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Improvement of Magnetic Properties Through The Synthesis of Ceramic Materials with Various Weight Ratios of BaTiO, $BiFeO_3$, and $BaFe_{12}O_{19}$ With Sol-Gel Method

Dwita.S[1*], Marlin.W[2] and Yuli.NM[1]

[1]*Study Program of Mechanical Engineering, Institu Teknologi Indonesia, Puspiptek Raya Street, Tangerang Selatan, Banten, Indonesia*

[2]*National Research and Innovation Regency (BRIN), Puspiptek Raya Street, Tangerang Selatan, Banten, Indonesia*

Electronic devices designed with multiferroic materials comprising both electrical and magnetic properties are needed for significant memory storage. Several studies have been carried out on multiferroic materials based on $BaTiO_3$, $BiFeO_3$, and $BaFe_{12}O_{19}$. However, none have obtained optimum multiferroic properties because they still show inadequate magnetic properties, especially energy values. The method used is sol-gel which could produce powder in nano size. The X-Ray Diffraction (XRD) and permagraph tests with metallographic observations using Scanning Electron Microscopy (SEM) were used to know phase of powder, value of magnetic properties and morphology of the powder. The ceramic compounds are mixing powder based on $BaTiO_3$, $BiFeO_3$, and $BaFe_{12}O_{19}$. Furthermore, the ratio of the weight composition of the materials varied by 1:1:1; 1:2:2; 2:1:1; 1:2:1 and 2:1:2. The result showed that the best magnetic properties were obtained at the weight composition ratio of 1:2:2 with a magnetic energy value of 48.0897×10^4 GkA/m. Based on SEM analysis, the sample with this weight ratio was dominated by the $BiFeO_3$ and $BaFe_{12}O_{19}$ phases with high magnetic properties.

Keywords: magnetic properties; multiferroic; sol-gel

I. INTRODUCTION

Over the last 5 years, several studies have been continuously carried out on the advanced materials in Indonesia's electronic devices, such as multiferroic material. It consists of more than one physical property, such as ferroelectricity, ferromagnetism, ferroelasticity, and ferrotoroidicity. One of the easiest characterisation methods of multiferroic material is its ability to respond to small external magnetic field effect in the form of a large electric voltage, thereby indicating the presence of a large MagnetoElectric (ME) coupling. An example of a high-quality multiferroic material is Bismuth Ferrite (BiFeO3) which needs to be a single-phase and nanoparticles to achieve the maximum effect (Dwita, S, Yuli, NM, Marlin, W 2019). Meanwhile, in reality, it is difficult to obtain single-phase $BiFeO_3$ material. This is because its formation is not stoichiometric, thereby creating impurities, such as $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$, that appear during the synthesis process. These impurities cause a large leakage current to reduce ferromagnetic properties, decreasing the value of the ME coupling and resistivity. Therefore, this study aims to carry out a nano-sized ceramic synthesis process combined with $BiFeO_3$, ferroelectric ($BaTiO_3$), and magnetic ($BaFe_{12}O_{19}$) material with the hypothesis that the impurity phase formed is replaced by ferroelectric and magnetic phases. These properties are added to the ceramic material to increase a large electric voltage response due to a small magnetic field effect. Furthermore, nanosize is needed to increase the surface area, which increases the interaction

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*Corresponding author's e-mail: dwita_suastiyanti@iti.ac.id

of ferroelectric and magnetic atoms (Mukesh, K, Mishra, RN, Mahaling 2018). The technology used for this synthesis process is sol-gel which requires simple equipment and a low process temperature applied to produce nano-sized powders.

