A CHEMICAL ROUTE TO THE SYNTHESIS OF Bi1-xMgxFeO3 (x=0.1 and x=0.07) NANOPARTICLE WITH ENHANCED ELECTRICAL PROPERTIES AS MULTIFERROIC MATERIAL

Dwita Suastiyanti ¹, Sri Yatmani ², Yuli Nurul Maulida ³

¹ Mechanical Engineering Study Program, Institut Teknologi Indonesia, Indonesia
² Electrical Engineering Study Program, Institut Teknologi Indonesia, Indonesia
³ Chemical Engineering Study Program, Institut Teknologi Indonesia, Indonesia

Abstract:
Bismuth ferrite (BiFeO3) is one of multiferroic material group, but it is difficult to produce BiFeO3 in single phase as multiferroic material because it occurs leakage of current arising from non-stoichiometric. So, to minimize it, it has already been engineering processed to synthesis BiFeO3 doped by Mg to produce Bi0.9Mg0.1FeO3 and Bi0.93Mg0.07FeO3. It used sol-gel method to produce the ceramics. The result of TGA/DTA (Thermo Gravimetric Analysis/Differential Thermal Analysis) test shows that the temperature of calcination is about of 150 and 175°C and temperature of sintering is about of 650°C. Characterization of the powder has already been done by using X-Ray Diffraction (XRD) test and electrical properties test. The results of XRD test show that the powder of Bi0.9Mg0.1FeO3 has minimum impurities with total oxide of 6.9% (bismite 3.5% and silenite 3.4%) at calcination temperature of 175°C for 4 hours and sintering at 650°C for 6 hours. Meanwhile at same parameter, Bi0.93Mg0.07FeO3 has more oxide phases with total oxide of 14.5% which consists of silenite (2.5%) and Bi2O4 (12%). Presence of oxide phases could cause leakage of current decreasing electrical properties. The values of electrical saturation polarization for ceramic having minimum total oxide (Bi0.9Mg0.1FeO3) is higher than ceramic having more oxide (Bi0.93Mg0.07FeO3). The value of electric saturation polarization for Bi0.9Mg0.1FeO3 is of 0.26 kv/cm and for Bi0.93Mg0.07FeO3 is of 0.11 kV/cm.

Keywords: Electrical; Saturation Polarization; Multiferroic; Sol-Gel; Ceramic.

Cite This Article: Dwita Suastiyanti, Sri Yatmani, Yuli Nurul Maulida. (2018). “A CHEMICAL ROUTE TO THE SYNTHESIS OF Bi1-xMgxFeO3 (x=0.1 and x=0.07) NANOPARTICLE WITH ENHANCED ELECTRICAL PROPERTIES AS MULTIFERROIC MATERIAL.” International Journal of Engineering Technologies and Management Research, 5(6), 103-112. DOI: 10.5281/zenodo.1313106.

1. Introduction

Ferroelectricity, ferromagnetism and ferro elasticity is a characteristic of materials which result in spontaneous polarization, magnetization and deformation. It could controlled by an applied electric field, magnetic field and stress [1]. These ferroic properties have been thoroughly used widely for years in various devices and components. Interesting potential applications arises for materials which possess two or three of ferroic properties at the same time. Those materials are called...
multiferroic materials. Some other similar properties (antiferromagnetism, ferrimagnetism, ferrotoroidicity) are often also considered ferroic [2]. Single multiferroics have two or all three ferroic properties in only one phase.

Bismuth ferrite (BiFeO$_3$/BF) material has an electrical polarization value at temperature of $T_C$ below ~810°C and magnetic properties at temperature of $T_N$-375°C, so the application of BiFeO$_3$ in functionality will be increased. At room temperature, bismuth ferrite has a rhombohedralperovskite structure with space group R3c. Bi and O ions together form a cubic close packing structure with Fe ion occupying an interstitial octahedron position. Bismuth ferrite (BF) has a rhombohedralperovskite structure, with almost cubic unit cell ($a_{rh} = 3.965$ Å, $a_{rh} = 89.40^\circ$) though it is usually described using hexagonal axes. Hexagonal c-axis is directed along [111] axes of pseudocubic cell and hexagonal cell ($a_{hex} = 5.58$ Å, $c_{hex} = 13.90$ Å) is consisted of six formula units of BiFeO$_3$. It is single multiferroic material, exhibiting ferroelectric and antiferromagnetic properties in the same phase. Aside from its multiferroicity, BFO exhibit properties which could be interesting to those dealing with pigments, solar cell materials, photocatalysts and optoelectronics thanks to a relatively small band gap of about 1.8–2.8 eV [3]. With very wide temperature range of multiferroic behavior ($T_C = 810^\circ$C, $T_N = 375^\circ$C), BF belongs to the materials with greatest potential for different kind of application, but still has unsolved problems in bringing out the best from its extraordinary properties. That is the reason for such numerous studies about BF in the last 15 years. Main obstacles which are still to be overcome are occurrence of currents leakage and insufficiently expressed magnetic properties. Low electrical resistivity of BF disables manifestation of ferroelectric behavior. The resistivity of BF was successfully improved by doping, especially in case of aliovalent ions.

