EFFECT OF CALCINATION HOLDING TIME ON BARIUM M-HEXAFERRITE (BaFe$_{12-x}$Zn$_x$O$_{19}$) MAGNETIC PROPERTIES WITH DOPING Zn IONS

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I. INTRODUCTION

Research in the field of magnetic materials is very intensive at the end of this decade. That is because the application of a magnetic material capable of covering the various aspects associated with today's advanced technology. One of the magnetic materials that has been developed is a magnetic material Barium M-Hexaferrite (BaM). Magnetic properties of BaM are easy to do engineering through the metal ions magnetic substitution mechanism, so can reach the range magnetization of the weakest to strongest magnetization properties. This material with properties can be applied to recording media, electromagnetic interference, magnetic fluids, microwave devices, and so on.

Hexaferrite has a large crystalline anisotropy and the location of resonances can be modified in a wide frequency range by ion substitution in hexaferrite. Beside that, hexaferrite are soft magnetic materials with relatively large permeability. Therefore, hexaferrite are promising candidates for development of anti-radar material [1]. Material barium M-Heksaferrit (BaFe$_{12}$O$_{19}$) has a high saturation magnetic polarization (78 emu/g), which consists of strong crystalline uniaxial anisotropy, high Curie temperature (450°C) and a large coercivity field (6700 Os), very good chemical stability and resistance to corrosion. Therefore there has a very large coercivity field, causes the anisotropic material properties increases so that the absorbing properties become weaker. To reduce the anisotropic properties so required doping mechanism. This study used ion Zn doping.

Barium M-phase compositions which doped with Zn ions through coprecipitation method had been found on the temperature calcination was 270°C for 4 h with $x = 0.4$ [2] and phase composition of barium M-hexaferrite which doped with Zn ions through the same method had been found on the temperature calcination was 100°C for 2 h with $x = 0.6$ [3]. The two studies indicate different holding time of calcination in the formation of M-phase barium hexaferrite, which means there is a connection holding time of calcination of the formed phase homogeneity. But the magnetism properties of BaM which had been doped Co and Zn ions can be used as an anti-radar material to be isotropic composite material in which PANI and BaM as a filler [4]. The substitution of materials with $x = 0.6$ had the absorption of -37.12 dB in the range of x-band (8.2 GHz -12.4). This is the background in this study, so in this study used methods of coprecipitation for the preparation of Barium M-Heksaferrit are synthesized by doping Zn$^{2+}$ ions and varied holding time or hold time heating at 150 °C to form barium M-hexaferrite as magnetic materials.

The addition of Zn as doping ions can disrupt the magnetic moment so that will affect the magnetic properties of barium M-hexaferrite product.

II. RESEARCH METHODOLOGY

A. Synthesis

Synthesis BaFe$_{12-x}$Zn$_x$O$_{19}$ made by coprecipitation method with the concentration to the value of $x = 0.6$. FeCl$_3$.6H$_2$O 27,589 g dissolved in 1839 mL distilled water and then stirred with a spatula to dissolve. 0,351 g Zn dissolved in 12 3O solution is mixed into the solution of BaCO$_3$ and Zn that has dissolved, stirring constantly with magnetic stirrer on a hot plate for 1 hour. After the mixed solution is perfect and the orange brown solution poured with 6.5 M HCl in 2,374 mL glass beaker and then stirred and heated until thoroughly homogeneous magnetic stirrer. And as much as 1,766 grams of BaCO$_3$ was added to the solution. The solution was stirred and heated with magnetic stirrer at temperature of 70-80°C for 2 hours as he poured a little distilled water (as BaCO$_3$ is soluble in weak acid) to dissolve the material (homogeneous clear solution). FeCl$_3$.6H$_2$O solution is mixed into the solution of BaCO$_3$ and Zn that has dissolved, stirring constantly with magnetic stirrer on a hot plate for 1 hour. After the mixed solution is perfect and the orange brown solution poured with 6.5 M NH$_3$OH 51,500 gr little by little until the solution settles like pasta.

