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Preparation and microwave absorbing properties in the X-band of natural ferrites from iron sands by high energy milling

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Abstract

Bulk natural ferrites based in iron sands were synthesized at room temperature by high energy ball milling. The reduced particle sizes of the ferrites were milled at 100 rpm at selected time intervals of 0, 2, 4, and 6 h. The as-milled products were then characterized by x-ray diffraction (XRD), a vibrating sample magnetometer (VSM) and a vector network analyzer (VNA). The results showed that the magnetite phase contents, their mean size and the saturated magnetization of the natural ferrites were about 95 nm and 36–50 emu g\(^{-1}\) without a new phase. The microwave absorbing characteristics were investigated by measuring the absorption of electromagnetic waves in the frequency range 7–12 GHz. The maximum reflection loss (\(RL\)) for the best process of milling (100 rpm, 6 h) of natural ferrites were \(RL_{m1} = -7.28\) dB in \(f_{m1} = 7.50\) GHz (\(\Delta f = 1.50\) GHz) and \(RL_{m2} = -4.31\) dB in \(f_{m2} = 10.28\) GHz (\(\Delta f = 2.57\) GHz). These results suggest that synthesized natural ferrites can be employed as effective microwave absorbers in various devices.

1. Introduction

Natural ferrites (\(Fe_3O_4\)) based in iron sands possess excellent magnetic and dielectric properties. These ferrite particles are generally used for microwave absorption, refractories, low magnetic materials, sensors and as magnetic carriers for drug targeting [1, 4]. Magnetic and structural properties of spinel ferrite particles are strongly influenced by their pure composition, microstructure and particle size, which are sensitive to the preparation methods. There are several methods for synthesizing nanosized magnetic spinel ferrite particles such as mechanochemical, co-precipitation, solid state reaction, hydrothermal, microwave assisted ball milling [3] and high energy ball milling [2, 5–7]. Here we used simple, cost effective low temperature synthesis and low cost raw materials which were capable of producing nanoparticles at a reasonably large scale compared to conventional chemical methods [9]. In this paper, a novel approach to the ferrite raw materials based in Lumajang iron sands was developed, using high energy ball milling at 100 rpm in milling time variations of 2, 4 and 6 h. The phase ferrite content and the microstructures’ magnetic properties were prepared by high energy ball milling. On this basis, the present work focuses on the dependence of the preparation factor (milling time), by high energy ball milling, on the microwave absorption of natural ferrites. The microwave absorption of natural ferrites of varying particle size were evaluated by the theory of the absorbing wall and VNA (vector network analyzer) measurements.

2. Methodology

Natural ferrite (\(Fe_3O_4\)) micro-nanoparticles were synthesized by extraction with a permanent magnet, using the milling route method. The raw materials used were \(Fe_3O_4\) from Lumajang iron sands. Specifically, \(Fe_3O_4\) was extracted from the iron sands using a quite strong (0.3–0.5 T) permanent magnet in a simple and hand made magnetic separator. The natural ferrite microparticles were synthesized by high energy ball milling in a Retsch planetary ball mill with tungsten carbide balls and jars. A ball-to-powder ratio of 20:1, a milling rotation speed of 200 rpm and a milling time of 2, 4, and 6 h were used in the experiments. The choice of ball-to-powder ratio and time ranges were based on previous studies on bulk cobalt ferrites and their effectiveness in particle size reduction [5]. Small amounts of the sample were withdrawn at preselected milling times to monitor the progress.
of the reduction in size and aggregation process, and to determine the corresponding structural and magnetic properties. The phase and structural characterizations were performed by an x-ray diffractometer (XRD) of JEOL-3530 (with Cu K\textsubscript{α1}; \(\lambda = 54\) Angstrom, 40 KV and 30 mA) which analyzed the particles’ size and phase purity. The magnetization was carried out by a vibrating sample magnetometer (VSM) of Oxford WSM 1.2 H. The microwave absorbing properties were evaluated using a VNA system (Agilent E 8364 C). The variation in the reflection loss in decibels (dB) with respect to frequency in the range of 7–12 GHz was studied.

