NANOPARTICLE FABRICATION OF $CO_xNi_{1-x}Fe_2O_4$ USING CO-PRECIPITATION METHODE AT LOW TEMPERATURE

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ABSTRACT

Nanoparticle $Co_xNi_{1-x}Fe_2O_4$ has been successfully synthesized using co-precipitation method at low temperature 120°C by variation of concentration value (x=0, 0.25, 0.5, 0.75, 1.0). Crystal structure and size of crystallite increase with increasing cobalt concentration. There is a difference of lattice between theoretical and experimental. The increasing of cobalt affected significantly to the expansion and lattice distortion occurred at the tetrahedral site and octahedral site. Because of the distortion, the crystallite where imperfectly formed and crystal defect occurred. It is indicated by the microstrain value that describes the magnitude of the strain in crystal.

Keywords: $Co_xNi_{1-x}Fe_2O_4$; nanoparticle; site A; site B; co-precipitation

Introduction

The aim of this research is ferrite type nanoparticles. Ferrite groups have the potential to be developed in various field of technology such as data storage, medical diagnostics, detectors microwave absorber, etc. The focus of the researchers are spinel group or known as spinel ferrite. Spinel ferrite has unique properties because of the typical crystalline structure of spinel structure. The spinel structure influenced by the configuration and distribution of ions in nanoparticle crystals affected by chemical composition during the synthesis process. The chemical formula of the spinel structure of crystal is MFe_2O_4 where M is divalent cation of the *3d* transition element. This crystal structure has cation that distorted in two sublattices, namely sublattice tetrahedral and octahedral.

The type sample of magnetic nanoparticle was studied were nickel ferrite ($NiFe_2O_4$) and cobalt ferrite ($CoFe_2O_4$). $CoFe_2O_4$ has a high saturation magnetization value, hard magnetic, and inverse spinel structure.[1,2] This nanoparticle been potential as nano-photocatalyst and nano absorbent for organic pollutan.[3] Nanoparticle NiFe2O4 is fine magnetic materials with high saturation magnetic characteristic, low coercivity, high magnetic permeability, low anisotropy, high currie temperature and low magnetostriction.[4,6] If the two materials are combined into a single $CoNiFe_2O_4$ unit, they will be producing new materials with crystal structures and different properties which have been potential to be a signal rectifier oscillator device.

The information about the structure of Co_xBi_{1-x} nanoparticle crystals still has a gap to research. This gives opportunity to study various information about $Co_xNi_{1-x}Fe_2O_4$ in relation to the influence of various synthesis parameters and chemical composition of the nanoparticles constituents with certain method. The co-precipitation method has selected in this research because the synthesis process is simple and relatively fast (not time-consuming),

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carried out at low temperature (120^{o}C), and nanoparticles that resulted have a size that tends to be more uniform compared to other methods. In addition, the co-precipitation method is also efficient because it does not have to require further processing in the form of calcination or sintering as was done by previous studies.

Methods

Nanoparticle $Co_xNi_{1-x}Fe_2O_4$ (0;0,25;0,5;0,75;1,0) has been synthesized by co-precipitation method. Chemicals used in research is $CoCl_2{\cdot}6H_2O$, $NiCl_2.6H_2O$, $FeCl_3.6H_2O$, HCl, NaOH (E Merk. Germany), and DI water. The mole ratio is used as presented in Table 1.

