Effect of bismuth substitution on magnetic properties of $CoFe_2O_4$ nanoparticles: Study of synthesize using coprecipitation method

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Abstract: The effect of bismuth ion substitution on the magnetic properties of cobalt ferrite nanoparticles was identified in this study. This method used in this study was coprecipitation method using 0.1 bismuth ion concentration. The results on hysteresis loop showed that the saturation magnetization of cobalt ferrite nanoparticles decreased with the substitution of bismuth ions, but the coercive field experienced the opposite. Saturation magnetization decreased from 57.97 to 51.19 emu / g, while coercive fields increased from 0.64 to 0.84 kOe.

Keywords: cobalt ferrite, bismuth ion, coprecipitation, magnetic properties

1. Introduction

Study conducted on cobalt ferrite nanoparticles behavior has been focused as concern by several experts. This occurs because cobalt ferrite nanoparticles have unique electrical, optical and magnetic structures and often show different results from previous studies (Shobana & Sankar, 2009). In general, spinel ferrite has the chemical composition of MFe_2O_4 (where M = Mn, Mg, Zn, Ni, Co, etc.) which is one of the most widely used magnetic materials because of the more flexible characteristics to be modified (Liu et al., 2004). Cobalt ferrite nanoparticles are inverse spinels with several advantages including high coercivity and moderate saturation magnetization, low losses in high frequency applications (Elkestawy et al., 2010; Lima et al., 2015a). These nanoparticles also have stable physical and chemical properties that have great potential when applied in the field of magnetic media which has high density, magnetic recording applications such as audio and video recording and high frequency devices due to several devices (Raut et al., 2014).

Ion substituted on ferritic cobalt greatly influences changes in its characteristics, especially electrical and magnetic properties according to the distribution of cations on the tetrahedral (A) and octahedral (B) sites (Panda et al., 2014). Research conducted by Kumar and Kar (2016) shows that strontium doping on cobalt ferrite decreases saturation magnetization. The results of research by Lima *et al.* (2015b) stated that the increase in the coercive field of ferrit cobalt doped with strontium. Cobalt ferrite with

Gd^{3+}, Nd^{3+} and Eu^{3+} doping each increases the coercive field and decreases saturation magnetization (Amiri and Shokrollahi, 2013). But research by Zare *et al.* (2015) show that Zn-Al doping decreases the coercive field and increases saturation magnetization. From some of these studies, changes in the magnetic properties of cobalt ferrite depend on the selection of doping material, so that it can be modified for certain purposes as it is maintain the miscroscopic and macroscopic parameters. Meanwhile, research on the effects of Bi^{3+} doping in ferrit cobalt particles is relatively small (Anjum *et al.*, 2016).

Bismuth ferrite is one of the single phase multi-ferroactive materials which is very potential to be used in the electronic field because it has low magnetic losses and high electrical resistivity (Eerenstein et al., 2016). It is estimated that Bi3+ can occupy tetrahedral and octahedral locations. Substitution of Fe^{3+} ions with Bi^{3+} can modify magnetic saturation and ceorcive fields (Kumar, 2016).

There are several method to synthesize used by experts to enhance cobalt ferrite such as sol-gel technique, powder metallurgy route, solution combustion, coprecipitation, hydrothermal, thermaldecomposition, microemulsion and solid state reaction (Chand *et al.,* 2011). Of the several synthesis methods, coprecipitation has attracted a lot of attention because it has various advantages including the relatively affordable costs, non-toxic precursors, time saving and can be fabricated on an industrial scale (Safi et al., 2015).

This study identified the effect of the effect of bismuth ion substitution on nanoparticles cobalt ferrite on its magnetic properties. To identify the magnetic properties of the samples obtained were characterized by Vibrating Sample Magnetometer (VSM). Thus, this article aims to identify the effect of bismuth substitution on nanoparticles cobalt ferrite in order to become an attractive reference source used in magnetic recording applications for high density information storage.

2. Materials and Research Methods

This study was classified by three main stages namely:

1) Creating the solution of NaOH, $CoFe_2O_4$, and $CoFe_{1.9}Bi_{0.1}O_4$
2) Synthesis of $CoFe_2O_4$, and $CoFe_{1.9}Bi_{0.1}O_4$ nanoparticles
3) Magnetic characterization of the samples

2.1. Creating the solution of NaOH, $CoFe_2O_4$, and $CoFe_{1.9}Bi_{0.1}O_4$

The NaOH solution is made by dissolving 19.2 grams of NaOH solids in 100 ml of aquabides. This dilution process is carried out in a measuring cup and stirred manually using a glass spatula until all solids dissolve.

