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INVESTIGATION OF MAGNETIC PROPERTIES OF DOPED $BiFe_{1-x}Zn_xO_3$ (X=0.1 AND X=0.07) BY LOW TEMPERATURE SYNTHESIS

Dwita Suastiyanti[1] and Ismojo[2]
[1]Mechanical Engineering Department, Institut Teknologi Indonesia, Indonesia
[2]Automotive Engineering Department, Institut Teknologi Indonesia, Indonesia
E-Mail: dwita.suastiyanti@iti.ac.id

ABSTRACT

One of the chemical compounds that have multiferroic properties is $BiFeO_3$. The multiferroic properties of the material would be better if the material has good magnetic properties as well. To obtain a high magnetic properties, the engineering process is carried out to synthesis $BiFe_{1-x}Zn_xO_3$ (x = 0.1 and 0.07) by doping Zn into $BiFeO_3$ compound. Engineering process performed by sol-gel method. Calcination in sol-gel method is carried out at a temperature of 150 and 175 ^oC for 4 hours and the sintering process at a temperature of 650 ^oC for 2, 4 and 6 hours. Characterization of the powder is modified done by using TGA / DTA test, X-Ray Diffraction (XRD) test and magnetic properties (Vibrating Sample Magnetometer) test. From the results of TGA / DTA test, it could be seen that the calcination process could be performed at temperatures of 150 and 175 ^oC and sintering process could be carried out at a temperature of 650 ^oC. From the result of XRD test, it is shown that the powder of $BiFe_{0.93}Zn_{0.07}O_3$ has minimum impurities (bismite 2.9% and iron 3.6%) at calcination temperature of 175 ^oC for 4 hours and sintering at 650 ^oC for 6 hours. But the most excellent magnetic properties belongs to powder of $BiFe_{0.9}Zn_{0.1}O_3$ with the value of magnetic polarization saturation of 0.65 emu/gram, while the value of magnetic polarization saturation for $BiFe_{0.93}Zn_{0.07}O_3$ is 0/45 emu/gram.

Keywords: magnetic, polarization, multiferroic, sol-gel.

INTRODUCTION

Characteristic of materials which result in spontaneous polarization, magnetization and deformation which can be controlled by an applied electric field, magnetic field and stress are called ferroelectricity, ferromagnetism and ferroelasticity, respectively [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 (BF) has a rhombohedral perovskite structure, with almost cubic unit cell (a_{rh} = 3.965 Å, α_{rh} = 89.40^o) 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 $BiFeO_q$. It is single multiferroic material, exhibiting ferroelectric and antiferromagnetic properties in the same phase. Aside from its multiferroicity, BF 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 [3-6]. With very wide temperature range of multiferroic behavior (TC = 830 ^oC, TN = 370 ^oC) [7], 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 leakage currents 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 [8-10].

Generally, conventional solid state reaction and/or rapid liquid phase sintering of Bi_2O_3 and Fe_2O_3 are adopted to prepare bulk BFO ceramic materials. Recently, wet chemical methods (sol-gel) have received great attention for the synthesis of BFO materials [11]. In this paper a synthesis procedure to obtain pure $BiFe_{0.9}Zn_{0.1}O_3$ and $BiFe_{0.93}Zn_{0.07}O_3$ powders and their structural and magnetic characterization have been outlined. It is used sol-gel method to obtain good magnetic properties providing good multiferroic properties too.

LITERATURE REVIEW

The structure and properties owned $BiFeO_3$ 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 $BiFeO_3$. Phase impurities that arise during synthesis usually as Bi_2O_3, $Bi_2Fe_4O_9$, and $Bi_{25}FeO_{39}$ [12]. This phase change stoichiometry and cause oxygen vacancies coupled with the emergence of iron oxide during processing. It causes leakage current. Single phase of $BiFeO_3$ has been difficult obtained because of the influence of thermodynamic and kinetic properties of the system. So to obtain material which has good magnetic properties, it has been done engineering process to obtain doped $BiFe_{0.9}Zn_{0.1}O_3$and $BiFe_{0.93}Zn_{0.07}O_3$.

For the characterization of magnetic properties using permagraph tool is a tool that could generate hysteresis loop curve that comes with the value of remanent induction (M_r) and the coercive force (H_c). At

the time of the measurement, it takes place a process of magnetization on the sample material permanently.

