Development of Magnetic Materials Based on Micro-Nano Particles Natural Ferrite as Microwaves Absorber Materials

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Abstract. Ferrite-based magnetic materials (ferrites) can be simple iron oxide compounds such as Fe$_2$O$_3$ or Fe$_3$O$_4$, and similar compounds containing other cations besides iron, such as BiFeO$_3$, CaFe$_4$O$_7$, and BaFe$_{12}$O$_{19}$. The solid phase of these compounds generally has varying magnetic properties, depending on the cation ($A^m$) which is the substitution of the iron cation (Fe$^{3+}$) in its crystal structure. In addition to the magnetic properties of interest, the compound in question also has strong absorption properties in electromagnetic waves in the frequency interval of 1 - 20 GHz (microwave), which is commonly used in the world of communication and radar technology. With these properties it is possible to develop these materials for electromagnetic shielding and stealth technology applications. As a magnetic element, ferrite material requires a conductive reflector element, to form a "core - shell" or "matrix - filler" system which results in absorption properties. The research that has been developed is in the form of Fe$_3$O$_4$ based micro-nano magnetic powder made from natural ferrite (iron sand). The synthesized of magnetic micro-nano particles using chemical extraction-milling and co precipitation methods. Morphology of micro-nano particles ferrites has been confirmed by using SEM and TEM. The results of measurements of absorption of microwaves using a Vector Network Analyzer showed that the ferrite nano particle powder has greater absorption power (Reflection Loss < - 20 dB) than micro particle powders with ≥ 99 % absorption in the "X-band" region. The extraction-milling method is simpler and more economical than the chemical coprecipitation method so that it is suitable to be an alternative method for producing large-scale ferrite powder.

1. Introduction

The science and technology of nano materials is currently being intensively developed in the international community, including the birth of smart magnetic materials. Materials included in this category are nanocomposites. Nanocomposites are composed of nanometer-sized components or phases. The physical properties of this material are very dependent on the type of constituent components, especially the physical properties of the filler. The choice of the matrix material and the control parameters of magnetic nanoparticles as fillers (size, shape, concentration) are carried out in accordance with the desired final properties as needed. One application of magnetic nano composites with a polymer matrix is as a protective material on electronic devices from electromagnetic wave interference (shielding effectiveness of electromagnetic interference) and microwave absorber materials (MAM, microwave absorber...
One material that has the ability to absorb microwaves is Fe$_3$O$_4$. Fe$_3$O$_4$ is generally obtained from commercial chemicals, but can also be obtained directly from natural resources [3].

The success of magnetic nano technology depends on the choice of synthesis method and preparation to obtain new properties before it is applied. Preparation methods that have been carried out to obtain magnetic nanoparticles with new properties are sol-gel, hydrothermal, micro-wave hydrothermal, reverse micelle synthesis, radio-frequency thermal plasma assisted synthesis, combination synthesis, precursors, high-energy crushing balls, micro-emulsions and coprecipitation [4, 5, 6]. Coprecipitation method is one method that has advantages in terms of ease of implementation (simple synthesis steps and is carried out at a temperature of 80 °C) to obtain nanoscale magnetic particles but still requires expensive costs. As a microwave absorber, absorption by magnetic particles is carried out in nanoscale sizes as well as high levels of purity using commercial materials, but the price is also expensive.

This paper discusses the synthesis and characterization of micro-absorbent materials made from natural nanoscale micro-scale ferrites, using coprecipitation and milling extraction methods. The milling extraction method was chosen to make magnetic micro particles because it is cheaper, simpler and faster to produce large quantities. Furthermore, a competitive comparison of absorption of microwaves from commercial and natural base materials, coprecipitation and milling extraction methods is examined with the characteristics of absorption of microwaves. The natural materials used are from Lumajang iron sand powder while the commercial materials used are FeCl$_3$.6H$_2$O and FeCl$_2$.4H$_2$O with high purity. Phase characterization and the average particle size of magnetic particles were carried out using X-rays Difractomery (XRD), morphology using Scanning Electron Microscope (SEM), and Transmission Electron Microscope (TEM). Measurement of microwave absorption is carried out with Vector Network Analyzer (VNA).

