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A CHEMICAL ROUTE TO THE SYNTHESIS OF $Bi_{1-x}Mg_xFeO_3$ (x=0.1 and x=0.07) NANOPARTICLE WITH ENHANCED ELECTRICAL PROPERTIES AS MULTIFERROIC MATERIAL

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Abstract:

Bismuth ferrite ($BiFeO_3$) is one of multiferroic material group, but it is difficult to produce $BiFeO_3$ 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 $BiFeO_3$ doped by Mg to produce $Bi_{0.9}Mg_{0.1}FeO_3$ and $Bi_{0.93}Mg_{0.07}FeO_3$. 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 $Bi_{0.9}Mg_{0.1}FeO_3$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, $Bi_{0.93}Mg_{0.07}FeO_3$ has more oxide phases with total oxide of 14.5% which consists of silenite (2.5%) and Bi_2O_4 (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 ($Bi_{0.9}Mg_{0.1}FeO_3$) is higher than ceramic having more oxide ($Bi_{0.93}Mg_{0.07}FeO_3$). The value of electric saturation polarization for $Bi_{0.9}Mg_{0.1}FeO_3$ is of 0.26 kv/cm and for $Bi_{0.93}Mg_{0.07}FeO_3$ is of 0.11 kV/cm.

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

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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^{o}C and magnetic properties at temperature of T_N-375^{o}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, 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 $BiFeO_3$. 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^{o}C, T_N = 375^{o}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_2O_3, $Bi_2Fe_4O_9$, 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+} 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+} 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+} 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-tions, but BF is not typical representative. Its antiferromagnetism is originating from Fe^{3+} ions, and is of G-type, meaning all first neighboring Fe^{3+} ions have opposite magnetic

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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, $Bi_2Fe_4O_9$, and sillenite type phase, $Bi_{25}FeO_{39}$) [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% $Bi_5O(OH)_9.(NO_3)_4$, $Fe(NO_3)_3.9H_2O$, HNO_3, H_2O, $Mg(NO_3)_2$ 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°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).

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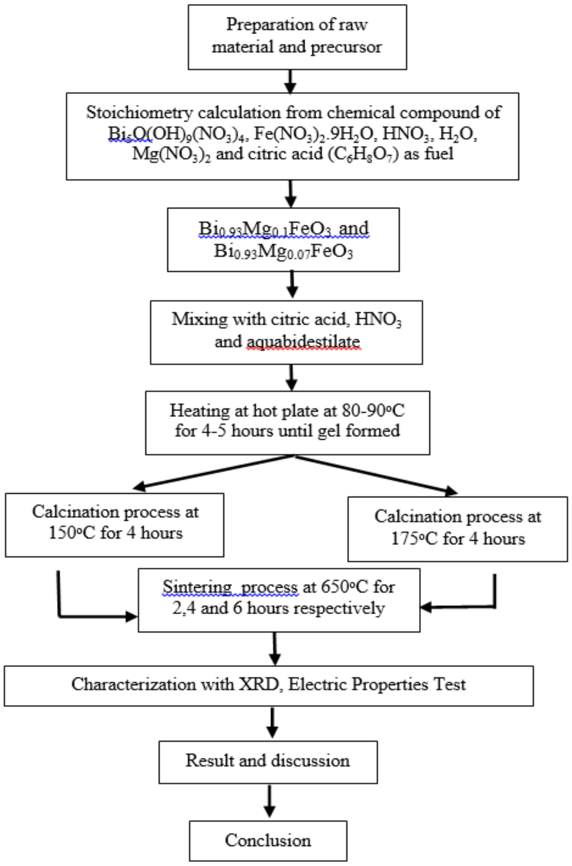
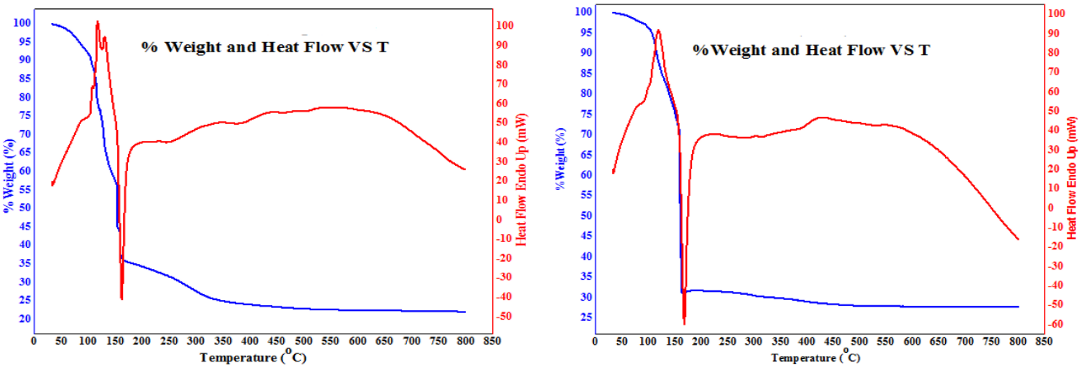


