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Characterization of Barium M-Hexaferrite with Doping Zn and Mn for Microwaves Absorbent

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Abstract. The research was conducted to examine the content of Fe and other metal in natural sand of beach Ampenan, Mataram, Indonesia which is expected to be used as microwave absorbent material. Characterizations of the electrical and magnetic properties Barium M-Hexaferrite (BaM) with Zn-Mn doping ($BaFe_{12-2x}Zn_xMn_xO_{19}$) are biosynthesized. The research carried out among others tested the metal content of Fe and other metals, synthesize $BaFe_{12-2x}Zn_xMn_xO_{19}$. The samples were characterized using Vibrating Sample Magnetometer (VSM) and Network Vector Analyzer (VNA) for the test properties of electricity and magnetism, as well as the absorption of microwaves. The results from the AAS (Atomic Absorption Spectroscopy) testing showed that each gram of magnetic minerals in the natural sand containing 16.27 mg Fe, which states that the majority of metal components content is 69.80% Fe metal with the Magnetite and Hematite phases. The result from VSM showed that the coercivity value decreased when doping ion concentration and calcination temperature increased (0.16 Tesla at 600^0C for x = 0.0 and 0.09 Tesla at 800^0C for x = 1.0). The value of magnetic saturation and the magnetic remanence decreased with increasing ion concentration (Ms = 4.94 emu/g at x = 0.0 decreased to 0.31 emu/g at x = 1.0) and Mr = 3.43 emu/g for x = 0.0 decreased to 0.06 emu/g at x=1.0. These indicates that the sample has been soft magnetic. The result from VNA showed that the electrical conductivity values measured in the range 8.0-15.0 GHz indicate that the sample is a semiconductor (1.62×10^{-2} S/cm). The result from VNA showed that the microwave absorption properties increased at higher concentration of doping ions and the calcination temperature would increase the value of Reflection Loss (RL). Maximum RL value of the sample is -14.37 dB at 15 GHz and the absorption coefficient of 96.34%. The $BaFe_{10.8}Zn_{0.6}Mn_{0.6}O_{19}$ sample can be applied as a microwave absorbent material on X-band to Ku-band frequency.

Introduction

Natural iron sand is an abundant natural material available in Indonesia. The distribution is very wide, spread along the banks of the Indian Ocean, from the province of Aceh to the island of Lombok [1], such as the West Coast of Sumatra, the South Coast of Java, Kalimantan, Sulawesi, Nusa Tenggara, and the Maluku Islands, but so far the related exploration activities have not been done thoroughly and systematically [2]. Lombok Island with a long coastline of 2.333 km, of course, has natural iron sand potential to be developed. The beach sand of Ampenan, Mataram City, is very black, so it is suspected of having high natural iron sand content, but the utilization of natural iron sand is currently less than optimal because it is only used as a mixture of cement, in fact, iron sand contains iron oxide which has the potential to be processed into various products with high selling value [3].

Sand iron compounds contain magnetite (Fe_3O_4) [4], hematite (α-Fe_2O_3) [5] as the main minerals (predominantly compound) and maghemite (γ-Fe_2O_3), silica (SiO_2) [6], alumina (Al_2O_3), rutile (TiO_2) [7], and ilmenite ($FeTiO_3$) [8] as a minor compound. The differences in levels of mineral content due to geological structure and mineralization processes in each region. These minerals have 88% magnetic properties. These minerals have the potential to be developed as an industrial material. For example, magnetite can be used as a base material dry ink (toner) on a copier and laser printer [9], in industries such as ceramics, catalysts, energy storage, magnetic data storage device, ferrofluids, as well as in medical diagnostics [10], absorbing radar waves [11], and microwave absorption [12].

This study focuses on the discussion of microwave absorbent material. One of the materials currently drawing attention to the microwave absorbent material is Barium M-hexaferrite ($BaFe_{12}O_{19}$) or better known as BaM. The BaM was applied as an absorbent material data recorder and microwave. The BaM has a high saturation magnetization (78 emu/g), large field coercivity is (6700 Oe), a high- temperature Curie (450ºC), good chemical stability and corrosion resistance, with electrical and magnetic properties that can be set to suit the application required [13]. However, the high of the magnetic field (coercivity field) causes BaM to have weak absorption properties making it less effective as the microwave absorbing the material. To solve these problems it is necessary to substitute or doping Fe^{3+} ions with other metal cations whose sized is almost the same (Al^{3+}, Ga^{3+}, and Cr^{3+}) [14], in order to lower the magnetic properties of BaM from hard magnetic to be soft magnetic. There are two approaches to substitution ionic, commonly used is the approach of using a single ion substitution and using multiple ion substitutions. The substitution double ion is a popular method in the study of BaM, and a number of studies have been undertaken to modify the properties of the magnetic as the use of double ion substitution (Mn-Ti, Co-Ti, Ni-Ti, and Zn-Ti) [15], Co–Zn, and Ni-Zn [16], as well as the Co-Mn [17]. The substitution that was performed in this study used a combination of elements of the transition metal is Zn-Mn, because both of these elements has a radius and configuration of the ionic similar to Fe^{3+} (ionic radius Fe = 0.065 nm; Zn = 0.074 nm; and Mn = 0.08 nm).

