Ni and Zn Substituted M-type Barium Hexaferrite Processed by Sol–Gel Auto Combustion Method

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Abstract. Barium hexaferrite (BaFe12O19) or BaM was synthesized by sol-gel auto combustion method with the new dopant elements, Ni and Zn, with mole fraction (0.2, 0.4, 0.6), pH (7, 9, 11) and sintering temperature (850, 950, 1050 °C) for 3 hours. Ni - Zn ions were substituted to Fe3+ ion of BaM in order to modify the magnetic properties such as magnetic saturation (Ms) and coercivity (Hc). Magnetic properties and microstructure were characterized by various instruments; XRD, SEM, FTIR, and VSM. It was obtained that the largest crystal size of BaM (588.049 nm) was found at X=0.6 , pH 11 and sintering temperature of 850 °C. It was found that from the VSM graphs that magnetic saturation (Ms) has reached a maximum of 95 emu/g at X=0.6 pH 11, sintering temperature at 1050 °C and coercivity (Hc) at 0.13 T. Considering these properties, BaM was qualified as a candidate for stealth technology materials.

1. Introduction
Stealth technology has been widely used in many national defense systems. The aim of this technology is to minimize the response of the electromagnetic wave fired by radar so the object undetectable. The ability to absorb these waves is influenced by a material called Radar Absorbent Material (RAM). This material is expected to have ability to absorb high energy waves and sensitive to the coming waves. The ability to absorb the wave is called magnetic saturation (Ms) and the sensitivity of the material when receive a wave is called magnetic coercivity (Hc). So that the material has to have a high value of magnetic saturation and low magnetic coercivity. Barium Hexaferrite (BaM) has been known as one of the material that is used as RAM. Zainuri reported that, BaM had a value of Hc = 6700 Oe while Ms = 72 emu / g and a curie temperature of 450 °C [1]. These properties indicated the high value of Ms and Hc. Producing BaM materials with high Ms and low Hc value, the Fe ions inside BaM have to be substituted with another ferromagnetic metal cations which have a similar atomic radius and electron configuration to Fe such as Ti, Zn, Mn, Ni, Co, etc [2]. M Jazireh Pour has dopped BaM with Mg-Ti within various dopant amount 0,1,2,3,4,5 using sol-gel method and it resulted the unsufficient magnetic saturation at 30 emu/gr [3]. The similar research using La-Ni as doppan was carried out by Talwinder and it was obtained the better magnetic saturation at 60.73 emu/gr and coercivity at 2.617 T [4].

In this research, new combination of dopant elements, Ni and Zn were added into BaM by sol-gel auto combustion method. This method had several advantages such as less processing time and
easier to obtain the reagent. The variations that were used in this research were the Ni-Zn mole fraction, pH value and sintering temperature.

2. Experimental analysis

2.1. Materials
All chemicals used to prepare the Barium hexaferrite (BaFe$_{12}$O$_{19}$) were reagent grade and used without further purifications. Barium nitrate (Ba(NO$_3$)$_2$), ferric nitrate (Fe(NO$_3$)$_3$9H$_2$O), zinc nitrate (Zn(NO$_3$)$_2$4H$_2$O), nickel nitrate (Ni(NO$_3$)$_2$6H$_2$O), citric acid (C$_6$H$_{12}$O$_7$H$_2$O) and ammonium hydroxide (NH$_4$OH) were supplied by Merck. Demineralized water was used during all synthesis and treatment process.

2.2. Preparation of Ni-Zn Doped Barium Hexaferrite (BaM)
Barium Hexaferrite (BaM) was produced by mixing Ba(NO$_3$)$_2$ and (Fe(NO$_3$)$_3$9H$_2$O solutions using a magnetic stirrer for 15 minutes. Ni (NO$_3$)$_2$6H$_2$O and Zn (NO$_3$)$_2$4H$_2$O (Ni-Zn X 0.2, 0.4, 0.6) were added then as doping materials. Citric acid was added as a reducing agent and then stirred for 15 minutes. After that, ammonia was added to obtain pH at 7, 9, and 11 and then stirred for 1 hour at room temperature. The next process was stirring at 80 °C for 3 hours to produce wet gels of BaM. Then the samples were heated in furnace at 250 °C for 3 hours to produce a dry gel of BaM (Auto combustion). Then, dry gel were crushed into a fine powder and sintered at temperature of 850, 950, 1050 °C for 3 hours.

