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Magnetic and microwave absorbing properties of Zn-substituted Barium M-Hexaferrite in X-band frequency range

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Abstract. In this study, Zn-doped Barium M-Heksaferrite ($BaFe_{11.7}Zn_{0.3}O_{19}$) powders have been prepared by coprecipitation processing from iron sand, $BaCO_3$ and Zn powders, followed by calcined $1000^\circ C$ for 5h. The powders were characterized by X-ray Diffractometry (XRD), Vibrating Sample Magnetometer (VSM), conductivity measurement and Vector Network Analyzer (VNA). The XRD patterns indicated that 2 phases, there were Barium M-Hexaferrite phase (dominant phase) and Hematite phase, with conductivity value on $6x10^6$ S/cm and be include as semiconductor material. The hysterisis curve showed that was a soft magnetic with coercivity field (Hc) on 0.0506 kOe. The powders was mixed on paint 10% of total weight and coated on steel grade AH36. The maximum of reflection loss on x-band frequency was -29.1 dB on frequency of 9.34 GHz and have almost 87.70% electromagnetic energy absorbed by Zn-doped Barium M-Heksaferrite ($BaFe_{11.7}Zn_{0.3}O_{19}$).

Keywords: barium m-hexaferite, zinc subtitution, reflection loss, radar absorbing material

1. Introduction

The widespread of technological devices that utilize electromagnetic waves (EM) was developed in wireless communiation system after the development of electromagnetic theory. Electromagnetic waves are emitted by resources of a certain wavelength used for different purposes, one of which is used as radio detection and ranging (RADAR) in military and commercial applications [1]. RADAR is an electromagnetic wave system that can be used as a detection tool, distance meter, and make a map of objects such as airplanes. By analyzing the radar reflected signal it can be determined the target location and through further analysis of the reflected signal can also be determined the target type. The radar detection on the target is based on Radar Cross Section (RCS). RCS is an area on the target that reflects signals coming by size, shape, or material of the target [2]. Along with the development of radar technology, a system was developed to avoid radar detection. This can be partially obtained by using materials that can absorb microwaves. This absorber uses magnetic and dielectric fillers to reduce the electric and magnetic field components from microwaves that reach the absorber [3].

In the process of absorption of electromagnetic radiation by absorbent materials, the characteristics of the complex permeability and permittivity of these materials play a very important role. Material that can be used a microwave absorber must be easily penetrated by microwaves and has a lossy filler that can convert microwave energy to another form of energy such as thermal energy. Magnetic material can be used as filler to covert microwave energy to thermal energy. In order to improve magnetic and microwave properties of magnetic fillers (i.e. hexaferrites in this case), the Fe^{3+} ion is usually substituted by divalent, divalent-tetravalent, trivalent cationic ion [4].
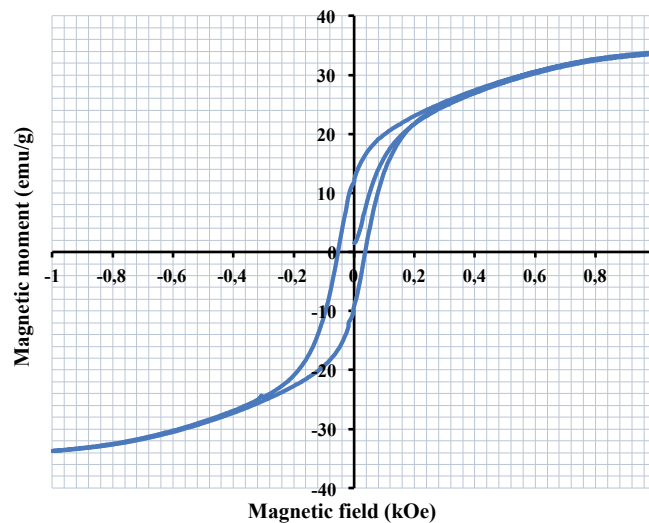
Figure 1. Results VSM analysis of Zn doped-Barium M-Hexaferite with x = 0.3