The magnitude of the magnetic properties of a material could be determined via hysteresis curve. From the curve, it could be known value of remanent induction (M_r), and the coercivity (H_c). When a magnetic material is in a state of magnetized (M = 0), given the external magnetic field H enlarged continuously, it will reach a maximum value at point M_s (dotted line). The value of M at the time was M_s (saturation magnetization). If the external magnetic field is lowered continuously, then the M-H curve does not follow the dotted line but follow the curve line. At the time of H=0 then the magnetic induction of M will have a value of M_r (remanent magnetic induction). To restore the required field of M=0, it needs H_c in negative value. If the magnetic field is continuous decreased, it would be reached the point of negative saturation magnetic induction (M_s). If the negative field of H is reversed, the curve will follow the line of $–H_s$-$M_rH_cM_s$ (curve line), until value of M_s reached again, in order to obtain hysteresis curve as shown in Figure-1

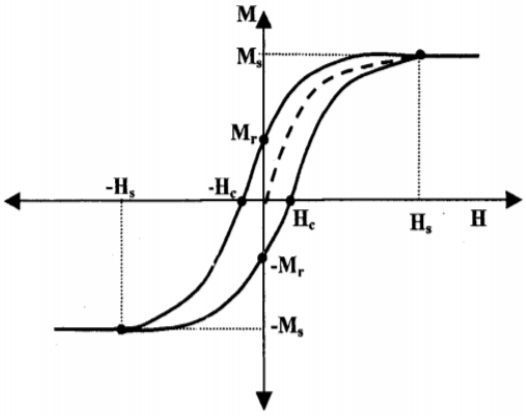

Figure-1. Hysteresis curve.

MATERIALS AND METHODS

The engineering process of $BiFe_{0.9}Zn_{0.1}O_3$ and $BiFe_{0.93}Zn_{0.07}O_3$ uses basiccompound of pro analysis Merck product with a purity of99.99% $Bi_5O(OH)_9.(NO_3)_4$, $Fe(NO_3)_3.9H_2O$, HNO_3, H_2O, $Zn(NO_3)_2$and citric acid $C_6H_8O_7$ as fuel. The basic compounds dissolved in aquabidestilate which was then heated on a hot plate at 80-90 ^oC to form a gel (approximately for 4 to5 hours). The gel that is formed is then heated in a furnace at a temperature of 150 and 175 ^oC 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 ^oC for 2, 4 and 6 hours respectively. The flowchart of the engineering process is shown in Figure-2.Testing by XRD were performed using an XRD of PW 1835 Phillips type with diffraction angle of 20^o-100^o 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 LINSEISL81-Series I / L81- STA (TGA-DTA). To know the magnetic properties, it used VSM (Vibrating Sample Magnetometer) device.

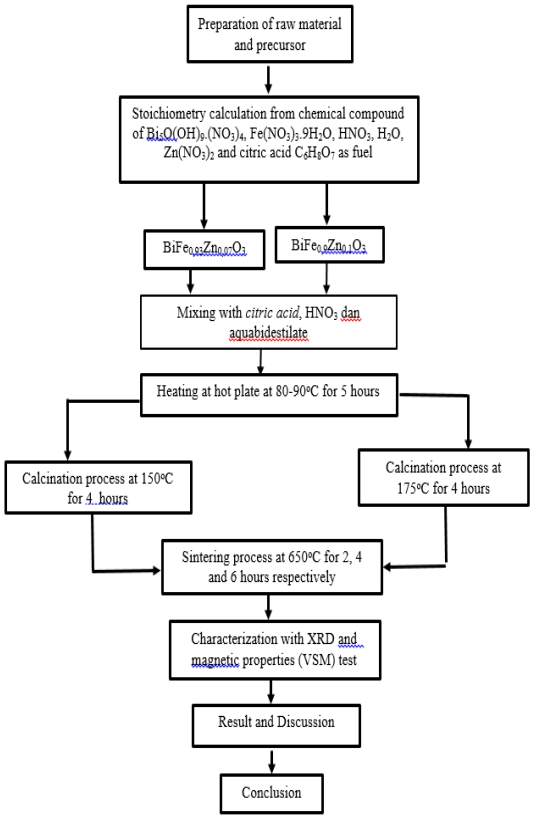

Figure-2. Flowchart of engineering process.

Figure-2 shows that the process (sol-gel) used low temperature of 150 and 175 ^oC for calcination and 650 ^oC for sintering process. If it was used conventional solid state reaction, it needs a higher temperature (up to 200 ^oC for calcination and up to 1000 ^oC for sintering process).

RESULTS AND DISCUSSIONS

The results of TGA/DTA test are shown in Figures 3 and 4. The data are used to determine the temperature of calcination and sintering process.

