Synthesis by Coprecipitation Method and Characterization of Nickel-doped Barium M-Hexaferrite (BaFe12O19)

by Susilawati Susilawati

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Synthesis by Coprecipitation Method and Characterization of Nickel-doped Barium M-Hexaferrite (BaFe$_{12}$O$_{19}$)

Susilawati*, Aris Doyan, and Munib
Faculty of Teacher Training and Education, University of Mataram, Jl. Majapahit No. 62 Mataram,
susilawatihambali@yahoo.co.id

***Abstract*-**Barium M-hexaferrite (BaFe$_{12}$O$_{19}$) as an absorber of microwaves has been synthesized by coprecipitation method and its effect on changes in temperature and dopant substitution were analyzed. Basic materials used in the synthesis were BaCO$_3$, FeCl$_{3-6}$H$_2$O and nickel metal. This study used a variation of calcination temperature of 80 °C, 400 °C, 600 °C and 800 °C for 4 hours with a variety of dopants 0; 0.4; 0.7 and 0.9.The results indicate that the formation of single phase and uniform distribution on M-barium hexaferrite (BaFe$_{12-x}$Ni$_x$O$_{19}$) at 800 °C calcination temperature and variations in dopant x = 0.7. The elements of barium are spread very evenly matched with the concentration of each element in the compound BaFe$_{12-x}$Ni$_x$O$_{19}$. The addition of the dopant concentration can increase the value of conductivity that is in the range of 10^{-6} to 10^{-4} with a coercivity value at x = 0.7 and calcination temperature of 800 °C at 0.05 T and magnetization value of 2.25 emu / g

Keywords: coprecipitation, Nickel-doped, Barium M-hexaferrite

1. Introduction

Barium Hexaferrite has stoichiometry with steady hexagonal structure as the oxide ferromagnetic with dielectric and magnetic characteristics largely used in the RF (*Radio Frequency*) application and *microwave*. Barium Hexaferrite (BaM) is grouped into 6 types based on the chemical formula and its crystal structure, namely M (BaFe$_{12}$O$_{19}$), Y (BaMe$_2$Fe$_{12}$O$_{22}$), W (BaMe$_2$Fe$_{16}$O$_{27}$), Z (Ba$_3$Me$_2$Fe$_{24}$O$_{41}$), X (Ba$_2$Me$_2$Fe$_{28}$O$_{46}$) and U (Ba$_4$Me$_2$Fe$_{36}$O$_{60}$) [1]. M, Y, W, Z, X, and U state the type of the Barium Hexaferrite determined by the number of iron and oxygen ion contents in the compound. While, M states a variable which can be changed by Zn, Ti, Co, Ga, Al ions, as well as other metal cation with the similar size based on the characteristics desired.

The electrical and magnetic characteristics of the Barium Hexaferrite substation mostly depend on its synthesis condition since it is caused by the dis-proportionality charge distribution in the substitution process of multivalent cation [2]. The magnetic material of barium M-hexsaferrite (BAM) has large crystal anisotropy and modifiable location resonance in a wide frequency range by ion substitution in hexsaferrite and soft to the relatively large permeability and has high saturation magnetic polarized and consists of strong anisotropy crystalline uniaxial, high Curie temperature and large coercivity terrain [3].

By the vast coercivity terrain, it causes the increasing material anisotropic characteristic so that its absorber characteristic is getting weaker, so it reduces the anisotropic characteristic so, the doping is required [4]. The doping in this study in the formation of BaFe$_{12}$O$_{19}$ is Ni by variation of calcinations temperature and doping used so that it results in BaFe$_{12-x}$Ni$_x$O$_{19}$.

