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### RESEARCH ARTICLE

## MAGNETIC PROPERTIES OF MAGNESIUM – DOPED BISMUTH FERRITE AS MULTIFERROIC MATERIAL PRODUCED BY SOL GEL METHOD AT LOW TEMPERATURE

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#### Abstract

The multiferroic properties of the material would be better if the material has good magnetic properties as well. Bismuth ferrite ( $\text{BiFeO}_3$ ) is one of multiferroic material group, but it is difficult to produce  $\text{BiFeO}_3$  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  $\text{BiFeO}_3$  doped by Mg to produce  $\text{Bi}_{0.9}\text{Mg}_{0.1}\text{FeO}_3$  and  $\text{Mg}_{0.93}\text{Mg}_{0.07}\text{FeO}_3$ . Engineering process performed by sol-gel method. 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°C and sintering process could be carried out at a temperature of 650°C. From the result of XRD test, it is shown that the powder of  $\text{Bi}_{0.9}\text{Mg}_{0.1}\text{FeO}_3$  has the least amount of 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. The powder has higher value of magnetic polarization saturation than  $\text{Bi}_{0.93}\text{Mg}_{0.07}\text{FeO}_3$  with the value of magnetic polarization saturation of 4.38 emu/gram, while the value of magnetic polarization saturation for  $\text{Bi}_{0.93}\text{Mg}_{0.07}\text{FeO}_3$  is 2.76 emu/gram.

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#### Introduction:-

Research of multiferroic materials has been widespread in recent years, especially with the discovery of the multitude of diverse multiferroic materials. The multiferroic material is a class of materials showing two or more ferrous phases and combining several ferroic properties, namely ferroelectric, ferromagnetic, ferroelasticity, and ferodicity. Electrical and magnetism phenomena have been combined in a common discipline since the 19th century that led to Maxwell's equations. Currently, several studies are focused on materials that combine electrical and ferromagnetic properties (Picozzi et al, 2009). The material is composed of ferroelectric-magnetic material is called multiferroic term. This magnetic characteristic is generated from interaction of exchange between magnetic dipoles derived from the skin of electron-filled orbitals. While the electrical properties occur due to the local electric dipole (Retno et al, 2009).

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In its publication, LW Martin et al (2010) reported a literature review about the research result of ferroelectric and ferromagnetic materials based on oxide and illustrated that the magnetoelectric and multiferroic phenomena. The magnetoelectric properties occur because of the coupling between the magnetized materials, however the degree of electric moment regularity so that magnetization and polarization could appear either by the influence of magnetic field or electric field.

The multiferroic material that has been successfully synthesized and shows the value of the MagnetoElectric (ME) coupling constant is ferrite-based multiferroic material (BiFeO<sub>3</sub>/BFO) (Dwita S, 2016). The material shows a voltage value of 130 volts when given the effect of external magnetic field only of 150 Gauss. The constant of ME is a constant showing the multiferroic properties of a material. The method used for the synthesis process is sol-gel method. But there is still a leakage of current in the BiFeO<sub>3</sub> so that the ME is not optimum. The size of nanoparticles in multiferroic materials with strong coupling of ferroelectric and magnetic properties provides an opportunity for potential applications in the field of information storage (Karpinsky, 2010). This means nanomultiferroic material is the right material for ultimate memory device. With these nanomultiferroic materials, each element of storage media is not only placed in two states but four states, two electrical polarization states and two magnetic states (Lebeugle et al., 2009).

In order to obtain large MagnetoElectric Coupling (coupling ME) effect resulting in stronger magnetic and electrical properties simultaneously in one material could be obtained by a single-phase bulk system or by fabricating the base material by substitution of one or more constituents (Zhang 2009). The bismuth ferrite (BiFeO<sub>3</sub> / BFO) material possesses an interesting feature that the magnetoelectric coupling allows manipulation of the ferroelectric polarization by magnetic field or control of the antiferromagnetic vector orientation by the electric field. This is particularly interesting for spintronics devices, as it could control the magnetization of ferromagnets, exchange coupling to a ferroelectric antiferromagnet through an electric field (Xue-Lian Yu et al., 2009). Bismuth ferrite or BFO is a material that exhibits ferroelectric and antiferromagnetic coexistence at room temperature (Sen et al., 2010).