2.3. Characterization
Phase characteristic, composition, and crystal structure were determined using X-Ray Diffraction (XRD) method. Scanning Electron Microscope (SEM) with maximum magnification up to 5000 times was carried out to analyze the morphological structure. Chemical bond of the BaM was examined using Fourier Transform Infrared (FTIR) method, while magnetic properties (magnetic saturation, coercivity and remanence) of BaM were analyzed using Vibrating Sample Magnetometer (VSM).

3. Result and discussion

3.1. XRD (X-Ray Diffraction) analysis
Figure 1a and Table 1 show that each sample has a crystal size range from 70.29 nm to 588.049 nm. The largest crystal size of BaM (588.049) nm is found at pH 11, X=0.6 and sintering temperature of 850 °C. The crystal size has increased significantly compared with the initial crystal size of BaM at 33.58 nm [5]. The temperature increase reduces the crystal size and the increase in pH affects BaFe$_{12}$O$_{19}$ crystal with Ni-Zn doping fraction of 0.6 to become much larger as showed in Table 1.

Figure 1b showed that the enhancement in pH increased the intensity of peak and the formation of BaFe$_{12}$O$_{19}$ single phase. In Figure 1c, based on PDF card 01-075-9113, at a temperature of 850 °C Barium Monoferrite (BaFe$_2$O$_4$) phase is formed and at 950 and 1050 °C, BaM (BaFe$_{12}$O$_{19}$) single phase is formed. However, the impurities, Fe$_2$O$_3$ phase, was found when heating temperature reached at 800°C and 850 °C. This condition was similar with the result of research conducted by Sozeri in the BaM material[6]. At sintering temperature of 950 and 1050 °C, the single phase of BaM was more formed and the the fewer impurity phases found.

3.2. SEM - EDX (Scanning Electron Microscopy) analysis
Figure 2 illustrates that all specimens have pores on the surface and the number increase along with the Ni-Zn mole fraction. With the addition of Ni-Zn mole fraction, the particles become more irregular and more pores on the surface. This particle characteristics was also obtained in BaM investigation.
carried out by L. Junliang which produced the polygonal shape [6]. The pores are formed due to the elongated crystal structure that formed needle-shaped crystals or tube. The irregular particle shape is caused by the stress in Barium Hexaferite crystal structure due to the difference in atomic radius between the doping elements Ni-Zn and Fe [7].

The influence of pH to particle size can be seen in figure 2a. From this figure, the increase in pH affects the particle size to become larger. Figure 2d-2f shows that with sintering temperature of 850 °C, BaFe$\text{10,8Ni}_{0,6}\text{Zn}_{0,6}\text{O}_{19}$ has more pores compared with the sintering temperature at 1050 °C. Therefore, the increase in sintering temperature stimulates the crystal size growth of BaFe$\text{10,8Ni}_{0,6}\text{Zn}_{0,6}\text{O}_{19}$. From the EDX result in Table 2, it can be observed that the substitution of Ni-Zn elements has been successfully carried out and the increment of wt% of Ni and Zn due to the increase of mole fraction and sintering temperature.

3.3. FTIR (Fourier Transform Infrared) analysis

Figure 4 and Table 3 show that all the samples have M – O (metal-oxygen) bond and the C = O bond. This proves that there is a bond between the Fe, Ba, Ni, and Zn metals with oxygen in the specimen. C = O bond shows the chemical bond between oxygen for combustion with carbon during the formation of Barium Hexaferite phase. C – H bond was also found in Figure 4 indicates the presence of citric acid reaction. The wavenumber range 1080-1300 cm$^{-1}$ shows the C – O bond and this is formed when the combustion reaction in BaM happened. The rest of product and water are shown by H-O bond at wavenumber of 2161.45 and 2360.68.