2. Materials And Methods

The basic material is barium carbonate (BaCO$_3$) dissolved with HCl and FeCl$_3$ dissolved with water. Then, both solution results are mixed and added the doping material in the form of liquid pure nickel element with 20000 rpm which then is reacted with NH4OH to make the mixture into precipitate. The reacting process of these materials is called as the coprecipitation method which is one inorganic compound synthesis methods based on the deposition of more than one substance together when passing through the saturation point. On the formation of barium ferrite-xNixO$_{19}$ BaFe$_{12}$ substitution, it uses the variations of x = 0; 0.4; 0.7; and 0.9 the sintering temperature of 32 °C, 400 °C, 600 °C and 800 °C [5].
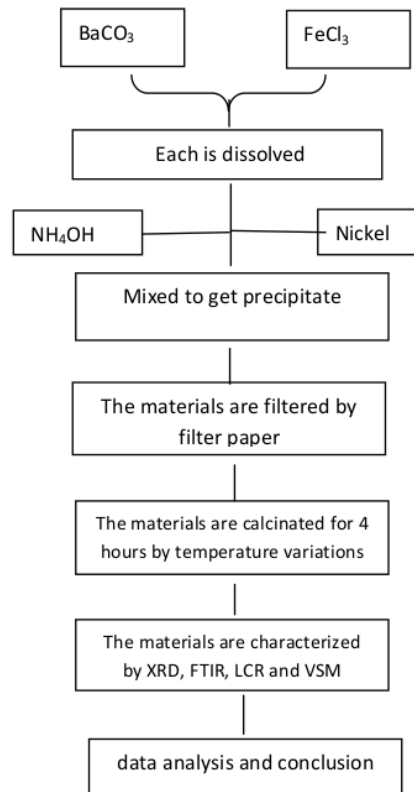Schematically, this study procedure is shown in Figure 1 below:

Figure 1. The flowchart of Barium M-hexaferrite $BaFe_{12-x}Ni_xO_{19}$
synthesis process using co precipitation method

3. Result and Discussion

The temperature change of variable x calcinations and concentration shows the tendency of powder color change of synthesis results along with the increasing temperature and dopant ion like in the Figure 2.
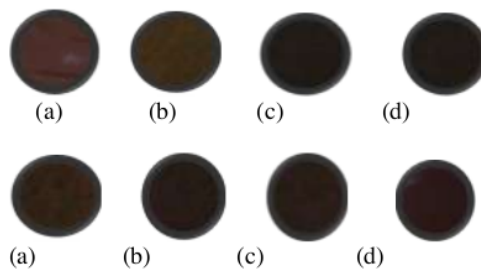

(a)   (b)   (c)   (d)

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

Figure 2. The temperature change of variable x calcinations and concentration to
the powder color change of $BaFe_{12-x}Ni_xO_{19}$

Based on Figure 2, it shows that at the same calcination temperature with the increasing dopant ion concentration, so it gets more color changes to brown-black powder. At temperatures above 800 °C, the sample tends to be blackish brown indicating all the content elements of H_2O and HCl 100% have been run out[5]. This indicates that the heating process of the basic material of $BaCO_3$ dissolved with HCl is in the perfect process. Whereas, by the same dopant ion concentration and the calcination temperature increase, these result in the powder color obtained to be increasingly dark brown [5].

a. **XRD analysis**

The barium M-hexaferrite powder in variation of x = 0,4 by the calcinations temperature of 800 °C so it forms $BaFe_{11,6}Ni_{0,4}O_{19,}$, the XRD testing is conducted to know the Ni dopant substitution. XRD used in this sample testing is the wave length of 1,541862 A with the brand of *Rigaku SmartLab* conducted in the testing in LIPI Fisika Serpong South Tangerang. Given the almost similar atomic radius so it can change the basic material structure, but only can cause little shift of diffraction pattern peak position (angle of 2θ). The substitution effect is very small shown in the Figure 3.
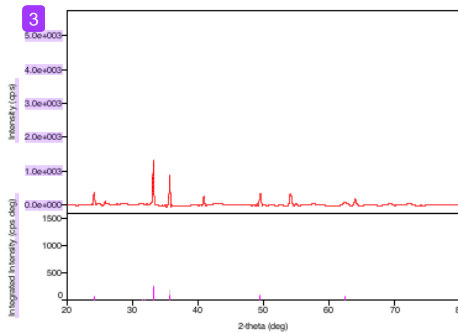

Figure 3. The pattern of XRD x=0,4 and temperature of 800 °C ($BaFe_{11,6}Ni_{0,4}O_{19}$)

Table 1. XRD Result Peak

No.	2-theta(deg)	Phase Name	Chemical Formula
1	24.22(2)	Unknown	Unknown
2	27.9302	Barium Iron Oxide	Ba_3FeO_5
3	28.5287	Unknown	Unknown
4	31.6708	Nickel Oxide (1,0,0)	$Ni_{1,334}O_2$
5	31.9202	Barium Iron Oxide (0,2,2) Nickel Oxide	Ba_3FeO_5 $Ni_{1,334}O_2$
6	33.238(7)	Barium Iron Oxide	Ba_3FeO_5
7	35.687(7)	Unknown	Unknown
8	49.528(14)	Barium Iron Oxide	Ba_3FeO_5
9	62.49(2)	Barium Iron Oxide	Ba_3FeO_5

