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The composition, nanocrystalline and magnetic properties of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ Ferrite nanoparticles synthesized at low temperature

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Abstract

The crystalline nanoparticles of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite were synthesized by chemical co-precipitation with precursor concentration of 0.1M, then modified by 0.25M solution of oleic acid in pentanol and finally heated at temperatures 120, 140, 160 and 180^{o}C for 6h in autoclave. The effect of heating temperature on crystallite size and magnetic properties of ferrite was studied. The analysis of XRD, EDS and TEM data of samples confirmed that all of samples heated at these temperatures are crystalline and their particle size is different with corresponding values 6, 6.5, 7 and 8 nm. The magnetic properties of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite measured by vibrating sample magnetometer (VSM) showed that the coercive force H_c and the remanence M_r of samples are about zero while the saturation magnetization M_s has values of 14.20, 25.39, 26.81, and 27.12 emu/g consequently.

Keywords: *crystalline nanoparticles, $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite, magnetic properties, superparamagnetism (SPM)*

1. Introduction

The superparamagnetic nanoparticles of Zn-Ni-Fe ferrite system are used currently for special applications such as target-directed medicine, cancer treatment, magnetic resonance imaging of improved resolution, increased radar wave absorption, ferrofluid, etc. [1,2]. Superparamagnetism (SPM) is a type of magnetism that occurs in small ferromagnetic or ferrimagnetic nanoparticles. Crystallite size of SPM is around a few to 10 nanometers, depending on the material. In the superparamagnetic nature, ferromagnetic or ferrimagnetic nanoparticles have coercive force $H_c = 0$ and remanence $M_r = 0$ like paramagnetic materials, but their saturation magnetization M_s is many times higher than that of paramagnetic materials [3, 4].

There are some of methods used for the synthesis of ferrite nanoparticles such as co-precipitation, sol-gel technique and hydrothermal method, etc. [5-7]. In this paper, nanoparticles of $Zn_{0,8}Ni_{0,2}Fe_2O_4$ ferrite were first synthesized by chemical co-precipitation, then modified by oleic acid and finally heated at different temperatures: 120, 140, 160 and 180^{o}C in 6h (autoclave heating). This study aims to understand how the heating temperature influences crystallite size and magnetic properties of the ferrite.
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2. Experimentals

2.1 Chemicals

The following chemicals such as $FeCl_3.6H_2O$ - Merck (Germany), $ZnCl_2$ - Merck (Germany), $NiCl_2.6H_2O$ - Merck (Germany), 1-Pentanol ($C_5H_{12}O$) - Merck (Germany), n-Hexane (C_6H_{14}) - (China), Oleic acid ($C_{18}H_{34}O_2$) - Sigma Aldrich (US) and Ethanol - (China) were used for synthesis.

2.2 Synthesis of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite

Each salt type was dissolved in double distilled water to the concentration 0.1 M. Solution of each salt was mixed and heated at 60^{o}C with a stirring speed of 500 rev/min. A 25 % ammonia solution was then added to the above mixture drop by drop while stirring kept constant. The addition of ammonia will stop when pH maintained at 8.5. To avoid agglomeration of particles, 0.5 M solution of oleic acid in pentanol was dropped in the mixture at 60^{o}C with stirring. The mixture was then heated to 80°C and stirring was stopped when the smell of ammonia disappears (about 1 h). Finally, to study the effect of heating temperature on crystallite size and magnetic properties of ferrite, the mixture was heated at temperatures 180, 160, 140 and 120°C for 6h in autoclave. Products were obtained in the form of precipitates and then separated from water by the magnet and washed several times by re-dispersing in n-hexane and precipitating with ethanol to remove salt residues and other impurities.

The formation of ferrite nanoparticles passed a two-step process. In the first step, hydroxide nanoparticles were co-precipitated from the metal salts and ammonia solution and then were capped from each other by oleic acid (co-precipitation step). The oleic acid initially reacted with the ammonia to form ammonium oleate. Additional heating decomposes ammonium oleate to ammonia gas and oleate ions, which attached to and surround the hydroxide nanoparticles. The mentions above can be expressed in the following chemical reactions:

$0.2Ni^{2+} + 0.8Zn^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow$
$0.2Ni(OH)_2 0.8Zn(OH)_2 2Fe(OH)_3\downarrow$ (1)

$NH_4OH + C_{17}H_{33}COOH$ (*heating*) $\rightarrow$
$C_{17}H_{33}COONH_4 + H_2O$ (2)

$C_{17}H_{33}COONH_4$ (*heating*) $\rightarrow C_{17}H_{33}COOH + NH_3$ (3)

$C_{17}H_{33}COO + Ni^{2+}/Zn^{2+}/Fe^{3+}$ (*heating*)
$\rightarrow C_{17}H_{33}COO(Ni/Zn/Fe)$ (4)

The second step consists of transformation of hydroxides into nanoferrites occurring when the samples were heated at appropriate temperatures in autoclave (ferritization step) as follows:

$0.2Ni(OH)_2 0.8Zn(OH)_2 2Fe(OH)_3$ (heating) $\rightarrow$
$Ni_{0.2}Zn_{0.8}Fe_2O_4 + 4H_2O$ (5)

At this step, the crystalline nanoparticles of ferrite are formed and grew up. The growth of ferrite nanoparticles is hindered by capped layer of metal oleate. As a result, crystalline nanoparticles of ferrite are obtained at appropriate heating temperature.

