $I23$ | 10.183 | 1055.758 | 9.310 |
| 0.15|       | 10.200 | 1061.176 | 9.260 |
increasing of remanence and saturation values which formed its magnetic properties were not affected by the existence of the secondary phases but were caused by Zn doping in the BFO structure.

3.3. Dielectric studies
The frequency dependence of the dielectric constant ($\varepsilon_r$) of $\text{Bi}_{1-z}\text{Zn}_z\text{FeO}_3$ ($z = 0, 0.05, 0.15$) at room temperature in the frequency range $50 \text{ kHz} – 2 \text{ MHz}$ shows in figure 3, respectively. From the figures, we can see that the decrease of $\varepsilon_r$ value with the increasing frequency exhibits the limitation change of polarization at a certain frequency rate. The dipoles of the sample can switch following the alternating electric field leading to an increase in total polarizability in the low-frequency region. Furthermore, when the frequency increases to the high-frequency region, the ability of dipoles to keep their orientation in alignment with the switching field at fast enough rates had decreased and hence a decrease in $\varepsilon_r$ values [2,17].

Below $100 \text{ kHz}$, the dispersion value of dielectric constant is decreasing from $\varepsilon_r = 5398.84$ for $z = 0$ to $\varepsilon_r = 3750.65$ for $z = 0.05$. Meanwhile, at $100 \text{ kHz}$ and above, the values of dielectric constant of both samples are similar ($\varepsilon_r = 1856.01$ for $z = 0$; and $\varepsilon_r = 1857.35$ for $z = 0.05$). The presence of Zn contained in the $z = 0.05$ sample which affects the density of BFO phase seems likely to decrease the dispersion of the dielectric constant [18].

![Figure 2](image.png)

**Figure 2.** Magnetic hysteresis curves of $\text{Bi}_{1-z}\text{Zn}_z\text{FeO}_3$ ($z = 0, 0.05, 0.15$) under $0 – 14 \text{ kOe}$ applied magnetic field at room temperature.
4. Conclusions
The effects of Zn-doped BFO on the structure, magnetic, and dielectric properties of the Bi$_{1-z}$Zn$_z$FeO$_3$ ($z = 0, 0.05, 0.15$) at room temperature have been studied. It was found that the lattice parameters of BFO are decreasing after the doping of Zn. The unit cell becomes denser which is caused by the presence of Bi$_{25}$FeO$_{40}$ as a secondary phase. Zn content has also induced the increase of magnetic saturation and the existence of antiferromagnetic phase which couples with the ferromagnetic ones. The increment of the coercivity value makes the ferromagnetism become more non-volatile. Furthermore, the doping of Zn makes the dielectric constant decreases at low-frequency values.

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References
[1] An J, Zhu L, Zhang Y and Tang H 2013 J. Environ. Sci. (China) 25 1213
[2] Pal J, Kumar S, Singh L, Singh M and Singh A 2017 J. Magn. Magn. Mater. 2017 441 339
[3] Liu Y, Qian Q, Yi Z, Zhang L, Min F and Zhang M 2013 Ceram. Int. 2013 39 8513
[4] Maria Č, Zagorac D, Batalovi K, Radakovi J, Stojadinovi B and Čebela M 2017 Ceram. Int. J. 43 1256
[5] Khomchenko VA, Paixão J A, Shvartsman V V, Borisov P, Kleemann W, Karpinsky D V., et al. 2010 Scr. Mater. 62 238
[6] Wu H, Xue P, Lu Y and Zhu X 2018 J. Alloys Compd. 731 471
[7] Gotardo R A M A M, Silva E F R F, R, Montanher D Z Z, Santos G M M, Silva K L, Cótica L F F, et al. 2017 Scr. Mater. 130 161

Figure 3. Dielectric constant as a function of frequency for Bi$_{1-z}$Zn$_z$FeO$_3$ ($z = 0, 0.05, 0.15$) at room temperature
[8] Bi L, Qingrong Y A O, Yihao S, Huaiying Z, Guanghui R A O. 2016 J. Rare Earths 34 396
[9] Khomchenko VA, Kiselev D A, Kopcewicz M, Maglione M, Shvartsman V V and Borisov P 2009 J. Magn. Magn. Mater. 321 1692
[10] Liu J, Deng H, Zhai X, Lin T, Meng X, Zhang Y, et al. 2014 Mater. Lett. 133 49
[11] Xu Q, Zai H, Wu D, Tang YK, Xu MX. 2009 J. Alloys Compd. 485 13
[12] Betancourt-Cantera L G, Bolarin-Miró A M, Cortés-escobedo C A, Hernández-Cruz L E, Sánchez-
De Jesús F. 2018 J. Magn. Magn. Mater. 2018 456 381
[13] De M, Hajra S, Tiwari R, Sahoo S, Choudhary R N P 2018 Ceram. Int. 44 11792
[14] Yao Q, Shen Y, Zhou H, Rao G, Deng J, Pan S. 2016 J. Rare Earths 34 396
[15] Kumar M, Yadav KL, Varma G D. 2008 Mater. Lett. 62 1159
[16] Zheng S, Wang J, Zhang J, Ge H, Chen Z, Gao Y F. 2018 J Alloys Compd. 735 945–9.
[17] Du Y, Cheng Z X, Shahbazi M, Collings EW, Dou S X, Wang X L. 2010 J. Alloys Compd. 490
637
[18] Lu J, Zhao H, Wu M, Lou X, Wu J. 2017 Mater. Des. 125 213
[19] Wang P, Cheng L, Zhang Y, Wu H, Hou Y, Yuan W, et al. 2017 Ceram. Int. 43 7424