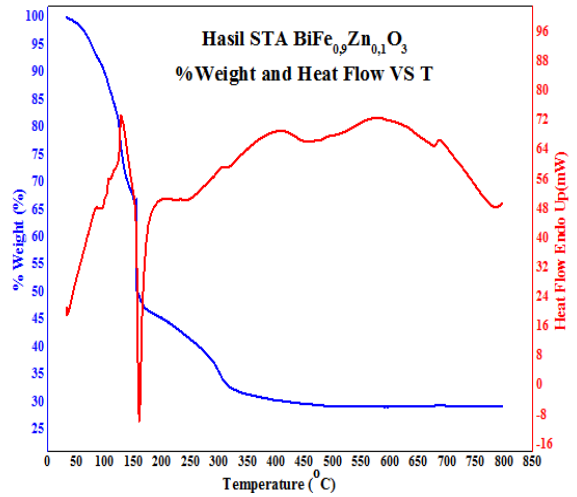

Figure-3. Graph of TGA/DTA test of $BiFe_{0.9}Zn_{0.1}O_3$ gel.

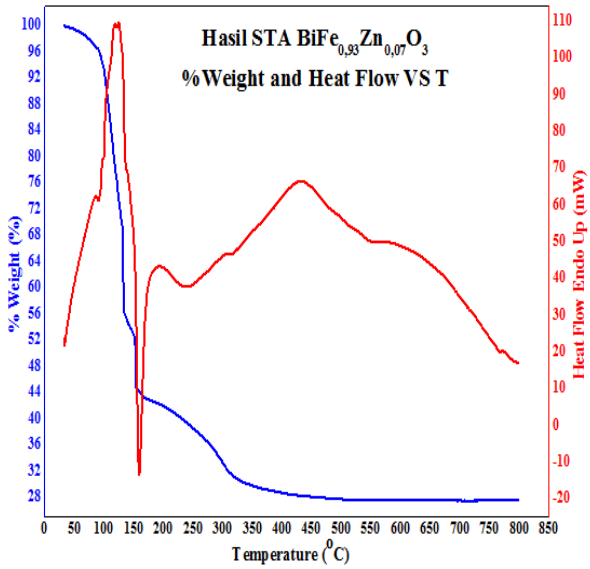

Figure-4. Graph of TGA/DTA test of $BiFe_{0.93}Zn_{0.07}O_3$ gel.

Figures-3 and 4 shows that weight reduction of both of ceramic powder is about at 150-200 °C approximately. The phase transition which happened 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.

To confirm the formation of phases, it is performed XRD test of sample for all parameters and the results are shown in Figure-5-16.

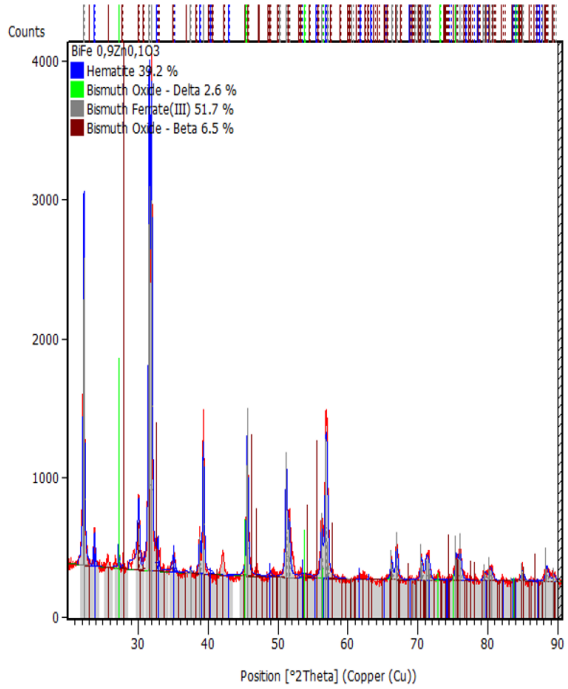

Figure-5. XRD pattern of $BiFe_{0.9}Zn_{0.1}O_3$, Calcination at 150 °C for 4 hours and sintering at 650 °C for 2 hours.

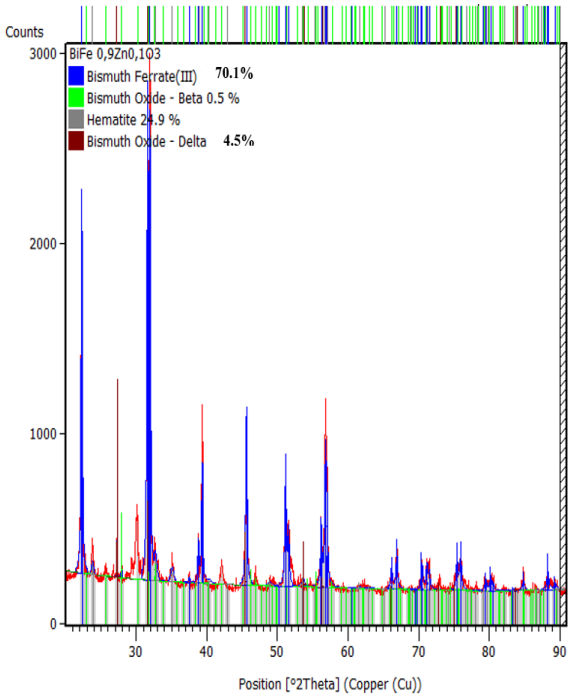

Figure-6. XRD pattern of $BiFe_{0.9}Zn_{0.1}O_3$, Calcination at 150 °C for 4 hours and sintering at 650 °C for 4 hours.

