

The effect of Doping of La^{3+} Ions on Multiferroic $\text{Bi}_{2-x}\text{La}_x\text{Fe}_4\text{O}_9$ ($x = 0; 0.2; 0.5; 1.0$) as Microwave Absorber

Yohanes Edi Gunanto*¹ and Wisnu Ari Adi²

¹Department of Physics Education, University of Pelita Harapan Karawaci, Tangerang 15811, Indonesia

²Center for Advanced Materials Science and Technology, Kawasan Puspittek Serpong Tangerang Selatan 15314, Indonesia

Abstract: The synthesis and characterization of $\text{Bi}_{2-x}\text{La}_x\text{Fe}_4\text{O}_9$ multiferroic material ($x = 0; 0.2; 0.5; 1$) have been used as microwave absorbers. $\text{Bi}_{2-x}\text{La}_x\text{Fe}_4\text{O}_9$ ($x = 0; 0.2; 0.5; 1$) material was made by solid state reaction with mechanical milling technique using high energy milling (HEM). X-ray diffraction (XRD) was used for characterization of formation phase and crystal structure, scanning electron microscopy-energy dispersive spectra (SEM-EDS) was used to characterize surface morphology and particle size, whereas vector network analysis (VNA) was used for characterization of absorption capability microwaves. The characterization results showed that all samples were in phase with orthorhombic crystal structure, Pbam space group. The average particle size was 578.5 nm with an almost homogeneous form. Meanwhile, the best sample in absorbing microwaves was obtained for $x = 0.2$ with reflection loss value (RL) around -21dB at 11.2 GHz frequency.

Keywords: crystal structure; microwave absorption; multiferroic; reflection loss.

*Corresponding author: yohanes.gunanto@uph.edu

<http://dx.doi.org/10.12962/j24604682.v16i2.5739>

2460-4682 ©Departemen Fisika, FSAD-ITS

I. INTRODUCTION

Multiferroic material was a compound exhibiting ferroic or antiferroic properties, such as ferromagnetic and ferroelectric in a single phase. In other words the multiferroic materials here have ferroelectric (antiferroelectric) and ferromagnetic (antiferromagnetic) properties which are also called magnetoelectric materials. Many researchers are interested in this multiferroic material, one of which is BiFeO_3 . This is due to its properties, namely its magnetization and dielectric at room temperature so that the material is highly applicable to sensors, data recorders or as microwave absorber [1-4]. To increase its ability, doping can be done on Bi atoms with La and or Nd [2, 5] or by doping Zn [3].

Recently, $\text{Bi}_2\text{Fe}_4\text{O}_9$ multiferroic material without doping [6-9], which was doped in Fe ($\text{Bi}_2\text{Fe}_{3.6}\text{Me}_{0.4}\text{O}_9$, where Me = Al or Ti) or doping position at Bi and Fe ($\text{Bi}_{2(1-x)}\text{Ho}_{2x}\text{Fe}_{4(1-y)}\text{Co}_{4y}\text{O}_9$) was developed [11]. The purpose of doping is to improve its ability as a photocatalyst [10] and also to increase its magnetodielectricity [11]. Several methods have been employed in preparing the $\text{Bi}_2\text{Fe}_4\text{O}_9$ sample, among others, using ethylenediaminetetraacetic (EDTA) [6], growth in p-type Si [8], polyol-mediated [9], modified Pechini [10], and solid state reaction [11]. From some of these studies, the crystal structure of $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_2\text{Fe}_{3.6}\text{Me}_{0.4}\text{O}_9$ was orthorhombic, except for $\text{Bi}_{2(1-x)}\text{Ho}_{2x}\text{Fe}_{4(1-y)}\text{Co}_{4y}\text{O}_9$ with x and y = 0.2 having rhombohedral structure. This is still a discussion for future possible research.

From several studies that have been carried out, the effect of supporting La^{3+} ions in addition to affecting the value of lattice parameters and microstructure can also increase its ability to absorb microwaves. But there are still differences in the magnetic saturation and coercivity values. J. J. Xu et al. [12] found that La^{3+} ion doping would increase magnetization and decrease coercivity, whereas X. Ren et al. [13] obtained the opposite results, both magnetization saturation (M_s) and coercivity (H_c), both of which will decrease due to the La^{3+} ion doping. This difference shows that there are still contradictions so it is interesting to discuss further.

