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Effects of Ni and Annealing Temperature on Crystal Structure and Magnetic Properties of MnNi-Fe₂O₄ Nanoparticles

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Abstract. Manganese nickel ferrite (MnNi-Fe₂O₄) nanoparticles have been synthesized by co-precipitation method. In this research, the effects of Ni concentration (0.2-0.8M) and annealing temperature (400-1000ºC) on the structural and magnetic properties of nanoparticles were studied. Ferrite samples were characterized by X-ray Diffractometer (XRD), Transmission Electron Microscope (TEM) and Fourier Transform Infrared (FTIR) spectroscope. The XRD patterns showed that nanoparticles possess cubic spinel structure that indicated by peaks of (220), (311), (400), (511) and (440). The crystallite size decreased with the increase of Ni concentration (23.5-4.5 nm) and increased with the increase of annealing temperature (14.8-49.3 nm). Stretching vibration on octahedral and tetrahedral of metal-oxygen from FTIR spectra was observed at 354.9 - 462.9 cm^{-1} and 586.3 - 601.7 cm^{-1}, respectively. Magnetic properties of ferrite sample were analyzed by Vibrating Sample Magnetometer (VSM). The saturation magnetization (*Ms*) lay in the range of 11.07 – 20.7 emu/g and the Coercivity (*Hc*) decreases with the increase of annealing temperature (217.0 – 167.0 Oe).
Keyword: MnNiFe₂O₄ magnetic nanoparticles, co-precipitation, annealing treatment.

1. Introduction

Magnetic nanoparticles are one of the nanoparticles that attract the attention of many researchers. The most studied magnetic nanoparticles are spinel ferrite which general formula MFe_2O_4 (M= divalent metals ion such as Cu, Mn, Mg, Zn, Ni, Co) due to the high permeability, good electrical resistivity, mechanical strength and chemical stability [1]. Spinel ferrite can be used in various applications such as magnetic resonance imaging (MRI), magnetic recording media, ferrofluids, biomedical [2], drug delivery and magnetic hyperthermia [3].

Manganese ferrite and nickel ferrite are examples of spinel ferrite material. Manganese ferrite is soft magnetic which has a partial inverse spinel structure with 80% Mn^{2+} ions in the tetrahedral site, 20% in the octahedral site, Mn^{3+} and Fe^{3+} ions distributed in tetrahedral and octahedral sites [4]. Nickel Ferrite is a soft magnetic material which has an inverse spinel structure where all Ni^{2+} ions in the octahedral site and Fe^{3+} ions in the tetrahedral site [5]. The structure and magnetic properties of spinel ferrite depend on the outer electron configuration, radius of divalent cation and distribution of cation at the different site [1]. To obtain certain magnetic properties such as high saturation magnetization, small coercivity both materials can be combined [6]. The combination of both nanoparticles with different concentrations can be obtained as $Mn_{1-x}Ni_xFe_2O_4$. Koseoglu [6] synthesis the $Mn_xNi_{1-x}Fe_2O_4$ (x = 0.2, 0.4 and 0.6) by
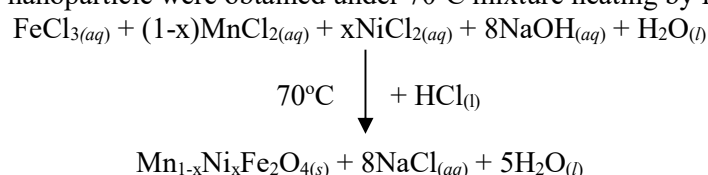
hydrothermal method. The crystallite size and saturation magnetization increasing with increasing Mn concentration. These results are similar to that of reported by Abdallah and Moyo [2] on $Mn_xNi_{1x}Fe_2O_4$ nanoparticles (x= 0.1, 0.3 and 0.5). A lot of research has been done with these combinations, but studies with a wider range of Mn concentrations are rarely reported.

