The Influence of Li-doping on the Microwave Absorption Properties of BiFeO₃ Nanoparticles

Een Taryana,a, b  Bambang Soegijono,a, †  HA. Notonegoro,c  Dedi d

a Department of Physics, Universitas Indonesia, Depok 16424, Indonesia
b Department of Electrical Engineering, Universitas Jenderal Achmad Yani, Cimahi 40513, Indonesia
c Department of Mechanical Engineering, Universitas Sultan Ageng Tirtayasa, Cilegon 42435, Indonesia
d Indonesian Institute of Sciences, Research Centre for Electronics and Telecommunication, Bandung 40135, Indonesia

† Corresponding author: naufal@ui.ac.id

Received: 20 February, 2021; Accepted: 23 May, 2021; Published: 29 May, 2021

The microwave absorbers based on BiFeO₃ have been widely used in the microwave absorbing region due to their excellent electromagnetic characteristics and properties. This study investigated the Li doping effect on the structure, magnetic properties, and microwave absorption efficiency of Bi₁₋ₓLiₓFeO₃ nanoparticles (x = 0.02, 0.04, and 0.06), which were created using the sol-gel method. The test results showed that the increase in the Li doping concentration affects the ferromagnetic properties of the material. The highest magnetic properties were obtained at a concentration of x = 0.06. The magnetic saturation value $M_s = 5.4 \text{ emu g}^{-1}$, the magnetic remanence value $M_r = 1.53 \text{ emu g}^{-1}$, and the coercive field $H_c = 106.73 \text{ Oe}$ were obtained from the concentration x = 0.06. The doping of x = 0.06 produced three absorption peaks, and the highest absorption peak was $-46 \text{ dB}$ at 11.22 GHz. To identify the microstructures and electromagnetic properties of the preliminary samples, X-ray diffraction, scanning electron microscopy, and vector network analysis studies were performed. The results showed that Bi₁₋ₓLiₓFeO₃ nanoparticles were successfully collected and that the prepared samples had excellent absorption properties. Overall, due to their outstanding microwave absorption efficiency, Bi₁₋ₓLiₓFeO₃ nanoparticles have numerous potential applications.

Keywords BiFeO₃; Li doping; Magnetic properties; Reflection loss

I. INTRODUCTION

Today, the use of electromagnetic waves has expanded to multiple fields, including telecommunications, military applications, and civilian projects. The rapid increase in the quantity of use and the propensity of the shift frequency to the domain of gigahertz (GHz) also contribute to the increase in electromagnetic interference (EMI). The presence of EMI negatively affects the performance of the devices that use microwaves, such as medical devices, wireless devices, radar systems, satellite communication systems, and antennas. The use of absorbing materials with variable absorption frequencies is considered as an effective method for fighting the effects of EMI. Information and communication technology production impacts the growing use of microwave frequencies within the 8–12 GHz (X-band) range [1]. This leads to microwave emissions that continue to increase all the time, so scientists have to create materials that can withstand this radiation.

Microwave absorbing materials are among the most powerful ways that are used for minimizing radiation [2]. Microwave absorbers is dependent the existence of permeability and permittivity. The reflection and attenuation characteristics of the investigated material are determined by the complex permeability and permittivity of the constituent material of microwave absorbers [3].

BiFeO₃ (BFO) is a multiferroic substance that is capable of operating simultaneously as a ferroelectric and ferromagnetic material [4]. BFO is a ferroelectric material with a perovskite structure ABO₃ and G-type antiferromagnetic. This material has high Curie temperature ($T_c \approx 830^\circ\text{C}$) [5] and Néel temperature ($T_N \approx 370^\circ\text{C}$) [6]. In this material, the interaction shapes of the electric and magnetic fields influence on the magnetic effect, which is an extremely interest-
ing investigation topic. This effect allows electric and magnetic fields to be regulated by the material’s magnetic and electrical properties [7], leading to the development of ferromagnetic, ferroelectric, and piezoelectrical characteristics.

