Enhanced calcination temperatures of Zn$_{0.6}$Ni$_{0.2}$Cu$_{0.2}$Fe$_2$O$_4$ on thermal, microstructures and magnetic properties using Co-precipitation method

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A B S T R A C T

Synthesis of Zn$_{0.6}$Ni$_{0.2}$Cu$_{0.2}$Fe$_2$O$_4$ has been successfully using the co-precipitation method at a calcination temperatures of 300 °C, 400 °C and 500 °C. Thermal properties, microstructures, and magnetic properties were obtained from the characterization of Thermogravimetric Analysis/Differential Scanning Calorimetry (TGA/DSC), X-ray Diffraction (XRD), Field Emission - Scanning Electron Microscope (FE-SEM). Vibrating Sample Magnetometer (VSM) used for analyses magnetic properties of ZnCuNi Ferrite. TGA/DSC results that the reduction of weight is 6.72% in range at 95 °C–100 °C and endothermic process occurs at temperatures below 100 °C. XRD results that confirmed that the higher calcination temperature that affects the growth of ZnNiCu ferrite crystals and the increase in the crystallite size are found within 17.75–20.15 nm. FE-SEM conducted that effect increase calcination temperature reduced particle size, faster diffusion of metal oxidation, and increasing the rate at which the cubic particles crystallize in spinel ferrite. The optimum conditions properties obtained for Zn$_{0.6}$Ni$_{0.2}$Cu$_{0.2}$Fe$_2$O$_4$ at a calcination temperature of 500 °C, $M_s = 31.79$ emu/g, $M_r = 12.06$ emu/g, $H_c = 331.06$ Oe, respectively.

1. Introduction

Magnetic spinel ferrites have been applied in power transformer in electronics, radar absorber materials (RAM) [1], hydrogen sulfide (H$_2$S) gas pollution [2], memory device [3], power supplies [4], wastewater treatment [5] and other electronic devices because of their high magnetic properties, excellent electrical properties, and low power loss [6–8]. The spinel ferrites with structural formula MFe$_2$O$_4$ (M = Cu, Zn, Ni, Mg, Co etc.) which is the spinel structure are based on a cubic lattice of the oxygen ions [9]. Soft magnetic of spinel ferrite properties conducted from interactions within metal oxide and particular positions to the oxygen in spinel crystalline structure [10,11].

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Several studies about synthesis of spinel ferrite were conducted by Li et al. [12] Cu-substituted NiZn ferrites of \((\text{Ni}_{0.7} \text{Zn}_{0.3})_{1-x} \text{Cu}_x \text{Fe}_2 \text{O}_4\) were prepared by solid-state reaction. The results that addition Cu in Ni–Zn ferrite can improve the permeability. Liu et al. [13] with addition of granulated sodium alginate were added directly into metal salt solutions to obtain respective ferrite oxide nanoparticles based on a solid-liquid ion-exchange reaction where maximum saturation magnetization, \(M_s\) of 37.26 emu/g at 20000 Oe with the \(\text{Ni}_{0.4} \text{Fe}_2 \text{O}_4\) nanoparticles. While Bhandare [14] reported that synthesized of \(\text{CoFe}_2 \text{O}_4\), \(\text{MnFe}_2 \text{O}_4\) and \(\text{ZnFe}_2 \text{O}_4\), with calcination temperatures at 400 °C, 600 °C and 800 °C is the phase formation behavior of samples can be considered as a combination spinel ferrite. Synthesize of \(\text{CuZnMg}\) ferrite spinel with calcination temperatures at 650 °C until 800 °C by Ansari et al. [15] reported that saturation magnetization increasing within increase calcination temperatures.

Indonesia have many island of Jawa, Sumatera, Kalimantan, Sulawesi, Nusa Tenggara Barat and Papua islands when the natural iron sand taken from island. Iron sand is a potential to be used as the magnetic-ferrite for raw materials. Setiadi et al. [16] reported that using natural iron sand taken from Buaya River in Deli Serdang, Sumatera Utara, Indonesia to get \(\text{Fe}_2 \text{O}_4\) single phase using the co-precipitation method. Rianna et al. [17] confirmed that the iron sand from Kata beach, Sumatera Barat, Indonesia has Fe content as precursors for synthesize of \(\text{BaFe}_{12} \text{O}_{19}\) for radar absorbing material (RAM).

