Synthesis and Structure, Magnetic and Electrical Properties  
Characterization of Core-Shell Structured Barium M-Hexaferrite/Polyaniline Composite Based on Natural Iron Sand

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Abstract-The synthesis of Barium M-Hexaferrite utilizing the method of coprecipitation and Barium Hexaferrite / Polyaniline composite had been done through the method of in situ polymerization to avoid agglomeration effect. Barium M-Hexaferrite was synthesized out of iron sand as the raw material and its magnetic properties was manipulated through Zn$^{2+}$ ion (BaFe$_{12}$O$_{19}$, ZnO$_{19}$) doping mechanism. The formation of Barium M-Hexaferrite phase was already confirmed by the XRD data, where the formation took place at the calcinations temperature of 1000°C. While the doping variation treatment resulted: for undoped M-Hexaferrite the coercive field and magnetic remanence were 0.1734 T and 8.334 emu/g respectively; for the doping concentration condition of x=0,3, the coercive field and magnetic remanence measurement yielded values 0.0506 T and 14.782 emu/g respectively. The composite’s conductivity under filler variation falls within 0.01-0.32 S/cm. According to SEM-EDX observation, it’s been concluded that the composite has a core-shell structure, that is Barium M-Hexaferrite acting as the core is covered with PANI. The average diameter of the composite is -10μm while the Barium M-Hexaferrite’s is -5μm.

Keywords – Iron sand, composite, polyaniline, Barium M-Hexaferrite, core-shell.

I. INTRODUCTION

The abundant presence of iron sand in Indonesia is considered as one of the natural sources that possesses an economic attraction. Little knowledge upon the content and advantages from the iron sand has made it mined and sold in a still raw form, thus resulting low selling price. To increase the selling price of the iron sand, it should be made use more in a still raw form, thus resulting low selling price. To increase and advantages from the iron sand has made it mined and sold be reduced by the substitution of Fe$^{3+}$ with divalent ions (Zn, Co, Ni, etc), through this substitution process it’s expected that Barium M-Hexaferrite will be able to be applied as electromagnetic wave absorber within X-band. This iron sand synthesized Barium M-Hexaferrite will be mixed up along with polyaniline, which is a conductive polymer, to form a composite, thus can further be manipulated in its microstructure, magnetic properties, and electrical properties. Conductive polymer is a sort of material having controllable conductivity which is done by adjusting the concentration level of the doping.

II. METHODS

A. Study Stage

The first step of this research was to prepare the fundamental materials following their corresponding mass and molar ratio (Fe$_{3}$O$_{4}$, BaCO$_{3}$, Zn powder, HCl and NaOH). Before being used, the iron sand was first purified to obtain a higher ferrite oxide purity level. Those compositions were then dissolved in HCl in a separated vessel for further being mixed up by the hot stirrer media. The next step was neutralization using 7 M NaOH solution. That solution was cleaned up from impurity contents. The obtained precursor was then calcinated at the temperature that was set by the DTA/TGA test result, this temperature was 1000°C hence resulting Barium M-Hexaferrite powder.

The second step was to composite the Barium M-Hexaferrite with in situ polymerization method in order to achieve core-shell structure with the Barium M-Hexaferrite as the core and polyaniline as the shell. To get it done, the first thing to do was mixing monomer solution with Barium M-Hexaferrite powder, next pouring in Amonium Peroxodisulfate (APS) and finally mixing all of them together using magnetic stirrer. Composite solution in a pasta form was then dried up until Barium M-Hexaferrite/polyaniline successfully produced.

The phase compositions analysis was done with the help of X-ray diffraction data that were collected from X-ray diffractometer using Cu$_{4+}$, 1,5418Å radiation source, operated at 40 kV voltage and 30 mA current. These diffraction data were taken within the angular range from 15$^0$ up to 65$^0$. Analysis of magnetic properties of Barium M-Hexaferrite was undertaken using VSM with induction magnetic field up to 1 Tesla. While for microstructure and atomic distribution analysis, SEM and EDX were utilized respectively.