The structure and magnetic properties of $MiNi$-Fe_2O_4 nanoparticles are strongly influenced by the annealing temperature [7]. Kumar *et al* [7] prepared $MnNiFe_2O_4$ nanoparticles with auto combustion method and evaporation method followed by annealing temperature treatment. The increase in annealing temperature can improve the crystallite size and saturation magnetization of nanoparticle.

There are many methods that can be used to synthesize manganese nickel ferrite ($MnNiFe_2O_4$) nanoparticles, such as auto combustion, evaporation method [7], sol gel [8, 9] ceramic method [5] hydrothermal [6] and co-precipitation [4]. From several methods that use to synthesize magnetic nanoparticles, the co-precipitation method is a commonly used method because it has several advantages such as, easy preparation, the material used is more flexible, more homogeneous [4] the shape and particles size can be controlled and low cost [10]. Therefore, this research study the effect of Mn concentration with a wider range (0.2-0.8) and annealing temperature on the crystal structure and magnetism properties of nanoparticles.

2. Materials and Method

$MnNi$-Fe_2O_4 nanoparticles was synthesized by co-precipitation method. The precursor used in the synthesis were $FeCl_3.6H_2O$ (Merck, Germany), $MnCl_2.H_2O$ and $NiCl_2.6H_2O$. The precursor was dissolved into 25 mL of distilled water for $MnCl_2.H_2O$ and $NiCl_2.6H_2O$ and 25 mL of distilled water for $FeCl_3.6H_2O$. Both of solution was stirrer for 3 minutes so that a homogeneous solution was obtained. Both of solutions were mixed into 1 solution with added 3.37mL HCL with stirrer for 3 minutes. The solution was then added in dropwise to 8 M NaOH (Merck, Germany) solution. The precipitation of $MnNi$-Fe_2O_4 magnetic nanoparticle were obtained under 70°C mixture heating by following reaction:

$$FeCl_{3(aq)} + (1\text{-}x)MnCl_{2(aq)} + xNiCl_{2(aq)} + 8NaOH_{(aq)} + H_2O_{(l)}$$

$$70°C \quad \bigg\downarrow \quad + HCl_{(l)}$$

$$Mn_{1\text{-}x}Ni_xFe_2O_{4(s)} + 8NaCl_{(aq)} + 5H_2O_{(l)}$$

Nanopowder were washed using distilled water to remove unreacted salts for six times. Nanopowder was dried using a furnace with a temperature of 90°C for 4 hours, continued by conducting heat treatment with annealing temperature variations of 400, 600, 800, and 1000°C. The sample was annealed at air pressure for 2 hours. Finally, $MnNi$-Fe_2O_4 nanoparticles were characterized using X-ray diffractometer (XRD) PANalytical type x'pert pro with Cu K-alpha 1.5406 Å, JEM-1400 jeol transmission electron microscope (TEM), Fourier Transform infrared (FTIR) spectroscope of the Shimadzu Prestige-21 brand. Magnetic properties were analysed using the VSM Riken Denshi co ltd. vibrating sample magnetometer (VSM).

3. Result and Discussion

3.1. Structure Studies

XRD patterns for $MnNiFe_2O_4$ (with Ni = 0.2-0.8M) and $Mn_{0.8}Ni_{0.2}Fe_2O_4$ (with temperature 400-1000°C) nanoparticles in room temperature is show in Figure 1. XRD pattern of both samples showed cubic spinel structure which were attributed by peaks (220), (311), (400), (511) and (440) as shown in Figure 1. These peaks were confirmed by JCPDS card no.74-2403 for $MnFe_2O_4$ and JCPDS card no.10-0325 for $NiFe_2O_4$. The crystallite size of the sample were calculated using Scherer's formula [4]:

