Investigation on the effect of Zirconium doping on the structural and electrical properties of BiFe$_{1-x}$Zr$_x$O$_3$ with $x = 0.01$, 0.03 and 0.05

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Abstract. Multiferroic material was interesting because it has many potential applications in sensors, spintronic devices, actuators, memory devices, microelectronic devices, and convertors. Material multiferroic has two or more primary ferroic properties in the same phase. BiFeO$_3$ is a multiferroic material that has two ferroic properties such as antiferromagnetism and ferroelectricity. BiFe$_{1-x}$Zr$_x$O$_3$ with $x = 0.01$, 0.03 and 0.05 have been prepared by sol-gel method to study effect structural and electrical properties. X-ray diffraction result shows that all of the samples have a hexagonal structure with space group R3c and lattice parameter, volume, density increased when the concentration of zirconium increased. Zr-substitution caused the dielectric constant decrease when the concentration of Zr increases at a lower frequency.

Keywords: Bi(FeZr)O$_3$, sol-gel method, structural, electrical

1. Introduction
Multiferroic material is defined as two or more primary ferroic properties in the same phase, such as ferroelectricity, ferromagnetism, antiferromagnetism and ferroelastic. Two requirements are needed to make multiferroics. First is the coexistence of magnetic and electrical dipoles, and the second is a coupling between different order parameters and need violation and time inversion simultaneously [1]. Multiferroic BiFeO$_3$ (BFO) is one of the most important multiferroic materials, which shows two ferroic properties such as ferroelectric ($T_c$, Curie temperature 1103 K) and antiferromagnetism ($T_N$, transition temperature from anti-ferromagnetism to para-magnetism 643 K). BFO having distorted rhombohedral perovskite structure with space group R3c and single-phase multiferroic [2]. BFO has several problems include: (i) difficult to synthesis single phase, (ii) the leakage current is too high and (iii) the magnetic properties in BFO are very weak [3].

Several types of research have been reported for synthesized of BiFeO$_3$ doping Zirconium. Mukherjee et al. [4] reported that BiFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.0$ and 0.05), synthesized by the chemical solution decomposition method, exhibited dielectric constant decrease when the concentration of Zirconium increase. Mahajan et al. [5] reported BaTiO$_3$ doping Zirconium at Fe-site assigned dielectric constant increase from ~1675 to ~10586 with diffuse phase transition. Mukherjee et al. [3] reported BiFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.0, 0.05, 0.10$, and $0.15$) show two relaxation regimes for the undoped samples while doped samples show only one relaxation. Based on previous several reports, there is no report for synthesized BiFe$_{1-x}$Zr$_x$O$_3$ with a concentration of Zr = 0.01, 0.03 and 0.05 with the sol-gel method to investigate electrical properties and structural properties at room temperature.
2. Experimental

BiFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.01$, $0.03$ and $0.05$) were prepared by the sol-gel method using Bi(NO$_3$)$_3$.5H$_2$O, Fe(NO$_3$)$_3$.9H$_2$O, Cl$_2$H$_12$O$_9$Zr and citric acid monohydrate. All precursors were mixed in water until the gel phase was formed. The gel was dried at 120°C to remove water, citric acid, and other compounds. The sample heated at 700 °C for 3 hours the sample was pressed at 5 kN into bulk and sintered at 800 °C. Phase identification and impurity were characterized by X-ray diffraction with Cu Ka radiation ($\lambda=1.5405$ Å) in the range $2\theta = 20° – 90°$ with a step size of 0.02°/s. The chemical composition was checked by X-ray Fluorescence PANalytical with Ag (source energy 50 kV). Dielectric properties of BiFeZrO$_3$ were characterization using RLC-Meter-PM 6303 in a frequency range of 100 Hz–1 MHz at room temperature.