In this research, multiferroic sampling $\text{Bi}_{2-x}\text{La}_x\text{Fe}_4\text{O}_9$ ($x = 0; 0.2; 0.5; \text{ and } 1.0$) was done by solid reaction method using high energy milling (HEM). We wanted to know the effect of La^{3+} ionic coating on crystal structure and its ability to absorb microwaves.

II. EXPERIMENT

With stoichiometric calculations, the $\text{Bi}_{2-x}\text{La}_x\text{Fe}_4\text{O}_9$ sample was prepared from a mixture of three raw materials Bi_2O_3 , Fe_2O_3 and La_2O_3 each with a purity of > 99%. Then the sample was milled with high energy milling (HEM) 1000 rpm for 5 hours then sintered at 800°C for 5 hours. The characterization of crystalline structures X-Ray Diffraction (XRD) type PAN analytical with Cu-K ($\lambda = 1,5406 \text{ \AA}$) was used. Moreover, SEM-EDS was used to characterize surface morphology, while for characterization of sample absorption proper-

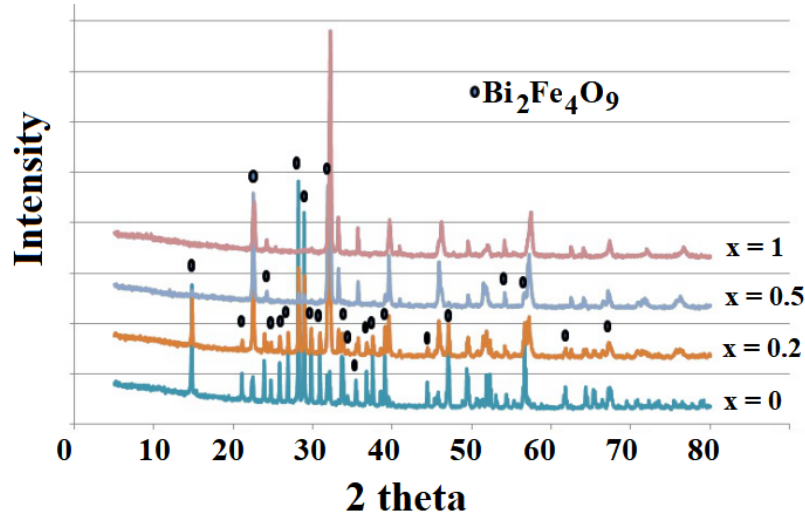


FIG. 1: Phase Diffraction Pattern $\text{Bi}_{2-x}\text{La}_x\text{Fe}_4\text{O}_9$ ($x = 0; 0.2; 0.5$ and 1.0).

TABLE I: Reflection loss (RL) for $\text{Bi}_{2-x}\text{La}_x\text{Fe}_4\text{O}_9$ samples with variation of x value.

x	RL (dB)	Freq. (GHz)
0	-20	10.9
0.2	-21	11.2
0.5	-18	11.0
1.0	-19	11.2

ties against microwaves, vector network analysis (VNA) was used. Specifically, for testing samples using VNA, the sample is prepared in the form of a compacted powder on top of the VNA holder that matches the X-band adapter (8-12 GHz).

III. RESULTS AND DISCUSSION

The result of X-ray diffraction pattern measurement can be seen in Fig.1. The refinement process was done by using GSAS program (*General Structure Analysis System*). The results can be seen in Fig.2. All samples indicated that they had not formed a single phase of $\text{Bi}_{2-x}\text{La}_x\text{Fe}_4\text{O}_9$, but there were still other phases detected, namely BiFeO_3 . Our guess is that the low sintering temperature is the cause of the incomplete phase formation. Samples without doping ($x = 0$) as well as with doping La ($x = 0.2, 0.5$, and 1) crystal structure are unchanged, i.e. remain orthorhombic with space group Pbam. Similar results are also obtained by some researchers [6-11], except for $\text{Bi}_{1.96}\text{Ho}_{0.04}\text{Fe}_{3.92}\text{Co}_{0.08}\text{O}_9$ which has a rhombohedral structure [11]. $\text{Ba}_2\text{Fe}_4\text{O}_9$ phase will be formed if the heating is greater than 600°C . With rising heating temperatures, the peaks of XRD patterns become higher and sharper. This causes the particle size to increase. Therefore to reduce particle size can be done by increasing the energy of milling [14].