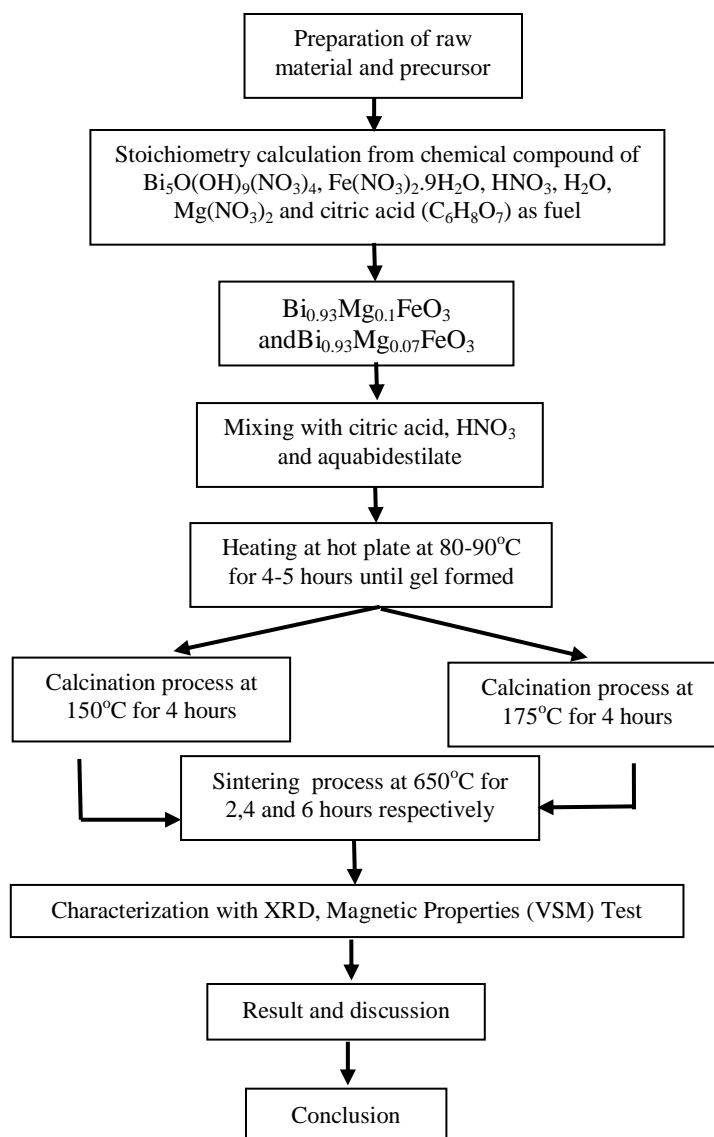
The BFO material has an electrical polarization value at temperature of T<sub>C</sub> below ~ 810°C and magnetic properties at temperature of T<sub>N</sub> - 375°C, so the application of BiFeO<sub>3</sub> in functionality will be increased. At room temperature, bismuth ferrite has a rhombohedralperovskite 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<sub>rh</sub> = 3.965 Å, α<sub>rh</sub> = 89.40°) though it is usually described using hexagonal axes. Hexagonal c-axis is directed along [111] axes of pseudocubic cell and hexagonal cell (a<sub>hex</sub> = 5.58 Å, c<sub>hex</sub> = 13.90 Å) is consisted of six formula units of BiFeO<sub>3</sub>. 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 (X.Yang, 2013). With very wide temperature range of multiferroic behavior (T<sub>C</sub> = 810°C, T<sub>N</sub> = 375°C) [7], BFO 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 BFO 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 BFO disables manifestation of ferroelectric behavior. The resistivity of BFO was successfully improved by doping, especially in case of aliovalent ions.

The structure and properties owned BiFeO<sub>3</sub> intensively studied by many researchers but are still hampered by the leakage of current problems arising from non-stoichiometric. It is difficult to obtain a single phase material of BiFeO<sub>3</sub>. Phase impurities that arise during synthesis usually as Bi<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>, and Bi<sub>25</sub>FeO<sub>39</sub> (Ke, Hua et al, 2010). This phase change stoichiometry and cause oxygen vacancies coupled with the emergence of iron oxide during processing. It causes leakage of current. Single phase of BiFeO<sub>3</sub> 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 Bi<sub>0.93</sub>Mg<sub>0.1</sub>FeO<sub>3</sub> and Bi<sub>0.93</sub>Mg<sub>0.07</sub>FeO<sub>3</sub>.

### Materials and Methods:-

The engineering process of Bi<sub>0.93</sub>Mg<sub>0.1</sub>FeO<sub>3</sub> and Bi<sub>0.93</sub>Mg<sub>0.07</sub>FeO<sub>3</sub> uses basic compound of pro analysis Merck product with a purity of 99.99% Bi<sub>5</sub>O(OH)<sub>9</sub>(NO<sub>3</sub>)<sub>4</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, HNO<sub>3</sub>, H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub> and citric acid C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> 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 CuK $\alpha$  radiation. Analysis (TGA) / Differential Thermal Analysis (DTA) aimed to observe changes in mass and heat of samples (still in gel qform) to the increase in temperature, using a TGA / DTA Thermal Balance Research type LINSEIS L81-Series I / L81- STA (TGA-DTA). To know the magnetic properties, it used VSM (Vibrating Sample Magnetometer) device.