Based on the figure 3 and table 1, it is shown the X-ray diffraction pattern by the nickel dopant concentration increase of 0,4, there is a peak in the angle of 31,6708 deg containing the foreign phase after it is conducted the nickel oxide increase and in the angle of 31,9202 deg, there is peak containing the iron barium of nickel oxide. By the dopant concentration increase, there are the foreign peaks as the compound of the dopant [6].

There is more stable diffraction pattern after the phase decomposition transformation at the temperature of 840 °C with a concentration x = 0,4, so that it forms a fairly stable single phase [4]. M-hexaferite barium phase formed at high temperatures (T ≥ 500 ° C) will form a single phase,

namely the hematite phase [7]. Besides, it also forms barium M-hexaferite at the temperature of 975 °C with doping concentration less than x = 0.8.

b. **FTIR analysis**

To find out the doping process of Ni dopant to the crystal structure bond, it is used Fourier Transform Infra Red Spectroscopy (FTIR) analysis. The analysis results using FTIR for the $BaFe_{12}-xNixO_{19}$ are as in Figure 4 and 5 below.
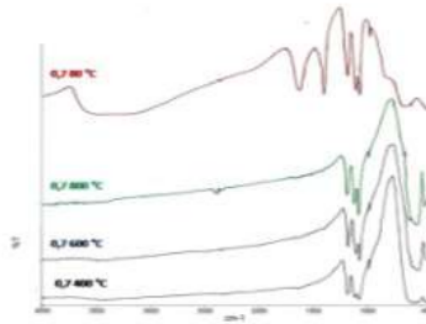

Figure 4. The Absorption Pattern of BaFe12-xNixO19 towards the changes in calcination temperature at x = 0.7

Based on Figure 4, it shows that for the dopant variation of x = 0,7, there is a significant shift in the peak by the increasing calcination temperature. At wave number of $1000\ cm^{-1} - 1500\ cm^{-1}$ at the same concentration, these will have more peaks along with the increasing calcination temperature which is the basic material of absorption peak indicated the bond changes. While the wave number $3400\ cm^{-1}$ is an -OH absorption where the higher the calcination temperature, the absorption is weakened. This is because H_2O decreases by the increasing of calcination temperature.
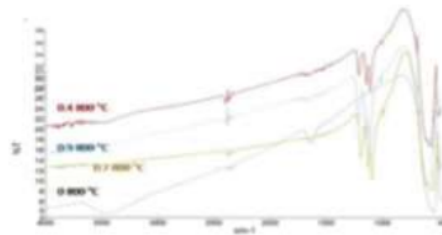

Figure 5. The Absorption Pattern of BaFe12 -xNixO19 towards the dopant ion concentration changes at T = 800 ° C.

Based on Figure 5, it shows that the wave number below $600\ cm^{-1}$, by the increasing calcination temperature, the peak tends to shift to the left. This shows that the wave number is a metal FeO at M-hexaferite phase of barium and hematite. At the calcination temperature of T = 800 °C, the peak shifts significantly by the increasing dopant concentration when compared to other calcination temperatures. At wave number $1000\ cm^{-1}$ -$1500\ cm^{-1}$ at the same calcination temperatures, these will get more peaks along by the increasing dopant concentration as the absorption peak of the basic material. While the wave number $3400\ cm^{-1}$ is -OH absorption where the higher concentration of dopant ions, the absorption is weakened.

The characteristics of vibration lower than $600\ cm^{-1}$ is the bond between oxygen atoms and metal ions (MO) and the peak will increasingly be in the range of $800-1500\ cm^{-1}$ showing the absorption peak of the basic material of $BaCO_3$ and also the absorption in the range of 2151.35 -

2923.88 cm^{-1} is OH absorption [8]. The OH absorption is in the range of 3640 cm^{-1} and in the range of 600-1650 cm^{-1} show more peak as the basic material absorption [9]. The vibration characteristics at 450 cm^{-1} and 570 cm^{-1} are the characteristic of the Fe-O bond as the characteristic of Ba ferrite [10].

c. SEM analysis

To determine the distribution of elements contained in the material barium M-hexaferrite (BaFe$_{12}$-xNixO$_{19}$), it is conducted using SEM-EDX tool. The sample data characteristics by Scanning Electron Microscopy (SEM) obtained are as in Figure 6 below.