Figure 1: Flowchart of Engineering Process

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.

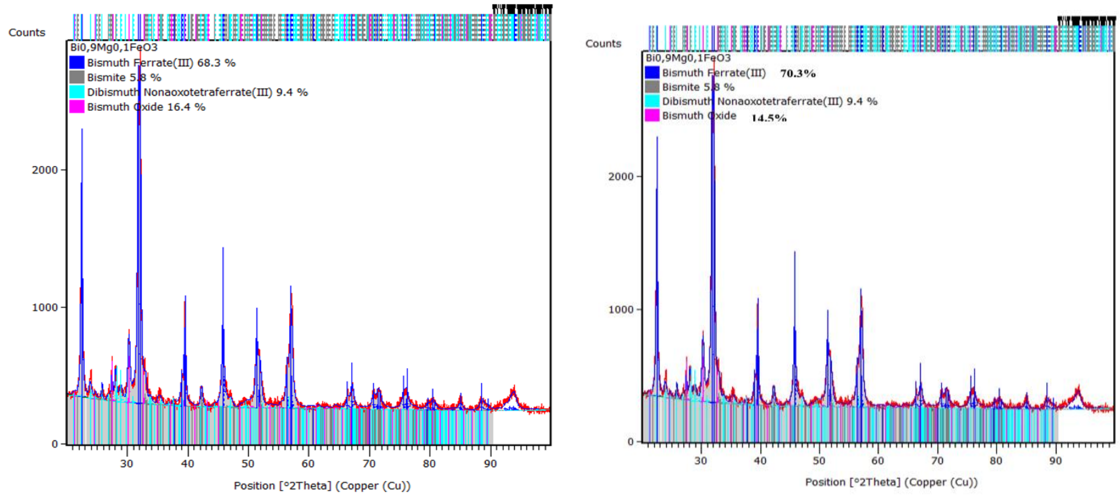


(a) (b)

Figure 2: Graph of TGA/DTA Test of $Bi_{0.9}Mg_{0.1}FeO_3$ Gel (a) and of $Bi_{0.93}Mg_{0.07}FeO_3$ Gel (b)