Then the solution was separated by its impurity using filter paper. The filtering precipitate was rinsed repeatedly with distilled water until reaching netral pH (pH = 7). The precipitate which had reached a neutral pH in the dry (drying) at temperature of 80°C for 4 hours so the sediment is turned into powder. Then the powder was tested by thermal (DTA / TGA) at temperature of 30°C-1100°C. Then XRD test was performed. The resulting powder was heated at temperature of 150°C with a variety of holding time calcination 2 hours, 4 hours, 6 hours, 8 hours, and 10 hours.
B. DSC (Differential Scanning Calorimetry)

DSC is a thermal analysis technique which is used to measure the energy absorbed or emitted by the sample as a function of time or temperature. When the thermal transitions occur in the sample, DSC calorimetry measurements of energy gives a transition from a given temperature. At DSC, the energy needed to make a difference in temperature between the sample and the comparison is close to zero is measured, which were analyzed at the same temperature, in hot or cold environment with a regular speed. Tests performed on samples with DSC ITS Robotics Building.

C. TGA (Thermo Gravimetric Analyzer)

TGA is a method used to measure the reduced mass of material when heated from room temperature to a high temperature around 900°C. On the micro scale, there are tools that can automatically record the weight of the sample at any time and the results are presented in graphical display. On continuous heating from room temperature, then at certain temperatures the material will lose significantly from its mass.

D. XRD (X-Ray Diffraction)

Phase identification of samples was done by synthesizing the results of X-Ray Diffraction testing Philips Type X’Pert MPD (Multi Purpose Diffractometer) at the Laboratory of X-ray Diffraction RC (Research Center) LPPM ITS Surabaya. These measurements will be performed at a voltage of 40 kV and current of 30 mA using Cu targets (λ = 1.54056 Å). Peak formed by the XRD results were matched by using the diffraction software (X’Pert High Score Plus).

E. SEM-EDX

SEM can produce a characteristic three-dimensional shapes that are useful for understanding the structure of the surface of a sample. Data obtained from SEM-EDX, among others can know the type or mineral elements contained in the samples obtained from SEM analysis and graphs of the energy value of the count obtained from EDX analysis. SEM-EDAX test conducted at the State University of Malang.

F. VSM

Vibrating Sample Magnetometer (VSM) is one measure the magnetization of the work based on the method of induction. VSM is used to determine the magnetic properties of materials. With this tool will obtain information about the magnitudes of magnetic properties as a result of changes in the external magnetic field is described in the hysteresis curve. In this study, the test will be done at Batan VSM Serpong Jakarta to obtain the magnetization hysteresis curve of a material, either as a function of temperature (up to 300 K) and as a function of the external field (up to ± 1.2 T).

III. RESULT AND DISCUSSION

A. Results Synthesis of Barium M-Hexaferrite Materials

The color of barium M-heksaferit powder is brownish yellow and the longer the holding time of calcination with holding time variation of 2, 3, 4, 5, 6, and 10 hours, the color of powdered barium M-heksaferit the dark. It can be shown in Figure 2.

B. Characterization of Barium M-Hexaferrite Samples

B.1 Analysis of the results of DSC/TGA in barium M-hexaferrite sample

Based on the above image, at a temperature of 20°C-125°C decreased the mass (mass loss) of 6.42%. This is due to the evaporation that results in loss of water content and solvent trapped in the precursor. At temperatures of 125 ° C-
225°C occurred at 18.14% mass loss. At 150°C, still declining of mass and increase of energy from the sample. Then at a temperature of 255°C-375°C, mass decreased by 20.72%. Exothermic peak appears at temperature of 280°C that is accompanied by a decrease of mass. This indicates the occurrence of phase decomposition and phase transformation. At temperatures of 560°C - 1100°C, a decrease in the steady phase, accompanied by a small exothermic peak temperature is as high as 825°C and a small endothermic peak at a temperature of 1040°C. Small endothermic peak can be found at a temperature of 975°C.

Based on research by Ariza N.K. (2012) on the material that barium M-hexaferrite doped Zn ions with low temperature have indicated the occurrence of phase transformation of barium M-hexaferrite (BaFe₁₂₋ₓZnx0₁₉) at the calcination temperature of 150°C for 4 hours. Through his research, the percentage of total 74.54% BaM phase has been successfully carried out by coprecipitation method.

Based on the results of DSC/TGA in Figure 3 indicated at 150 ºC there is a sharp decrease in mass in the TGA curve. This phase is one form of Fe oxide with a cubic structure [5]. Identification of phases in the samples that have not been heated (precursor) shows the most dominant phase is the phase of hematite formed. The peaks which indicate of hematite phase, among others, at 2θ: 33.89º, 36.72º, 38.97º, 46.43º and 56.30º. While the peak which indicate BaM phase at 2θ: 33.89º, 36.72º, 38.97º, 46.43º and 56.30º. The highest peak in the precursor indicated hematite phase, but after sample is heated so that a phase shift into BaM phase.