(a)   (b)
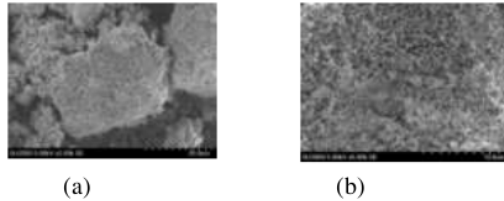
Figure 6. The photo of SEM BaFe12-xNixO19 at x = 0.9 and T = 800 ° C with a magnifications of (a) 2000 and (b) 5000

Based on figure 6, the powder size is still difficult to determine because the powder is clustered and the observable range clearly is still limited, because the particle dimensions of powder has reached the nano order. There is particle size powder increase by the increasing dopant ion concentration variable and calcination temperature [11].

The element results of EDX from barium M-hexaferite (BaFe$_{12-x}$Ni$_x$O$_{19}$) show the content of material composition of barium M-hexaferite containing the main element of Fe, Ba, C, O and Ni. This is based on the color *backscatter* observation like in the figure 7 below.
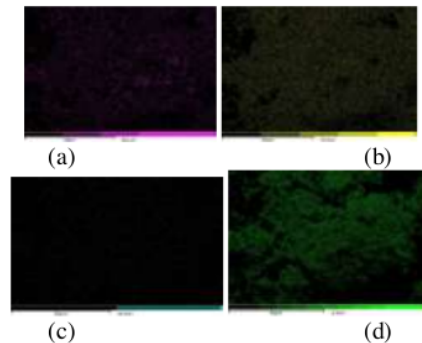

(a)   (b)

(c)   (d)

Figure 7. The element spread of BaFe$_{12-x}$Ni$_x$O$_{19}$ at x=0,9 and T = 800 °C (a) Ba (b) Fe (c) Ni and (d) O

In Figure 7, it shows the element content spread of barium is evenly spread based on the concentration of each element in BaFe$_{12-x}$Ni$_x$O$_{19}$ compound. This is based on the fact that the spread will be evenly based on the component in BaM itself [12].

d. TEM Analysis

The TEM analysis is used to identify the particle dimension of barium M-hexaferrite powder qualitatively. The TEM results obtained are shown in the figure 8 below.
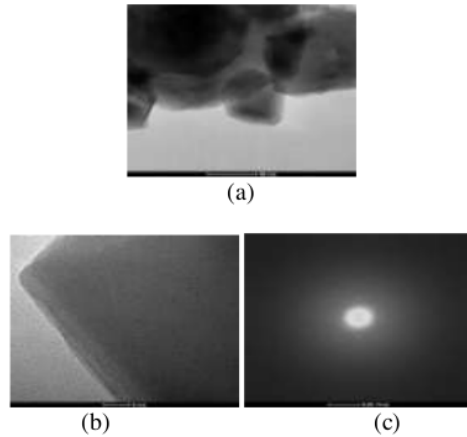
(a)

(b)   (c)

Figure 8. The photo of TEM at x = 0,7 by T = 800 °C

Based on the figure 8, it shows clearly that in the particle structure of BaM. There is a change by the increasing dopant ions. At the high temperature and high doping concentration, it will form a structure with hexagonal shape [13]. This is seen clearly in figure 8 (a) showing the similar particle size distribution by the smallest size crystal reaching 20 nm so that it can be said that this material is nano-material like in the figure 8 (b) with orde around 5 nm. While the intra-particles distance is seen clearly in the figure 8 (c) that the particle size has reached the nano orde.

e. LCR analysis

The measurement by LCR meter of temperature variation with the concentration is still x = 0,7, it is obtained the results like in the figure 9 below.
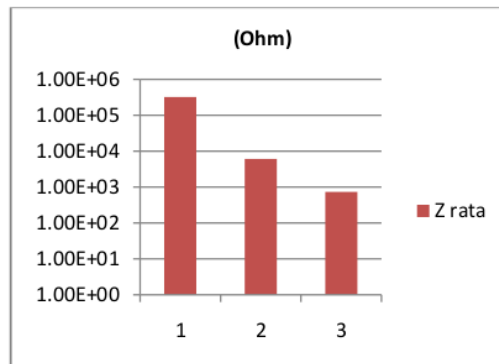

Figure 9. The Resistivity Graph of Barium M-Hexaferrite ($BaFe_{12-x}Ni_xO_{19}$)

Based on the figure 9 above, it is seen that there is a close relationship between the dopant ion concentration increase and its resistivity value. The higher the dopant ion concentration its show that the lower its resistivity value.