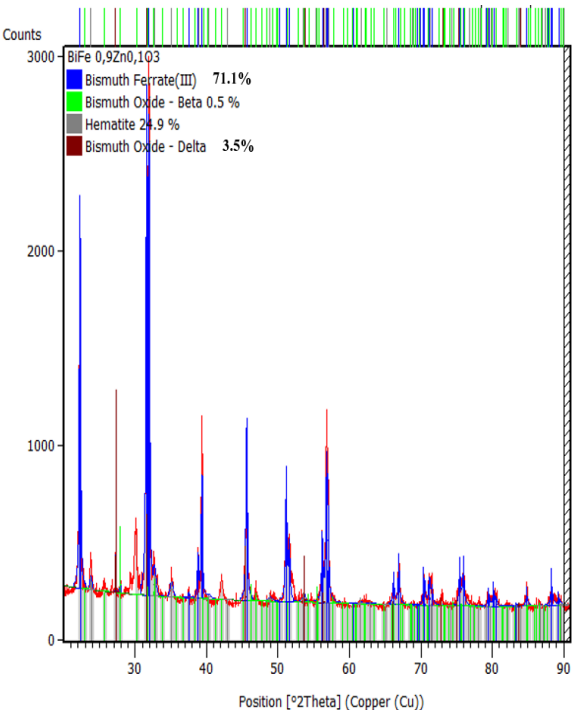

Figure-7. XRD pattern of $BiFe_{0.9}Zn_{0.1}O_3$, Calcination at 150 ºC for 4 hours and sintering at 650 ºC for 6 hours.

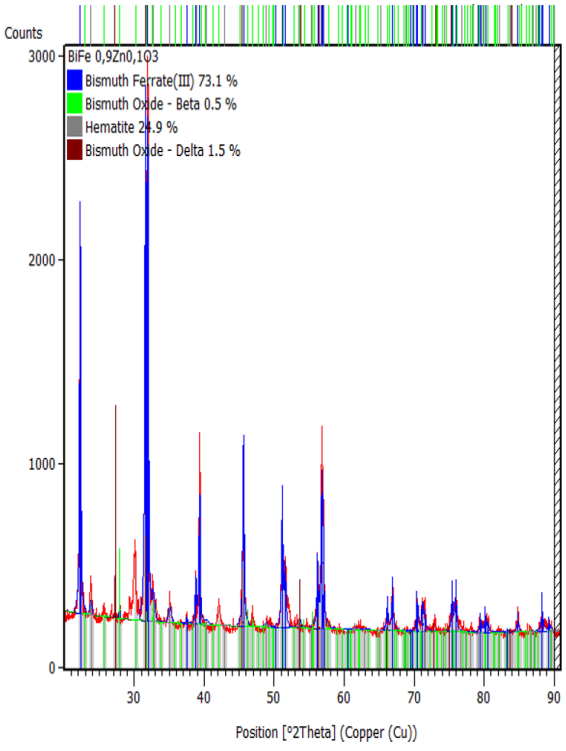

Figure-8. XRD pattern of $BiFe_{0.9}Zn_{0.1}O_3$, Calcination at 175 ºC for 4 hours and sintering at 650 ºC for 2 hours.

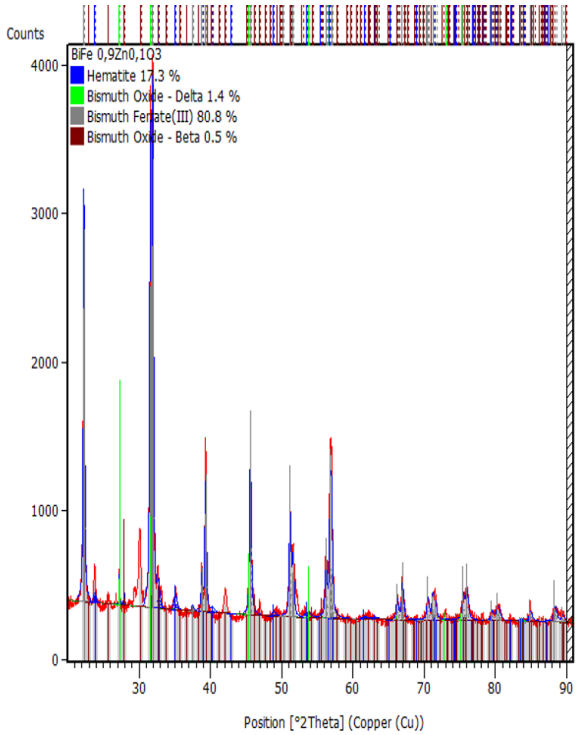

Figure-9. XRD pattern of $BiFe_{0.9}Zn_{0.1}O_3$, Calcination at 175 ºC for 4 hours and sintering at 650 ºC for 4 hours.