Multiferroic materials have attracted research interest in recent years due to the simultaneous presence of ferromagnetic, ferroelectric, and ferroelastic properties in a single phase (Eerenstein W, Mathur N, Scott J, 2006; Cheong S-W, Mostovoy M, 2007). Bismuth ferrite ($BiFeO_3$) is one of the most promising multiferroic compounds used to develop spintronics, sensors, optical filters, memory, and data storage devices (Scott J, 2007; Park T-J *et. al.,* 2007; Selbach SM *et al.,* 2007). $BiFeO_3$ material has a rhombohedral distorted perovskite structure with space group R_3c, which coexistence with ferroelectric and magnetic substances at Curie temperature T_C and antiferromagnetic Neel temperatures of 826-845˚C and = type G, T_N = 360-380˚C.

The application of $BiFeO_3$ is limited irrespective due to the presence of impurities such as $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$. Consequently, it is difficult to obtain single-phase $BiFeO_3$, which is not stoichiometrically formed. This impurity phase causes a decrease in ferromagnetic properties, with the occurrence of a large leakage current, decrease in magnetoelectric coupling and resistivity (Mukesh K, Mishra R.N, Mahaling, 2018). Many methods have been used to synthesise $BiFeO_3$ powder. According to Guohua Dong *et al.* (2014), conventional solid-state reaction methods cannot produce single-phase $BiFeO_3$. Conversely, the synthetic chemical method (sol-gel) produces $BiFeO_3$, which is better when the powder particles are nano-sized.

Several studies have highlighted the use of nitric acid in the washing processes, which is calcined to remove impurities. An instance is the solid-state reaction method used to obtain single-phase $BiFeO_3$. However, subsequent washing results obtained coarser powders and poor reproducibility.

Based on the background of the problems above, such as the high level of difficulty in obtaining good quality multiferroic properties in $BiFeO_3$ powder due to impurities, Nanoceramics was synthesised using ferroelectric and magnetic compounds, such as $BaTiO_3$ and $BaFe_{12}O_{19}$. The nanosize of the ceramic produced is necessary in order to form a wider surface capable of increasing the interaction between magnetic and electrical properties to obtain a strong MagnetoElectric (ME).

The multiferroic nature of a material is highly dependent on the magnetic properties of the constituent material. The contribution of good magnetic properties leads to the high value of the ME constant of multiferroic materials, such as $BaFe_{12}O_{19}$ material. Ferromagnetic properties also make a good contribution to the multiferroic properties of a material by reducing energy consumption when applied as the ultimate memory device. Dwita S has succeeded in synthesising single-phase and nano-sized $BaFe_{12}O_{19}$ (barium hexaferrite/BHF) powder using the sol-gel method due to its good magnetic properties with an intrinsic coercivity value of 453.2 kA/m (Dwita Suastiyanti, 2013).

II. MATERIALS AND METHOD

This study was carried out using 3 powder constituent compounds, namely $BaTiO_3$, $BiFeO_3$, and $BaFe_{12}O_{19}$. These compounds were synthesised using the wet chemical method (Sol-gel) as follows: Several basic compounds were used to synthesise $BaTiO_3$, such as Barium Nitrate ($Ba(NO_3)_2$), $C_6H_8O_7$, Titanium Dioxide (TiO_2), and Nitric Acid (HNO_3), and heated for 4-5 hours to form a gel. This was followed by the calcination and sintering processes at a temperature of 150°C, 450°C, and 700°C for 1, 2, and 4 hours.