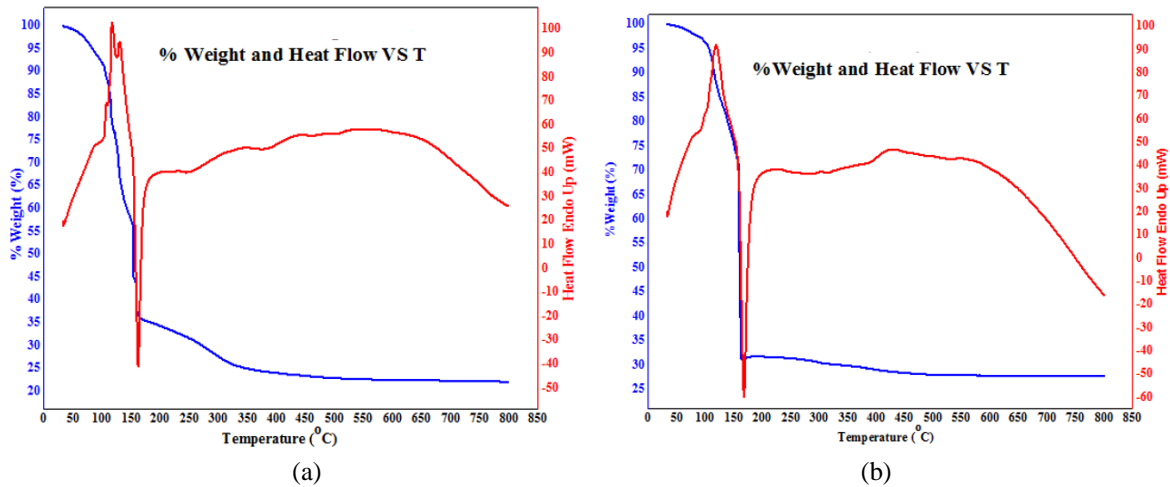


**Figure 1:-**Flowchart of Engineering Process

Figure 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).

## Results and Discussions:-

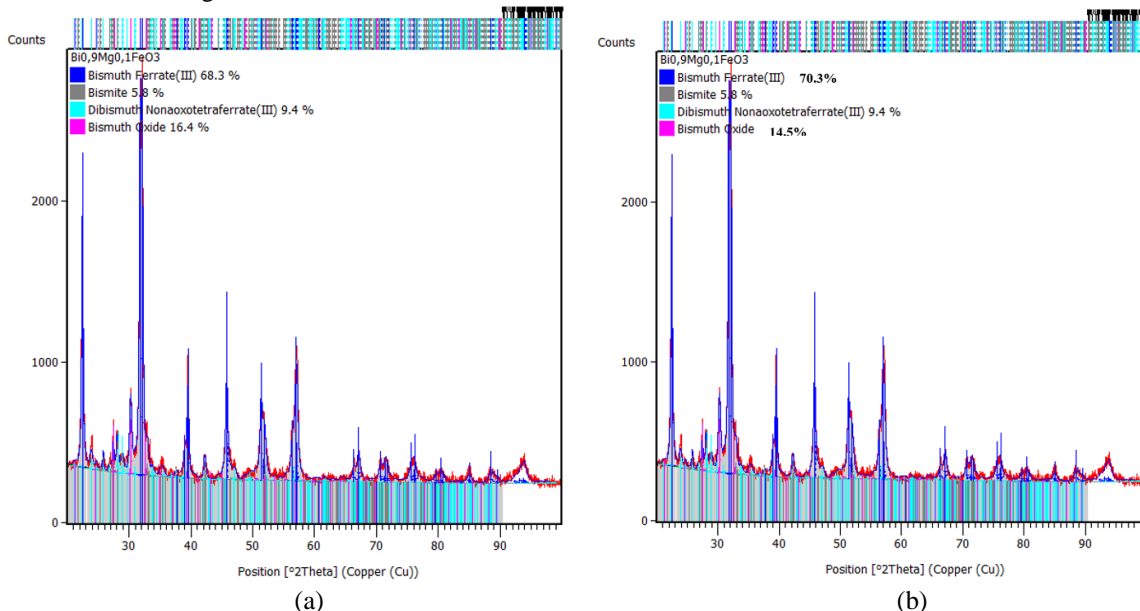
The results of TGA/DTA test are shown in Figure 2. The data are used to determine the temperature of calcination and sintering process.