$$t = \frac{K\lambda}{\beta \cos\theta}$$

where K is structure factor (0.9) and β is full width at half maximum at peaks 311. Lattice parameter (a) and inter planar spacing (d) have been calculated with formula $a = d\,(h^2+k^2+l^2)^{1/2}$.
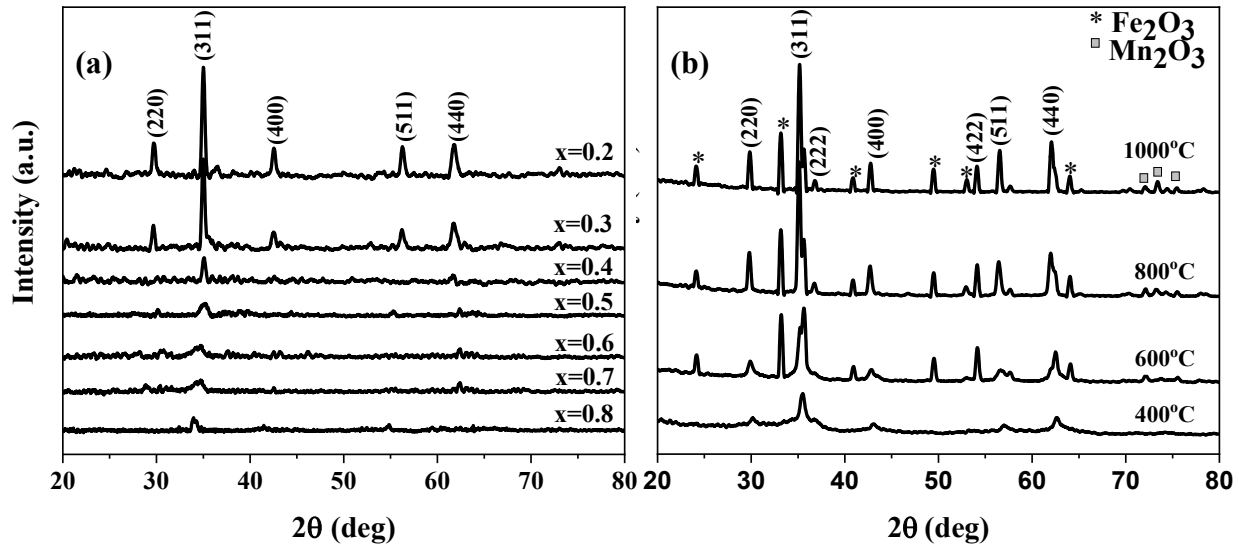

Figure 1. XRD patterns of $Mn_{1-x}Ni_xFe_2O_4$ nanoparticles with Ni concentration (Ni = 0.2-0.8M), (b) XRD patterns $Mn_{0.8}Ni_{0.2}Fe_2O_4$ nanoparticles with annealing temperature in the range of 400-1000°C.

The crystallite size and lattice parameter decrease with the increase Ni concentration. The decrease of lattice parameter with an increase Ni concentration due to the replacement of Mn ions with smaller radii ions of Ni [2]. On the other hand, crystallite size and lattice parameter increase with the increase in annealing temperature. The increase in crystallite size due to the nucleation and crystal growth rate increase. The relation between Ni concentration and annealing temperature with crystallite size shown by Figure 2.
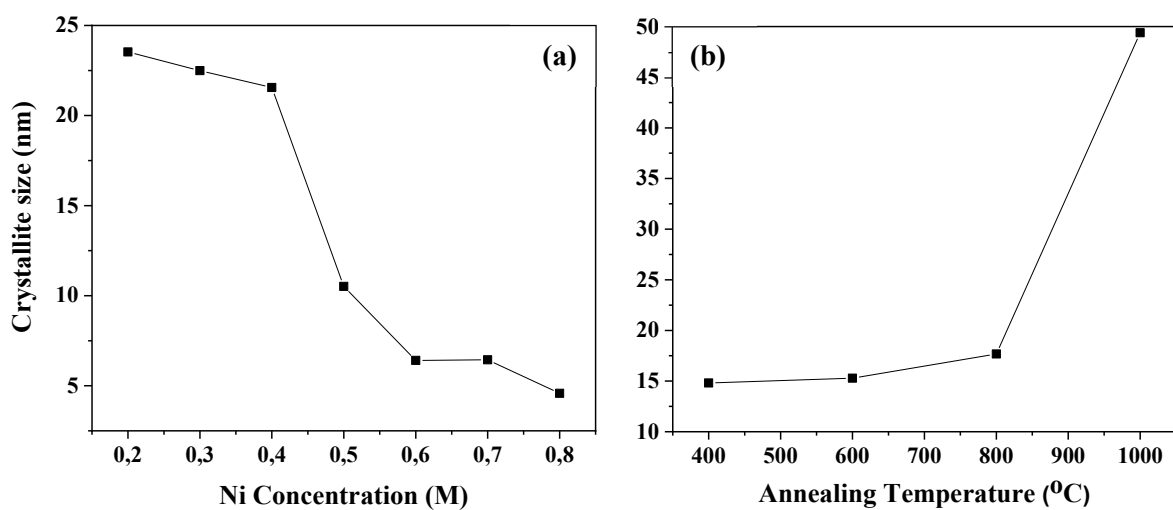