Recently, Barium M-Hexaferrite has been studied broadly because this material has excellent chemical stability and dielectric properties, high magnetocrystalline anisotropy and saturation magnetization and can be obtained at low cost and exhibits ferromagnetic resonance for microwave [5]. But the material has a high coercivity field, the field required for magnetization to be zero thus affecting the outer field is also high. This is a problem that should be avoided, because the high field coercivity causes the anisotropic properties are increasing so as to make the nature of the absorbs become increasingly weak. The problem can be solved by substitution of Fe^{3+} ions having radius of 0.69 Å with other metal cations having almost the same size [6]. In this study, the synthesis of barium m-hexaferrite used iron stone from Tanah Laut, south kalimantan, Indonesia as magnetic material with Fe^{3+} ion was replaced by Zn^{2+} ion to decrease magnetic properties. In the end was obtained Zn doped-Barium M-heksaferrite ($BaFe_{11.7}Zn_{0.3}O_{19}$).

2. Materials and methods
Following reagent chemicals were used to synthesize $BaFe_{11.7}Zn_{0.3}O_{19}$; iron stone (Fe_3O_4), $BaCO_3$, Zn, Hydrochloric acid and Ammonium hydroxide solution. This research began with the extraction process to produce iron powder from natural ironstones. Then, the powder is washed with alcohol (96%) using an ultrasonic cleaner to reduce and eliminate impurity. Hydrochloric acid solution is used as a solvent from a mixture of iron powder, $BaCO_3$ and Zn which is then stirred using a magnetic stirrer for 30 min at 70 °C. In the dissolution of the iron powder was filtered and evaporated at 100 °C, so that the resulting is $FeCl_2.FeCl_3$ solution. The third solution was mixed at 70 °C for 45 min and added ammonium hydroxide solution slowly until pH scale on 9 (precipitation). It was cleaned until pH scale on 7 and dried. The prekusor was calcined at 1000 °C for 5h to produce the crystalline phase. The Zn doped-Barium M-Hexaferrite was characterized by X-Rays Diffraction (Cu Kα radiation, λ = 1.54060 Å). The measurement of hysteresis of the samples was done using Vibrating Sample Magnetometer (OXFORD VSM 1.2H) and the sample conductivity value was obtained by two point probe methods.

The coating process requires Zn doped-Barium M-Hexaferrite, grade A type AH36 of steel plate, Agatha ship paint, dan thinner. The Zn doped-BaM and paint were mixed with ratio 1:10 and stirred for 10 min with velocity of ± 8000 rpm. The mixture is diluted with thinner and then used to coat the steel plate. Coating thickness is 4 mm. Vector Network Analyzer (VNA ADVANTEST type-3770) is used to measure microwave absorption on X-band frequency.

3. Results and discussion

3.1. Analysis of magnetic properties
The magnetism of Zn doped-Barium M-Hexaferrit material with x = 0.3 ($BaFe_{11.7}Zn_{0.3}O_{19}$) can be seen from the result of VSM measurement in figure 1. Based on the hysteresis curve $BaFe_{11.7}Zn_{0.3}O_{19}$ obtained

the maximum magnetization value ~33.87 emu/g, coercivity field (Hc) ~0.0506 kOe, and magnetization remanesi (Mr) ~14.782 emu/g. If the magnitude is compared to the Barium M-Hexaferrit without doping material ($BaFe_{12}O_{19}$) in Rosyidah's study [7], it can be concluded that there is a decrease in the value of the coercivity field (Hc) and the increase of the maximum magnetization value and the magnetization of remanence (Mr) in the material.