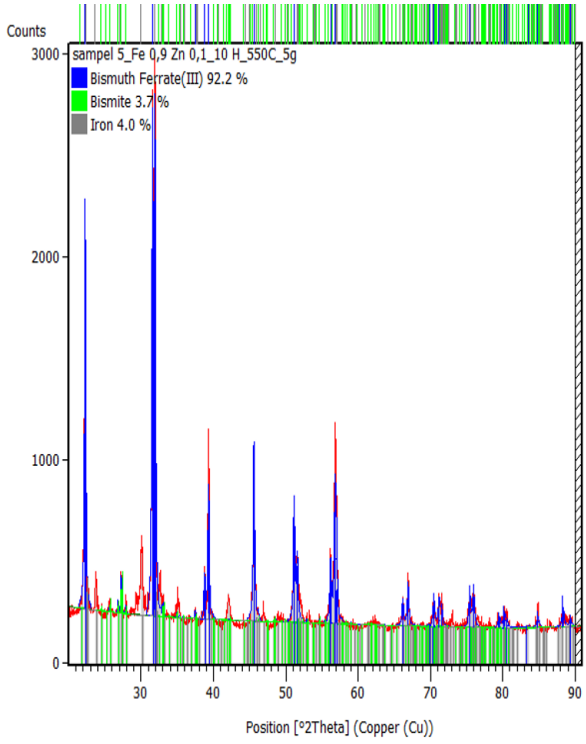

Figure-10. XRD pattern of $BiFe_{0.9}Zn_{0.1}O_3$, Calcination at 175 ºC for 4 hours and sintering at 650 ºC for 6 hours.

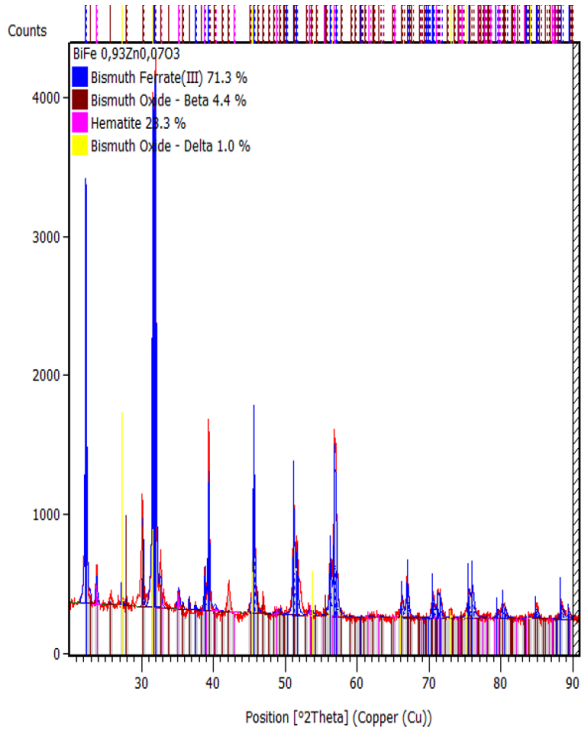

Figure-11. XRD pattern of $BiFe_{0.93}Zn_{0.07}O_3$, Calcination at 150 ºC for 4 hours and sintering at 650 ºC for 2 hours.

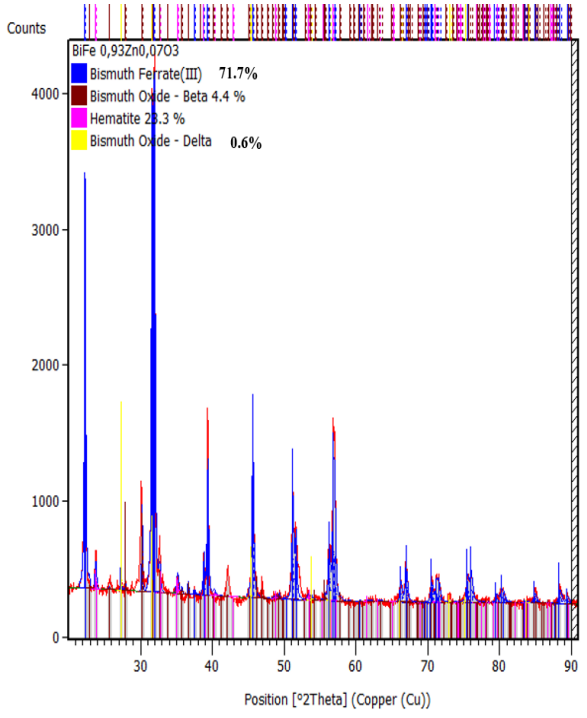

Figure-12. XRD pattern of $BiFe_{0.93}Zn_{0.07}O_3$, Calcination at 150 ºC for 4 hours and sintering at 650 ºC for 4 hours.