3. Results and discussion

3.1. Structural analysis

Figure 1 shows Le-bail fitting material BiFeO$_3$ doping Zr with concentration $x = 0.01$, $0.03$ and $0.05$. The Le-bail fitting plotted from database Crystallography Open Database (COD) such as BiFeO$_3$ with number 96-100-1091, Bi$_2$Fe$_4$O$_9$ with number 96-153-0919 and Bi$_{25}$FeO$_{40}$ with number 96-403. All samples have a hexagonal structure with space group R3c and have some peak impurity, such as Bi$_2$Fe$_4$O$_9$ and Bi$_{25}$FeO$_{40}$. This impurity because of the decomposition of BiFeO$_3$ at a temperature of 790–1040 K during the cooling process from the sintering process [6].

Table 1 shows the crystallographic of BiFeZrO$_3$ as-sintered at 800 °C for 3 hours. Based on table 1, the lattice parameter and volume increased when the concentration of Zr increased. The lattice parameter and volume increased because of ionic radii Zr$^{4+}$ (0.72 Å is greater than ionic radii Fe$^{3+}$ (0.65 Å) [7].

![Figure 1](image-url). Rietveld refinement of XRD patterns of BiFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.01$, $0.03$, and $0.05$) using Highscore Plus software. The experimental data are indicated by the black dots and the calculated data by the red solid line overlaying them, and blue bottom curves line shows the difference between experimental and calculated data.
The crystallite size decrease when concentration of Zr increased in the range of 76.22–71.04 nm. The reduction in crystallite size indicated the increase in lattice strain inside the lattice due to ionic size mismatch and consequently induced local structural disorder and reduction in nucleation rate [7]. The perovskite structure can be described by Goldschmidt’s tolerance factor (t) which is an indicator of stability and structure distortion in the sample following equation:

$$t = \left(\frac{r_{Bi} + r_{O}}{\sqrt{2}}\right)(1-x)r_{Fe} + x r_{Zr} + r_{O})$$

where $r_{Bi}$, $r_{Fe}$, $r_{Zr}$ and $r_{O}$ are the ionic radii of the Bi, Fe, Zr and O [6]. Tolerance factor (t) for BiFeO$_3$ doping Zr slight decrease with increasing concentration of Zr. Changes in t lead to distortions in BFZO structure and are expected to cause a change in Bi-O and Fe-O bond lengths and subsequently alter Fe-O-Fe angle [8]. According to the above relation, the tolerance factor (t) was found to be 0.8399, 0.8393 and 0.8386, indicating the distortion in the lattice parameter.

3.2. X-ray fluorescence

X-ray Fluorescence (XRF) was performed to knowing the elemental composition of BiFe$_{1-x}$Zr$_x$O$_3$. Based on table 2, weight experimental slightly difference with weight calculation. This difference is due to the measurement, synthesis, and limitations of XRD detecting elements with small atomic numbers. Table 3 shows a comparison between the atomic ratio experimental with atomic ratio calculation. It can see that slightly different values between experimental and calculation. It may be due to the synthesize process.

| Table 1. The crystallographic parameters of BiFe$_{1-x}$Zr$_x$O$_3$ (x = 0.01, 0.03 and 0.05). |
|-----------------|-----------------|-----------------|
| Structure parameter | x = 0.01 | x = 0.03 | x = 0.05 |
| Phase | Hexagonal | Hexagonal | Hexagonal |
| Space Group | R3c (161) | R3c (161) | R3c (161) |
| Lattice Parameter | | | |
| a (Å) | 5.581 | 5.582 | 5.583 |
| b (Å) | 5.581 | 5.582 | 5.583 |
| c (Å) | 13.879 | 13.874 | 13.873 |
| Volume (Å$^3$) | 373.879 | 374.298 | 375.031 |
| Crystallite Size (nm) | 76.22 | 72.80 | 71.04 |
| Density (g/cm$^3$) | 8.33 | 8.35 | 8.37 |
| R-Factor (%) | | | |
| Re | 4.470 | 4.946 | 4.837 |
| Rp | 4.441 | 5.092 | 5.015 |
| Rwp | 5.699 | 6.582 | 6.441 |
| (Goodness of fit) $\chi^2$ | 1.45 | 1.77 | 1.68 |
| Tolerance Factor (t) | 0.8399 | 0.8393 | 0.8386 |