**B.2 Identifikasi Fasa Barium M-Heksferit (BaFe₁₂₋ₓZnx0₁₉) dengan Difraksi Sinar-X (XRD)**

In the barium M-hexaferrite material with x = 0 (no doping Zn ions) which was calcined at 150°C with holding time 4 hours, there are many peaks that indicate phase impurities. This is another phase of BaO, ZnO, BaCl₂, and BaCO₃. While the BAM phase at x = 0 is still about 23%, while the hematite phase amounted to 25%, the remainder is an impurity phase. The peak position of the BaM at x = 0 position 20 is 36.1°, 50.6°, 53.3°, 57.5° and 65.7°. When given a doping zinc ions with x = 0.6 with the same heating treatment, a shift in the peak so that the position of the peak phase of the BaM to be 35.3°, 39.7°, 46.3° and 56.4°. In the presence of doping Zn ions at x = 0.6 has resulted in a shift in the peak phase of the BAM to the left. The radius of Zn²⁺ ions is greater than the radius of Fe³⁺ ions, so that Zn²⁺ ions are substituting Fe³⁺ ions lead to the distance between the diffraction grating becomes larger. This causes the diffraction angle becomes smaller.

**Table 1 Phase composition of BaM without calcination and with calcination at 150°C with a variation of holding time**

<table>
<thead>
<tr>
<th>Holding Time</th>
<th>Volume Fraction(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BaM Phase</td>
</tr>
<tr>
<td>0 h (Precursor)</td>
<td>23.36</td>
</tr>
<tr>
<td>2 h</td>
<td>28.31</td>
</tr>
<tr>
<td>3 h</td>
<td>50.93</td>
</tr>
<tr>
<td>4 h</td>
<td>72.54</td>
</tr>
<tr>
<td>5 h</td>
<td>66.92</td>
</tr>
<tr>
<td>6 h</td>
<td>39.58</td>
</tr>
<tr>
<td>10 h</td>
<td>31.59</td>
</tr>
</tbody>
</table>

Phases formed during calcination by giving another variation of holding time between phase BAM (BaFe₁₂₋ₓZnx0₁₉), hematite (γ-Fe₂O₃), BaCO₃ and BaCl₂. Hematite phase (γ-Fe₂O₃) is a metastable phase formed at low temperatures. This phase is one form of Fe oxide with a cubic structure [5]. Identification of phases in the samples that have not been heated (precursor) shows the most dominant phase is the phase of hematite formed. The peaks which indicate of hematite phase, among others, at 2θ: 26.57°, 35.26° and 61.2°. While the peak which indicated BaM phase at 2θ: 33.89°, 36.72°, 38.97°, 46.43° and 56.30°.

**B.3 Barium M-Hexaferrite Microstructure Analysis**

Based on the results of SEM imaging, it was found that the grain size was about 0.5 μm. Agglomeration particles due to
magnetic dipole interaction between particles. Testing of samples by SEM-EDAX can know the percentage of constituent elements in these materials when calcined at a temperature of 150°C for 4 h. Table 2 shows the percentage by weight (weight percent) and the percentage of atoms (atomic percent) making up the material. Samples when calcined at this temperature with a holding time 4 hours, heavy element Fe has the highest percentage (47.41%) compared to the other elements. This can be caused because the amount of material is used during the process of coprecipitation also great. Ba and Zn elements have a smaller percentage as the elements is the amount used in the coprecipitation process is also less. On the elements Cl, the percentage obtained by 4.47% element due to the loss of Cl content when the calcination process and partly because of coprecipitation reactions.