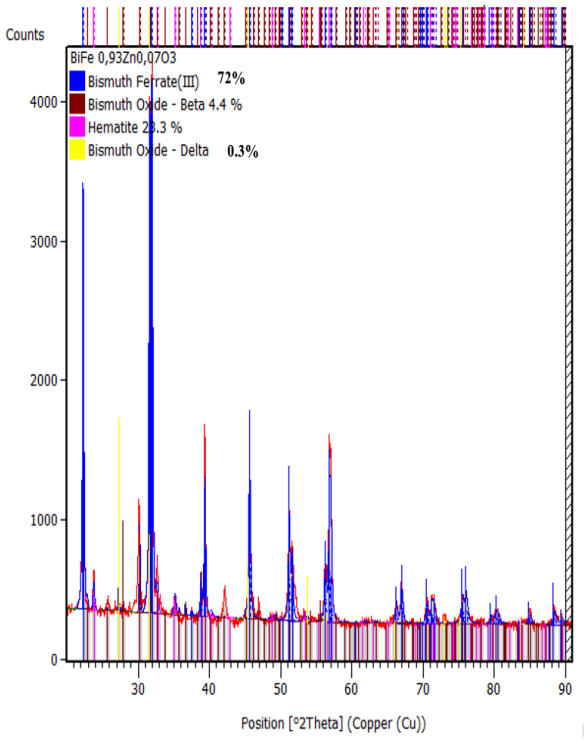

Figure-13. XRD pattern of $BiFe_{0.93}Zn_{0.07}O_3$, Calcination at 150 ºC for 4 hours and sintering at 650 ºC for 6 hours.

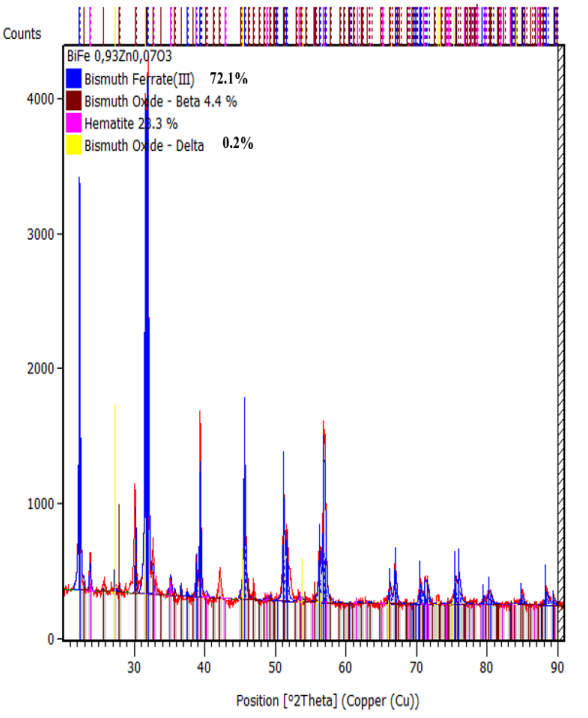

Figure-14. XRD pattern of $BiFe_{0.93}Zn_{0.07}O_3$, Calcination at 175 ºC for 4 hours and sintering at 650 ºC for 2 hours.