2. Experimental Details
2.1 Synthesized Micro Particles Fe$_3$O$_4$

Natural ferrite (Fe$_3$O$_4$) micro-nanoparticles have been synthesized by extracted with permanent magnet and milling route method. The starting raw materials used were Fe$_3$O$_4$ from Lumajang iron sands. Specifically, Fe$_3$O$_4$ from iron sands were extracted by using a quite strong (0.3-0.5 Tesla) permanent magnet in simple and hand made magnetic separator. So, microparticles natural ferrite were synthesized processed by high energy ball milling in a Planetary Ball Mill Fritsch Pulverisette 5 with tungsten carbide balls and jars. A ball to powder ratio of 20:1, a milling rotation speed at 200 rpm and milling time in 3, 5, and 7 hours, were used in our experiments. Small amounts of sample were with drawn at pre selected milling times to monitor the progress of the size reduction or aggregation process and determine the corresponding structure and phase of magnetic.

2.2 Synthesized Nano Particles Fe$_3$O$_4$

Natural ferrite Fe$_3$O$_4$ nanoparticles were synthesized by coprecipitation method using powder extracted and crushed of iron sand powder. Furthermore, the extracted Fe$_3$O$_4$ micro powder was dissolved in HCl at around 70 °C and stirred for about 20 minutes in a magnetic stirrer by referring to the reaction: Fe$_3$O$_4$ + 8 HCl $\rightarrow$ 2 FeCl$_3$ + FeCl$_2$ + 4H$_2$O

After the solution is formed, filtering is done using filter paper. The filtered liquid was dissolved in NH$_4$OH then stirred and heated in a magnetic stirrer at 70 °C for 20 minutes with referring to the reaction: 2FeCl$_3$ + FeCl$_2$ + 4H$_2$O + 8NH$_4$OH $\rightarrow$ Fe$_3$O$_4$ + 8NH$_4$Cl + 8H$_2$O

The resulting reaction is then filtered separated from the impurity and washed repeatedly with distilled water until clean from the impurity. The material obtained is then dried in an oven at 100 °C for about 1 hour. Nano particle powder was crushed to obtain Fe$_3$O$_4$ nanoparticles and ready for further testing. As a
reference for making Fe₃O₄ nanoparticles, synthesis is carried out by coprecipitation method using FeCl₃·6H₂O and FeCl₂·4H₂O which refers to the reaction equation (2).

The phase and structural characterizations were performed by X-ray diffractometer (XRD) of JEOL-3530 (with Cu Kα₁: λ = 54 Angstrom, 40 KV and 30 mA) for analyzing particles size and phase purity. The microwave absorbing properties were evaluated using a Vector Network Analyzer system (Agilent E 8364C). Variation of reflection loss in Decibel (dB) with respect to frequency in the range 8 – 12 GHz was studied.

3. Results and Discussion
3.1 X-ray diffraction and morphology analysis.
To observe the magnetite phase content of Fe₃O₄ on micro and nano scales, samples were characterized by XRD devices with the results shown in Figures 1 and 2. Based on Figure 1 it is known that there are diffraction patterns with three highest or main peaks at 20 angles different for micro samples nano ferrite with a different treatment. The three main highest peaks are at an angle of 20 of 27.76°; 35.46° and 62.66° which show the angle of the magnetite phase. Qualitative analysis using software match! which shows the presence of other phases (impurities) contained in iron sand other than magnetite, SiO₂, then quantitative analysis is done using the Rietica program to determine the composition of each phase in a material. This Rietica analysis uses the Rietvield equation by refinement of the peaks of the diffraction pattern so that the results of the matching data are in accordance with the model. The model used for samples without milling treatment, samples with milling treatment at 200 rpm for a variation of time 3 hours, 5 hours, and 7 hours is a magnetite model with COD 9007706 which has a cubic structure with a lattice parameter a = 8.3969 Å and an angle of 90°/g113 and an angle of 90°/g113 and SiO₂ model with COD 9006295 which has a monoclinic structure with a lattice parameter a = 6.8513 Å; b = 7.3761 Å; c = 6.7085 Å and β = 101,918°.