The structure and properties owned BF intensively studied by many researchers but are still hampered by the current leakage problems arising from non-stoichiometric. It is difficult to obtain a single phase material of BF. Phase impurities (oxide phases) that arise during synthesis usually as Bi$_2$O$_3$, Bi$_2$Fe$_4$O$_9$, and Bi$_25$FeO$_39$ [4,5]. This phase changes stoichiometry and causes oxygen vacancies coupled with the emergence of iron oxide during processing. It causes leakage of current. Single phase of BF without oxide phases has been difficult obtained because of the influence of thermodynamic and kinetic properties of the system. So to obtain material which has good electrical properties applying as multiferroic material, it has been already done engineering process producing Bi$_{0.93}$Mg$_{0.1}$FeO$_3$ and Bi$_{0.93}$Mg$_{0.07}$FeO$_3$.

The resistivity of BF was improved by doping successfully, in case of aliovalent ions [6]. Opinions are divided in case of doping with isovalent ions. Smaller content of volatile Bi$_3^{3+}$ ions explains improvement of resistivity by A-site1 substitution with isovalent ions causing less pronounced unstoichiometry. For this reason, although slightly decreasing ferroelectric polarization by the elimination of its cause (Bi$_3^{3+}$ ions with lone 6s2 electron pair) [1]. For synthesis of BF with improved ferroelectric properties, used substitution of A-site ion. There are also some studies reporting higher current density in isovalently substituted BF [7]. Substitution of Bi$_3^{3+}$ in BF was additionally reported to promote formation of perovskite BF phase, reducing the amount of secondary phases in this way [8]. More success in obtaining highly resistive BF has been achieved in two-dimensional materials in the form of thin films. Antiferromagnetic materials still do not have many applica-ions, but BF is not typical representative. Its antiferromagnetism is originating from Fe$_3^{3+}$ ions, and is of G-type, meaning all first neighboring Fe$_3^{3+}$ ions have opposite magnetic
spin directions. What is interesting in BF is that these spins are not completely opposite, and there is some small resulting moment. This kind of structure is called canted spin structure, and it usually leads to weak ferromagnetism, but in BF, magnetic spins have another level of organization arranging them in spiral structures with a period of 62 nm, destroying magnetization in bulk material [9]. This means that limiting the growth of its particles or grains under 62 nm is one way of creating ferromagnetism in BF. The other way, substitution of Bi$^{3+}$ ions with isovalent ions of different size could be breaking of spiral spin structure [10].

Another important obstacle in BF application is difficulty in obtaining pure and dense BF ceramics. BF phase exhibits instability area between 447°C and 767°C in which it is spontaneously decomposed to secondary phases (mullite type phase, Bi$_2$Fe$_4$O$_9$, and sillenite type phase, Bi$_2$5FeO$_{39}$) [11,12]. It is hard to conduct sintering of powder and in the same time to completely avoid this temperature interval. Together with the large bismuth loss at high temperatures, this is a huge barrier for densification of BF ceramics. That is the reason why so many studies about BF operate with powders. Magnetic properties are manifested and could be easily measured in powders, but for electrical and multiferroic properties, and also applications based on them, it is usually necessary to make dense ceramics. Mechanisms of isovalent substitution-driven improvement of resistivity, polarization and magnetization are still not known, but there are implications that it is mainly driven by the average size of the A-site ion, and not by the dopant nature. The most probable reason is change in the Goldschmidt tolerance factor and, therefore, lowering the angle of the Fe-O-Fe bonds, which controls both magnetic and conduction properties leading also to structural transition. For this reason, an attempt of improving purity, electrical and magnetic properties of BF by doping with Mg (magnesium element) was conducted in this study and synthesized by the auto-combustion (sol-gel) method.