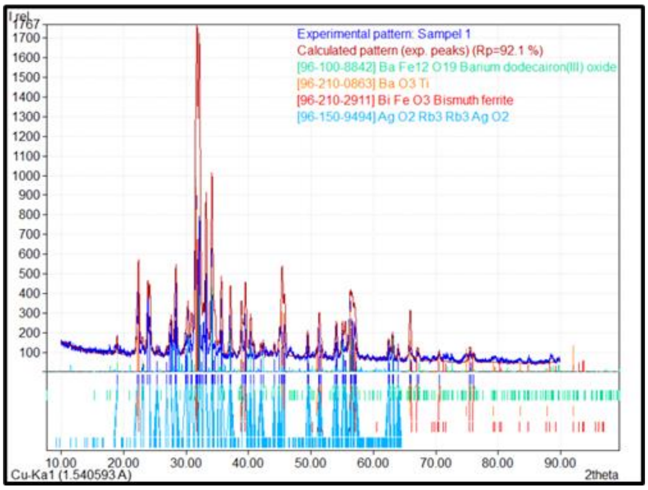
The synthesis of $BiFeO_3$ was carried out using the basic compound pro analysis Merck product with a purity level of 99.99%. The alloys used were Bi.O(OH), $_9(NO_3)_4$, $Fe(NO_3)_3.9H_2O$, HNO_3, H_2O, and citric acid. All compounds were dissolved in aquabidestilate, heated on a hot plate at a constant temperature of 80 - 90°C to form a gel within 4-5 hours. The gel was heated in a furnace at a calcination temperature of 200°C for 1 hour to evaporate water and elements such as C, N, and H. In addition, after producing the $BiFeO_3$, the sintering process is carried out for 6 hours at a temperature of 600°C.

The synthesis of $BaFe_{12}O_{19}$ was carried out using several basic materials, such as $Ba(NO_3)_2$, $Fe(NO_3)_3.9H_2O$, $C_6H_8O_7$ (citric acid), and aqua bidestilata. Meanwhile, the neutralised solution was continuously stirred and evaporated to dryness by heating at 80°C - 90°C on a hot plate to form a gel within 4-5 hours. The obtained gel was heated at 150°C for 4 hours, followed by a calcination process at 450°C for 24 hours. This was also followed by the sintering process carried out at a temperature of 1000°C for 10 hours.

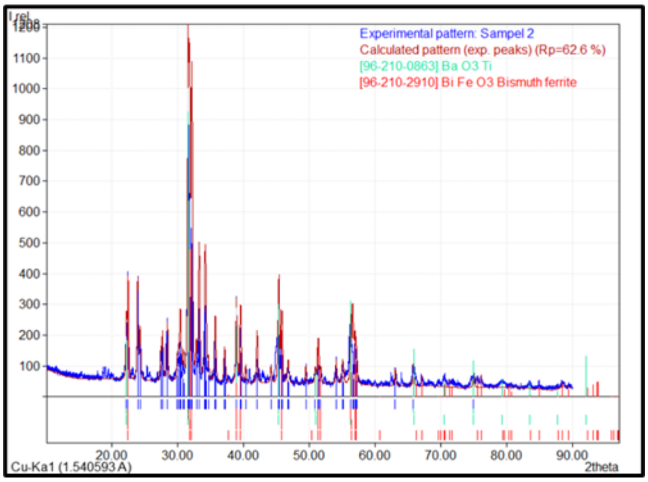
The $BaTiO_3$, $BiFeO_3$ and $BaFe_{12}O_{19}$ powder materials obtained are mixed at weight ratios of $BaTiO_3$: $BiFeO_3$: $BaFe_{12}O_{19}$ in values of 2:1:2, 1:2:2, 2;1:1, 1;2:1 and 1:1:1. The mixed powder pressed into pellets and finally, it is sintered at a temperature of 1200°C for 4 hours.

III. RESULTS AND DISCUSSION

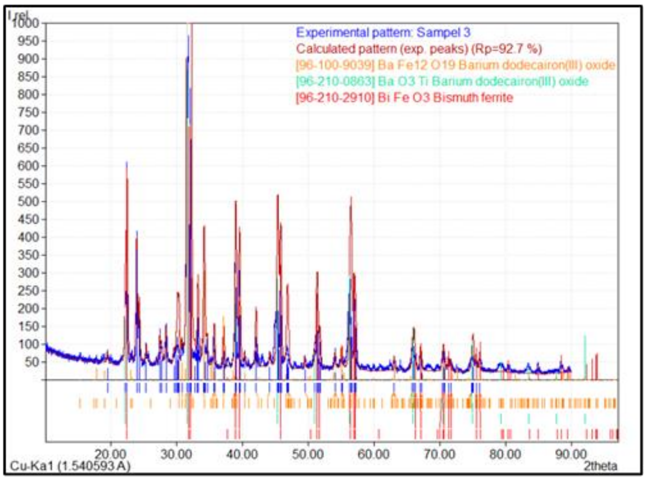
Samples in the form of pellets are tested X-Ray Diffraction, Figures 1(a) to (e) provide 5 sample results of the X-Ray Diffraction test.