In making ferrite cobalt solution, 0.02 mol of $Co(NO_3)_2.6H_2O$ and 0.01 mol of $Fe(NO_3)_3.9H_2O$ are mixed into 200 ml of aquabides ($CoFe_2O_4$). Furthermore, 0.01 moles of $Co(NO_3)_2.6H_2O$, 0.019 moles of $Fe(NO_3)_3.9H_2O$, and 0.001 moles of $Bi(NO_3)_3.5H_2O$ were mixed into 200 ml of aquabides for the manufacture of ferrite cobalt solution with bismuth substitution ($CoFe_{1.9}Bi_{0.1}O_4$). Different from making NaOH solution, mixing each solution of $CoFe_2O_4$, and $CoFe_{1.9}Bi_{0.1}O_4$ using a hotplate and magnetic stirrer with the aim of the solution being homogeneous. The solution is each distrer with a rotating speed of 250 rpm for 20 minutes at room temperature.

2.2. *Synthesis of $CoFe_2O_4$, and $CoFe_{1.9}Bi_{0.1}O_4$ nanoparticles*

NaOH solution with a total volume of 100 ml was put into the burette while 200 ml ferrit cobalt solution was placed in a glass jar and placed on the hotplate. Cobalt ferrite solution distrer with a rotational speed of 250 rpm while being heated to a temperature of 95 ° C. After the ferritic cobalt solution reaches a temperature of 95 ° C, the NaOH solution is dropped in a solution of cobalt ferrite until the NaOH solution is used up mixed. NaOH droplets are set at a rate of 2 ml per minute. During the synthesis process, the temperature of the solution is maintained at a temperature of 95 ° C. The synthesized solution is deposited for one night. After sediment and liquid are separated, liquid is removed so that the remaining deposits (Kiran and Sumathi, 2017).

2.3. *Magnetic characterization*

The tool used to identify the magnetic properties of the sample was the Dexing Magnet Ltd vibrating sample magnetometer VSM 250 type. After that the magnetic properties of the samples were analyzed based on the hysteresis loop of the data obtained. The magnetic properties identified include coercive field, remanent magnetization and saturation magnetization.

3. Results and Discussion

The hysteresis loop of the samples synthesized at 95°C and annealed at 800°C for 5 hours is shown in Fig. 1. The magnetic property of the samples were measured at room temperature.

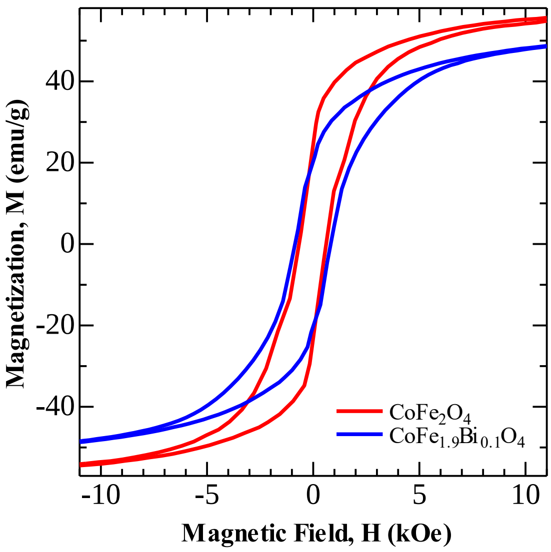

Figure 1. Hysteresis loop of $CoFe_2O_4$, dan $CoFe_{1.9}Bi_{0.1}O_4$ nanoparticles synthesized at 95°C and annealed at 800°C for 5 hours

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Figure 1. showed that the cobalt ferrite with and without bismuth substituted have the same typical hysteresis loop but have different width and saturation point specifically of the loop. It is obvious that the bismuth substituted cobalt ferrite has shorter hysteresis loop than the cobalt ferrite without bismuth substituted. The bismuth substituted of cobalt ferrite impact the magnetic properties of the sample as shown in Table 3. Table 3 shows changes in coercive field, saturation magnetization, remanent magnetization, and the squareness ratio of the $CoFe_2O_4$, and $CoFe_{1.9}Bi_{0.1}O_4$ samples.