Figure 2. (a) Relation between Ni concentration with crystallite size (b) Relation between annealing temperature with crystallite size.

The XRD patterns of annealed samples at temperatures above 400 indicates the formation of hematite phase (α-Fe_2O_3). The intensity of this phase increases until annealing temperature of 800^oC, then decreases at further temperatures [7]. The formation of α-Fe_2O_3 creates two coincide peaks of 311 in the XRD pattern. Peaks with a smaller angle corresponds to $NiFe_2O_4$ and a higher angle corresponds to $MnFe_2O_4$ as the lattice parameter of $NiFe_2O_4$ is higher than of $MnFe_2O_4$ [11].

Bonding analysis of atom in sample were identified base on spectra provided by FTIR as shown Figure 3. Two strong absorption bands between 354.90 cm^{-1} and 601.79 cm^{-1} are showed of cubic spinel phase. The bands centered at about 460 cm^{-1} and 601 cm^{-1} are due to vibration at octahedral (B) and tetrahedral (A). There are some absorption bands in octahedral which showed some metal which vibration with oxygen. The difference absorbance position between tetrahedral (A) and octahedral (B) is related distance metal ions to oxygen. There is some absorption at the octahedral site caused by the differences ions radii in the site. The band corresponding to wavenumber about 1056 cm^{-1} on the sample is associated with vibration Fe-O-H. Two bands about 1600 cm^{-1} and 3400 cm^{-1} were related with bending and stretching of O-H-O bonds which showing the presence of free absorbed water [12] and this band disappear after annealing at 800^oC.
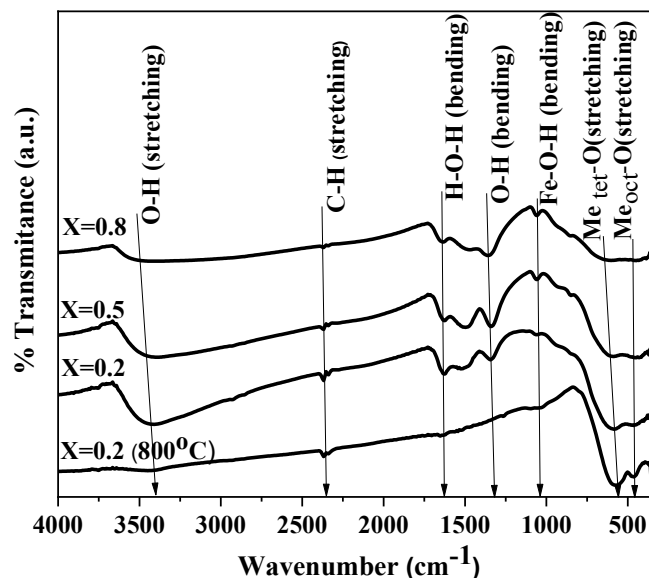