There are different methods used in the synthesis of BaM such as solid state reaction [18], ball milling [19], sol-gel [20], and co-precipitation [21]. In this study, we used the coprecipitation method. The advantages of this method are, it used low temperatures and it was easy to control the particle size so the time that required is shorter. The products are expected to have a smaller particle size and more homogeneous than the solid-state method and the sol-gel method [22]. Based on the description, the focus of this study was to synthesize and to characterize of electrical and magnetic properties of BaM that will be used as a microwave absorbing materials based on natural sand with varying the doping concentration of Zn-Mn and calcination temperature.

Method

The sample used in this research was natural sand taken from Ampenan Beach, Mataram City. Coastal sand samples were weighed 50 grams using a calibrated digital balance and measured for the magnetic mineral content to determine the percentage of magnetic mineral content in natural sand. The measurements were made by bringing a 1.48T magnet permanent magnet to the natural sand where the iron sand attached to the magnet is a magnetic mineral. The magnetic minerals obtained from natural sand are then analyzed by their metal content using AAS equipment of PerkinElmer Analyst 400 type. Furthermore, analysis of elements and compounds contained in natural iron sand was done using XRF type Rigaku Supermini 200.

Iron sand was then synthesized into BaM by Zn-Mn metal doping using coprecipitation methods with varying x-value concentrations (x = 0.0, 0.6, 1.0) and the calcination temperature T = 600 ºC. The synthesis was done by dissolving iron sand and $BaCO_3$ powder respectively with HCl solution while stirring with magnetic stirrer. It was then inserted a Zn-Mn metal doping that has been dissolved with H_2O while still stirring with a magnetic stirrer. The mixture was precipitated by mixing NH_4OH solution and filtered. The precipitate and filtration were then dried by means of a diesel at 80°C for 2 hours. The dried sample was then crushed until smooth to obtain BaM powder with Zn-Mn metal properties and microwave absorption by samples were carried out using advantest type RNA70 type VNA equipment operating at a wave frequency range of 300 kHz - 20 GHz.

Result and Discussion

The results of iron sand separation and AAS testing are shown in table 1, where the percentage of minerals found on the natural sand of Ampenan Beach Indonesia is very large reaches 96%, with the average content of Fe metal in each gram of 16.27 mg. This proves that the sand of Ampenan Beach has the potential to produce natural magnetic minerals.

Table 1. The result of Iron Sand Percentage and AAS Analysis.

No	Sample Name	Magnetic Minerals (%)	Fe Content (mg/gram)
1	Amp-A	96.23	16.87
2	Amp-B	95.95	15.68

Table 2 shows that based on XRF test the dominant element contained in iron sand is Fe element of 69.80%, followed by Si element of 11.60%. This strengthens the results of AAS testing (Table 1) in which Fe content has a high value.

Table 2. The result of XRF Analysis.

No	Elements	%mass	Compounds	%mass
1	Fe	69.80	Fe_2O_3	60.80
2	Si	11.60	SiO_2	17.80
3	Ti	6.71	TiO_2	7.46
4	Al	4.49	Al_2O_3	6.18
5	Ca	2.08	CaO	1.99
6	another	< 1	Another	< 1.5

Fig. 1 shows the difference in BaM conductivity values without doping and with Zn-Mn metal doping using two adapters with different test frequency ranges. Testing using the adapter type WR-90 (8-12 GHz) and WR-75 (10-15 GHz). The BaM powder has the conductivity value in the range of 7.01×10^{-4} up to 1.20×10^{-2} S/cm. The $BaFe_{10.8}Zn_{0.6}Mn_{0.6}O_{19}$ powder has the conductivity value in the range of 8.31×10^{-4} up to 1.98×10^{-3} S/cm. While $BaFe_{10}Zn_{1,0}Mn_{1,0}O_{19}$ powder has the conductivity value in the range of 8.67×10^{-4} up to 1.62×10^{-2} S/cm. The data indicate that the powder sample tested is a semiconductor, in which the semiconductor material has a conductivity value ranging from 10^{-7} to 10^{3} S/cm. To be applied as a microwave absorbent mineral, the mineral must be a semiconductor, because the semiconductor material can convert microwave energy into heat energy. When microwaves about the surface coated with microwave absorbent material, it will form an electric field on the surface of the absorber, then it will flow as the surface current. When the current flows in the absorber, the microwave energy is converted into heat energy.