![Figure 1. XRD pattern of (a) iron sand, Fe₃O₄ micro particles synthesized by milling (b) 3 h, (c) 5 h, and (d) 7 h](image-url)
The results of the analysis of the magnetite phase composition of the magnetic separation samples before and after the grinding process have different values, where an increase or addition of magnetite composition when given milling treatment with high speed and in a longer processing time. The composition of the magnetite phase increases with the addition of the speed and time of the grinding process, this is due to the reduction in particle size, crystalline and grain size which is getting smaller, causing more magnetite composition or composition than before the grinding process. Samples with the most magnetite phase compositions were obtained from grinding at a speed of 200 rpm for 7 hours, namely 99.99% of the initial magnetic phase composition before being given a grinding treatment of 66.16%. However, when the addition of the magnetite phase composition will cause the impurity phase composition, ie SiO₂, to decrease because most of the sample is filled with magnetite material.

The magnetite phase of F₃O₄ from the iron sand extract was observed by matching the XRD spectra (Figure 2) with the reference phase spectra in PDF (powder diffraction file) number 24-0734. Matching results showed that the magnetite phase F₃O₄ was dominantly formed with a concentration of > 90% and was supported from the XRF test results which showed a Fe element content of 76.92%. This shows that the natural iron sand taken from the Regoyo Lumajang River is feasible as raw material for synthesis of F₃O₄ nano particles. The thin diffraction spectra shows that F₃O₄ particles in iron sand powder are still in the order above the nanometer. The identities of the two XRD spectra show that the magnetite phase is formed in the form of a single phase with no detected impurity phase. Crystal size is calculated using the equation:

\[ D = \frac{k \cdot \lambda}{(FWHM - FWHM \text{ standart}) \cdot \cos \theta} \]

Figure 2. XRD patern of (a) iron sand, (b) F₃O₄ nano based iron sand, and (c) Fe₃O₄ based FeCl₃.6H₂O and FeCl₂.4H₂O

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where D = the size of the average crystal (nm), k = the form factor of the crystal (range 0.9), \( \lambda \) = the wavelength of the X-ray (Cu-Kα = 0.1540151), FWHM = width of half the highest wave crest and \( \theta \) = diffraction angle. Obtained crystallite sizes as shown in Table 1. The crystalline size of F₃O₄ made with
base material (FeCl₃.6H₂O and FeCl₂.4H₂O) 11.2 nm has a smaller size compared to that made from the basic ingredients of iron sand. This difference is due to the high level of purity which makes ferrite phase easy to form when coprecipitation takes place with the pH maintained at 7, on the other hand the reaction to the formation of ferrite phase from iron sand takes place more slowly because of the presence of impurity resistance. The presence of the impurity phase causes inhibition of the formation and growth of the Fe₃O₄ phase where the thermal energy is held back by the non-magnetic phase boundary so that the penetration of the Fe₃O₄ phase takes place slowly [7].

| No  | Fe₃O₄          | Particles Size |
|-----|----------------|----------------|
| 1   | Raw materials  | 155.4 (μm)     |
| 2   | Milled 3 hours | 3.39 (μm)      |
| 3   | Milled 5 hours | 2.84 (μm)      |
| 4   | Milled 7 hours | 2.42 (μm)      |
| 5   | Coprecipitation| 17.6 (nm)      |

The size of Fe₃O₄ micro nano magnetic particles synthesized from chemicals (FeCl₃.6H₂O and FeCl₂.4H₂O) and iron sand, confirmed in exact morphological pictures using SEM and TEM are shown in Figures 3 and 4. Morphology SEM showed that ferrite micro-scale particles which are square in shape while TEM morphology showed the magnetic nanoparticles of Fe₃O₄ from both of them close to spherical shape.

Figure 3. SEM images of (a) iron sand, Fe₃O₄ micro particles synthesized by milling (b) 3 h, (c) 5 h, and (d) 7 h
3.2 Electromagnetic wave absorbing properties.

The absorption of radar waves by micro ferrite nano particles made from magnetic powder extracted from Lumajang iron sand was measured using a Vector Network Analyzer. Absorption power of radar waves is known from the Reflection Loss value calculated using equation [8]:

\[
RL(dB) = 20 \log_{10} \left| \frac{Z_{in} - 1}{Z_{in} + 1} \right|
\]

where \( Z_{in} = \left( \frac{\mu_r}{\varepsilon_r} \right)^{\frac{3}{2}} \tanh \left[ \frac{2\pi}{c} \sqrt{\mu_r \varepsilon_r \omega \mu_0} \right] \), \( c \): light speed, \( \omega \): angular frequency, \( j = \sqrt{-1} \): imaginer unit, \( \nu \): frequency, \( \mu_0 \) dan \( \varepsilon_0 \): permeability dan permitivity.