Surface morphology can be seen in Fig.3. The shape of the particles is still heterogeneous with a size between 150-500 nm. The results are not much different obtained by J. Zhao *et al.*, with a heating temperature of 700°C , the average particle size ranges from 200-450 nm [7]. As the heating temperature increases, the average particle size will rise from 1-2 nm to sinter 850°C , to 5-10 nm for sinter 880°C [1].

VNA measurements were performed to characterize the absorbance properties of materials against microwaves. Microwave absorption in the sample can be seen based on the reflection loss value, the greater the negative value of reflection loss (RL) the greater the absorption of material to microwave. The result of characterization with VNA can be seen in Fig.4. The sample with doping $x = 0.2$ has the largest reflection loss (RL) value, which is about -21 dB at 11.2 GHz frequency. The full results of the characterization of VNA can be seen in Table 1. The La^{3+} ion doping does not necessarily increase the ability to increase microwave absorption (RL). Only the value of $x = 0.2$ will increase the value of RL, while for $x = 0.5$ and 1.0 it will actually reduce the value of RL. This shows the maximum value of La^{3+} in increasing the RL value. The addition of La^{3+} ions up to 0.2 causes an increase in magnetic saturation and decreases coercivity so that the material is soft magnetism which results in the material being a good microwave absorber [12]. The value of $x = 0.2$ is the optimal value, because the excessive addition of La^{3+} ions ($x = 0.5$ and 1.0) decreases the ability to absorb microwaves due to magnetic saturation and coercivity, both of which decrease [13].

Microwave absorption of the material depends on the density of the material which is the amount of material (thickness). Our estimation is the more dense the material created, the greater absorption possibility is. This is as a result of close or dense distance between the grains in the material. Likewise, the material thickness affects the absorption that the possibility of power to be reflected in the material leads to smaller transmitted power. With a particle size of about 100-130 nm