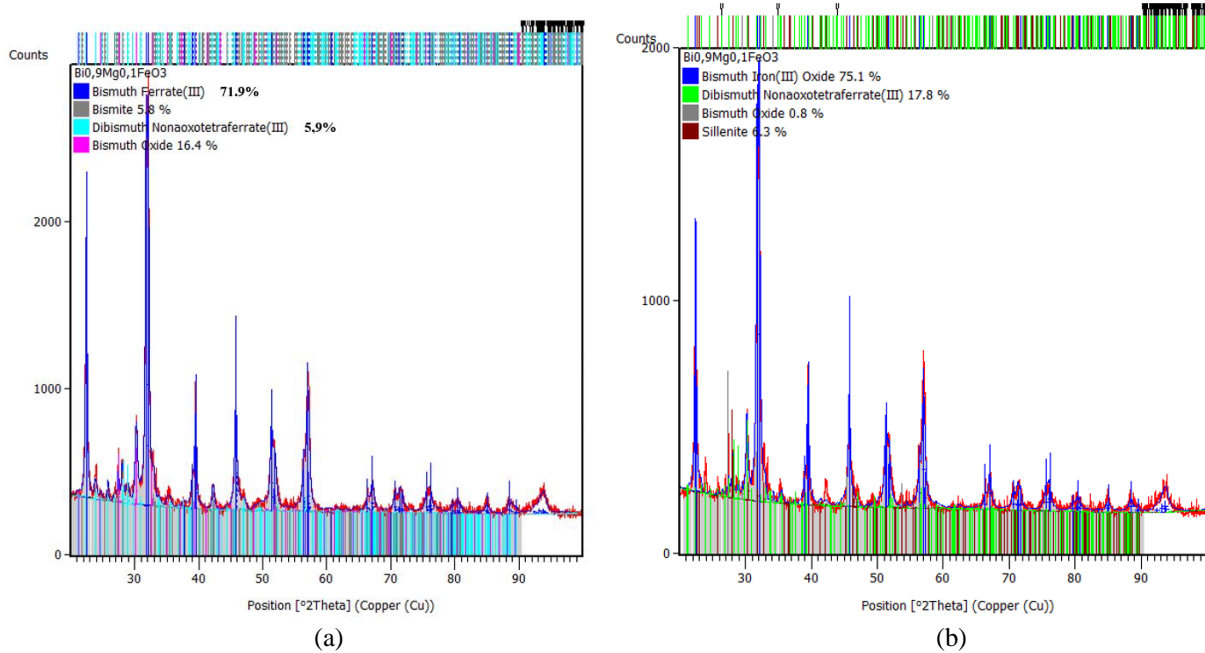
**Figure 2:-**Graph of TGA/DTA Test of  $\text{Bi}_{0.9}\text{Mg}_{0.1}\text{FeO}_3$  Gel (a) and  $\text{Bi}_{0.93}\text{Mg}_{0.07}\text{FeO}_3$  Gel (b)

Figure 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. So for this research, it is used 150 and 175°C for calcination process and 650°C for sintering process.

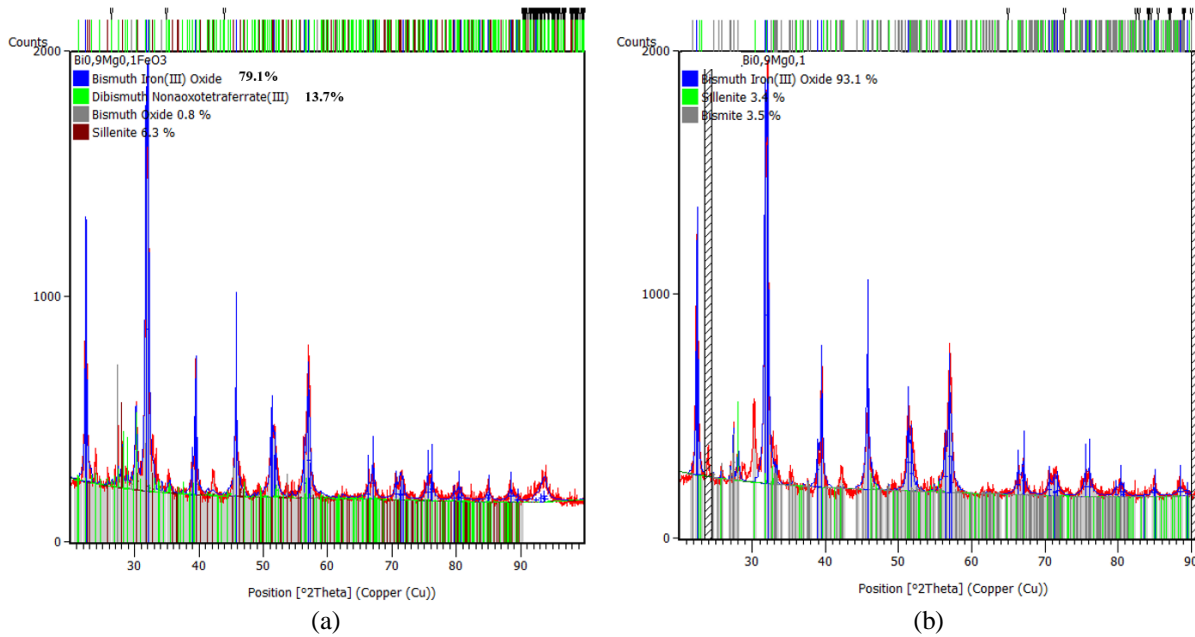
To confirm the formation of  $\text{Bi}_{0.9}\text{Mg}_{0.1}\text{FeO}_3$  phases, it is performed XRD test of sample for all parameters and the results are shown in Figure 3-5.