3. Result and discussion

3.1. X-ray diffraction patterns and magnetic properties

Figure 1 is the XRD pattern of Fe\textsubscript{3}O\textsubscript{4} powder from milling at 2, 4 and 6 h at 100 rpm and without milled raw materials from iron sands. We analyzed the spectra of raw materials according to the reference of PDF number 24-0734 for Fe\textsubscript{3}O\textsubscript{4}. It showed the magnetic phase of Fe\textsubscript{3}O\textsubscript{4} with content >95%. These results are in accordance with the test of oxide content using x-ray fluorescence (XRF), in which the FeO total content was 66.16%. This indicates that ferrite nanoparticles are a single phase magnetite and have quite stable magnetic properties in the air.

An analysis of the crystal size according to the diffraction peak showed that the Fe\textsubscript{3}O\textsubscript{4} crystals in iron sands were in the order of micrometer size. The mean crystal size was calculated using Scherrer’s formula for the strongest peak:

\[
D = \frac{0.9\lambda}{\beta\cos \theta}
\]  

Figure 1. X-ray spectra Fe\textsubscript{3}O\textsubscript{4} powder by milling at 100 rpm, (a) without milling, (b) 2 h, (c) 4 h, (d) 6 h.

Table 1. Magnetite phase contents, crystal size and magnetization of natural ferrite.

<table>
<thead>
<tr>
<th>Fe\textsubscript{3}O\textsubscript{4} Contents (% wt)</th>
<th>Crystal size (nm)</th>
<th>(M_s) (emu g(^{-1}))</th>
<th>(M_r) (emu g(^{-1}))</th>
<th>(H_c) (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without milling</td>
<td>66.16</td>
<td>100 ± 0.018</td>
<td>43.70</td>
<td>9.71</td>
</tr>
<tr>
<td>Milling (100 rpm; 2 h)</td>
<td>95.53</td>
<td>99 ± 0.021</td>
<td>37.00</td>
<td>11.00</td>
</tr>
<tr>
<td>Milling (100 rpm; 4 h)</td>
<td>98.90</td>
<td>97 ± 0.023</td>
<td>37.00</td>
<td>12.80</td>
</tr>
<tr>
<td>Milling (100 rpm; 6 h)</td>
<td>99.59</td>
<td>91 ± 0.022</td>
<td>35.00</td>
<td>12.40</td>
</tr>
</tbody>
</table>

where \(D\) is the mean crystallite size in nm, \(\beta\) is the full-width at half maximum and \(\theta\) is the Bragg angle.

The size of the Fe\textsubscript{3}O\textsubscript{4} particles from the iron sands may have affected their magnetic properties. Their magnetic properties include their ability to absorb electromagnetic waves. The smaller the particle size, the greater the surface area that was penetrated by electromagnetic waves. Magnetic dipole moments which result in more active particles are one of the properties of absorbing electromagnetic waves. Milling had a significant effect on the particle size and the results showed the decreasing crystal size of Fe\textsubscript{3}O\textsubscript{4} particles by ball milling. The values of crystal size as a function of milling time were on a nanometer scale which did not change the phase of spinel Fe\textsubscript{3}O\textsubscript{4}, as shown in figure 1 and table 1. The values of the crystal size were calculated from the most intense (1 3 1) XRD peak using the Debye Scherer formula, which showed the effectiveness in 6 h at 100 rpm for reducing particle size was the same as Mattei et al’s [11] result.
Magnetic hysteresis loops observed in the natural ferrites at room temperature are shown in figure 2. It can be seen in figure 2 that the saturation of magnetization was not reached even at the maximum applied field of 1 T. The magnitude of the magnetic field required to reach saturated magnetization depended on the size of the particles. The saturated magnetization values were also closely related to the size of the crystal. According to the domain theory, the smaller the crystal size (micro to nano meter scale), then the lower the number of domains and tends to a single domain [8]. This situation resulted in a smaller magnetic dipole moment and the consequence was a lower saturated magnetization. Improving magnetization for smaller domains is therefore easier than repairing it for multiple domains.