BFO, which has ferroelectric and ferromagnetic effects at room temperature, has been widely investigated as a microwave absorbent material. Intensive research has been performed to make the microwave absorption more powerful. Engineering the properties of BFO is generally done by doping. With doping in Bi and Fe elements, the characteristics of BFO change. As engineering efforts are made for better properties and the EM absorbing application, the option of doping elements into BFO was performed. The doping for Bi is elements that have 3+ ions (La, Nd, Y) and 2+ ions (Ca, Ba, Sr) [8], and doping for Fe are metallic transition elements such as Cr, Zn, Mn, Ti, and Zr [9].

The conducted research has shown that doping in BFO improves the absorption value of microwave absorbers. For example, Li et al. [10] studied BFO doped with Ca, where the bandwidth increased to be 3.4 GHz in X-band frequency. Furthermore, Li et al. [11] studied La-substituted BFO and found that the resulting minimum reflection loss (RL) increased from −12 to −30 dB at a frequency of 11.5 GHz. The doping of other elements, such as Ba, Mn, Zn, Nd, Y, and Gd on BFO, was also performed. It increased the magnetic and electrical properties, further enhanced their RL compared with undoped BFO [12–17].

In this research, we observed the magnetic properties and microwave absorption of BFO after Li doping. We conducted the present experiment with the aim of obtaining better microwave absorbing materials. The synthesis process was performed using the sol-gel method. This method was chosen to have better homogeneity in low temperature and produce nano-sized particles so that resulting in energy saving.

II. EXPERIMENT

In a sol-gel process, Bi$_{1-x}$Li$_x$FeO$_3$ (for $x = 0.02$, 0.04, and 0.06) was synthesized. All the reagents were procured and used without further purification with ultra-high purity bismuth nitrate pentahydrate, Bi(NO$_3$)$_3$·5H$_2$O, and lithium acetate dihydrate, CH$_3$COO$\cdot$2H$_2$O, dissolved in deionized water. A HNO$_3$ solution was placed in a beaker. In another beaker, iron nitrate nonahydrate, Fe(NO$_3$)$_3$·9H$_2$O, was dissolved in deionized water. Both solutions were mixed under continuous magnetic stirring. Tartaric acid was applied to the homogeneous precursor solution as a chelating agent, and the resulting solution was continually stirred and heated to approximately 80°C until a viscous gel was formed. The obtained gel was dried overnight, preheated to 400°C, and then thoroughly ground with a mortar and a pestle. The resulting powder was annealed at 600°C for four hours to acquire a fine crystalline substance.

The Bi$_{1-x}$Li$_x$FeO$_3$ ($x = 0.02$, 0.04, 0.06) structure was defined at room temperature using X-ray diffraction (XRD) (D-8 Advance, Bruker, with Cu Ka$_1$, $\lambda = 1.5405$ Å). The magnetic properties of the tablet samples were tested using Permagraph C (Magnet Physik). Morphology and the elemental composition of the samples were characterized by a scanning electron microscope and an energy dispersive spectrometer (JEOL), respectively. Dielectric constants were tested with an LCR meter (Fluke, PM 6306). The microwave absorbing behavior was then measured in the X-band frequency using a vector network analyzer (Advantech).

III. RESULTS AND DISCUSSION

A. Phase analysis

Figure 1(a) displays the XRD spectrum of the Li-doped BFO nanoparticles. The samples exhibited the BFO phase as shown by the rhombohedral crystal structure and $R3c$ space group, according to the reference of Crystallography Open Database No. 96-210-2910, and similar with previous reported [17–19]. The diffraction peaks of the samples shifted toward the lower angle area at a wide concentration of $x$ (0.02 and 0.04) and shifted to the higher angle on $x = 0.06$ as shown in Figure 1(b), which is consistent with the previous study [18].