**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) Sintering at 650°C for 4 Hours (b)



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



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

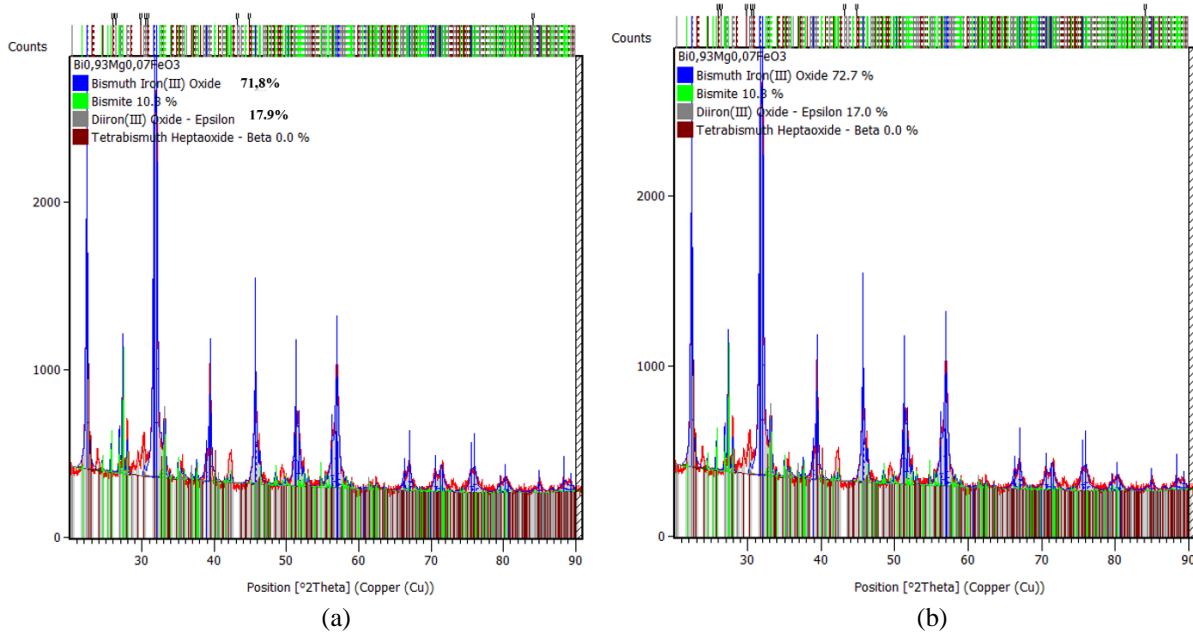
As we know that  $\text{BiFeO}_3$  phase is still hampered by the leakage of current problems arising from non-stoichiometric. It is difficult to obtain a single phase material of  $\text{BiFeO}_3$ . Oxide phases such as  $\text{Bi}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_4$  and  $\text{Bi}_{25}\text{FeO}_{39}$  (sillenite) could change stoichiometry and cause oxygen vacancies coupled with the emergence of iron oxide during processing. It causes leakage of current. Figures 3-5 show 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 Table 1 (taken from Figures 3-5).

**Table 1:-**Percentage ofOxide Phases in  $\text{Bi}_{0.93}\text{Mg}_{0.07}\text{FeO}_3$

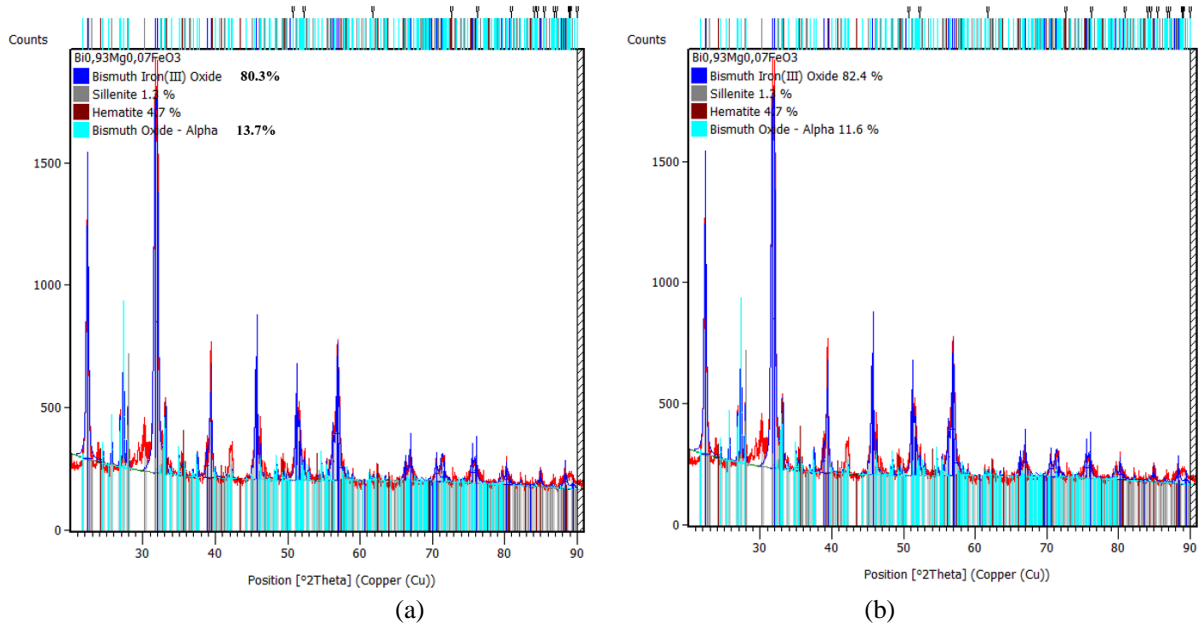
Treatment	Bismite ( $\text{Bi}_2\text{O}_3$ )(%)	$\text{Bi}_2\text{O}_4$ (%)	Silenite ( $\text{Bi}_{25}\text{FeO}_{39}$ )(%)	Total Oxides (%)
Calcination 150°C, sinter 650°C,2 hours	5.8	16.4	0	22.2
Calcination 150°C, sinter 650°C,4 hours	5.8	14.5	0	20.3
Calcination 150°C, sinter 650°C,6 hours	5.8	16.4	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