2. Materials and Methods

To obtain ceramics of Bi$_{0.9}$Mg$_{0.1}$FeO$_3$ and Bi$_{0.93}$Mg$_{0.07}$FeO$_3$ uses basic compound of pro analysis Merck product with a purity of 99.99% Bi$_5$(OH)$_9$.(NO$_3$)$_4$, Fe(NO$_3$)$_3$.9H$_2$O, HNO$_3$, H$_2$O, Mg(NO$_3$)$_2$ and citric acid C$_6$H$_8$O$_7$ as fuel. The basic compounds dissolved in aquabidestilate which was then heated on a hot plate at 80-90°C to form a gel (approximately for 4 to 5 hours). The gel that is formed is then heated in a furnace at a temperature of 150 and 175°C for 4 hours respectively. The goal is to evaporate the water and the elements C, N and H. The powder obtained was then carried out by heating (the sintering process) in the furnace at temperature of 650°C for 2, 4 and 6 hours respectively. The flowchart of the engineering process is shown in Figure-1. Testing by XRD were performed using an XRD of PW 1835 Phillips type with diffraction angle of 20°-100° and using CuKα radiation. Analysis (TGA) / Differential Thermal Analysis (DTA) aimed to observe changes in mass and heat of samples (still in gel form) to the increase in temperature, using a TGA / DTA Thermal Balance Research type LINSEIS L81-Series I / L81-STA (TGA-DTA).
Fig. 1 shows that the process (sol-gel) used low temperature of 150 and 175°C for calcination and 650°C for sintering process. If it was used conventional solid state reaction, it needs a higher temperature (up to 200°C for calcination and up to 1000°C for sintering process).

3. Results and Discussions

The results of TGA/DTA test are shown in Fig. 2. The data are used to determine the temperature of calcination and sintering process.

Figure 2: Graph of TGA/DTA Test of Bi₀.₉Mg₀.₁FeO₃ Gel (a) and of Bi₀.₉₃Mg₀.₀₇FeO₃ Gel (b)
Fig. 2 shows that weight reduction of both of ceramic powder is about at 150-200°C approximately. The phase transition which is happen at the temperatures range, shown that calcination process occurs at the temperatures of 150-200°C. The next phase transition occurs at temperatures of 600-650°C (characterized by the occurrence of heat flow reduction). It is shown that sintering process occurs at the temperatures range. Based on the test result, it is used 150 and 175°C for calcination temperatures and 650°C for sintering temperatures.

To confirm the formation of phases, it is performed XRD test of sample for all parameters and the results are shown in Fig. 3-8.

Figure 3: XRD Pattern of $\text{Bi}_{0.9}\text{Mg}_{0.1}\text{FeO}_3$ Calcination at 150°C for 4 Hours and Sintering at 650°C for 2 Hours (a) and for 4 Hours (b)

Figure 4: XRD Pattern of $\text{Bi}_{0.9}\text{Mg}_{0.1}\text{FeO}_3$, Calcination at 150°C for 4 Hours and Sintering at 650°C for 6 Hours (a) and Calcination at 175°C for 4 Hours and Sintering at 650°C for 2 Hours (b)
Figure 5: XRD Pattern of Bi$_{0.9}$Mg$_{0.1}$FeO$_3$, Calcination at 175°C for 4 Hours and Sintering at 650°C for 4 Hours (a) and for 6 Hours (b)

Figure 6: XRD Pattern of Bi$_{0.93}$Mg$_{0.07}$FeO$_3$, Calcination at 150°C for 4 Hours and Sintering at 650°C for 2 Hours (a) and for 4 Hours (b)
As we know that BiFeO$_3$ phase is still hampered by the leakage of current problems arising from non-stoichiometric. It is difficult to obtain a single phase material of BiFeO$_3$. Oxide phases change stoichiometry and cause oxygen vacancies coupled with the emergence of iron oxide during processing. It causes leakage of current. Fig.3-8 show that ceramic powder still has oxide phases.
It causes decreasing of electric properties. Data of formation of oxide phases could be tabulated at Table 1 and 2 (taken from Fig. 3-8).