Crystal structures by Rietveld analysis for three variations of the Li-doping BFO samples are shown in Table 1. It can be seen that the lattice parameters of Li-doping BFO have changed. The position of the Li atom in the BFO structure was identified by inserting the Li atom and its site occupancy in the Bi position using Rietveld analysis. The position of the Li atom is shown in Table 2. There is a shift of the O atom following the shift of the Fe atom. As a result of this Li doping, the Bi atom position shifted in the z-axis direction.

![Figure 1: (a) XRD patterns of Bi$_{1-x}$Li$_x$FeO$_3$. (b) An enlarged diffraction peak between 22° and 23°.](image-url)
Addition of Li to BFO reduced the Fe–O–Fe bond angle and increased the Bi/Li–O–Bi/Li bond angle. Of course, this can increase the magnetic properties of the material due to the antiferromagnetic moment of Fe$^{3+}$, which is less collinear [18]. Generally, the Fe–O bonds are elongated, in contrast to the Bi–O bonds, which are shortened. The increase in the Fe–O bond length was expected to increase the ability of relaxing the charge. The Li doping also led to changes in the lattice parameters, and the increase in the Li concentration tended to increase lattice parameter values.

B. Morphological analysis

Figure 2 shows field-emission scanning electron microscopy images of the undoped BFO sample. The particles in the BFO phase are seen to stay together for the branched-chain formations, such as coral [Figure 2(a)]. The particles have various sizes, approximately ~152 nm in diameter, and some particles were agglomerated to form chunks [Figure 2(b)]. The sample size is still more extensive than the length of the cycloid antiferromagnetic range so that it cannot contribute to the increase in its ferromagnetic properties.

Figure 3(a) shows a microstructure for the Bi$_{0.94}$Li$_{0.06}$FeO$_3$ sample. The BFO particles experienced agglomeration (a white arrow) with the variation in the lump size. The agglomerates are composed of small particle grains. Some of them are 70 nm in size but are still larger than the antiferromagnetic cycloid BFO formation (> 64 nm), as shown in Figure 3(b). This indicates that the resulting particle size could not affect the increase in the magnetic properties of the Li-doped BFO samples, however, the increase in the magnetic properties was more influenced by the Li doping concentration itself.

C. Magnetic properties

The magnetic properties of the Li-doped BFO samples in the Bi$_{1−x}$Li$_x$FeO$_3$ composition system ($x$ = 0.02, 0.04, 0.06)

| Crystal System  | $x = 0$   | $x = 0.02$ | $x = 0.04$ | $x = 0.06$ |
|-----------------|-----------|------------|------------|------------|
| Space Group     | $R3c$     | $R3c$      | $R3c$      | $R3c$      |
| Phase Contribution (%) | 100       | 100        | 100        | 100        |
| $a$ (Å)         | 5.5791    | 5.5793     | 5.5785     | 5.5795     |
| $b$ (Å)         | 5.5791    | 5.5793     | 5.5785     | 5.5795     |
| $c$ (Å)         | 13.8694   | 13.8723    | 13.8711    | 13.8731    |
| Volume (Å$^3$)  | 373.3727  | 373.965    | 373.828    | 374.017    |

| Bond Angle      | $156.7$   | $154.7$    | $154.3$    | $154.7$    |
| Bi/Li–O–Bi/Li  | $109.0$   | $111.8$    | $111.6$    | $111.8$    |
| Bi/Li–O–Fe     | $102.7$   | $105.2$    | $105.0$    | $105.2$    |