3.4. VSM (Vibrating Sample Magnetometer) analysis

From figure 5, it can be known that the enhancement of the mole fraction decreases the Ms, Hc, and Mr value. Regarding the doping mechanism, Ni has a tendency to substitute the Fe$^{3+}$ ions at 4f$_2$ position (spin down) if the mole fraction is at a value of 0.1. When the mole fraction was larger than 0.1, it will replace the Fe$^{3+}$ ions in the 12k position (spin up) which will reduce the value of Ms and vice versa. Thus, the value of Ms has declined. [8]. The reduction of coercivity happened because the magnetic anisotropic value become lower. This properties significantly affect the magnetic performance and direction of magnetic domain [9].

Figure 5 also shows that the value of Hc decreases when pH increased, but at X=0.6 and pH 9 the value of Hc was higher than at pH 11. Although, the value of Ms does not indicate the similar trend with pH enhancement. The enhancement of pH value will increase with the value of Ms [4]. This is because the formation rate of single phase BaFe$_2$O$_4$ becomes higher. It also affects the crystal size and magnetic domain to be much bigger and it leads to a higher amount of spins with uniform direction that increases the capacity of the magnetization [10]. This condition is obtained when the addition of doping element has reached X=0.6. However, the impurities in BaFe$_2$O$_4$ are still found at X=0.2 and X=0.4 and these will reduce the magnetic characteristics.

The effect of sintering temperature on the magnetic properties is generally related with the effect of sintering temperature as reported in research by Sozeri [6]. The difference is at the value of coercivity that obtained by Sozeri [6] increased up to 1100 °C and then slightly declined at temperature of 1200 °C. These properties value increase is supported by the investigation in BaM materials conducted by Mosleh that used sintering temperature from 750 to 950 °C [11]. In this research, it has obtained Ms and Hc optimum at 95 emu/g and 0.13 Tesla, respectively, at X=0.6, pH 11 and sintering temperature of 1050 °C. Based on high Ms and low Hc value of BaM, this material can be used in stealth technology.
Figure 1. XRD at X=0.6 T=850, 950, 1050 °C (a) pH 7, (b) pH 9, (c) pH 11

Figure 2. SEM at 5000x Magnification; T=950 °C pH 7 (a) X=0.2, (b) X=0.4, (c) X=0.6 and X=0.6 pH 11 (d) T=850 °C, (e) T=950 °C, (f) T=1050 °C
Figure 3. EDX at Specimen pH 7 X=0.6

Figure 4. FTIR at X=0.6 T=850, 950, 1050 °C (a) pH 7, (b) pH 9, (c) pH 11
Figure 5. VSM at T=950 °C X=0.2, 0.4, 0.6 (a) pH 7, (b) pH 9, (c) pH 11

Table 1. Crystal Size of Barium Hexaferrite

| Mol Fraction | pH | Sintering Temperature (°C) | Crystal Size (nm) |
|--------------|----|----------------------------|-------------------|
| 0.6          | 7  | 850                        | 199.65            |
|              |    | 950                        | 102.05            |
|              |    | 1050                       | 189.19            |
|              | 9  | 850                        | 199.65            |
|              |    | 950                        | 70.29             |
|              | 11 | 850                        | 588.05            |
|              |    | 950                        | 199.65            |
|              |    | 1050                       | 83.13             |


Table 2. Wt% of Ni and Zn Elements

| pH | Mol Fraction | Ni (Wt%) | Zn (Wt%) | Sintering Temperature (°C) | Ni (Wt%) | Zn (Wt%) |
|----|--------------|----------|----------|---------------------------|----------|----------|
|    |              |          |          |                           |          |          |
| 7  | 0.2          | 01.01    | 01.99    | 850                       | 2.01     | 4.08     |
|    | 0.4          | 02.49    | 04.90    | 7                         | 3.90     | 6.93     |
| 9  | 0.6          | 03.56    | 07.92    | 1050                      | 1.80     | 2.17     |
|    | 0.2          | 02.08    | 01.82    | 850                       | 2.08     | 4.41     |
| 11 | 0.4          | 06.28    | 05.65    | 9                         | 2.66     | 2.31     |
|    | 0.6          | 02.70    | 02.35    | 1050                      | 2.66     | 2.31     |
|    | 0.2          | 02.77    | 03.84    | 850                       | 1.11     | 2.00     |
| 6  | 0.4          | 03.32    | 05.94    | 11                        | 6.00     | 7.38     |
|    | 0.6          | 06.00    | 07.38    | 1050                      | 6.11     | 5.43     |