The decrease in the coercivity field value of the Zn doped-Barium M-Hexaferrite ($BaFe_{11.7}Zn_{0.3}O_{19}$) indicates a change of magnetic properties from hard magnetic ($BaFe_{12}O_{19}$) to soft magnetic ($BaFe_{11.7}Zn_{0.3}O_{19}$). The change can occur because of the Zn^{2+} ion as a doping that goes into the structure $BaFe_{12}O_{19}$ to replaces Fe^{3+} ion, so it is able to ruffle the magnetic domain arrangement and minimize the total magnetic moment. In hexagonal structures of Barium M-Hexaferrite consist of 8 Fe^{3+} ions with spin up condition and 4 Fe^{3+} ions with spin down condition [8]. In one unit of the molecule there are 6 ↑ Fe^{3+} ions occupying the octahedral position in the RS block, 1 ↑ Fe^{3+} ion occupies the bipiramidal trigonal position in the R block, 2 ↓ Fe^{3+} ions occupy the octahedral position on the block S, 2 ↓ Fe^{3+} ions occupies the tetrahedral position of the S block , and 1 ↑ Fe^{3+} ion occupy the octahedral position on the block S. Each Fe^{3+} ion contributes a magnetic moment of 5 μ_B, so that the total magnetic moment per unit of molecule is 20 μ_B (($6 + 1-2-2 + 1$) $* 5 \mu_B = 20 \mu_B$). The substitution of Fe^{3+} ions by Zn^{2+} ions it can reduce the amount of magnet bohr from 5 μ_B (Fe^{3+}) and then be replaced to 0 μ_B (Zn^{2+}) in which substitution takes place simultaneously in spin-down and spin-up of sublattices, can decrease coercivity field [7].

Engineering of magnetism from hard magnetic to soft magnetic is useful in the absorption mechanism by the dissipation of electromagnetic wave energy of soft magnetic material whose magnetic domain is easily driven by a small magnetic field. The energy required in the magnetization process can be calculated from the hysteresis curve area where the soft magnetic material has a narrow curve so that the energy required in the magnetization process is relatively small. The properties of magnetic materials are also influenced by the magnetic material crystalline size where the size of the crystal can inhibit the movement of the domain wall. On the small crystal size, many the grain boundaries are formed so as to cause obstacles to the movement of the domain wall are more too, which is resulting in increased resistance to the demagnetization field. So it means the coercivity field (Hc) is also getting larger [9].

In determining the magnetic properties of a material not only seen from the field of coercivity but also can be seen from the parameters of maximum magnetization magnitude and magnetization remanence. The maximum magnetic value of Barium M-Heksaferrite increased from 16 emu/g to 34 emu/g and the magnetization remanence value of Barium M-Heksaferrite also increased from 8.334 emu/g to 14.782 emu/g after doping Zn^{2+}. This is because the substitution of Zn^{2+} ions is tend to occupy the tetrahedral position, and in the Barium M-Heksaferrite structure, the tetrahedral position has a structure opposite to the octahedral position. The octahedral position produces the total magnetic moment. Therefore, the reduction of negative magnetic moment can occur as a result of substitution of Zn^{2+} ions to Barium M-Heksaferrite structure. With the increase of the maximum magnetization value of Zn doped- Barium M-Heksaferrite, this means that the ability of particles to maintain the dominance of magnetic domains also increases. Physically, when the material is given an external magnetic field, the magnetic moment will be polarized in the direction of the given external magnetic field. The more of the orientation direction of the magnetic dipole moment, it will require more energy for the polarization process so that the maximum magnetization value is also higher.

3.2. Analysis of microwave absorption

The result of reflection loss measurements on AH36 steel before and after coating process is done by using VNA in the X-Band frequency range (8-12GHz) shown in figure 2. Based on result, the reflection loss value of the material is -29.1 dB at a frequency of 9.34 GHz with a reflection coefficient value of 0.0351 Γ so that 87.70% of the microwave energy was absorbed. The reflection loss is defines the energy value of the lost electromagnetic wave after the material (absorbed energy). While the reflection coefficient with symbol Γ is the ratio of the reflected wave to the coming wave. If the reflection coefficient Γ is zero, then it can be interpreted that the load impedance matched with channel impedance and no wave reflected by the material.