| Table 2. XRF characterization results for BiFe$_{1-x}$Zr$_x$O$_3$ (x = 0.01, 0.03 and 0.05). |
|-----------------|-----------------|-----------------|
| BiFe$_{1-x}$Zr$_x$O$_3$ | (% weight experimental) | (% weight calculation) |
| Bi | Fe | Zr | Bi | Fe | Zr |
| x = 0.01 | 75.441 | 15.725 | 0.459 | 78.7272 | 20.9267 | 0.3452 |
| x = 0.03 | 79.106 | 17.5 | 1.235 | 78.5177 | 20.4491 | 1.03 |
| x = 0.05 | 78.955 | 17.219 | 2.039 | 78.3085 | 19.9742 | 1.717 |
3.3. Electrical properties.
Electrical properties for BiFe$_{1-x}$Zr$_x$O$_3$ using impedance spectroscopy. The measurement results are impedance ($Z$) and phase angles ($\phi$). The results of impedance measurements are plotted in the form of Nyquist plots and Bode plots. Figure 2a shows the Nyquist plot of BFZO at room temperature. It shows that the semicircle decreased with decreased concentration of zirconium and indicating impedance BFZO decrease when the concentration of Zr decreased. Figure 2b shows the Bode plot of BFZO, indicating impedance value increase with concentration Zr increase and impedance value increase when frequency decrease also impedance close to zero with high frequency. Figure 3a shows impedance real ($Z'$) as a function frequency at room temperature. Impedance real ($Z'$) value increase when the concentration of Zr increased and impedance real ($Z'$) close to zero when frequency $> 10^1$. Figure 3b shows impedance imaginary ($Z''$) as a function temperature. Impedance imaginary value ($Z''$) increase when the concentration of Zr increased and impedance imaginary ($Z''$) value close to zero when frequency $> 10^2$. The maximum peak for all samples indicated a relaxation mechanism at room temperature.

Figure 4a shows dielectric constant ($\varepsilon'$) of BFZO at room temperature as a frequency in the range 100 Hz–1 MHz. The value of dielectric constant decreases with concentration zirconium increase and shows relaxation at a lower frequency. The same result was also obtained by Mukherjee [3], BFZO shows relaxation can be due to the grain boundary condition. Figure 4b shows tan loss at room temperature of BiFe$_{1-x}$Zr$_x$O$_3$ with $x = 0.01, 0.03$ and $0.05$. Increasing tan loss is observed with an increase of Zr-doping can be due to decreased grain boundary resistance.

| BiFe$_{1-x}$Zr$_x$O$_3$ | Atomic ratio experimental | Atomic ratio calculation |
|-------------------------|---------------------------|-------------------------|
|                         | Bi  | Fe  | Zr  | Bi  | Fe  | Zr  |
| x = 0.01                | 1   | 0.776 | 0.01 | 1   | 0.99 | 0.01 |
| x = 0.03                | 1   | 0.82  | 0.03 | 1   | 0.97 | 0.03 |
| x = 0.05                | 1   | 0.813 | 0.049 | 1   | 0.95 | 0.05 |

Figure 2. (a) Nyquist plot and (b) Bode plot of BiFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.01, 0.03$ and $0.05$) at room temperature.
Figure 3. (a) Real and (b) Imaginary part of impedance as a function of frequency of BiFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.01, 0.03$ and $0.05$) at room temperature.

Figure 4. Frequency dependence on (a) Dielectric constant and (b) Dielectric loss of BiFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.01, 0.03$ and $0.05$) at room temperature.

4. Conclusion

BiFeO$_3$ doping Zr at Fe-site (BiFe$_{1-x}$Zr$_x$O$_3$, $x = 0.01, 0.03$ and $0.05$) have been successfully synthesized by sol-gel method. The XRD analysis confirms all samples show a hexagonal phase with space group $R3c$. Doping of Zr content increased lattice parameter, volume, and density when the concentration of Zr increased. And crystallite size decrease when the concentration of Zr increased. The dielectric constant value increased when the concentration of Zr increased.

Acknowledgments

This work was financially supported by Ministry of Research and Technology (KEMRISTEK/BRIN) Republic of Indonesia under research grant Hibah Penelitian Tesis Magister (PTM) 2020 with contract number NKB492/UN2.RST/HKP.05.00/2020.
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