| Treatment | Bismite (Bi2O3) (%) | B2O4 (%) | Silicate (Bi42FeO39) (%) | Total Oxides (%) |
|-----------|---------------------|----------|--------------------------|------------------|
| Calcination 150°C, sinter 650°C, 2 hours | 5.8 | 16.4 | 0 | 22.2 |
| Calcination 150°C, sinter 650°C, 4 hours | 5.8 | 14.5 | 0 | 20.3 |
| Calcination 150°C, sinter 650°C, 6 hours | 5.8 | 16.4 | 0 | 22.2 |
| Calcination 175°C, sinter 650°C, 2 hours | 0 | 0.8 | 6.3 | 7.1 |
| Calcination 175°C, sinter 650°C, 4 hours | 0 | 0.8 | 6.3 | 7.1 |
| Calcination 175°C, sinter 650°C, 6 hours | 3.5 | 0 | 3.4 | 6.9 |

| Treatment | Bismite (Bi2O3) (%) | Fe2O3 (%) | Silicate (Bi42FeO39) (%) | Total Oxides (%) |
|-----------|---------------------|----------|--------------------------|------------------|
| Calcination 150°C, sinter 650°C, 2 hours | 10.8 | 17.9 | 0 | 28.7 |
| Calcination 150°C, sinter 650°C, 4 hours | 10.8 | 17.0 | 0 | 27.8 |
| Calcination 150°C, sinter 650°C, 6 hours | 0 | 4.7 | 13.7 | 19.7 |
| Calcination 175°C, sinter 650°C, 2 hours | 0 | 4.7 | 13.0 | 17.6 |
| Calcination 175°C, sinter 650°C, 4 hours | 0 | 0 | 2.5 | 14.5 |
| Calcination 175°C, sinter 650°C, 6 hours | 0 | 0 | 2.5 | 14.5 |

Table-1 shows that Bi0.9Mg0.1FeO3 powder still has impurities (oxide phases), but increasing time of sintering and calcination temperature could decrease amount of total oxides. There is total oxides of 6.9% at sintering 650°C for 6 hours and calcination temperature of 175°C. While Bi0.93Mg0.07FeO3 powder has more total oxides at same parameters (Table 2). The presence of oxide phases in the powder will affect the electric properties of the powder, shown in Fig.9.

Figure 9: Electric Properties of Bi0.9Mg0.1FeO3 Calcination at 175°C, 4 Hours, Sintering at 650°C, 6 Hours (a) and of Bi0.93Mg0.07FeO3 Calcination at 175°C, 4 Hours, Sintering at 650°C, 6 Hours (b)
Figure 9 shows that ceramic with minimum amount of total oxides (Bi$_{0.9}$Mg$_{0.1}$FeO$_3$) has higher value of electric saturation (0.26 kV/cm for Bi$_{0.9}$Mg$_{0.1}$FeO$_3$ and 0.11 kV/cm for Bi$_{0.93}$Mg$_{0.07}$FeO$_3$). The value of electric saturation for ceramic of other parameters, shown in Table 3 and 4.

Table 3: Electric Saturation Polarization for Bi$_{0.9}$Mg$_{0.1}$FeO$_3$

| Treatment                                      | Electric Saturation (kV/cm) | Total Oxides (%) |
|------------------------------------------------|----------------------------|------------------|
| Calcination 150°C, sinter 650°C, 2 hours       | 0.07                       | 22.2             |
| Calcination 150°C, sinter 650°C, 4 hours       | 0.10                       | 20.3             |
| Calcination 150°C, sinter 650°C, 6 hours       | 0.13                       | 22.2             |
| Calcination 175°C, sinter 650°C, 2 hours       | 0.17                       | 7.1              |
| Calcination 175°C, sinter 650°C, 4 hours       | 0.21                       | 7.1              |
| Calcination 175°C, sinter 650°C, 6 hours       | 0.26                       | 6.9              |

Table 4: Electric Saturation Polarization for Bi$_{0.93}$Mg$_{0.07}$FeO$_3$

| Treatment                                      | Electric Saturation (kV/cm) | Total Oxides (%) |
|------------------------------------------------|----------------------------|------------------|
| Calcination 150°C, sinter 650°C, 2 hours       | 0.01                       | 28.7             |
| Calcination 150°C, sinter 650°C, 4 hours       | 0.02                       | 27.8             |
| Calcination 150°C, sinter 650°C, 6 hours       | 0.05                       | 19.7             |
| Calcination 175°C, sinter 650°C, 2 hours       | 0.07                       | 17.6             |
| Calcination 175°C, sinter 650°C, 4 hours       | 0.10                       | 17.0             |
| Calcination 175°C, sinter 650°C, 6 hours       | 0.11                       | 14.5             |