The magnetic properties of a material are closely related to their magnetic domains, which can be single or multiple. In general, the smaller the size of the crystals in the substance the more likely it is to have a single domain state. Conversely the greater the crystal size, the more likely it is to have multiple magnetic domains. This trend is in agreement with the decrease in crystal size evidenced by XRD estimations. The coercivity field is the magnetic field required to make zero magnetization in the substance. Based on table 1 and figure 2, the coercivity field tended to rise with the decrease in the ferrites’ crystal size. Remanence magnetization of the ferrites was also measured in this study. The greater the magnetic remanence value was, the larger the field was required to be to eliminate the magnetization. This was because remanence magnetization remained when a substance was not influenced by an external field [11]. Remanence magnetization values could not be compared with the field as this tended to increase coercivity of natural ferrite.

3.2. Microwave absorption
Based on the measured data of the scattering parameter, if we assume that a single layer of Fe$_3$O$_4$ particles is attached to a metal plate, then the electromagnetic wave absorption properties can usually be evaluated by the theory of the absorbing wall [8, 11]:

\[
RL = 20 \log \left( \frac{Z - 1}{Z + 1} \right) \quad \text{where} \quad Z = \sqrt{\frac{\mu}{\varepsilon}} \cdot \tanh \left( \frac{2\pi f t}{\lambda} \sqrt{\mu\varepsilon} \right)
\]  

(2)

where $RL$ denotes the reflection loss in decibel unit, $Z$ is the input characteristic impedance at the absorbers/air interface, $t$ is the thickness of an absorber in millimeters, $\lambda$ is the wavelength, $\varepsilon$ and $\mu$ are the measured relative complex permittivity and permeabillity, respectively. The calculated frequency dependence reflection loss of Fe$_3$O$_4$ particles were milled with one thickness and this is shown in figure 3. From the graph, frequency dependence reflection loss can be analyzed by several microwave absorption parameters; the minimum reflection loss ($RL_m$), the matching frequency ($f_m$) and the absorbed frequency range (bandwidth). These parameters are shown in table 2. Figure 3 and table 2 show that the Fe$_3$O$_4$ particles had double matching frequencies in 7–12 GHz with matching reflection loss lower than $-20$ dB. The increase in milling time (2–6 h), meant that the particles absorbed microwaves at a matching frequency to the X-band. The strongest values of reflection loss in the microwave absorbing Fe$_3$O$_4$ particles were milled at 100 rpm in 6 h, $RL_{m1} = -7.28$ dB, $f_{m1} = 7.50$ GHz, bandwidth = 1.57 GHz and $RL_{m2} = -4.31$ dB, $f_{m2} = 10.08$ GHz and bandwidth = 2.35 GHz. This phenomenon occurred because of factors such as their spherical shape and the size of the crystal, with the smallest crystal size at about $91 \pm 0.022$ nm. The spherical shape and small crystal size meant that these particles had the largest surface area and highest density, where the surface area was an important factor of microwave absorbing materials [6]. This was supported by the lowest magnetic saturation value (35.00 emu g$^{-1}$) compared to other milling time variations, where the microwaves were absorbed more effectively by nanoscales particles.
Natural ferrite (Fe$_3$O$_4$) micro-nanoparticles were synthesized from iron sands by milling at 100 rpm at 2, 4, and 6 h. The XRD pattern confirmed that the samples of magnetite Fe$_3$O$_4$ had a single phase. The samples prepared from iron sands contained several elemental impurities, which acted as dopants substituting some part of Fe in the spinel structure, without forming any other individual phase. The crystal sizes were found to be 99 ± 0.021 nm, 97 ± 0.023 nm and 91 ± 0.022 nm at 2, 4 and 6 h, respectively. The magnetic measurements showed superparamagnetic natural ferrite samples had improvements in remanence and coercivity with increasing crystal size. The saturated magnetization samples were low and decreased with decreasing particle size. The value of the nanoparticles $M_s = 35$ emu g$^{-1}$ (6 h) were lower than the value of the microparticles of natural ferrite that were not milled $M_s = 43.70$ emu g$^{-1}$. The microwave absorbing characteristics were investigated via measuring the absorption of electromagnetic waves in the frequency range 7–12 GHz. The maximum reflection loss ($RL_m$) and matching frequency ($f_m$) of best process milling (100 rpm; 6 h) of natural ferrites were $RL_{m1} = -7.28$ dB in $f_{m1} = 7.50$ GHz ($\Delta f = 1.50$ GHz) and $RL_{m2} = -4.31$ dB in $f_{m2} = 10.28$ GHz ($\Delta f = 2.35$ GHz).

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