Tabel 1. The mole ratio precursor

Reagen	Ratio
$CoCl_2.6H_2O$	1
$NiCl_2.6H_2O$	1
$FeCl_3.6H_2O$	2

For the value of x varied (0, 0.25, 0.5, 0.75, dan 1.0). The co-precipitation method begins with prepare Fe_2Cl_3, $CoCl_2$, dan $NiCl_2$ solution. Fe_2Cl_3, $CoCl_2$, dan $NiCl_2$ solution stirred at room temperature with speed 500 rpm for 3 minutes until homogeneous. The metal salt solution added with 3,37 ml HCl and stirred by rate 500 rpm at room temperature for 5 minutes. After that, this solution was dripped with a dropping rate ± 2 ml/min using a burette into NaOH solution which being sterilized at 120^{o}C with a stirring rate of 1000 rpm for 60 minutes. The precipitate formed is deposited on a permanent magnet for 30 minutes until the temperature is at room temperature, then rinse with 150 mL of distilled water and deposited again on a permanent magnet for 30 minutes. The slurry was heated in a furnace at 90^{o}C for 5 hours to produce solid pieces of nanoparticles $CoxNi1\text{-}xFe_2O_4$ and then it crushed to powder. Finally, nanoparticles were characterized using X-Ray diffraction characterization (XRD) using X-Ray wavelength (CuKα1) of 1.5406 Å step to observe the crystal structure and nanoparticle phase and data is processed using Origin Software.

Result and Discussion

The diffraction peaks formed in the XRD spectrum in each sample can be assumed that the sample is crystalline. This is characterized by the appearance of diffraction peaks. The diffraction peaks of nanoparticles are (311) in the diffraction patterns confirms that all the samples exhibit a cubic spinel structure having space group Fd3m.[7] Determination of the diffraction peaks is adjusted to the JCPDS card No 79-1744 ($CoFe_2O_4$) and JCPDS Card No. 74-2018 ($NiFe_2O_4$). The diffraction peaks are formed shifted as the concentration of x increase from x=0 to x=1, because of differences in composition between Co and Ni. Besides that, the synthesis method also affected the shift of diffraction peaks. The synthesis method has an effect on the $CoNiFe_2O_4$ nanoparticle crystals formed. XRD data processing used software origin 9.0, which from the diffraction peaks can be estimated crystallite size and lattice parameter of nanoparticle $CoxNi1\text{-}xFe_2O_4$ (x=0,0.25,0.5,0.75,1.0). The concentration of the XRD spectrum shown in Figure 1 displayed phase of γ-Fe_2O_3. The phase peaks γ-Fe_2O_3 also undergo a shift with increasing nickel concentration in nanoparticle $CoxNi1\text{-}xFe_2O_4$. The form of γ-Fe_2O_3 did not give a significant effect on the crystalline structure of nanoparticle, but it has a significant effect on the moment magnetic of nanoparticle which has an impact to the magnetic properties.[8] The phase presence of γ-Fe_2O_3 can be caused by a synthesis process which is not perfect, so it is assumed the phase of $Co_xNi_{1-x}Fe_2O_4$ that formed is not perfect. The parameter value of experimental lattice (a_{ex}) and crystallite size can be calculated by the Scherrer[9] and presented in Table 2.

$$D \frac{k\lambda}{B\,Cos\theta} \quad (1)$$

The average cation radius at A site (rA) and B site (rB) can be calculated by equation[9]:

$$rA=(C^A{}_{Co}{}^{2+})(r^A{}_{Co}{}^{2+})+(C^A{}_{Fe}{}^{3+})(r^A{}_{Fe}{}^{3+}) \quad (2)$$

$$rB=1/2*((C^B{}_{Ni}{}^{2+})(r^B{}_{Ni}{}^{2+})+(C^A{}_{Fe}{}^{3+})(r^A{}_{Fe}{}^{3+})) \quad (3)$$

where the CA value shows the ion concentration found of A-site (tetrahedral) and

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CB value of B site (octahedral). Lattice parameters experimentally (a_{exp}) give result different than theoretical lattice parameters (a_{th}). It is due to the calculation of theoretical lattice parameters based on the ionic radius of each element in CoxNi1-xFe2O4. Theoretical calculation of lattice parameters can be calculated by the equation 4:

$$a_{th} = \frac{8}{3\sqrt{3}}\left[r_A + R_0 + \sqrt{3}(r_B + R_0)\right] \quad (4)$$

rA and rB are radius cation-anion found at A site and B site.