### Table 1

<table>
<thead>
<tr>
<th>Composition</th>
<th>Calcination temperature(°C)</th>
<th>Sample Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Zn}<em>{0.6} \text{Ni}</em>{0.4} \text{Cu}_{0.2} \text{Fe}_2 \text{O}_4)</td>
<td>0</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>C</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>D</td>
</tr>
</tbody>
</table>

**Fig. 1.** The results synthesized of samples A, B, C, and D.

**Fig. 2.** TGA/DSC curve of sample A.
Based on the previous studies review, the synthesis of $\text{Zn}_{0.6}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Fe}_{2}\text{O}_{4}$ ferrite was conducted for studies of thermal, microstructures and magnetic properties. In study that used Zn, Ni, and Cu as doping materials and natural iron sand from Lombok Island, Indonesia as content material for the synthesis of $\text{Zn}_{0.6}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Fe}_{2}\text{O}_{4}$ using the co-precipitation method. Then, the effect of the calcination temperature variations on thermal, microstructure, magnetic properties, of $\text{Zn}_{0.6}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Fe}_{2}\text{O}_{4}$ synthesized from natural iron sand will be presented.

2. Materials and methods

In this research, the synthesis of $\text{Zn}_{0.6}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Fe}_{2}\text{O}_{4}$ used the coprecipitation method. $\text{ZnCl}_2$, $\text{CuCl}_2$, $\text{NiCl}_2$ and natural iron sand from Lombok Island, Indonesia are the main precursors. Firstly, 16 gr of iron sand were dissolved in 50 ml of HCl (37%) and mixture is stirred until homogeneous for 30 min under a room temperature, then filtered using filter paper of Whatmann (Grade 40 Circles). The solution when the mixed with $\text{ZnCl}_2$, $\text{CuCl}_2$, $\text{NiCl}_2$ which have been dissolved with 25 ml of distilled water. After that the mixed solution is dropped into NaOH solution which concentrates 3 M. This synthesis process is carried out at a temperature of 100 °C and the solution is stirred with a magnetic stirrer at a speed of 500 rpm for 2 h. After 2 h the solution was precipitated and washed 7 times to get a PH of 7, then it was dried in the oven for 15 h at a temperature of 100 °C until the powder was obtained. The powder was calcined at temperature variations of 300 °C, 400 °C and 500 °C for 2 h with a heating rate of 10 °C/min. The last powder properties were analyzed using Thermogravimetric Analysis/Differential Scanning Calorimetry (TGA/DSC) for only powder before calcination, X-ray diffraction (Rigaku Smartlab), vibrating sample magnetometer (VSM250 Dexcel Magna Ltd), field emission scanning electron microscopy (JEOL). The $\text{Zn}_{0.6}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Fe}_{2}\text{O}_{4}$ powder was also produced by the same method as a comparison. The samples name for each variation are shown in Table 1 and Fig. 1.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>(2\theta) (deg.)</th>
<th>FWHM (deg.)</th>
<th>(a) (Å)</th>
<th>(D) (nm)</th>
<th>(\varepsilon\times10^{-5})</th>
<th>(\delta\times10^{15}) line/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>35.51</td>
<td>0.70</td>
<td>8.42</td>
<td>11.91</td>
<td>6.44</td>
<td>3.17</td>
</tr>
<tr>
<td>B</td>
<td>35.49</td>
<td>0.69</td>
<td>8.39</td>
<td>12.09</td>
<td>6.42</td>
<td>3.18</td>
</tr>
<tr>
<td>C</td>
<td>35.48</td>
<td>0.64</td>
<td>8.39</td>
<td>13.04</td>
<td>6.11</td>
<td>2.88</td>
</tr>
<tr>
<td>D</td>
<td>35.47</td>
<td>0.56</td>
<td>8.40</td>
<td>14.89</td>
<td>5.65</td>
<td>2.46</td>
</tr>
</tbody>
</table>

Fig. 3. XRD Pattern: (a) Powder of samples A, B, C and D (b). Magnification of the XRD patterns in the fields of (311).
Fig. 4. (a) FE-SEM characterization of samples A, B, C and D, (b) Histograms of Particle Size Distribution of samples A, B, C and D.
Fig. 5. EDX spectroscopy of samples A, B, C and D.
3. Results and discussions

Fig. 2 shown TGA/DSC to investigated calcination temperatures, a thermal decomposition analysis and understand the phase evaluation during ZnNiCu ferrite formation. The TGA curve shows the reduction of weight is 6.72% in range at 95 °C–100 °C. The reduction of weight losses at a temperatures above 100 °C. This indicates that the change into ferrite is already complete at 100 °C. The decomposition of Sample A was found temperature ranges within 200 °C–600 °C from DSC curve [13]. The DSC curve shows that endothermic process occurs at temperatures below 100 °C. This is due energy generated during thermal decomposition is the oxidation reaction in Sample A.

The XRD analysis of Zn$_{0.6}$Ni$_{0.2}$Cu$_{0.2}$Fe$_2$O$_4$ powder before calcination, and after calcination temperatures of 300 °C, 400 °C, and 500 °C are shown in Fig. 3 (a). As seen from XRD pattern shows that all phase confirmed Zn$_{0.6}$Ni$_{0.2}$Cu$_{0.2}$Fe$_2$O$_4$ in all sample. Then the calcination temperature was increased to 300 °C up to 500 °C form Zn$_{0.6}$Ni$_{0.2}$Cu$_{0.2}$Fe$_2$O$_4$ no significantly secondary phase of Hematite (Fe$_2$O$_3$) [18]. The lattice constant and crystal growth increase with increasing temperature calcination. The XRD pattern in Fig. 3 showed that all (220), (311) and (440) peak have high intensity, which is the (311) peak confirming to type of spinel ferrite [12].