Figure 3. The FTIR spectra of MnNi-Fe_2O_4 nanoparticles

The morphology and selected area diffraction (SAED) image of sample before and after annealing as shown in Figure 3 by transmission electron microscopy (TEM) analysis.
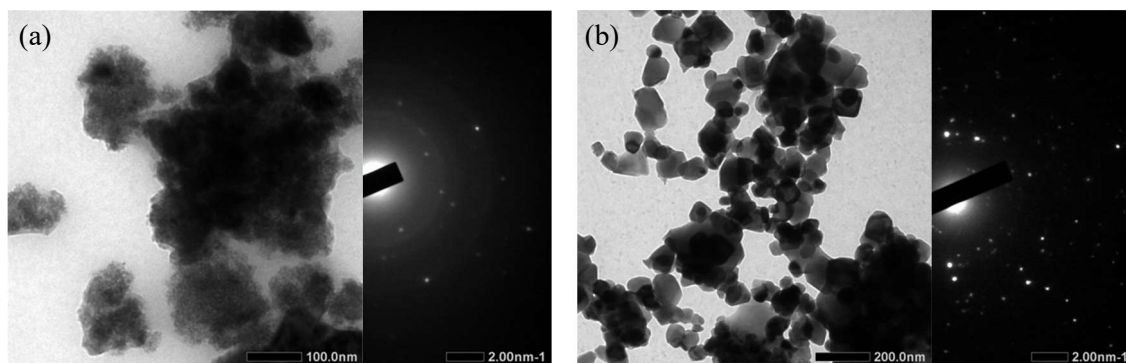

Figure 4. TEM images of MnNi-Fe_2O_4: (a) as prepared, (b) annealing at 800^oC.

The obtained MnNi-Fe$_2$O$_4$ nanoparticles were agglomerated, as shown in Figure 4(a), therefore the grain size of nanoparticles was not observed. Meanwhile, Figure 4(b) shows MnNi-Fe$_2$O$_4$ nanoparticles and easily recognizable as individual particle. The average grain size of annealed sample nanoparticles is about 85 nm. The reduce of agglomeration after annealing process is due to lower surface energy and magnetic moments interaction on nanoparticles. Selective area electron diffraction (SAED) image of as prepared MnNi-Fe$_2$O$_4$ showed single crystal formation. After the annealing process, sample showed polycrystalline formation with a few additional spots. The new spot formation due to new formation of α-Fe$_2$O$_3$ during the annealing process.