The results of measurements of radar wave absorption are shown in Figure 5 and the calculation of the Reflection Loss values are shown in Table 2. This reflection loss value can determine the characteristics of wave absorption properties where reflection loss value is very high the material is a good absorbent material. One of microwave absorber materials in this study is magnetic material made from iron sand because it has magnetic properties that are high enough and easy to obtain and has a large magnetic saturation value, which serves to widen the frequency of absorption. This magnetic material-based absorber produces high permeability so that the range of electromagnetic waves absorbed will be wider, one of which is magnetite. The particle size of the sample in micro order is a magnetic material which has the property of absorbing microwaves through the interaction of the magnetic dipole moment contained in the magnetite sample. The surface of the particle as the first medium to experience interaction with microwaves, the surface area affects the energy of microwaves absorbed by spin magnetic coupling.
Figure 5. Microwave absorbing properties of Fe₃O₄ micro particles (a) Fe₃O₄ nano particles, (b) milled 7 h, (c) milled 5 h, (d) milled 3 h, and (e) Fe₃O₄ without milled

Table 2. Reflection Loss of microwave absorbing micro nano natural ferrites.

| Fe₃O₄         | RL (dB) | Frequency (GHz) | (%) absorption |
|--------------|---------|-----------------|----------------|
| Raw materials| -12.15  | 11.60           | 50.92          |
| Milled 3 hours| -13.80  | 10.80           | 73.85          |
| Milled 5 hours| -14.57  | 11.60           | 81.71          |
| Milled 7 hours| -15.89  | 11.61           | 88.01          |
| Kopresipitasi| -16.98  | 11.60           | 93.43          |

Based on the absorption graph of microwave magnetite samples without grinding treatment, given a mechanical treatment in the form of a grinding process with variations in speed and time of milling and chemical processes using the coprecipitation method shown in Figure 5. The results of the absorption of microwaves in the 8-12 GHz frequency range shows a decrease in the value of Reflection Loss (RL) in almost the same frequency range, the difference is the magnitude of the reflection loss of each sample. One of them is size reduction which is able to influence the maximum reflection loss level. Maximum absorption with the highest value of reflexion loss occurs in magnetite samples with a treatment speed of 200 rpm over 7 hours occurred at a frequency of 11.61 GHz with a value of -15.89 dB.

Where as at the same frequency, the minimum absorption was obtained in samples of iron sand coprecipititation process with nanoscale particle size with a reflection loss value of -16.98 dB. The absorption of microwaves increases with the smaller size of crystals and grains due to reduction through the milling process with greater speed and time and the chemical dissolution process. This is because a large particle size can cause a small surface area so that the absorption of microwave energy by the magnetic dipole moment becomes small [3, 9].

In addition, the presence of impurities or impurities in the form of non-magnetic materials causes relatively little absorption. Magnetite material is able to absorb microwaves due to the content of magnetic dipole moments that interact with each other and move from low energy levels to high energy that require energy, so that when microwaves come they will be absorbed and transformed into the energy needed by
magnetic dipoles to move around. Interaction of magnetic dipole moments will produce potential energy differences that correspond to the distance of each magnetic dipole moment that interacts, so that the frequency of microwaves that can be absorbed varies.

4. Conclusion
The ferrite nano micro particles have been synthesized as a radar wave absorber made from ferrite powder from iron sand using extraction milling and coprecipitation methods. The maximum absorption with highest reflection loss value occurs in magnetite samples with a treatment milling speed of 200 rpm for 7 hours (size 2.42 μm) occurs at a frequency of 11.61 GHz with a value of -15.89 dB. Whereas at the same frequency, maximum absorption was obtained in samples of iron sand coprecipitation process with nanoscale particle size (17.6 nm) with a reflection loss value of -16.98 dB. Ferrite micro particles from iron sand synthesized by the milling extraction method are more competitive to produce radar absorbing materials on a large scale.

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