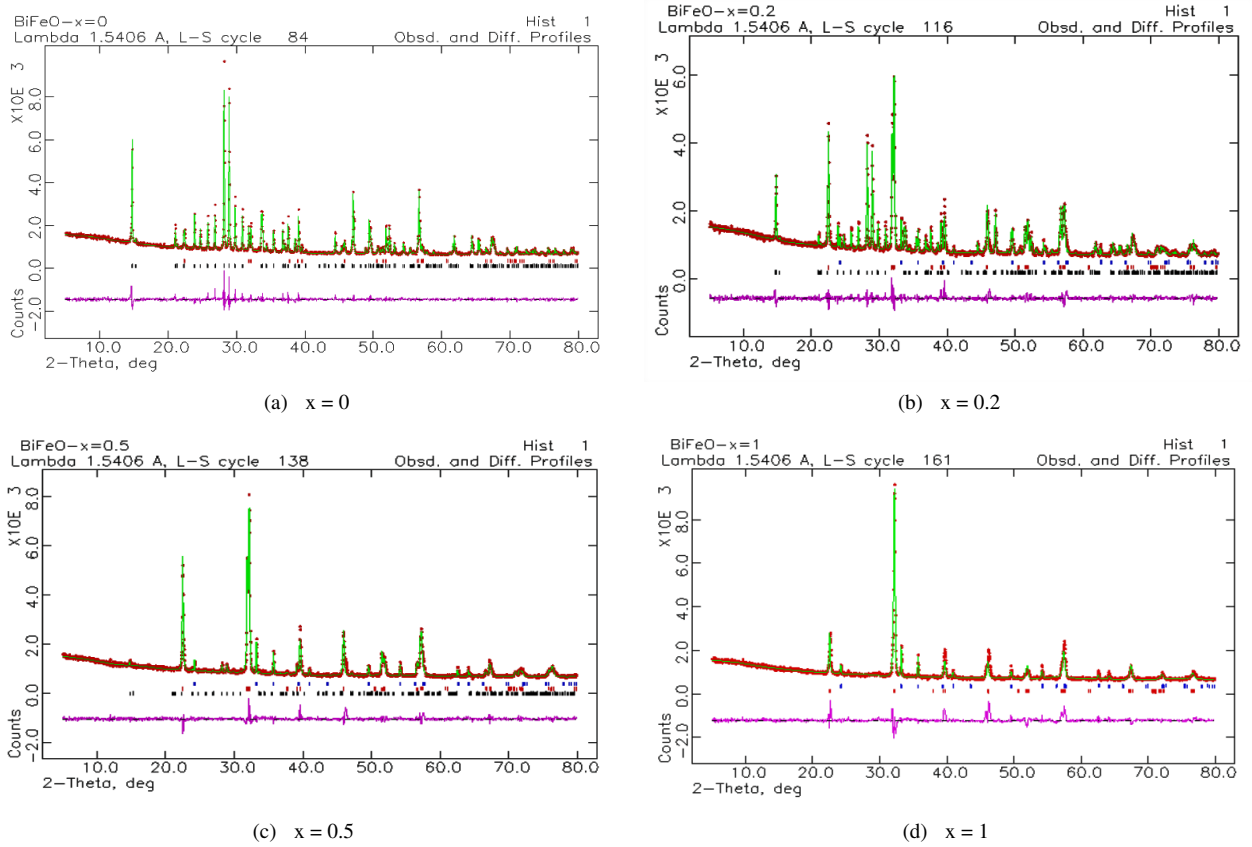


FIG. 2: Result of refinement with GSAS program for $x = 0; 0.2; 0.5; \text{ and } 1.0$.

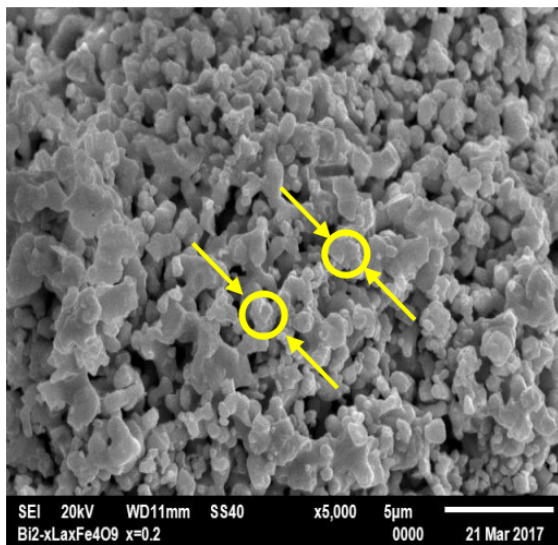


FIG. 3: Grain morphology for $x = 1.0$ using SEM.

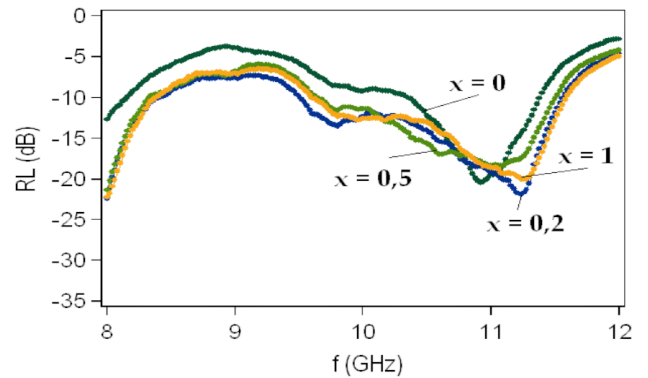


FIG. 4: The reflection loss curve as a frequency function for the sample $\text{Bi}_{2-x}\text{La}_x\text{Fe}_4\text{O}_9$.

IV. CONCLUSIONS

Multiferroic $\text{Bi}_{2-x}\text{La}_x\text{Fe}_4\text{O}_9$ material has been successfully synthesized by the solid reaction method using high energy milling. The structure of the crystal is orthorhombic with the P 6mm space group and the average particle size is 500 nm. The $\text{Bi}_{2-x}\text{La}_x\text{Fe}_4\text{O}_9$ multiferroic material can be applied to microwave absorbers. The addition of La^{3+} ions does not necessarily increase the ability of the material to absorb mi-

and a sample thickness of 6 mm obtained RL -29.89 dB at 10.3 GHz [3].

crowaves (RL). RL values for values $x = 0.5$ (-18 dB) and 1.0 (-19 dB) are even smaller when compared to RL values for $x = 0$ (-20 dB). For samples with La^{3+} doping value = 0.2

and a thickness of 2 mm, the best reflection loss (RL) value is around -21 dB at a frequency of 11.2 GHz.