Fig. 3 (b) suggested that there is a peak shift from sample A in the field of (311) towards a larger angle of 2θ for samples B, C, and D. As seen from Fig. 3(b) there is an increase in the intensity and an increase in FWHM values. This is due to the higher calcination temperature that affects the growth of ZnNiCu Ferrite crystals and the increase in the crystallite size are found within 17.75–20.15 nm. The calculated values of structural parameters are given in Table 2. The increase of the crystal size (17.75–20.15 nm), but decrease of lattice parameter, $a$ (8.49–8.40 Å), lattice strain, $ε$ (6.44–5.65) and dislocation, $δ$ (3.17–2.46) of larger angle (2θ) for all sample. The addition Zn, Ni, and Cu to Fe will affect in the metal oxidation of Fe [19]. The angle of the diffraction peak increases because the radius difference of ion r(Fe) = 0.63 Å is smaller than that of the ion r(Zn) = 0.74 Å, r(Ni) = 0.69 Å and r(Cu) = 0.72 Å [20–22]. In the increase of calcination temperature causes the ion radius that are formed to experience heat vibrations thereby increasing the peak intensity [23,24].

Fig. 4 (a) presented the surfaces morphologies of Zn$_{0.6}$Ni$_{0.2}$Cu$_{0.2}$Fe$_2$O$_4$ in before calcination (A), and calcination temperature at 300 °C (Sample B), 400 °C (Sample C) and 500 °C (Sample D). The FESEM images exhibited the formed crystallites are well homo- geneous an aggregation spinel plate lea particles coated by some small cubic grains with random particle average size of 0.1 μm. It is difference in the morphology with changing spinel ferrite type due to the degree of agglomeration. This may be also due to the different behavior of spinel (softmagnetic) part in each composition with previous analysis [25,26].

The particle size distribution shown in Fig. 4 (b) that all sample tends to have a narrow peak range, within 20–55 nm. As seen in histograms, the increase in the calcination temperature could random shifted the peak to constant particle sizes with average range 25–40 nm for samples A, B and D, and the peak particle sizes for sample C is 28–32 nm, respectively. It can be show higher calcination temperature could affects, reduced particle size, faster diffusion of metal oxidation, and increasing the rate at which the particles crystallize in spinel ferrite [3]. Therefore, the particle size growth was conducted at various calcination temperatures of 300 °C, 400 °C,
500 °C tends to enhance its size with the increasing on the number of oxygen vacancies. Then, effects addition of ZnNiCu have larger ionic radius than Fe and an oxygen vacuum. Li et al. [12] confirmed that the effect calcination at 800 °C increase particle size.

As seen Fig. 5, the energy dispersive X-ray spectrum (EDX) of the Samples A, B, C and D. The spectra confirmed that the presence of the variation elements. The weight and atomic percentages of zinc, nickel, copper, iron and oxygen basically confirm to the chemical formula.

In Fig. 6 and Table 3 showed that magnetic hysteresis curves and magnetic properties for all samples. The various of calcination temperature prepared all samples due to softmagnetic but their effects on magnetic properties [27]. The coercivity decreases with increasing calcination temperatures of Samples B, C and D. The saturation, remanance increases with increasing calcination temperature of Samples B, C and D as the grain size increases with same studies previous [28]. Hence, based on these results and discussions, the effect of calcination temperatures of ZnCuNi ferrites can be obtained thermal reductions above 100 °C, single crystal Zn0.6Ni0.3Co0.1Fe2O4 ferrite with cubic particle crystals and increasing of magnetic properties. Several research from researchers Ni et al. [29] influences calcination temperatures of 400°C–800 °C can be pure single phase spinel structure and good magnetic properties, then uniform in both morphology and particle size distribution with sizes varied in the range of 13–145 nm. Then Wang et al. [30] reported metal co-doped (Ni,Zn)Fe2O4 having a saturation magnetization of 57.3 emu/g with calcination temperature at 1000 °C for 2 h.

4. Conclusions

Zn0.6Ni0.3Co0.1Fe2O4 was successfully synthesized from the natural iron sand of Lombok Island, Indonesia using co-precipitation method, before calcination and the calculation temperatures were varied: 300 °C, 400 °C, and 500 °C for 2 h. The optimum condition sample was obtained sample D at the calcination temperature of 500 °C with the pure single phase of ZnNiCu ferrite. The magnetic behaviors of the samples suggested that the values are Ms = 31.79 emu/g, Mr = 12.06 emu/g, Hc = 331.06 Oe, respectively.

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