Calcined powder with higher temperature (175°C) will contain fewer oxide phases as well as the longer sintering time, it will contain less amount of oxide phases too. The least amount of oxide phases belong to powder calcined at 175°C and sintered for 6 hours.

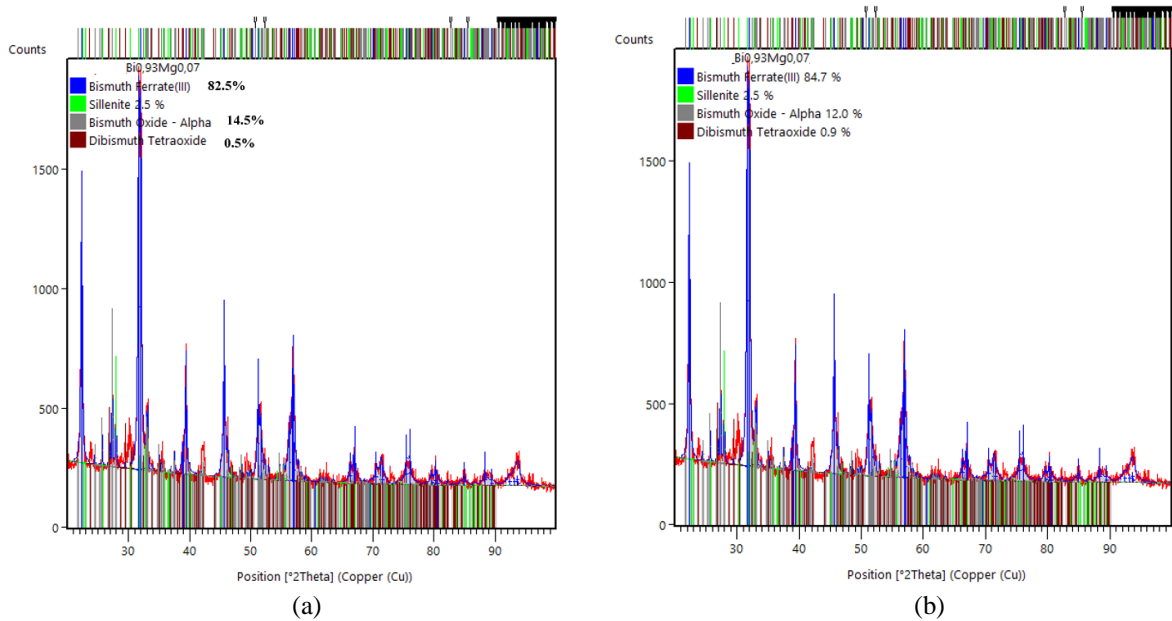
To confirm the formation of  $\text{Bi}_{0.93}\text{Mg}_{0.07}\text{FeO}_3$  phases, it is performed XRD test of sample for all parameters and the results are shown in Figure 6-8



**Figure 6:-**XRD Pattern of  $\text{Bi}_{0.93}\text{Mg}_{0.07}\text{FeO}_3$ , Calcination at 150°C for 4 Hours and Sintering at 650°C for 2 Hours (a) Sintering at 650°C for 4 Hours (b)



**Figure 7:-**XRD Pattern of  $\text{Bi}_{0.93}\text{Mg}_{0.07}\text{FeO}_3$ , Calcination at 150°C for 4 Hours and Sintering at 650°C for 6 Hours (a) Calcination at 175°C for 4 Hours and Sintering at 650°C for 2 Hours (b)