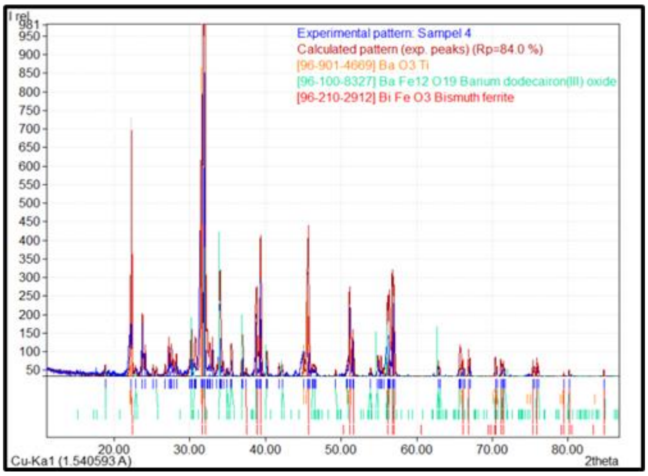
(a)



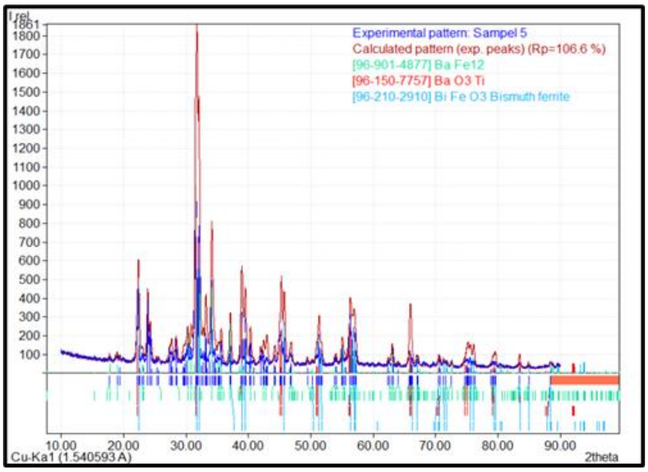
(b)



(c)



(d)



(e)

Figure 1(a) – (e): Diffraction pattern of $BaTiO_3$:$BiFeO_3$: $BaFe_{12}O_{19}$ composite with different mixing ratio of weight percentage = 2:1:2, 1:2:2, 2:1:1, 1:2:1, 1:1:1

Figures 1(a) to (e) show that all powder samples have a weight ratio, which corresponds to the following calculation results:

1. Weight ratio of $BaTiO_3$: $BiFeO_3$: $BaFe_{12}O_{19}$ = 40,6% : 18,8% : 40,6% (Sample 1)
2. Weight ratio of $BaTiO_3$: $BiFeO_3$: $BaFe_{12}O_{19}$ = 20,1% : 40,2% : 40,2% (Sample 2)
3. Weight ratio of $BaTiO_3$: $BiFeO_3$: $BaFe_{12}O_{19}$ = 49,9% : 25,1% : 25,1% (Sample 3)
4. Weight ratio of $BaTiO_3$: $BiFeO_3$: $BaFe_{12}O_{19}$ = 23,9% : 52,2% : 23,9% (Sample 4)
5. Weight ratio of $BaTiO_3$: $BiFeO_3$: $BaFe_{12}O_{19}$ = 32,8% : 33,1% : 33,3% (Sample 5)

The obtained diffraction pattern is complex because it consists of 3 different compounds ($BaTiO_3$, $BiFeO_3$ and $BaFe_{12}O_{19}$). There are no impurities observed.