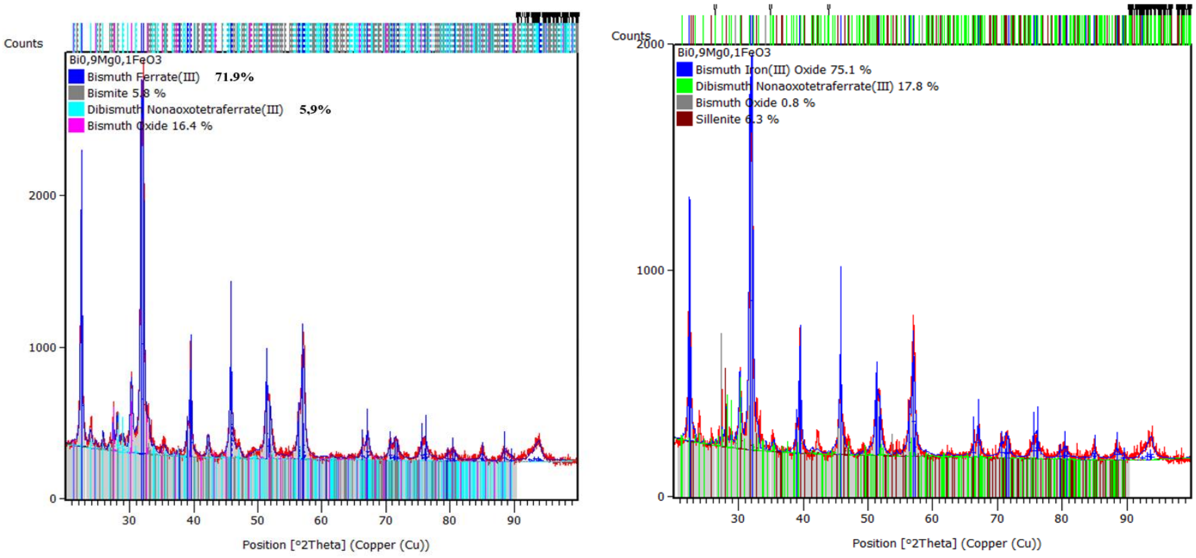
Fig.2 shows that weight reduction of both of ceramic powder is about at 150-200°C approximately. The phase transition which is happen at the temperatures range, shown that calcination process occurs at the temperatures of 150-200°C. The next phase transition occurs at temperatures of 600-650°C (characterized 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.



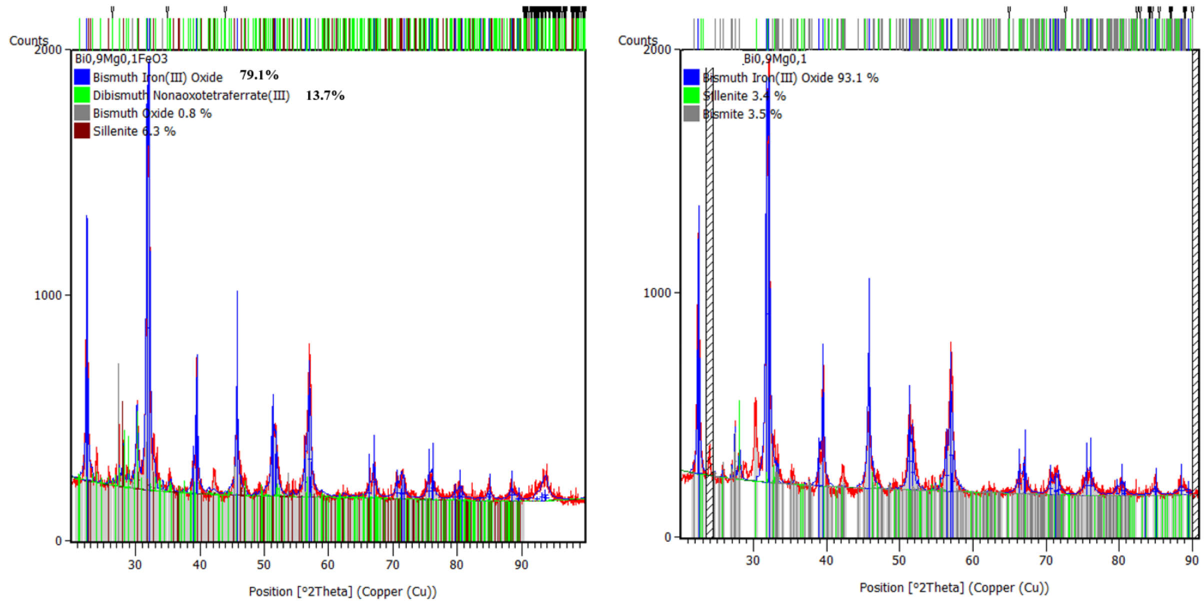
(a) (b)