3.2. Magnetic Properties

The magnetic properties of all samples were measure by using vibration sample magnetometer (VSM) at room temperature, as shown in Figure 5 and 6 (Ni concentration) and Figure 7 (annealing temperature). Figure 4 shows that the saturation magnetization tends to increase with the increase of Ni concentration. This result is in accordance with those reported by Airimioaei *et al* [13] and in contrast with the reported result by Hu *et al* [14] for bulk ferrite. The minimum and maximum magnetization are 5.9 emu/g and 24.6 emu/g respectively. The coercivity (*Hc*) increases with the increase in Ni concentration from 0.2 to 0.6 M and decreases for further concentrations.
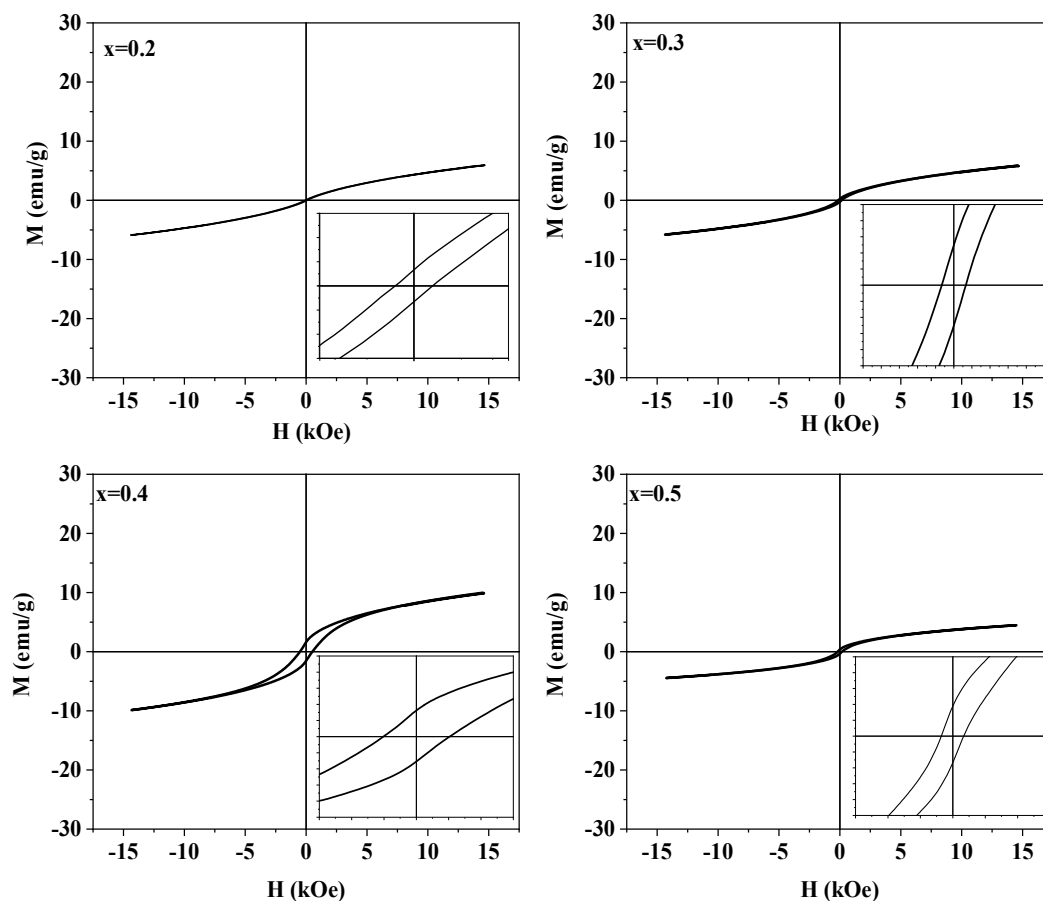

Figure 5. The hysteresis loop of Mn$_{1-x}$Ni$_x$Fe$_2$O$_4$ nanoparticles with Ni concentration (Ni = 0.2-0.5M)

The annealed sample in Figure 5 shows saturation magnetization tends to increase by increasing the annealing temperature. The increase in saturation magnetization is related to the increase grain size as a result of the increase of annealing temperature. The saturation magnetization decreases at 600°C

caused by the non-magnetic phase of ferrite (α-Fe_2O_4) which is most formed at this temperature. This phase decreases with the increase in annealing temperature and might disappears at higher temperature.
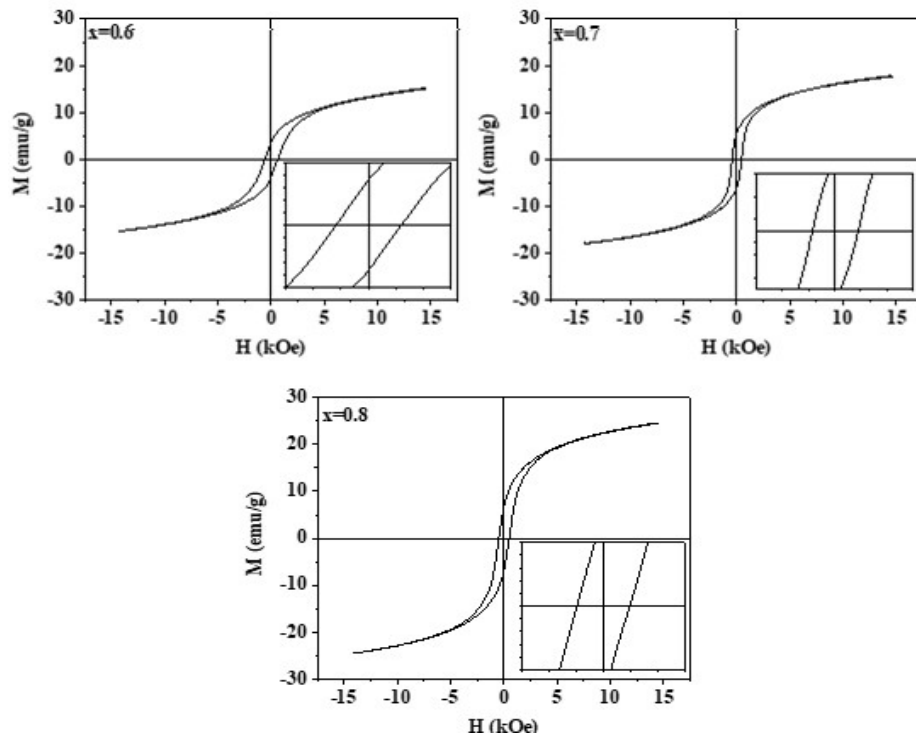