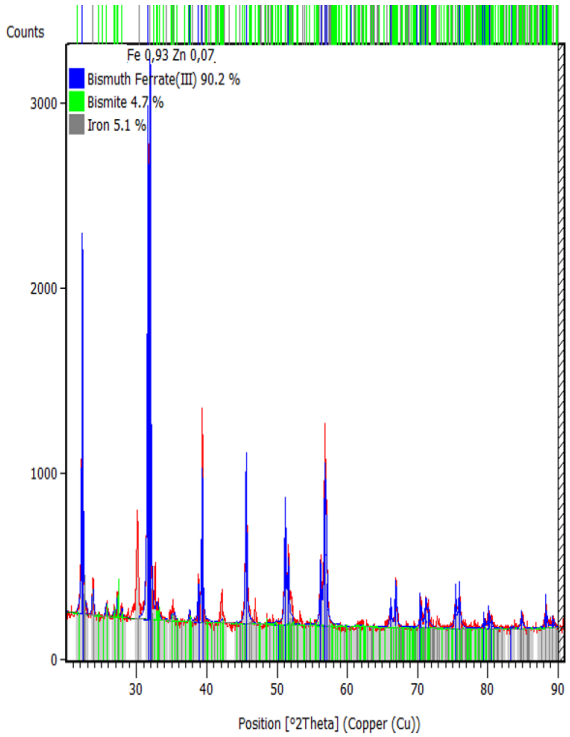

Figure-15. XRD pattern of $BiFe_{0.93}Zn_{0.07}O_3$, Calcination at 175 ºC for 4 hours and sintering at 650 ºC for 4 hours.

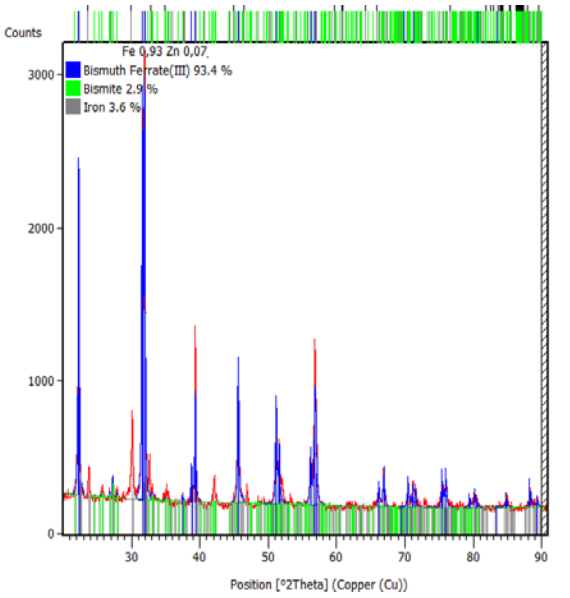

Figure-16. XRD pattern of $BiFe_{0.93}Zn_{0.07}O_3$, Calcination at 175 ºC for 4 hours and sintering at 650 ºC for 6 hours.

As we know that $BiFeO_3$ phase is still hampered by the current leakage 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 current. Figures 5-16 shows that powder from some parameters still have oxide phases. It causes decreasing of magnetic properties. Data of formation of oxide phases could be tabulated at Tables 1 and 2 (taken from Figures 5-16).

Table-1. Percentage of oxide phases in $BiFe_{0.9}Zn_{0.1}O_3$.

Treatment	Bi_2O_3-β (%)	Bi_2O_3-δ (%)	Fe_2O_3 (%)
Calcination 150 ºC, sinter 650 ºC,2 hours	6.5	2.6	39.2
Calcination 150 ºC, sinter 650 ºC,4 hours	0.5	4.5	24.9
Calcination 150 ºC, sinter 650 ºC,6 hours	0.5	3.5	24.9
Calcination 17 5ºC, sinter 650 ºC,2 hours	0.5	1.5	24.9
Calcination 175 ºC, sinter 650 ºC,4 hours	0.5	1.4	0
Calcination 175 ºC, sinter 650 ºC,6 hours	0	0	0

Table-2. Percentage of oxide phases in $BiFe_{0.93}Zn_{0.07}O_3$.

Treatment	Bi_2O_3β (%)	Bi_2O_3δ (%)	Fe_2O_3 (%)
Calcination 150 ºC, sinter 650 ºC,2 hours	4.4	1.0	23.3
Calcination 150 ºC, sinter 650 ºC,4 hours	4.4	0.6	23.3
Calcination 150 ºC, sinter 650 ºC,6 hours	4.4	0.3	23.3
Calcination 175 ºC, sinter 650 ºC,2 hours	4.4	0.2	23.3
Calcination 175 ºC, sinter 650 ºC,4 hours	0	0	0
Calcination 175 ºC, sinter 650 ºC,6 hours	0	0	0

Table-1 shows that $BiFe_{0.9}Zn_{0.1}O_3$ powder has no impurities (oxide phases) with calcination temperature of 175 ºC for 4 hours and sintering temperature of 650 ºC for 6 hours. While $BiFe_{0.93}Zn_{0.07}O_3$ powder has no impurities (oxide phases) with calcination temperature of 175 ºC for 4 hours and sintering temperature of 650 ºC for 4 and 6 hours (Table-2). These powder that has no oxide phases, do not have current leakage problem, because there are no oxygen vacancies coupled with the emergence of oxide during processing. It supports with a high magnetic properties shown in Figures 17 and 18.