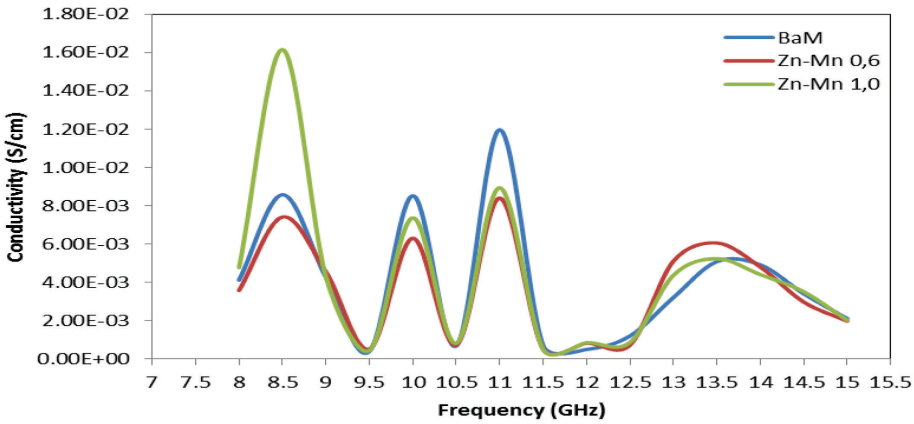
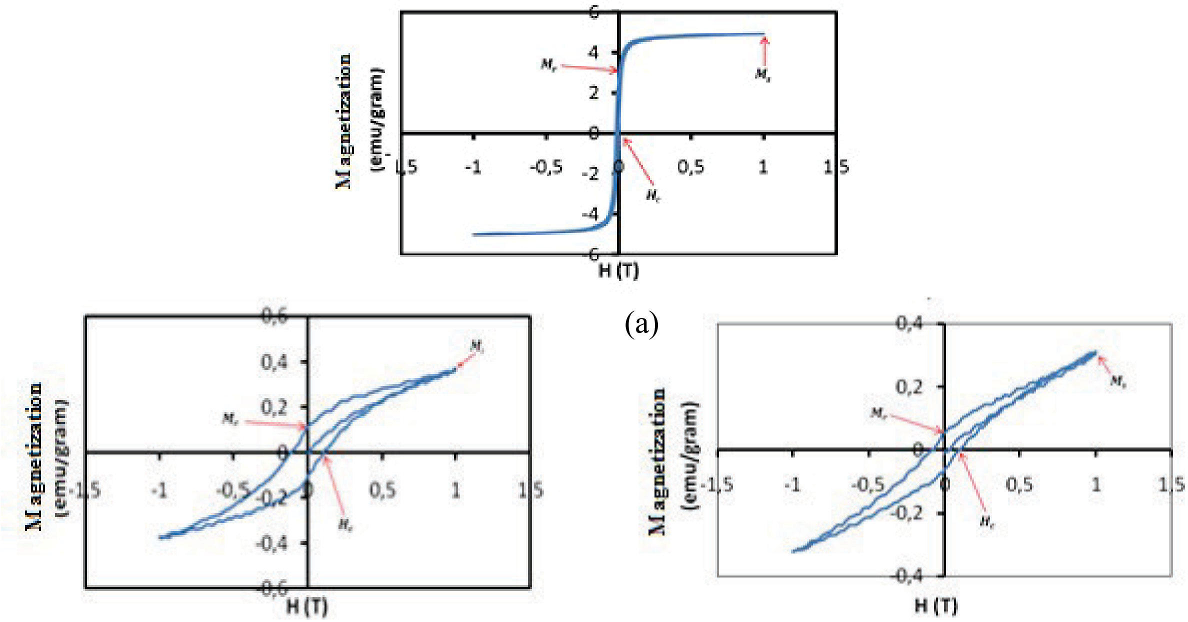


Fig. 1. Graph of Frequency (GHz) relationship with the conductivity value (S/cm) powder $BaFe_{12-2x}Zn_xMn_xO_{19}$.