The permagraph test results with various variations showed that the largest magnetic energy was obtained at the ratio of $BaTiO_3$: $BiFeO_3$: $BaFe_{12}O_{19}$ in values of 1:2:2 to obtain 48.09 x10^4 GkA/m. This is because the content of magnetic material ($BaFe_{12}O_{19}$) in the sample is 2x more than ferritic ($BaTiO_3$). This value is greater than the magnetic energy of the sample, which consists of $BiFeO_3$ and $BaFe_{12}O_{19}$ at weight ratio of 1:1 of 9.89 x 10^4 GkA/m (Dwita Suastiyanti, 2019). Therefore, the contribution of the magnetic properties of the permanent magnet material ($BaFe_{12}O_{19}$) is large enough to increase the magnetic energy by 5 times.

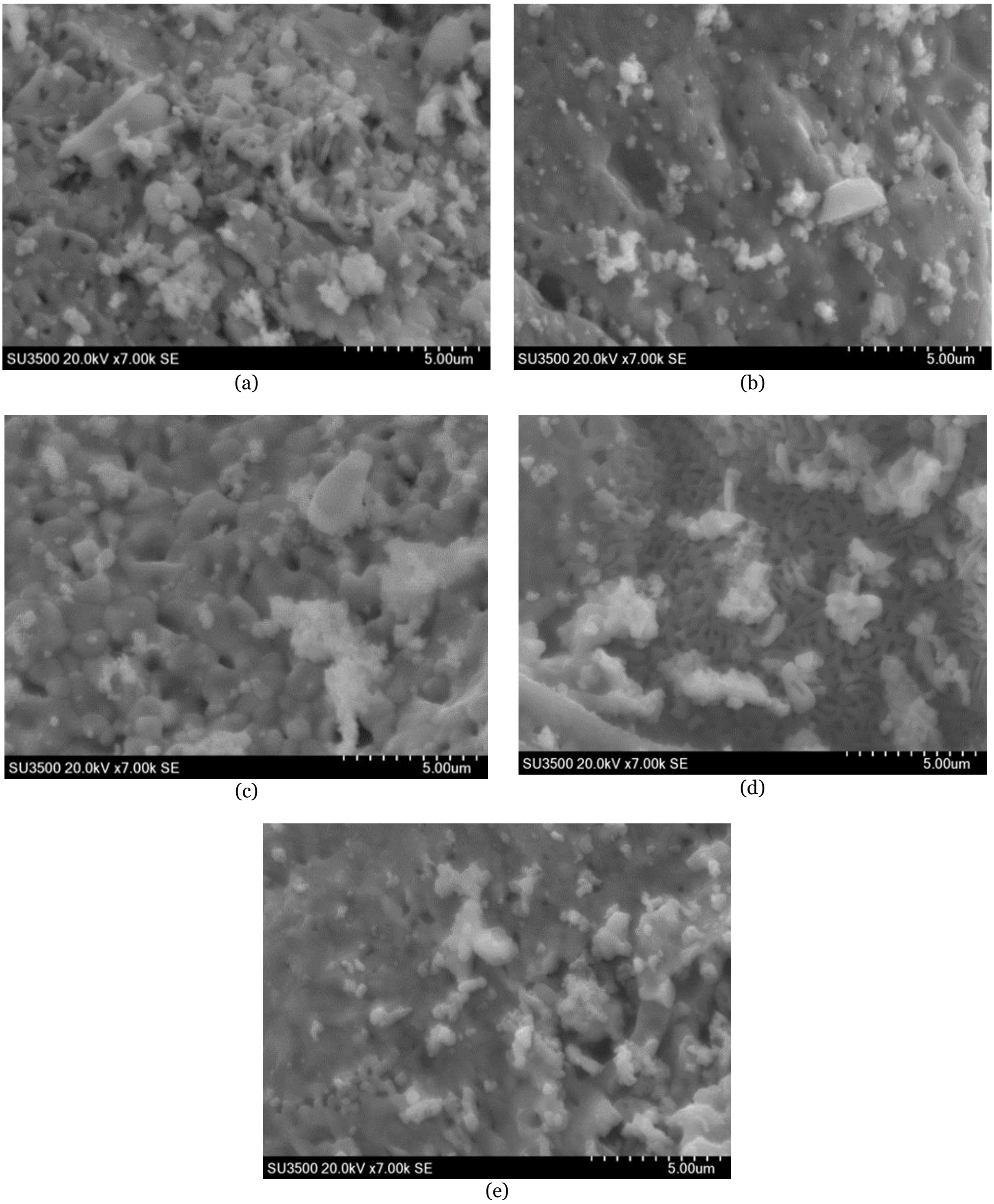
Table 1 showed that the highest coercivity value obtained is due to the influence of crystallite growth, which led to the formation of a single domain system. The coercivity obtained from this research is a hard magnetic classification with a regular magnetic moment in single-domain particles. Furthermore, the smaller the particle size, the more magnetic the orientation. This increases the interaction between particles and their anisotropic energy, therefore, the demagnetised process requires a larger external field. Magnetic energy is also determined by the amount of remanence (Mr) of a material. It is a residual magnet found in the material after the external magnetic field is removed. The remanence magnetisation obtained from this study increased along with a significant rise in the percentage of magnetic material, as shown in Table 1.