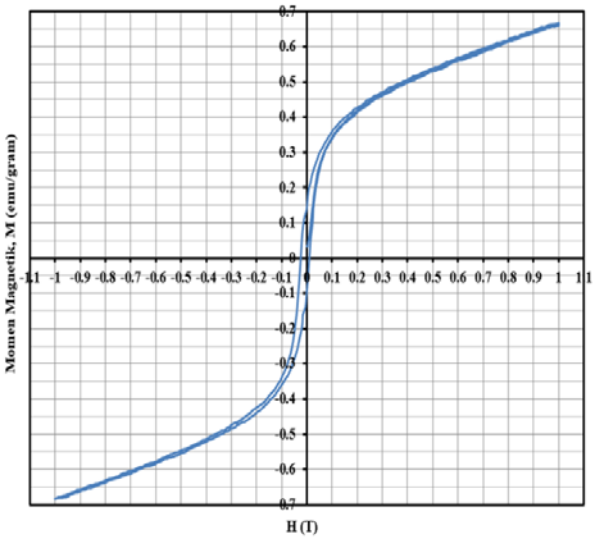

Figure-17. Magnetic properties of $BiFe_{0.9}Zn_{0.1}O_3$ with Calcination at 175 ºC (4 Hours), sintering at 650 ºC (6 hours).

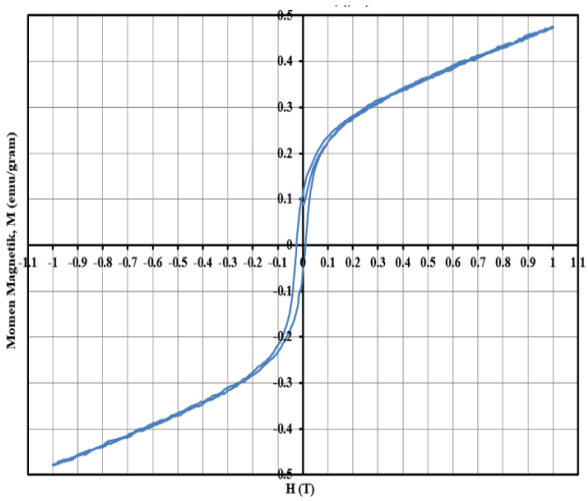

Figure-18. Magnetic properties of $BiFe_{0.93}Zn_{0.07}O_3$ with Calcination at 175 ºC (4 hours), sintering at 650 ºC (6 hours).

Figures 17 and 18 shows that the curve is hysteresis and $BiFe_{0.9}Zn_{0.1}O_3$has magnetic saturation polarization of 0.65 emu/gram higher than of $BiFe_{0.93}Zn_{0.07}O_3$of 0.48 emu/gram. While remnant values of both sample are same approximately of 0.01-0.05 T. The values of magnetic saturation polarization for both sample are higher and better than of other sample with different parameters, shown in Tables 3 and 4.

Table-3. Magnetic saturation polarization for $BiFe_{0.9}Zn_{0.1}O_3$.

Treatment	Magnetic saturation (emu/gram)
Calcination 150 ºC, sinter 650 ºC,2 hours	0.19
Calcination 150 ºC, sinter 650 ºC,4 hours	0.29
Calcination 150 ºC, sinter 650 ºC,6 hours	0.34
Calcination 175 ºC, sinter 650 ºC,2 hours	0.41
Calcination 175 ºC, sinter 650 ºC,4 hours	0.48
Calcination 175 ºC, sinter 650 ºC,6 hours	0.65

Table-4. Magnetic saturation polarization for $BiFe_{0.93}Zn_{0.07}O_3$.

Treatment	Magnetic saturation (emu/gram)
Calcination 150 ºC, sinter 650 ºC,2 hours	0.10
Calcination 150 ºC, sinter 650 ºC,4 hours	0.21
Calcination 150 ºC, sinter 650 ºC,6 hours	0.28
Calcination 175 ºC, sinter 650 ºC,2 hours	0.34
Calcination 175 ºC, sinter 650 ºC,4 hours	0.37
Calcination 175 ºC, sinter 650 ºC,6 hours	0.48

Tables 3 and 4 show that powder with oxide phases has lower of magnetic saturation. 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.

CONCLUSIONS

Sol-gel method at low temperatures (calcination temperature of 175 ºC and sintering temperature of 650 ºC) could produce powder of BiFe0.9Zn0.1O3and BiFe0.93Zn0.07O3. Especially for sintering time of 6 hours and calcination temperature of 175 ºC, the both powder have no oxide phases, then it will not occur leakage current. The presence of oxide phases could decrease magnetic properties due to leakage current. The highest value of magnetic saturation polarization belongs to $BiFe_{0.9}Zn_{0.1}O_3$ powder.

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for Research and Technology DIKTI, the Republic of Indonesia.

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