Table 3 and 4 show that powder with more amount of oxide phases has lower of electric saturation. The presence of oxide phases could cause leakage of current, decreasing electric saturation consequently. Time sintering which is less than 6 hours, still leaves oxide phases. This is because oxide phases formed have not been entirely transformed into a bismuth ferrite in sinter time of less than 6 hours.

4. Conclusions

Longer time of sintering in producing Bi$_{0.9}$Mg$_{0.1}$FeO$_3$ and Bi$_{0.93}$Mg$_{0.07}$FeO$_3$ ceramics by sol-gel method, could decrease amount of total oxides. Meanwhile lower amount of total oxides could increase value of electric saturation because there is minimum leakage of current. The optimum parameter used for synthesis Mg doped BiFeO$_3$ is calcination temperature of 175°C for 4 hours and sintering temperature of 650°C for 6 hours and for $x = 0.1$.

Acknowledgements

The authors would like to thank to the Ministry of Research and Technology DIKTI, The Republic of Indonesia under Research Grant of Researchbased on Competency 2018, letter of number decree of 044/KM/PNT/2018, March 6th, 2018, Ministry for Research and Technology DIKTI, The Republic of Indonesia and letter of number decree of 32/KP/LPKT-ITI/III/2018, March 29th, 2018, Institut Teknologi Indonesia, the Republic of Indonesia.
References

[1] N.A. Hill, A. Filipputi, Why Are There Any Magnetic Ferroelectrics, J. Magn. Magn. Mater, 2002,242-245, 2002, 976-979.

[2] W. Eerenstein, N.D. Mathur, J.F. Scott, Multiferroic and Magnetoelectric Materials, Nature 442, 2006, 759-765.

[3] X. Yang, Y. Zhang, G. Xu, X. Wei, Z. Ren, G. Shen, G. Han, Phase and Morphology Evolution of Bismuth Ferrites via Hydrothermal Reaction Rout, Mater. Res. Bull, 48, 2013, 1694-1699.

[4] Ke, Hua et al, Factors Controlling Pure Phase Multiferroic BiFeO3 Powders Synthesized by Chemical Co-Precipitation, Journal Alloy and Compounds. 2010.

[5] Dwita S, M. Wijaya, Synthesis of BiFeO3 Nanoparticle and Single Phase by Sol-Gel Process for Multiferroic Material, ARPN Journal of Engineering and Applied Sciences, 11(2), 2016, 901-905.

[6] G. Catalan, J.F. Scott, Physics and Application of Bismuth Ferrite, Adv. Mater 21, 2009,2463-2485.

[7] L.Luo, W. Wei, X. Yuan, K. Shen, M. Xu, Q. Xu, Multiferroic Properties of Y-Doped BiFeO3, J. Alloy Compd. 540, 2012,36-38.

[8] S.K. Pradha, B.K. Roul, Electrical Behavior of High Resistivity Ce-Doped BiFeO3 Multiferroic, Physica B 407, 2012, 2527-2532.

[9] D. Lebeugle, A. Mougin, M. Viret, D. Colson, L. Ranno. Electric Field Switching of The Magnetic Anisotropy of a Ferromagnetic Layer Exchange Coupled to The Multiferroic Compound BiFeO3, Physical Review Letters. 2009.

[10] F. Bao Lin, X. Hao, X. Zhao Xian, Structure and Multiferroic Properties of Y Doped BiFeO3 Ceramics, Chin. Sci. Bull, 55, 2010,452-456.

[11] Dwita S, Ismojo, FTIR Spectrum of BiFeO3 Ceramic Produced by Sol-Gel Method Based on Variation of Sinter and Calcination Treatment, The International Journal of Engineering and Science (IIES), 5(5), 2016,114-117.

[12] Dwita S, Sifat Magnetoelektrik Pada Material Keramik Berbasis Keramik, Jurnal Teknik Mesin Institut Teknologi Indonesia 2(1), 2018, 26-29.

*Corresponding author.
E-mail address: dwita.suastiyanti@iti.ac.id