| Bond Distance   | $1.675$   | $1.693$    | $1.693$    | $1.694$    |
| O–O (1) (Å)     | $1.612$   | $1.621$    | $1.620$    | $1.621$    |
| O–O (2) (Å)     | $2.099$   | $2.101$    | $2.257$    | $2.247$    |
| Fe–O (1) (Å)    | $1.945$   | $1.962$    | $2.112$    | $2.101$    |
| Fe–O (2) (Å)    | $2.598$   | $2.529$    | $2.527$    | $2.529$    |
| Bi/Li–O (1) (Å) | $2.234$   | $2.256$    | $2.262$    | $2.256$    |
| Bi/Li–O (2) (Å) | $3.07$    | $3.052$    | $3.077$    | $3.052$    |
are shown in Figure 4(a). The increase in the Li concentration in the BFO structure increased the ferromagnetic properties because of the smaller Fe−O−Fe angle (Table 1) and the shift in the O atom position. The decrease in the magnetic saturation value \( M_s \) at \( x = 0.04 \), which was lower than that at \( x = 0.02 \), was due to the decrease in the position of the Fe atom along the z-axis in the BFO structure (Table 2).

The magnitude of the increase in the magnetization value of the Li-doped BFO can be seen in Table 3. The increase in the Li doping concentration also led to an increase in the values of \( M_s, M_r, \) and \( H_c \), which represent the magnetic saturation value, the magnetic remanence value, and the coercive field, respectively, as shown in Figure 4(b). The O−O and Fe−O bond extensions accordingly contributed to the increased magnetic properties \([19]\). The magnetic characteristics could be improved due to fluctuation in the ion oxidation valence and the changes in the crystal structure by the Li doping.

**Table 2: Positions of the atoms in the Li-doped BFO structure.**

| Li \( x \) | Atom | Wyckoff position | s.o.f.\(^a\) | \( x \) | \( y \) | \( z \) | B \(^b\)/10^4 pm^2 |
|---|---|---|---|---|---|---|---|
| 0 | O | 18b | 1 | 0.1 | 0.311 | 0.093 | 0.2 |
|   | Fe | 6a | 1 | 0 | 0 | −0.011 | 0.68 |
|   | Bi | 6a | 1 | 0 | 0 | 0.210 | 1 |
| 0.02 | O | 18b | 1 | 0.093 | 0.313 | 0.102 | 0.5 |
|   | Fe | 6a | 1 | 0 | 0 | 0 | 0.5 |
|   | Bi | 6a | 0.98 | 0 | 0 | 0.221 | 0.5 |
|   | Li | 6a | 0.02 | 0 | 0 | 0.221 | 0.5 |
| 0.04 | O | 18b | 1 | 0.093 | 0.313 | 0.102 | 0.5 |
|   | Fe | 6a | 1 | 0 | 0 | −0.001(9) | 0.5 |
|   | Bi | 6a | 0.96 | 0 | 0 | 0.221(9) | 0.5 |
|   | Li | 6a | 0.04 | 0 | 0 | 0.221 | 0.5 |
| 0.06 | O | 18b | 1 | 0.093 | 0.313 | 0.102 | 0.5 |
|   | Fe | 6a | 1 | 0 | 0 | 0 | 0.5 |
|   | Bi | 6a | 0.94 | 0 | 0 | 0.221 | 0.5 |
|   | Li | 6a | 0.06 | 0 | 0 | 0.221 | 0.5 |

\(^a\) Site-occupancy factors.

\(^b\) Isotropic displacement parameter.
D. Microwave absorption characteristic

Microwave absorption is a process in which wave energy is attenuated. Energy is generated by a substance and then converted into other forms of energy. Therefore, this energy does travel through the material. The RL is a measured common unit for representing microwave absorption performance. The material’s absorption efficiency expressed in decibels (dB), where a material which has an absorption level with less reflection and a more negative RL, shows more significant absorption. The absorption value reflects how much energy is lost in the microwave absorption process. To evaluate the RL, the absorbing layers placed on an ideal metal plane [20, 21]. The transmission line theory, which quantifies in the usual case of an incidence wave, the layer can be defined as

\[
\text{RL} = 20 \log \left( \frac{Z_{\text{in}} - 1}{Z_{\text{in}} + 1} \right),
\]

where the normalized input impedance \(Z_{\text{in}}\) of an absorption layer can be defined as

\[
Z_{\text{in}} = \frac{\mu_r}{\varepsilon_r} \tanh \left( j \frac{2\pi}{c} \sqrt{\mu_r \varepsilon_r} f d \right)
\]

where \(\mu_r\) and \(\varepsilon_r\) are the relative permeability and permittivity of the samples, respectively, \(j\) is an imaginary number, \(c\) is the speed of light, \(f\) is the microwave frequency, and \(d\) is the thickness of the absorber.