Table 3. Peak of Barium Hexaferrite

| pH  | Mol Fraction | Peak List | Sintering Temperature (°C) | Peak List |
|-----|--------------|-----------|----------------------------|-----------|
|     |              | M – O Stretching | C = O Stretching |                          | M – O Stretching | C = O Stretching |
| 7   | 0.2          | 566.98 | 538.01 | 1457.05 | 850 | 773.61 | 566.04 | 1438.84 |
| 9   | 0.4          | 565.81 | 538.95 | 1457.95 | 950 | 767.90 | 539.04 | 1445.70 |
| 11  | 0.6          | 567.07 | 538.60 | 1448.02 | 1050 | 700.05 | 570.19 | 1098.88 |
| 11  | 0.2          | 568.86 | 540.23 | 1467.02 | 850 | 859.10 | 567.61 | 1438.52 |
| 9   | 0.4          | 569.01 | 538.44 | 1406.86 | 950 | 852.77 | 568.13 | 1457.52 |
| 11  | 0.6          | 568.13 | 540.03 | 1457.52 | 1050 | 857.04 | 545.50 | 1423.42 |
| 11  | 0.2          | 567.08 | 538.60 | 1448.02 | 850 | 865.44 | 567.61 | 1435.36 |
| 6   | 0.4          | 569.53 | 539.95 | 1463.85 | 11 | 853.96 | 569.81 | 1469.59 |
| 6   | 0.6          | 569.81 | 541.71 | 1469.59 | 1050 | 906.60 | 567.32 | 1096.57 |

Table 4. Hc, Ms, and Mr of Barium Hexaferrite

| pH  | Mol Fraction | Magnetic Properties | Sintering Temperature (°C) | Magnetic Properties |
|-----|--------------|---------------------|----------------------------|---------------------|
|     |              | Hc (Tesla) | Ms (emu/gr) | Mr (emu/gr) |                          | Hc (Tesla) | Ms (emu/gr) | Mr (emu/gr) |
| 7   | 0.2          | 0.24     | 95.48     | 55.90      | 850 | 0.15     | 94         | 51         |
| 9   | 0.4          | 0.22     | 95.45     | 51.29      | 7   | 0.12     | 85         | 40         |
| 11  | 0.6          | 0.12     | 84.89     | 39.62      | 1050 | 0.11    | 74.5       | 38         |
| 11  | 0.2          | 0.23     | 99.27     | 58.22      | 850 | 0.12     | 80.7       | 39.7       |
| 9   | 0.4          | 0.18     | 86.42     | 49.25      | 9   | 0.19     | 88.4       | 48.2       |
| 11  | 0.6          | 0.19     | 88.45     | 48.20      | 1050 | 0.03    | 90.9       | 35.6       |
| 11  | 0.2          | 0.16     | 91.18     | 52.19      | 850 | 0.18     | 80.3       | 43.4       |
| 6   | 0.4          | 0.20     | 84.54     | 48.84      | 11 | 950 | 0.15     | 90.7       | 48.6       |
| 6   | 0.6          | 0.15     | 90.69     | 48.59      | 1050 | 0.13    | 95         | 49         |
Conclusions
1. The addition of doping ions Ni-Zn leads to decrease in the value of coercivity (Hc) and magnetic saturation (Ms). The lowest coercivity (0.12 T) is found at pH 7 and X=0.6.
2. The enhancement in pH increases the magnetic saturation (Ms) and the crystal size of BaM. Otherwise it leads to an impairment of the coercivity (Hc). The largest crystal size (588.049 nm) is found at X=0.6, pH 11 and sintering temperature at 850 °C.
3. The addition of sintering temperature produces the impairment in the crystal size of BaFe_{12}O_{19}, otherwise it increases the coercivity (Hc) and magnetic saturation (Ms) of Barium Hexaferrite that has been doped by Ni and Zn. The smallest crystal size is 70.29 nm observed at X=0.6, pH 9 and sintering temperature of 1050 °C. The highest value of magnetic saturation (Ms) is 95 emu/g with coercivity (Hc) of 0.13 T observed at X=0.6, pH 11 and sintering temperature of 1050 °C.

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