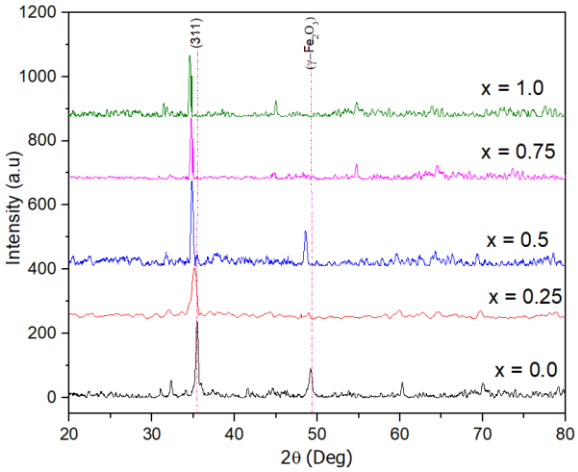

Figure 1. XRD Spectrum

Table 2. Value of lattice parameters, crystallite size,$Co_xNi_{(1-x)}Fe_2O_4$ nanoparticle

X	Sample	2θ	FWHM	hkl	a_{exp} (Å)	a_{th}(Å)	t(nm)	microstrain
0.0	$NiFe_2O_4$	35,46	0,33	311	8,39	7,80	50,09	0.32
0.25	$Co_{0.25}NiFe_2O_4$	35,12	0,31	311	8,47	7,82	53,93	0.32
0.5	$Co_{0.5}Ni_{0.5}Fe_2O_4$	34,85	0,29	311	8,53	7,84	56,64	0.31
0.75	$Co_{0.75}Ni_{0.25}Fe_2O_4$	34,75	0,26	311	8,56	7,85	64,03	0.31
1.0	$CoFe_2O_4$	34,59	0,26	311	8,59	7,87	64,00	0.31