Magnetic material in this research is formed from two phases. By XRD results of the samples. Figure 3 shows characteristic diffraction peaks corresponding to the Barium M-Hexaferrite and Hematit structure. The dominant phase that is Barium M-Hexaferrite phase ($BaFe_{11.7}Zn_{0.3}O_{19}$) and
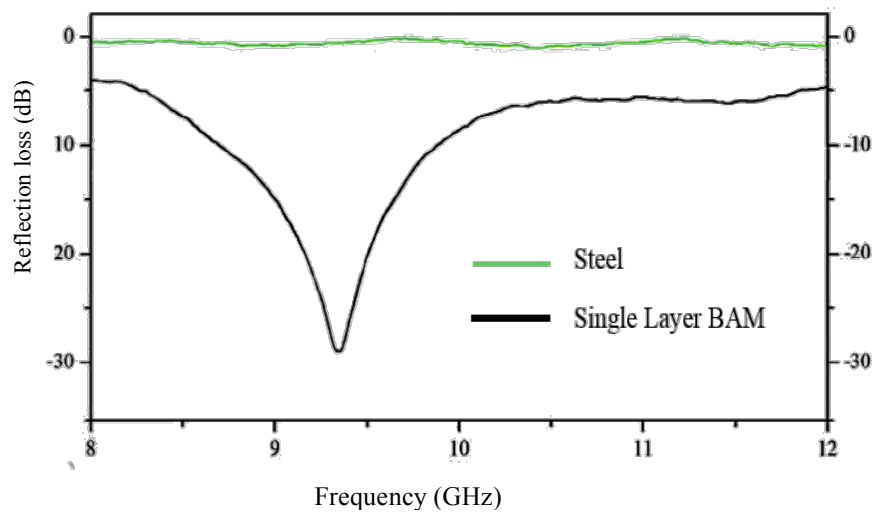
Figure 2. Graph of reflection loss at X-Band frequency
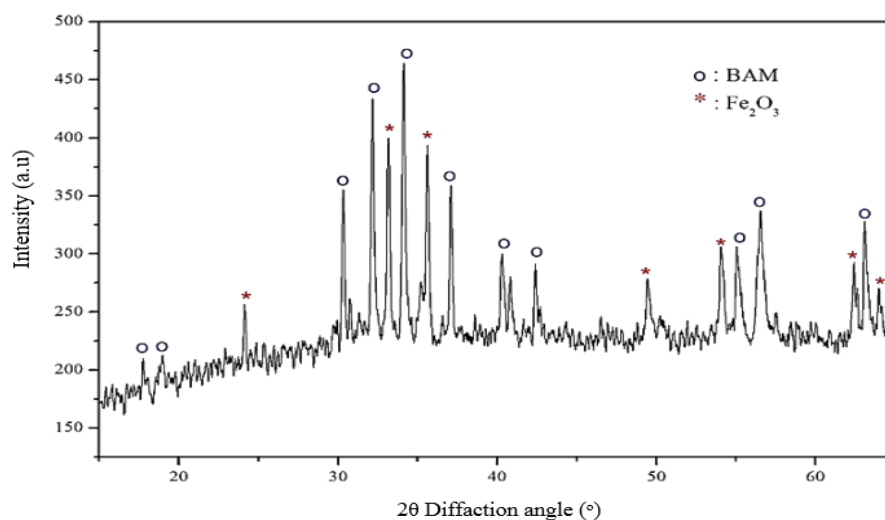
Figure 3. X-Ray Diffraction Pattern of Barium M-Hexaferite $BaFe_{11.7}Zn_{0.3}O_{19}$

secondary phase is Hematite phase (Fe_2O_3). For Barium M-Hexaferrite phase formed is 56.64% and Hematite phase formed is 43.36%. Physically, calcination process aims to getting formation of the desired phase. But, the hematite phase appears as a secondary phase after calcination at 1000 °C. This is because iron sand have Fe^{2+} and Fe^{3+} ions, only Fe^{3+} ions are required to form hexagonal structure. Furthermore, the remaining Fe^{2+} and Fe^{3+} ions in the solution bind to O^{2-} ions to form Fe_3O_4 compounds.