III. RESULT AND DISCUSSION

A. Thermal Analysis

Thermal analysis was done using DTA/TGA. The following is the result of thermal analysis.
From figure 1 it can be seen that there is mass reduction of about 19% taking place within 25-400°C temperature range, this identifies the presence of water vaporization and hydroxide (OH-) decomposition. Test result suggests that there was some endothermic process happened at about 1100°C that indicates the occurrence of polymorphic transition in the sample. It was concluded from the analysis that Barium M-Hexaferrite would be formed at at least 1000°C for it to become the main product. Therefore the chosen temperature at which the calcinations process of Barium M-Hexaferrite precursor powder was run was taken at 1000°C.

B. Phase Analysis of The X-Ray Diffraction

It can be seen from figure 3 that during the calcinations process of precursor powder it’s not only Barium M-Hexaferrite that was formed but also alpha hematite (α-Fe$_2$O$_3$) found to be present, this substance is a stable phase of iron (III) oxide that comes from the heating process of magnetite phase (Fe$_3$O$_4$) inside iron sand. Figure 3 also indicates a diffraction pattern under variation of Zn$^{2+}$ ion doping condition, where Zn$^{2+}$ ion having 0.074 nm ionic radius was dissolved into the crystal structure of Barium M-Hexaferrite replacing Fe$^{3+}$ ion having 0.064 nm in tetrahedral position. This statement can be proved from the fact that there’s a slight displacement of the peak position around 2θ that can indicate the replacement of Fe$^{3+}$ ion with Zn$^{2+}$ ion that has greater ionic radius than Fe$^{3+}$ does. So that the distance between crystal planes becomes farther after Zn$^{2+}$ ion doping. Aside of those, there’s also lattice parameter change a and c that’s caused from the ionic radius difference between Zn$^{2+}$ and Fe$^{3+}$. This increase of lattice parameter confirms the pre-statement that Zn$^{2+}$ would substitute the position of Fe$^{3+}$ throughout the structure of Barium M-Hexaferrite.

Table 1. Relative phase composition of Barium M-Hexaferrite for different doping concentrations

<table>
<thead>
<tr>
<th>Doping Variation (X)</th>
<th>% weight Barium M-Hexaferrite</th>
<th>% weight Hematit</th>
<th>GoF</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>43.45</td>
<td>56.55</td>
<td>1.8</td>
</tr>
<tr>
<td>0.3</td>
<td>62.64</td>
<td>37.36</td>
<td>1.6</td>
</tr>
<tr>
<td>0.5</td>
<td>62.04</td>
<td>37.96</td>
<td>1.5</td>
</tr>
<tr>
<td>0.7</td>
<td>64.66</td>
<td>35.34</td>
<td>1.5</td>
</tr>
<tr>
<td>0.9</td>
<td>88.61</td>
<td>11.39</td>
<td>6.44</td>
</tr>
</tbody>
</table>

C. Microstructure Analysis Using SEM

Sample in this observation was BaFe$_{11.7}$Zn$_{0.3}$O$_{19}$. Figure 5 below shows the result.

From the test result above it is seen that Barium M-Hexaferrite crystal that had been already synthesized possesses hexagonal shape with 5μm diameter and is aligned.
along c axis. This agrees with the theory that says that Barium M-hexaferrite has hexagonal crystal structure characterized by two lattice parameters: hexagonal plane width, a, and crystal height, c, with a = 0.588 nm and c = 2.32 nm[3].

The following is the SEM EDX test result of the core-shell structured Barium M-Hexaferrite/PANi composite. Sample to be tested in this measurement was Barium M-Hexaferrite/PANi composite for doping variation x = 0.3.

![Figure 6. The morphology of Barium M-Hexaferrite/PANi composite](image)

Barium M-Hexaferrite particles retained their shape after undergoing polymerization process and didn’t agglomerate. In figure 6 particles of PANi are of brighter intensity than those of Barium M-Hexaferrite. Larger molecular weight of PANi atom than that of Barium M-Hexaferrite atom is the cause of this.

![Figure 7. The distribution of composition’s atom constituting Barium M-Hexaferrite/PANi composite](image)

To be able to prove the formation of core-shell structured Barium M-Hexaferrite/PANi composite, one can look at EDX’s result of Barium M-Hexaferrite/PANi composite. It’s observed that the compositions constituting PANi particle are distribute in such a way so that engulfing the surface of Barium M-Hexaferrite particles. The distribution doesn’t only occupy the edge of Barium M-Hexaferrite particles but also covers the entire surface of Barium M-Hexaferrite itself. This proves that the resulting Barium M-Hexaferrite/PANi composite is of core-shell structure.