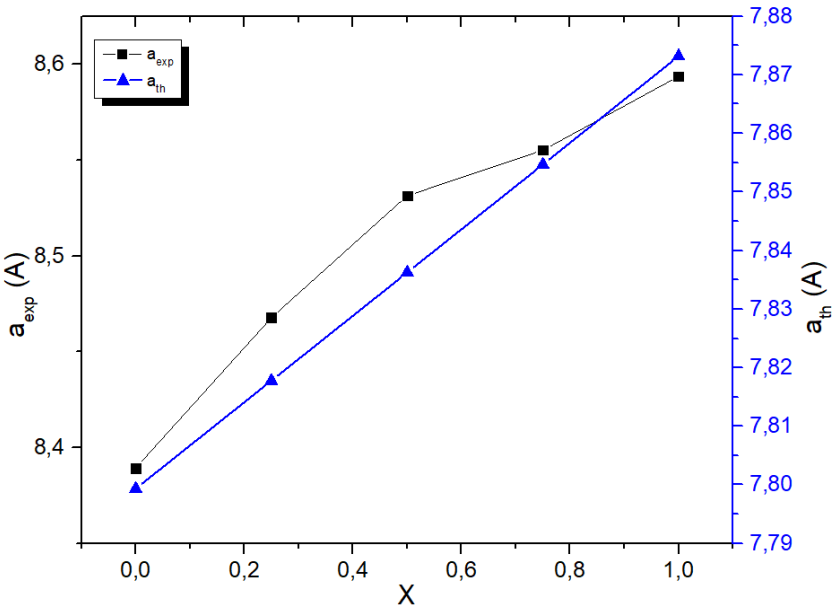

Figure 2. a_{exp} vs a_{th}

Table 2. Effect of Co (x) concentration of R_A and R_B values

x	U	R_A	R_B
0,00	0,68	6,26	3,64
0,25	0,68	6,24	3,62
0,50	0,67	6,21	3,59
0,75	0,67	6,19	3,57
1,00	0,67	6,17	3,55

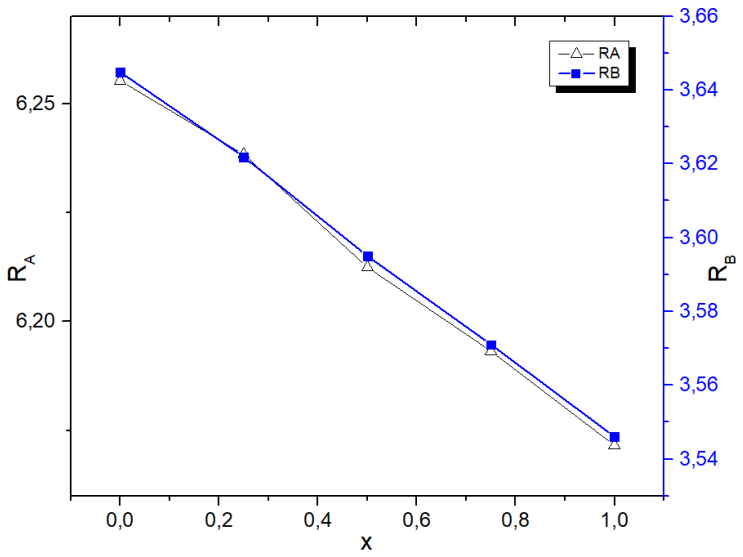

Figure 3. The Co (x) concentration effect on R_A and R_B

Based on Table 2, the lattice parameters increased with increasing the content of cobalt in $Co_xNi_{1-x}Fe_2O_4$ both theoretically (a_{th}) and experimentally (a_{exp}). It graphically is shown in Figure 2.

Increasing lattice parameters can be affected by ion substitution, replacing a larger radius of ionic with smaller ionic radius. The cobalt element that has an ionic radius of 0,75 A replace the nickel element which has an ionic radius of 0,69 A. Co^{2+} ions in this nanoparticle are present on A site tetrahedral and Ni^{2+} ions on B site octahedral. Fe3+ ions are distributed in both sites, tetrahedral and octahedral. Distribution of cations in the nanoparticle is assumed by the equation[10]:

$$[Co_x^{2+}Fe^{3+}{}_{1-x}]_A[Ni_{1-x}Fe^{3+}{}_{1-x}]_B \quad (5)$$

Increasing of cobalt concentration in CoxNi1-xFe2O4 nanoparticle affected to the bond length between cation-anion on tetrahedral site (R_A) and octahedral site (R_B). The bond length can be calculated by equation 6 – 7. [9-11] As a result of changes in the bond length of cation-anion assumed that distortion occurs in both sites. The addition of cobalt concentration in $CoFe_2O_4$ nanoparticle due to lattice expansion occurs in A site and shrinkage in B site which is illustrated by equation 8 and equation 9. R_A and R_b value are shown in Table 2.

$$R_A = a\sqrt{3}(\delta + \tfrac{1}{8}) \quad (6)$$

$$R_B = a\sqrt{3\delta^2 - \tfrac{\delta}{2} + \tfrac{1}{16}} \quad (7)$$

$$\delta = U - 0.375 \quad (8)$$

$$U = \left[(rA + Ro)\tfrac{1}{\sqrt{3a}} + \tfrac{1}{4}\right] \quad (9)$$

Based on Table 2, R_A and R_B value was decreased with increasing of cobalt element. It graphically is shown in Figure 3.

The trigonal deviation from the coordinate of oxygen atom which found on B site octahedral is expressed as U. The shrinking of the U value state due to distribution on tetrahedral site and octahedral site with increasing of cobalt concentration.

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Conclusion

The $Co_xNi_{1-x}Fe_2O_4/SiO_2$ nanoparticle have been successfully synthesized with various element of (x=0.0 , 0.25, 0.5, 0.75, 1.0) using co-precipitation method. The result of XRD diffractogram represented that the nanoparticle has a crystalline form with a crystallite size of 50.09 to 64. The form of nanoparticles is not perfect because the synthesis process at low-temperature result strain in crystal so assumed happen deviation for both sites, A site and B site.

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