Figure 5 shows the reflection loss in the 8–12 GHz range for the Bi\(_{1-x}\)Li\(_x\)FeO\(_3\) sample with a layer thickness of 2 mm. It can be seen that the increase in the Li doping level can improve the microwave absorption effect. Li doping with \(x = 0.02\) produced three absorption peaks of \(\leq -10\) dB [22], and they are approximately \(-15, -31.3,\) and \(-31.3\) dB at 9.6, 9.9, and 11.62 GHz, respectively. That with \(x = 0.04\) only produced two peaks, and they are approximately \(-34.05\) and \(-15.5\) dB at 9.9 and 11.52 GHz, respectively. For \(x = 0.06\), the absorption peaks are approximately \(-16.9, -46,\) and \(-21.4\) dB at 9.9, 10.08, and 11.22 GHz, respectively. This is due to the increased electromagnetic match caused by the higher magnetization [23].

The results of the dielectric relaxation measurements for the Li-doped BFO samples based on the relative dielectric permittivity value \(\varepsilon'\) in the frequency range between 100 kHz and 1 MHz are shown in Figure 6. In the sample with \(x = 0.02\) and 0.04, the curve \(\varepsilon'\) exponentially decreased as the frequency increased (the inset of Figure 6). At \(x = 0.06\), the value of \(\varepsilon'\) continued to increase with the increase of the frequency. The Li doping at \(x = 0.06\) enhanced the relaxation ability of the charge in the sample. Its dielectric constant at the frequency of 100 kHz was still higher, thus contributing to the increase in the RL (dB) values of Bi\(_{1-x}\)Li\(_x\)FeO\(_3\) \((x = 0.02, 0.04, 0.06)\) in our results, as the RL value is directly proportional to \(\varepsilon_r\), which is in line with Eqs. (1) and (2).

**IV. CONCLUSION**

In this study, the composition system \((x = 0.02, 0.04, 0.06)\) of Bi\(_{1-x}\)Li\(_x\)FeO\(_3\) was synthesized using the sol-gel process. The increase in the concentration of Li doping led to magnetic saturation and magnetic remanence and caused the coercive field values to increase. Therefore, doping Li on the Bi sites was found to be a very effective strategy for simultaneously improving both ferromagnetic and electrical behaviors. For \(x = 0.02\) and 0.06, three absorption peaks were produced by Li doping, while the sample with \(x = 0.04\) produced two absorption peaks. The Bi\(_{1-x}\)Li\(_x\)FeO\(_3\) sample

![Figure 5](image1.png)  
**Figure 5:** Reflection loss (RL) of Bi\(_{1-x}\)Li\(_x\)FeO\(_3\).

![Figure 6](image2.png)  
**Figure 6:** Relative permittivity \(\varepsilon'\) of the Bi\(_{1-x}\)Li\(_x\)FeO\(_3\) samples.
with $x = 0.06$ reached the minimum RL value of $-46$ dB at 11.22 GHz at a thickness of 2.0 mm.

Acknowledgments

We acknowledge the financial support and research facilities granted by Hibah Penelitian Disertasi Doktor No: NKB-3001/UN2. RST/HKP.05.00/2020 from the Ministry of Research, Technology, and Higher Education of Indonesia (RIST EK-DIKTI), and the authors would like to thank Research Unit for Clean Technology and Research Center for Electronics and Telecommunication for providing instrument facilities.

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