### D. Analysis of Magnetic Properties using VSM

The followings are the results of magnetic properties measurement for each doping variation.

![Figure 8. VSM’s result of Barium M-Hexaferrite for each concentration of Zn^{2+} ion doping](image)

From the hysteresis curve resulted from VSM for each doping variation displayed above, one can make a table relating the values of remanent magnetization (Mr) and coercivity (Hc) for each doping variation. This is provided in table 2.

<table>
<thead>
<tr>
<th>X</th>
<th>Coercive field, Hc (Tesla)</th>
<th>Remanence, Mr (emu/gram)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1734</td>
<td>8.334</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0506</td>
<td>14.782</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0591</td>
<td>10.243</td>
</tr>
<tr>
<td>0.7</td>
<td>0.0528</td>
<td>8.667</td>
</tr>
<tr>
<td>0.9</td>
<td>0.0801</td>
<td>10.095</td>
</tr>
</tbody>
</table>

For doping addition x = 0.3; 0.5; 0.7; 0.9 the value of coercivity is smaller compared to BaM without doping. This result suggests that the addition of doping would reduce the significant amount of energy loss so that it exhibits soft magnetism characteristic. In line with the purpose of adding Zn^{2+} ion doping in this research, it’s expected that the magnetic domains within BaM become again disoriented in all direction.

The magnetic properties of Barium M-Hexaferrite are inherited from Fe^{3+} ion having 5μb magnetic moment. The distribution of magnetic moments within Barium M-Hexaferrite structure are 1↑ trigonal bipiramidal +7↑2↓ oktahedral +2↓ tetrahedral, this means the total magnetic moment for Barium M-Hexaferrite is 4↑ = 20μb[3]. Magnetic saturation of Barium M-Hexaferrite can be made higher by the substitution of non magnetic ions such as Zn^{2+}. It’s because Zn^{2+} ions likely tend to occupy tetrahedral position, meanwhile inside Barium M-Hexaferrite structure the tetrahedral position yields structure that opposes octahedral position wherein it’s the octahedral position that produces total magnetic moment. That explains why the substitution of Zn^{2+} ions can reduce the negative magnetic moment thus increasing total magnetic moment as well as decreasing coercive field.
E. Analysis of Electrical Conductivity using two point probes

Electrical conductivity is the ability of some materials to carry the electric current. Not all materials have electrical conductivity. The conductivity of Barium M-Hexaferrite/Polyaniline composite was contributed from PANi that have a high concentration of Bipolaron as charge carrier on PANi. The following is the result of Barium M-Hexaferrite/PANi composite's conductivity.

Figure 9. Barium M-Hexaferrite/PANi composite's conductivity

The value of conductivity is smaller compared to PANi after had composited with BaM. It's could because of electrostatic's flux between BaM and PANi thus Bipolaron as charge carrier be hard to get a move.

The value of composite's conductivity is increase into 0.32 S/cm after Barium M-Hexaferrite was adding Zn$^{2+}$ ion. It's because unbalanced charge on Barium M-Hexaferrite after adding Zn$^{2+}$ ions thus leftover of the ions be negative charged so that can be increasing the electrical composite's conductivity.

IV. CONCLUSION

The experiment already done concludes that the synthesis of Barium M-Hexaferrite (BaM) from natural iron sand with average size of $5\mu$m has been successfully conducted. The coercive field and magnetic remanence of BaM before doping yielded the value 0.1734 T and 8.334 emu/gram respectively. Magnetic properties of BaM has been successfully reduced with optimum doping concentration at $x = 0.3$, coercive field at 0.0506 T, and magnetic remanence at 14.782 emu/gram.

Synthesis of core-shell structured BaM/PANi composite has also been successfully carried out, where BaM acts as the core and PANi as the shell. The average diameter of the composite is $\approx 9\mu$m and and the filler's diameter is $5\mu$m. And the composite's conductivity for varying concentration $x = 0; 0.3; 0.7$ in the filler lies within 0.01-0.32 S/cm range.

BIBLIOGRAPHY