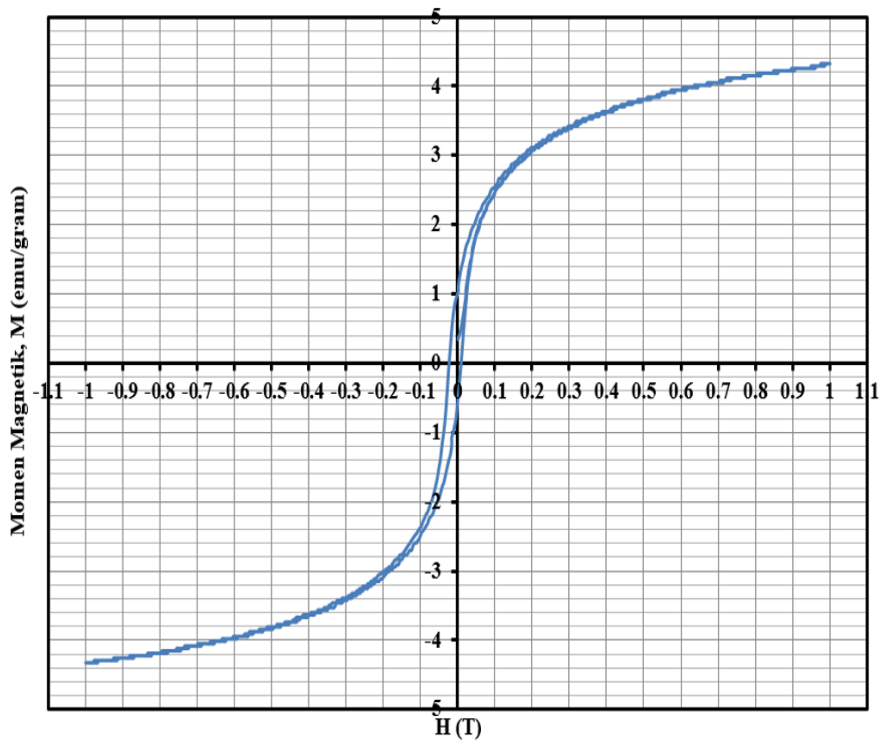
**Figure 8:-**XRD Pattern of  $\text{Bi}_{0.93}\text{Mg}_{0.07}\text{FeO}_3$ , Calcination at 175°C for 4 Hours and Sintering at 650°C for 4 Hours (a) Sintering at 650°C for 6 Hours (b)

Figure 6-8 show that  $\text{Bi}_{0.93}\text{Mg}_{0.07}\text{FeO}_3$  still has oxide phases such as bismite ( $\text{Bi}_2\text{O}_3$ ),  $\text{Fe}_2\text{O}_3\text{-}\epsilon$ ,  $\text{Bi}_4\text{O}_6$ , silenite ( $\text{Bi}_{25}\text{FeO}_{39}$ ) and  $\text{Bi}_2\text{O}_4\text{-}\alpha$ . The presence of these oxide phases may cause a leakage of current which could reduce magnetic properties of the material. Data of formation of oxide phases could be tabulated at Table 2 (taken from Figures 6-8).

**Table-2;-**Percentage ofOxide Phases in  $\text{Bi}_{0.93}\text{Mg}_{0.07}\text{FeO}_3$

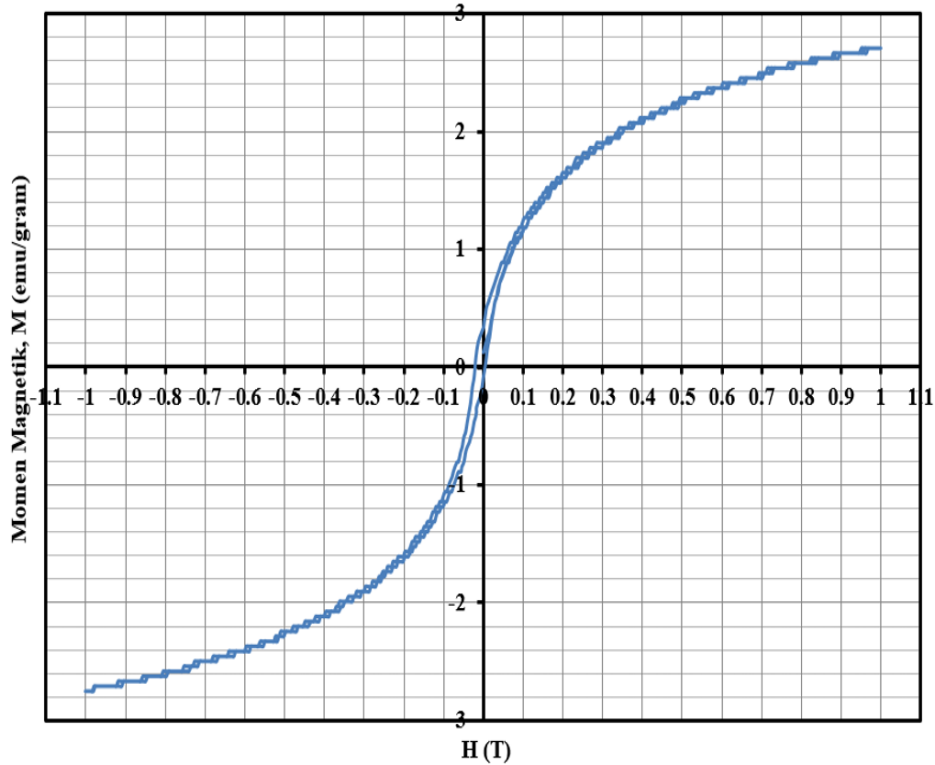
Treatment	Bismite ( $\text{Bi}_2\text{O}_3$ )(%)	$\text{Fe}_2\text{O}_3$ (ε)(%)	Silenite ( $\text{Bi}_{25}\text{FeO}_{39}$ )(%)	$\text{Bi}_2\text{O}_4$ (%)	TotalOxides (%)
Calcination 150°C, sinter 650°C,2 hours	10.8	17.9	0	0	28.7
Calcination 150°C, sinter 650°C,4 hours	10.8	17.0	0	0	27.8
Calcination 150°C, sinter 650°C,6 hours	0	4.7	1.3	13.7	19.7
Calcination 175°C, sinter 650°C,2 hours	0	4.7	1.3	11.6	17.6
Calcination 175°C, sinter 650°C,4 hours	0	0	2.5	14.5	17
Calcination 175°C, sinter 650°C,6 hours	0	0	2.5	12	14.5