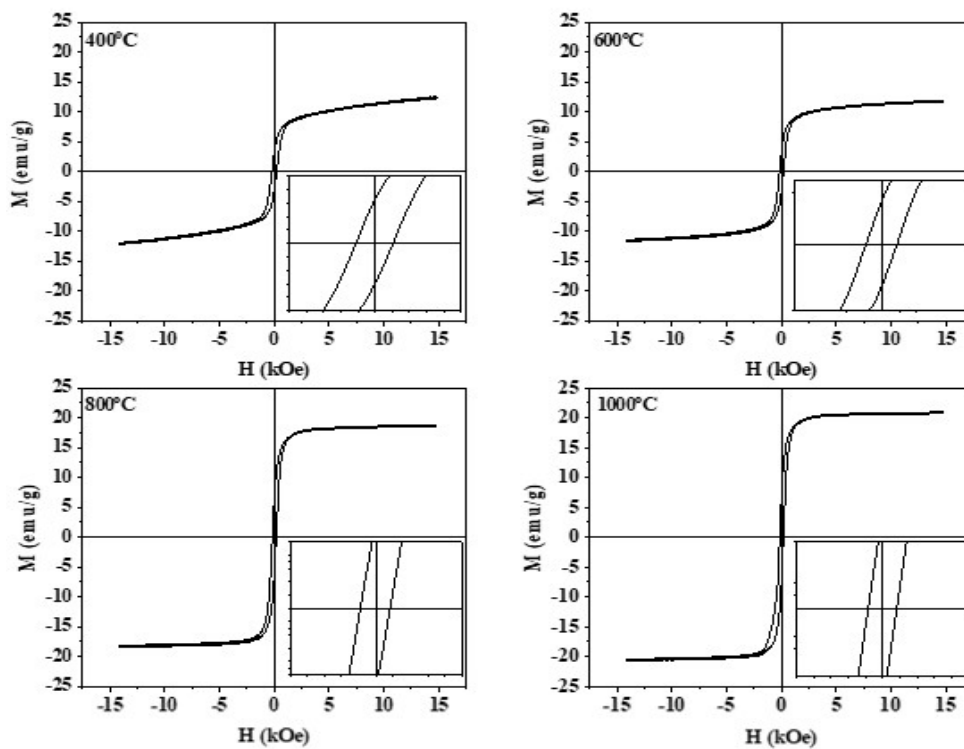**Figure 6.** The hysteresis loop of $Mn_{1-x}Ni_xFe_2O_4$ nanoparticles with Ni concentration (Ni = 0.6-0.8M)

Figure 7. The hysteresis loop of $Mn_{0.8}Ni_{0.2}Fe_2O_4$ nanoparticles with annealing temperature in the range of 400-1000°C

4. Conclusion

The spinel ferrite of MnNi-Fe$_2$O$_4$ nanoparticles has been successfully synthesized by co-precipitation method. The crystallite size of samples influenced by Ni concentration and annealing temperature. The other phase of ferrite (α-Fe$_2$O$_4$) is formed at a temperature of 600 and decreases with an increase in annealing temperature. Annealing temperatures tend to reduce the agglomeration of nanoparticles. The magnetic properties of both sample such as saturation magnetization, remanent magnetization is increase with the increase Ni concentration and annealing temperature.

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