Figure 3: XRD Pattern of $Bi_{0.9}Mg_{0.1}FeO_3$ Calcination at 150°C for 4 Hours and Sintering at 650°C for 2 Hours (a) and for 4 Hours (b)



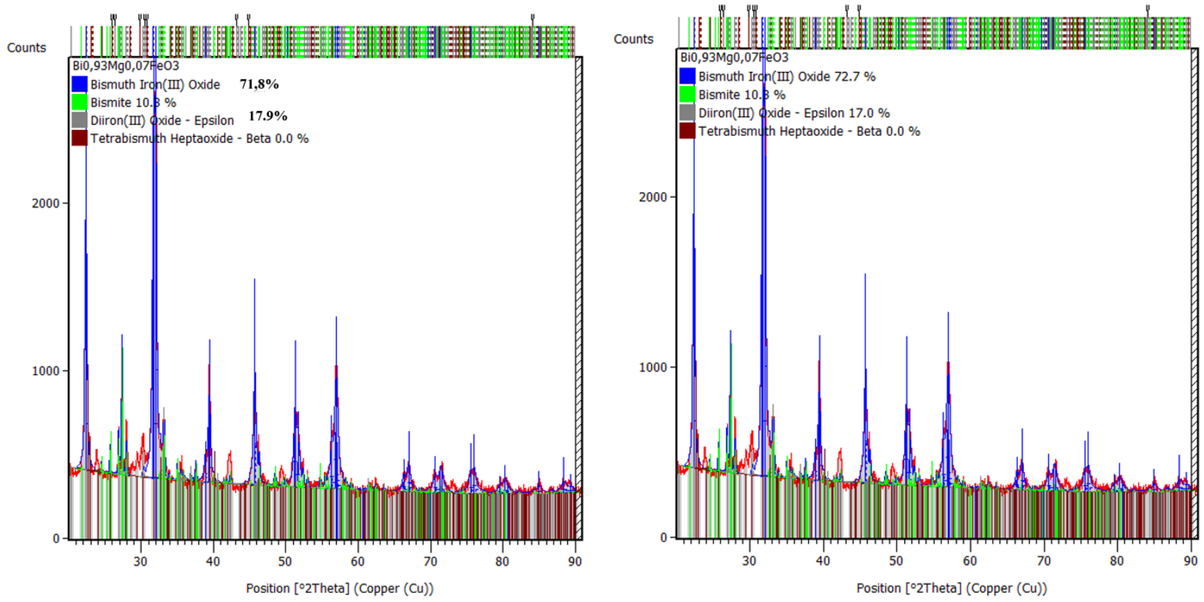
(a) (b)

Figure 4: XRD Pattern of $Bi_{0.9}Mg_{0.1}FeO_3$, 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)