Fig. 2 shows the hysterical curve of the BaM sample without doping and with Zn-Mn metal doping. Hysteresis curve analysis showed that doping resulted in a change of magnetic properties of BaM. The BaM without doping has a small coercivity value, while saturation and remanent are higher (Fig. 2a). The BaM which has been substituted by doping (Zn-Mn with x = 0.6) increased conductivity value, but the value of saturation and remanent decreased (Fig. 2b). While BaM with high doping (Zn-Mn with x = 1.0) the coercivity decreased followed by the saturation value and the remanent became smaller (its character approaches soft magnet) (Fig. 2c), coercivity, saturation, and remanence values can be seen in Table 3.

Table 3. Magnetic properties of $BaFe_{12-2x}Zn_xMn_xO_{19}$.

Sample	Magnetic Properties		
	Ms (emu/gram)	Hc (T)	Mr (emu/gram)
Zn-Mn 0.0	4.94	0.02	3.43
Zn-Mn 0.6	0.37	0.11	0.11
Zn-Mn 1.0	0.31	0.09	0.06



(b) (c)

Fig. 2. Magnetic hysteresis curves of $BaFe_{12-2x}Zn_xMn_xO_{19}$ (according to Tabel 4), (a) BaM without Zn-Mn addition, (b) $BaFe_{11.8}Zn_{0.6}Mn_{0.6}O_{19}$, (c) $BaFe_{10}Zn_{1.0}Mn_{1.0}O_{19}$.

Fig. 3 shows the permeability value and permittivity of the sample in complex numbers, the real value indicates the amount of microwave energy stored in the material and the imaginary value indicates the amount of microwave energy which is dissipated in the form of energy loss [23]. This combination of real and imaginary values is the determinant of the working frequency area of microwave absorbent material.

Fig. 4 shows the results of BaM material absorption coefficient values without doping and with Zn-Mn metal doping using a WR-75 (10-15 GHz) VNA type. The BaM powder without doping has a maximum absorption coefficient value at a frequency of 15 GHz of 91.62% and the lowest at 11 GHz frequency of 26.28%. The powder $BaFe_{10.8}Zn_{0.6}Mn_{0.6}O_{19}$ has a maximum absorption coefficient value at the frequency of 15 GHz of 96.34% and the lowest at 11 GHz frequency equal to 31.67%. While $BaFe_{10}Zn_{1.0}Mn_{1.0}O_{19}$ powder has the highest absorption coefficient at 15 GHz frequency of 95.99% and the lowest at 8.5 GHz frequency of 28.29%. These data suggest that the higher the doping used the higher the material absorption coefficient at the lower microwave frequency.

The reflection loss (RL) of magnetic material needs to be known for the application of Radio Detection and Ranging (RADAR). The RL show the capability of a material to absorb the microwave which can be measured using VNA. The result of RL analysis using VNA with adapter type WR-75 as shown in Fig. 5.