Fig. 6  SEM of Barium M-Heksaferit that was calcinated at 150ºC for 4 hours

Table 2 Constituent elements of the BaM material when calcination of 150ºC for 4 hours

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CK</td>
<td>16.95</td>
<td>33.88</td>
</tr>
<tr>
<td>OK</td>
<td>27.72</td>
<td>41.60</td>
</tr>
<tr>
<td>CIK</td>
<td>04.47</td>
<td>03.02</td>
</tr>
<tr>
<td>BaL</td>
<td>00.81</td>
<td>00.14</td>
</tr>
<tr>
<td>FeK</td>
<td>47.41</td>
<td>20.38</td>
</tr>
<tr>
<td>ZnK</td>
<td>02.64</td>
<td>00.97</td>
</tr>
<tr>
<td>Matrix</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

B.4 Analysis of Magnetization Properties of Barium M-Heksaferrit by Using VSM

Based on the VSM, the hysteresis curve of barium M-hexaferrite material that has been in the doping Zn²⁺ ions has a narrow area of the curve. So that this material has a soft magnetic properties. Holding time at 4 hours, the maximum magnetization obtained is 0.55 emu / g. However, this value is still very much when compared with the value saturation magnetization (Ms) on the material barium M-hexaferrite (BaFe₁₁,Zn₀.₅O₁₉) is 78 emu / g. The maximum magnetization value indicates the ability of nanoparticles to maintain unidirectional magnetic domains when they were subjected to an external magnetic field. So that when the number of maximum magnetization of the magnetic moments have led to a larger value, which means ability to rectify the magnetic domains are also great.

Fig. 7 Hysteresis loop of barium M-hexaferrite with holding time calcination

Table 3 Magnetic properties of barium M-hexaferrite powder that is calcined at a temperature of 150°C for 4 hours

<table>
<thead>
<tr>
<th>Holding Time</th>
<th>Coercivity Hc (kA/m)</th>
<th>Remanent Mr (T)</th>
<th>Saturation Ms (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 h</td>
<td>0.0095</td>
<td>0.018</td>
<td>0.49</td>
</tr>
<tr>
<td>3 h</td>
<td>0.0013</td>
<td>0.011</td>
<td>0.44</td>
</tr>
<tr>
<td>4 h</td>
<td>0.0082</td>
<td>0.011</td>
<td>0.45</td>
</tr>
<tr>
<td>5 h</td>
<td>0.0095</td>
<td>0.011</td>
<td>0.51</td>
</tr>
<tr>
<td>6 h</td>
<td>0.013</td>
<td>0.012</td>
<td>0.49</td>
</tr>
<tr>
<td>10 h</td>
<td>0.019</td>
<td>0.014</td>
<td>0.53</td>
</tr>
</tbody>
</table>

The presence of dopant ions substitute Zn²⁺ to Fe³⁺ ions and randomize domain so that the field direction of the sample coercivity is reduced. On the hysteresis loop (Fig. 7), indicating the longer holding time, the value of the coercivity field Hc is increasing. In the holding time 2 hours, Hc values obtained = 0.0095 kA / m, then the value is decreased in 4-hour holding time becomes 0.0082 kA / m. In the holding time 10 hours increased Hc value and its value to 0.019 kA / m. In the holding time 2 hours obtained the maximum is 0.018 Mr. T with a maximum magnetization 0.49 emu/g. Bohr magneto concept in this material lies in the spin magnetic moment caused by the material to orient the magnetic domains so as to achieve maximum magnetization which shows the magnitude of the magnetization in this material.

calcination with different holding times will give different magnetization values which can be shown by the hysteresis loop in Figure 7. This is due to them by grain growth and crystal defects during calcination time so the impact on the appearance of the phases when the calcination process. Grain growth by diffusion processes play a role in inhibiting the movement of domain walls. Crystal growth resulted in the growth of the powder particles of barium M-hexaferrite so could result in a magnetization process becomes more difficult due to the larger particle size of magnetic domains [2].

IV. CONCLUSION AND RECOMMENDATION

Synthesis of barium M-hexaferrite (BaFe₁₁,Zn₀.₅O₁₉) was successfully carried out by coprecipitation method. Hematite phase (γ-Fe₂O₃) increased with increasing holding time of heating, while the decline phase of BAM. In this study obtained values ranging from 0.0082 coercivity Hc kA/m to 0.019 kA/m, the value remanensi range 0.01 to 0.018 Tesla Tesla, and the maximum magnetization values ranging from 0.44 emu/g to 0.55 emu/g. The most volume
fraction of barium M-hexaferrite phase 72.54% at 150°C temperature with holding time 4 hours as a soft magnetic material, the value of the coercivity and remanence 0.0082 kA/m and 0.01 Tesla and have the highest magnetization value is 0.55 emu/g. The use of magnetic fields of more than 1 Gauss is highly recommended for further research in order to identify the exact value of saturation magnetization in the material barium M-heksaferit.

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BIBLIOGRAPHY