Table 1. VSM data of the $CoFe_2O_4$, dan $CoFe_{1.9}Bi_{0.1}O_4$ nanoparticles synthesized at 95°C and annealed at 800°C for 5 hours

Sample	*Mr* (emu/g)	*Ms* (emu/g)	*Hc* (kOe)	Mr/Ms	ηB
$CoFe_2O_4$	23.68	57.97	0.64	0.41	2.43
$CoFe_{1.9}Bi_{0.1}O_4$	20.40	51.19	0.84	0.40	2.29

The presence of bismuth ions decrease the remanent and saturation magnetization of cobalt ferrite. Remanent magnetization decreased from 23.68 to 20.40 emu/g, and from 57.97 to 51.19 emu/g due the process of saturation magnetization. The decrease of remanent and saturation magnetization was in line with the results from study done by several experts namely Rafiee & Rahpeyma (2015), Safi et al. (2015) dan Kiran & Sumathi (2017).

Distribution of cations on tetrahedral and octahedral sites, as well as interactions between tetrahedral and octahedral greatly influence the magnetic properties of ferrit spinel (Panda et al., 2015). The decrease of saturation magnetization can be analyzed by the presence of bismuth ions occupying octahedral site. Strains of force constants in Fe–O and O-H bond in tetrahedral or octahedral site affect the redistribution of cations. The change of saturation magnetization is caused by the strain induced magnetization of breaking the magnetic ion chains with the substitution of non-magnetic ions, include bismuth ions (Kumar & Kar, 2016). Another reference explains that the decrease in saturation magnetization is due to the magnetic dilution of the ferrite system in the presence of magnetic ion replacement (Fe^{3+}) with non magnetic as substitute material (which in the case was ion Bi^{3+}) (Isfahani et al., 2011). The bismuth ion substituted on cobalt ferrite nanoparticles enters the octahedral site which causes antiparallel spin coupling and canting spin. This effect weakens the octahedral and tetrahedral site exchange interactions that match the Yafet-Kittel model (Yafet & Kittel, 1952). From several angles, the sub-grid of the octahedral site is divided into two parts which are opposite. This has a big effect on the average magnetization (Li et al., 2007) and causes saturation magnetization to decrease.

The analysis was also confirmed using the theory of magnetic moment calculations (Magneton Bohr). The Bi^{3+} ion has a magnetic moment ηB per ion of 5 ηB while the magnetic moment of Co^{2+} ion is 3 ηB. Therefore, the substitution of bismuth ions causes a decrease in the magnetic moment of cobalt ferrite nanoparticles which results in decreased saturation magnetization (Routray et al., 2017).

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The value of the magnetic moment per unit in Bohr magneton (B) is calculated by the following formula:

$$\eta B = \frac{M \times M_s}{5585},$$

where M is molecular weight of $CoFe_2O_4$, or $CoFe_{1.9}Bi_{0.1}O_4$, and M_s is saturation magnetization (emu/g) from each sample (Manjusha et al., 2015).

Based on Figure 1, it is certainly seen that coercive field increase after Bi^{3+} ion was substituted to cobalt ferrite nanopartikel. Coercive field increased from 0.64 to 0.84 kOe as shown in Table 1. These results are in line with previous research conducted by Gore et al. (2015) and Routray et al. (2017). Increased coercive fields are associated with increased anisotropy and constant magnetostriction. In this study obtained a relatively low coercivity value. This shows that domain wall movements follow the dominant mechanism of magnetization and magnetically specimen samples tend to become softer. Magnetic properties are suitable for application to magnetic recording devices (Yang et al., 2011; Yang et al., 2013). Coercive field increases due to the formation of nanocrystalline structures and the incorporation of bismuth ions into cobalt ferrite nanoparticles which shows that the direction of magnetization approaches stable alignment with the axis (Gore et al., 2015).

With a larger coercive field value this bismuth subtituted cobalt ferrite yields more a square hysteresis curve than cobalt ferrite non subtituted bismuth. Based on these result, the bismuth subtituted cobalt ferrite is harder to remove the magnetic properties than cobalt ferrite non subtituted bismuth.

4. Conclusion

The substitution of bismuth ion on cobalt ferrite nanoparticles through co-precipitation method was successfully carried out. This is proven by the change in magnetic properties of cobalt ferrite nanoparticles after substitution of bismuth ions. The hysteresis loop showed that the saturation magnetization of cobalt ferrite nanoparticles decreased with the substitution of bismuth ions, but the coercive field experienced the opposite.

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