Table 3. Conductivity value

Radius	1,17	1,174	1,17
Area	1,07	1,08	1,07
Width	3,94	3,3	3,14
Conductivity	1,01E-06	6,33E-05	5,51E-04

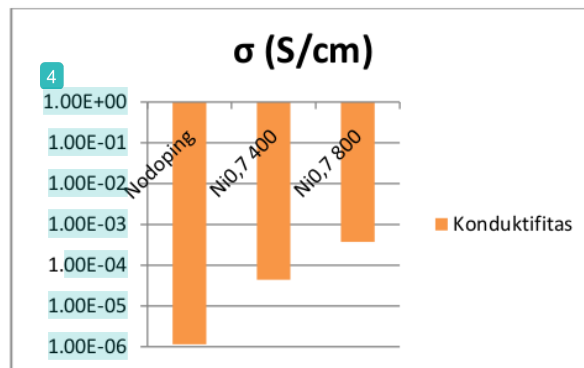**Figure 10**. Conductivity Value of Barium M-Hexaferrite (BaFe$_{12-x}$Ni$_x$O$_{19}$)

From table 3 above, it is obtained that the higher the dopant ion concentration so the higher the conductivity value.

This conductivity is in the range of 10^{-6} until 10^{-4} (figure 10). By the dopant ion increase, so the conductivity value is getting higher [14].

f. VSM analysis

      The synthesis results of barium M-hexaferrite are characterized by the magnetic characteristic using *vibrating sample magnetometer* (*VSM*) in the Science and Technology Science of Advanced Material BATAN. The measurement result is the hysteresis curve showing the magnetisation (M) and coercivity (H) like shown in Figure 11. Based on the literature about barium M-hexaferite without doping (x = 0), it has the coercivity of 0,0782 T and the magnetization of 0,02 emu/gram. The BaM characteristics have the coercivity value of 0,0005 T and magnetization value of 0,02 emu/gram [15].
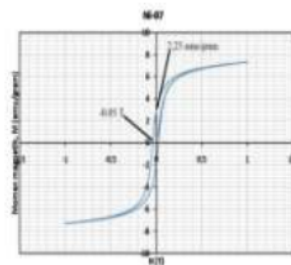

Figure 11. Hysteresis curve in calcinations temperature of 800 °C at x = 0,7

In figure 11, it shows that the hysteresis curve in barium M-hexaferrite sample with the dopant ion concentration of x = 0,7 and the calcination temperature of 800 °C have the coercivity value of 0,05 T and the magnetization value of 2,25 emu/gram. This is greater than the one without doping (x = 0). The best radar absorber material is in the low coercivity value and high magnetization that is around 0,1104 T and 29 emu/gram at x = 0,4 [16]. It has coercivity value of 0,0506 T and magnetization value of 14,782 emu/gram at x = 0,3 [17].

While, based on the heating time, it is obtained that the coercivity value is 0,0082 T and the magnetization value is 0,55 emu/gram at the heating for 4 hours [18]. The higher the calcination temperature used so the coercivity and magnetization values will increase. At T < 800 °C, it has coercivity value below 0,025 T and the magnetization below 0,53 emu/gram [19]. This shows that in this study by calcinations temperature T ≥ 800 °C, it is obtained the coercivity value of 0,05 T and magnetization of 2,25 emu/gram.

4. Conclusion

Based on the results and discussion that the barum M-hexaferrite powder has been synthesized sucessufully using coprecipitation method by diffraction pattern forming stable enough caused by the dopant at the temperature of 800 °C for 4 hours at x = 0,7 and these show that it forms the single phase. The elements of barium are spread evenly based on the concentration of each element in $BaFe_{12-x}Ni_xO_{19}$ compound.

The dopant concentration increase can increase the conductivity value in the range of 10^{-6} until 10^{-4} with the coercivity value at x = 0,7 and the calcinations temperature of 800 °C is 0,05 T and the magnetization values if 2,25 emu/gram.

Acknowledgements

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