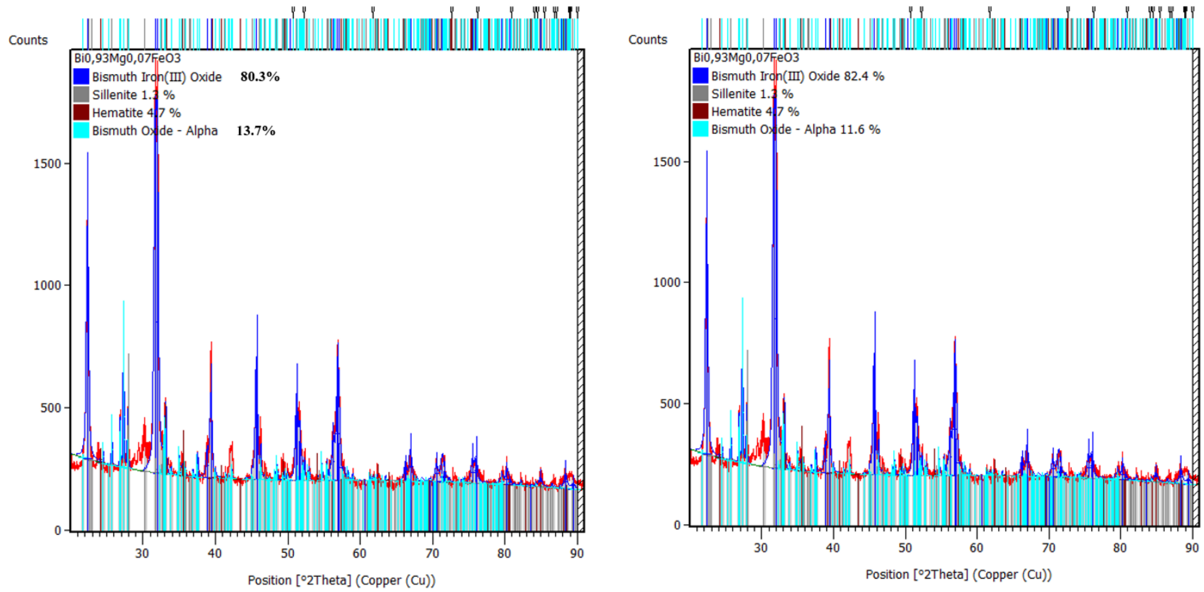
(a) (b)

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)



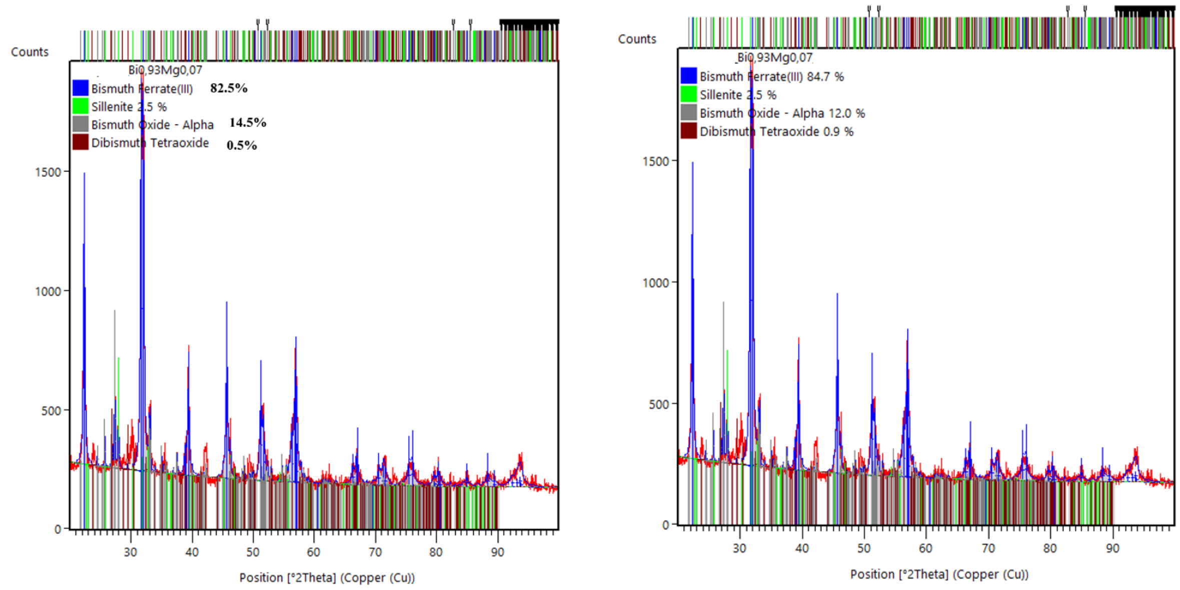
(a) (b)

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)



(a) (b)

Figure 7: XRD Pattern of $Bi_{0.93}Mg_{0.07}FeO_3$, 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)



(a) (b)

Figure 8: XRD Pattern of $Bi_{0.93}Mg_{0.07}FeO_3$, Calcination at 175°C for 4 Hours and Sintering at 650°C for 4 Hours (a) and for 6 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).