-
- [1] A.K. Pradhan, *et al.*, "Magnetic and electrical properties of single-phase multiferroic BiFeO_3 ", *Journal of Applied Physics*, vol. 97, pp. 093903, 2005.
- [2] K. Guo, R. Zhang, T. He, H. Kong, and C. Deng, "Multiferroic and in-plane magnetoelectric coupling properties of BiFeO_3 nano-films with substitution of rare earth ions La^{3+} and Nd^{3+} ", *Journal of Rare Earths* vol. 34, Issue 12, pp. 1228-1234, December 2016.
- [3] S. Bi, J. Li, B. Mei, X.J. Su, C.Z. Ying, and P.H. Li, "Effect of Zn doping on the microwave absorption of BFO multiferroic materials", *IOP Conf. Series: Materials Science and Engineering*, vol. 292, 012105, 2017 (doi:10.1088/1757-899X/292/1/012105).
- [4] S. Li, *et al.*, "Ultrafast microwave hydrothermal synthesis of BiFeO nanoplates", *J. Am. Ceram. Soc.*, vol. 96, no. 10, pp. 31553162, 2013 (doi: 10.1111/jace.12473).
- [5] Y. Li, X. Fang, M. Cao, "Thermal frequency shift and tunable microwave absorption in BiFeO_3 family", *Scientific Reports*, vol. 6, ArticleNumber:24837, 2016.
- [6] J. Zhao, T. Liu, Y. Xu, Y. He, and W. Chen, "Synthesis and characterization of $\text{Bi}_2\text{Fe}_4\text{O}_9$ powders", *Journal of Materials Chemistry and Physics*, vol. 128, pp. 388-391, 2018.
- [7] H. Yang, J. Dai, L. Wang, Y. Lin, F. Wang, and P. Kang, "A novel approach to prepare $\text{Bi}_2\text{Fe}_4\text{O}_9$ flower-like spheres with enhanced photocatalytic performance", *Scientific Reports*, vol. 7, 2017 (doi:10.1038/s41598-017-00831-3).
- [8] M. Santhiya, K.S. Pugazhvadivu, K. Tamilarasan, and C. Ranganasami, "Influence of sputtering power on the structure and electrical properties of $\text{Bi}_2\text{Fe}_4\text{O}_9$ thin film", *Acta Metall. Sin. (Engl. Lett.)*, 2017 (doi:10.1007/s40195-017-0537-z).
- [9] A. Kirsch, M.M. Murshed, P. Gaczynski, K.D. Becker, and T.M. Gesing, " $\text{Bi}_2\text{Fe}_4\text{O}_9$: structural changes from nano-to micro-crystalline state", *Z. Naturforsch.*, vol. 71, no.5b, pp. 447-455, 2016.
- [10] X. Yuan, L. Shi, J. Zhao, S. Zhou, and J. Guo, "Tunability of magnetization and bandgap in mullite-type $\text{Bi}_2\text{Fe}_4\text{O}_9$ ceramics through non-magnetic ions", *Scripta Materialia*, vol. 146, pp. 55-59, 2018.
- [11] S.R. Mohapatra, S.D. Kaushik, and A.K. Singh, "Enhanced antiferromagnetic transition and magnetodielectric study in cobalt and holmium co-substituted multiferroic $\text{Bi}_2\text{Fe}_4\text{O}_9$ ", *Mater. Res. Express*, vol. 5, pp. 016107, 2018.
- [12] J.J. Xu, *et al.*, "Electromagnetic and microwave absorbing properties of Co_2 Z-type hexaferrites doped with La^{3+} ", *Journal of Magnetism and Magnetic Materials*, vol. 321, no. 19, pp.3231-3235, 2009. (doi: 10.1016/j.jmmm.2009.05.039).
- [13] X. Ren and G. Xu, "Electromagnetic and microwave absorbing properties of NiCoZn -ferrites doped with La^{3+} ", *Journal of Magnetism and Magnetic Materials*, vol. 354, pp. 44-48, March 2014.
- [14] M. Ahmadzadeh, A. Ataie, E. Mostafavi, "The effects of mechanical activation energy on the solid-state synthesis process of BiFeO_3 ", *Journal of Alloys and Compounds*, vol. 622, pp. 548556, 2015.