Heat treatment can form a new phase according the temperature, in this case the Barium M-Hexaferite precursor forms $BaFe_{11.7}Zn_{0.3}O_{19}$ and Fe_3O_4 transforms into the Hematite stable phase (Fe_2O_3). That is mean, in addition to eliminating impurities, this process can produce precursors into stable phase Barium M-Hexaferite have a crystal structures that bonds between particles are more compact/strong. When the particles gets heat energy, so that the atoms in the structure will have activation energy to vibrate and construct the structure in a more stable state. Atoms can diffuse interstitially and substitutionally. In this study, Fe^{3+} ions diffuses substitution by Zn^{2+} ions in the structure of Barium M-Hexaferite have occured. Referring to Amalia's study [10] that the Hematite particle also has the ability to absorb microwaves with a reflection loss of -28.69 dB at frequencies below X-Band (6-8 GHz). So that the secondary phase of hematite is expected not to reduce the ability in terms of microwave absorption, because basically ferrite materials have good magnetism properties.

Electromagnetic waves consist of two components, the electric field components and magnetic field components are perpendicular to each other. Electromagnetic wave energy is the resultant of electric field energy and magnetic field energy. To optimize the absorption of electromagnetic waves, the material must have an electrical loss component and a magnetic loss (magnetical loss) component capable of interacting with both electric and magnetic fields in electromagnetic waves. The absorption mechanism can be observed from distributed loading properties using electrical and magnetic materials that allow the absorption of microwave energy by the material. The electrical properties of materials are included in the semiconductor material range, but are still weak enough to affect the absorption mechanism of the electrical losses component. While the magnetism of material contribute in the mechanism of magnetic loss (magnetical losses). This material is a soft magnetic where the total magnetic moment is smaller. With a small total magnetic moment it means that the magnetic domain is easily moved by an external magnetic field small too, so that the electromagnetic energy can be dissipated as a magnetic loss. Based on the electrical conductivity value, the RAM (Radar Absorbing Material) is in the range of conductivity value of semiconductor material that is between 10^{-8} - 10^{3} S/cm. Conductivity measurement of Zn doped-Barium M-Hexaferrite is relatively small (6×10^{-6} S/cm), this result indicates the ability of Barium M-Hexaferrite to deliver very weak electrical currents. Therefore this material needs to be combined with other materials with high conductivity values to improve microwave absorption properties. Basically, when microwaves arrive at microwaves absorbers, electric fields will form on the surface of the absorber. Then there will be a flow of current on the surface of the absorber. When the current flows on the absorber surface, the energy from the microwave will be converted thermal energy [11].

The results of absorption bandwidth in this study are able to cover the overall frequency of X-Band that is 8-12 GHz frequency, but there is a characteristic absorption peak at a certain frequency range. This indicates that the maximum material absorption capacity in that frequency. Single layer of coating materials tend to form absorption peaks at frequencies 8.6-10 GHz with 1.4 GHz absorption bandwidth. The bandwidth shows the effectiveness of the material to reduce the energy of electromagnetic waves, so that reflected electromagnetic waves are very weak.

4. Conclusions

Research on powder synthesis of Zn doped-Barium M-Hexaferrite by coprecipitation method has been conducted. Powder obtained by 56.64% of Barium M-Hexaferite phase and 43.36% of Hematite phase (Fe_2O_3), can absorbing 87.70% of microwave energy with RL 29.1 dB. However, it has a relatively low conductivity value $\sim 6 \times 10^{-6}$ S/cm. So it needs to be combined with high conductivity materials to improve the microwave absorbing properties. Single layer coating of Zn doped-Barium M-Hexaferrite have absorption bandwidth is 1.4 GHz on X-Band frequency range in 8.6-10 GHz bandwidth. So it is able to cover the overall frequency of X-Band is the frequency of 8-12 GHz.

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