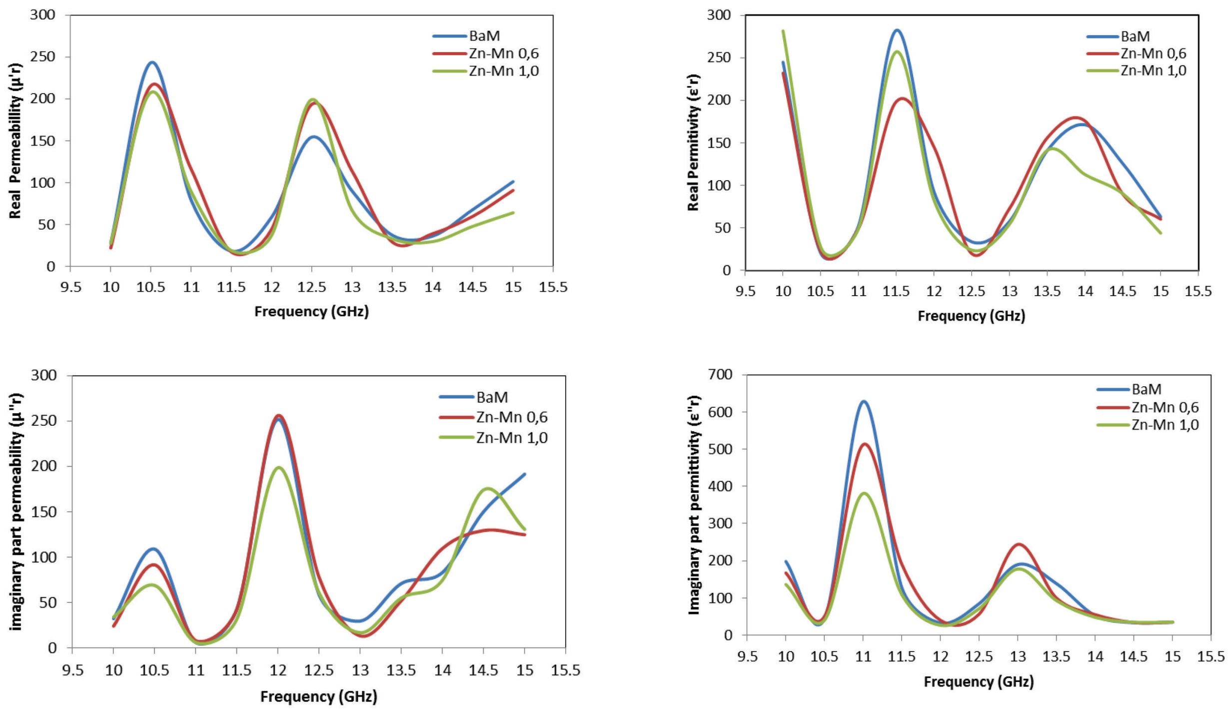


Fig. 3. The permeability and permittivity value of sample $BaFe_{12-2x}Zn_xMn_xO_{19}$.

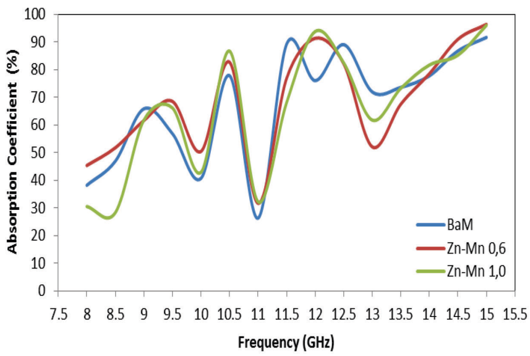


Fig. 4. The absorption coefficient (%A) of $BaFe_{12-2x}Zn_xMn_xO_{19}$ at 10-15 GHz.

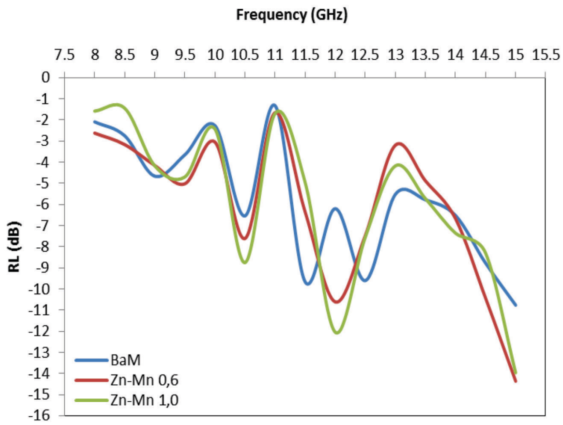


Fig. 5. The reflection loss (RL) of $BaFe_{12-2x}Zn_xMn_xO_{19}$ at 10-15 GHz.

Non-doped BaM powder ($BaFe_{12}O_{19}$) has the lowest RL value of -1.32 dB at 11 GHz and the highest RL value of -10.77 dB at a frequency of 15 GHz. $BaFe_{10.8}Zn_{0.6}Mn_{0.6}O_{19}$ powder BaM (BaM with doping concentration Zn-Mn x = 0.6) has the lowest RL value of -1.65 dB at 11 GHz frequency and the highest RL value of -14.37 dB at frequency 15 GHz. As for $BaFe_{10}Zn_{1.0}Mn_{1.0}O_{19}$ powder (BaM with doping concentration Zn-Mn x = 1.0) has the lowest RL value of -1.44 dB at 8.5 GHz frequency and the highest RL value of -13.93 dB at frequency 15 GHz. Referring to these RL <-20 dB, it can be seen as the potential users of this Zn-Mn doped BaM as a microwave absorbing materials.

Conclusion

The BaM synthetic powder has been successfully synthesized with Zn-Mn metal doping of iron sand as the base material. The synthesis of $BaFe_{12-2x}Zn_xMn_xO_{19}$ has been a semiconductor, where the more doping is given the greater the coercivity value of the material. The synthesized $BaFe_{12-2x}Zn_xMn_xO_{19}$ powder has a coercive field value, saturation magnetization, and a smaller remanence magnetization that is affected by the increasing amount of doping given, so it is soft magnetic. The last $BaFe_{12-2x}Zn_xMn_xO_{19}$ powder can be used as a microwave absorbent material because it has a reflection loss value <-20 dB.

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