Table 1. Magnetic properties of samples

No	Weight Ratio of BTO:BFO:BHF	Remanence (10^4G)	Coercivity (kA/m)	Magnetic Energy (10^4 GkA/m)
1	2:1:2	0.079	563.9	44.55
2	1:2:2	0.081	593.7	48.09
3	2:1:1	0.045	211.3	9.51
4	1:2:1	0.064	447.6	28.65
5	1:1:1	0.059	400.5	23.63

The observation results of the microstructure using a Scanning Electron Microscope with a 7, 000x magnification, as shown in Figures 2(a) to (e) indicate that the particle size is not homogeneous. Furthermore, the particles are not fully compact with the appearance of numerous vacancies. The least porosity possessed by the sample with a ratio of 1:2:2 is in line with the value of the largest magnetic energy, as shown in Figure 2(b).

The minimum porosity causes the particles to be in a single domain with the formation of a regular magnetic moment. This causes increasing large porosity rate at the smallest magnetic energy obtained in the third sample (2:1:1 ratio), as shown in Figure 2(c).



(a) (b) (c) (d) (e)

Figure 2(a) – (e): Morphology of $BaTiO_3$, $BiFeO_3$, $BaFe_{12}O_{19}$ Composite with different mixing ratio weight percentage = 2:1:2, 1:2:2, 2:1:1, 1:2:1, 1:1:1

IV. CONCLUSION

In conclusion, this study obtained the largest magnetic energy value at a ratio of 1:2:2, which correspond to the minimum porosity and a greater percentage of magnetic ceramic ($BaFe_{12}O_{19}$) possessed by the sample. Particles which are not fully compact with the appearance of numerous vacancies have the smallest magnetic energy. The least porosity possessed by the sample with a ratio of 1:2:2 is in line with the value of the largest magnetic energy, as shown in Figure 1(b). The XRD test confirmed all samples consisted of 3 compounds $BaTiO_3$, $BiFeO_3$ and $BaFe_{12}O_{19}$ with a weight % of 2:1:2, 1:2:2, 2:1:1, 1:2:1 and 1:1:1 with no impurities observed.

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