Table 2 shows that powder which has the least amount of oxide phases is powder that is calcined at 175°C and sintered at 650°C for 6 hours. The longer the sinter time, the less of oxide phases found in the powder. The amount of oxide phases present in the powder will affect the magnetic properties of the powder, as the magnetic properties of the powder shown in Figure 9 and 10.



**Figure 9:-**Magnetic Properties of  $\text{Bi}_{0.9}\text{Mg}_{0.1}\text{FeO}_3$  with Calcination at 175°C (4 Hours), Sintering at 650°C (6 Hours)





**Figure 10:-**Magnetic Properties of  $\text{Bi}_{0.93}\text{Mg}_{0.07}\text{FeO}_3$  with Calcination at  $175^\circ\text{C}$  (4 Hours), Sintering at  $650^\circ\text{C}$  (6 Hours)

Figures 9 and 10 show value of magnetic properties of  $\text{Bi}_{0.9}\text{Mg}_{0.1}\text{FeO}_3$  and  $\text{Bi}_{0.93}\text{Mg}_{0.07}\text{FeO}_3$  which has little oxide phases. Meanwhile magnetic properties of other parameters showed in Table 3 and 4.

**Table3:-** Magnetic Saturation Polarization for  $\text{Bi}_{0.9}\text{Mg}_{0.1}\text{FeO}_3$

Treatment	Magnetic Saturation (emu/gram)
Calcination $150^\circ\text{C}$ , sinter $650^\circ\text{C}$ , 2 hours	2.05
Calcination $150^\circ\text{C}$ , sinter $650^\circ\text{C}$ , 4 hours	2.29
Calcination $150^\circ\text{C}$ , sinter $650^\circ\text{C}$ , 6 hours	3.06
Calcination $175^\circ\text{C}$ , sinter $650^\circ\text{C}$ , 2 hours	3.89
Calcination $175^\circ\text{C}$ , sinter $650^\circ\text{C}$ , 4 hours	4,08
Calcination $175^\circ\text{C}$ , sinter $650^\circ\text{C}$ , 6 hours	4.38

**Table4:-** Magnetic Saturation Polarization for  $\text{Bi}_{0.93}\text{Mg}_{0.07}\text{FeO}_3$

Treatment	Magnetic Saturation (emu/gram)
Calcination $150^\circ\text{C}$ , sinter $650^\circ\text{C}$ , 2 hours	0.98
Calcination $150^\circ\text{C}$ , sinter $650^\circ\text{C}$ , 4 hours	1.03
Calcination $150^\circ\text{C}$ , sinter $650^\circ\text{C}$ , 6 hours	1.09
Calcination $175^\circ\text{C}$ , sinter $650^\circ\text{C}$ , 2 hours	2.41
Calcination $175^\circ\text{C}$ , sinter $650^\circ\text{C}$ , 4 hours	2.65
Calcination $175^\circ\text{C}$ , sinter $650^\circ\text{C}$ , 6 hours	2.76

Table 3 and 4 show that powder which is calcined at higher temperature ( $175^\circ\text{C}$ ) and sintered for longer time (6 hours) has a higher value of magnetic saturation (2.76 emu/gram for  $\text{Bi}_{0.9}\text{Mg}_{0.1}\text{FeO}_3$  and 4.38 emu/gram for  $\text{Bi}_{0.93}\text{Mg}_{0.07}\text{FeO}_3$ ). Longer time of sintering and higher temperature of calcination could produce powder with minimum of oxide phases (Table 1 and 2), so it could reduce leakage of current. It is expected that the value could contribute to increase MagnetoElectric (ME) constant to have high quality of multiferroic material. This phenomenon will be proven in subsequent research.

**Conclusion:-**

Sol-gel method at low temperatures (calcination temperature of 150 and 175°C and sintering temperature of 650°C) could produce powder of  $\text{Bi}_{0.9}\text{Mg}_{0.1}\text{FeO}_3$  and  $\text{Bi}_{0.93}\text{Mg}_{0.07}\text{FeO}_3$ . Powder ( $\text{Bi}_{0.9}\text{Mg}_{0.1}\text{FeO}_3$ ) which is produced by calcination temperature of 175°C and sintering temperature of 650°C for 6 hours has the least amount of oxide phases (total oxide of 6.9%). The powder has also the highest value of magnetic saturation (4.38 emu/gram) due to leakage of current minimum belong to  $\text{Bi}_{0.9}\text{Mg}_{0.1}\text{FeO}_3$ .

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