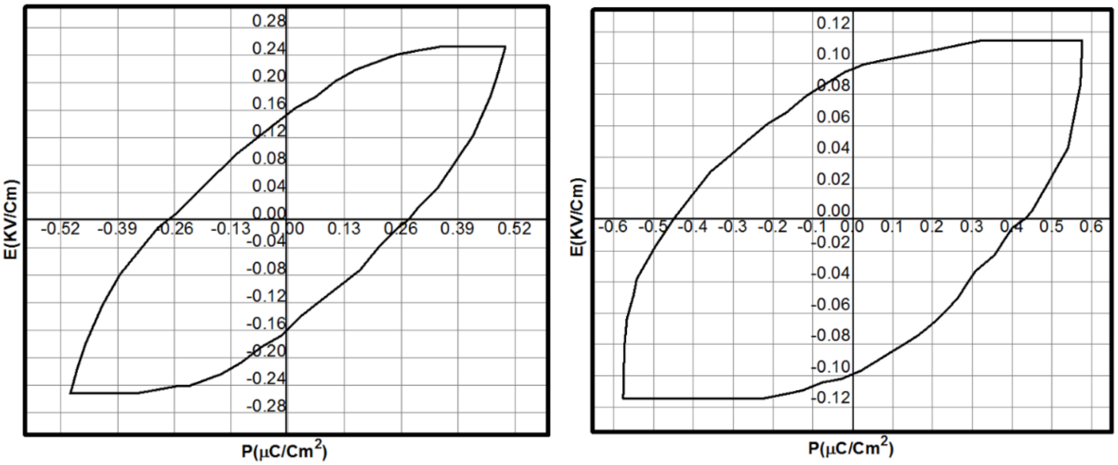
Table 1: Percentage of Oxide Phases in $Bi_{0.9}Mg_{0.1}FeO_3$

Treatment	Bismite (Bi_2O_3) (%)	Bi_2O_4 (%)	Silenite ($Bi_{25}FeO_{39}$) (%)	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

Table 2: Percentage of Oxide Phases in $Bi_{0.93}Mg_{0.07}FeO_3$

Treatment	Bismite (Bi_2O_3) (%)	Fe_2O_3 (ε) (%)	Silenite ($Bi_{25}FeO_{39}$) (%)	Bi_2O_4 (%)	Total Oxides (%)
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-1 shows that $Bi_{0.9}Mg_{0.1}FeO_3$ 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 $Bi_{0.93}Mg_{0.07}FeO_3$ 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.



(a) (b)

Figure 9: Electric Properties of $Bi_{0.9}Mg_{0.1}FeO_3$ Calcination at 175°C, 4 Hours, Sintering at 650°C, 6 Hours (a) and of $Bi_{0.93}Mg_{0.07}FeO_3$ 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^{o}C, sinter 650^{o}C,2 hours	0.07	22.2
Calcination 150^{o}C, sinter 650^{o}C,4 hours	0.10	20.3
Calcination 150^{o}C, sinter 650^{o}C,6 hours	0.13	22.2
Calcination 175^{o}C, sinter 650^{o}C,2 hours	0.17	7.1
Calcination 175^{o}C, sinter 650^{o}C,4 hours	0.21	7.1
Calcination 175^{o}C, sinter 650^{o}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^{o}C, sinter 650^{o}C,2 hours	0.01	28.7
Calcination 150^{o}C, sinter 650^{o}C,4 hours	0.02	27.8
Calcination 150^{o}C, sinter 650^{o}C,6 hours	0.05	19.7
Calcination 175^{o}C, sinter 650^{o}C,2 hours	0.07	17.6
Calcination 175^{o}C, sinter 650^{o}C,4 hours	0.10	17.0
Calcination 175^{o}C, sinter 650^{o}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^{o}C for 4 hours and sintering temperature of 650^{o}C for 6 hours and for x = 0.1

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