2.3 Characterization

Structure of ferrite was studied by X-ray diffraction (XRD). Microstructure was observed by Transmission Electron Microscope (TEM). Chemical composition of ferrite was determined by Energy Dispersive X-rays Spectroscopy (EDS). Magnetic properties of ferrite were measured by Vibrating Sample Magnetometer (VSM)

3. Results and Discussion

3.1 Chemicals composition

Chemical composition of $Zn_{0,8}Ni_{0,2}Fe_2O_4$samples was determined by EDS. Figure 1 shows EDS spectra of sample heated at 180°C which confirm appearing of Fe, Zn, Ni and O.

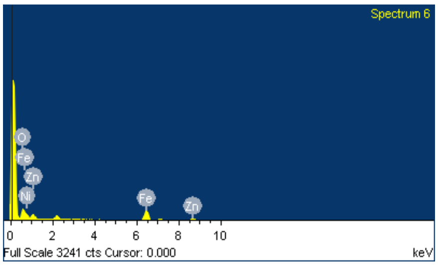

Fig. 1 The EDS spectrum of $Zn_{0,8}Ni_{0,2}Fe_2O_4$ samples heated at 180°C

The table 1 shows chemical composition of $Zn_{0,8}Ni_{0,2}Fe_2O_4$ samples heated at 180°C compared with theoretical composition. There is also a little difference of compositions found which can be negligible

Table 1: Chemical composition of $Zn_{0,8}Ni_{0,2}Fe_2O_4$ sample heated at 180°C

Element	Weight by EDS (%)	Theoreticle weight (%)
O K	25.20	26.71
Fe K	45.99	46.74
Ni K	5.01	4.84
Zn K	23.81	21.70

3.2 Microstructure

Crystal structure of samples was studied by XRD. Figure 2 shows diffraction patterns for as-synthesized samples heated at different temperatures: 120, 140, 160 and 180°C for 6h in autoclave. Observed diffraction peaks of the heated samples are corresponding to the (220), (311), (400), (422), (511) and (440) standard powder diffraction lines of Fe-Zn-Ni ferrite [8]. The sample heated at 120°C is not completely crystallized because only three diffraction peaks with low intensity are observed. Thus, it is believed that the ferritization occurs completely at temperatures from 140 to 180°C.

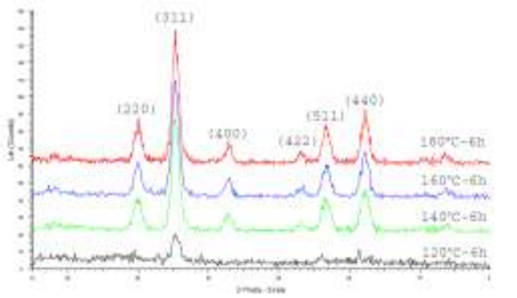

Fig. 2 XRD pattern of Zn0.8Ni0.2Fe2O4 samples heated at different temperatures

The crystallite size of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ferrite was determined by Scherrer formula [9]:

$$d = \frac{K\lambda}{\beta . \cos\ \theta}\ ; \qquad (6)$$

where d is average crystallite size, $K = 0.9$, $\lambda_{Cu\text{-}K\alpha}$ = 1.54056 Å, β - FWHM in radians, θ - Wulf-Bragg angle ($2\theta = 35.23^o$)

Values of average crystallite size and corresponding β of heated samples are shown in table 2.

Table 2: Average crystallite sizes of heated samples determined by Scherrer formula

Samples	2θ (degree)	β (FWHM) (radian)	Crystallite size (nm)
Heated at 180°C/6h	35.23	1.042	7.9
Heated at 160°C/6h	35.23	1.176	7.1
Heated at 140°C/6h	35.23	1.213	6.8
Heated at120°C/6h	35.23	1.299	6.4

For TEM analysis of heated ferrites, the powder specimens were dispersed in n-hexane and then treated by ultrasonication for about 30min. A few drops of the suspension were made on a carbon-coated copper grid and left to dry in the air. Figure 3 shows the TEM images of samples heated at different temperatures for 6h in autoclave.

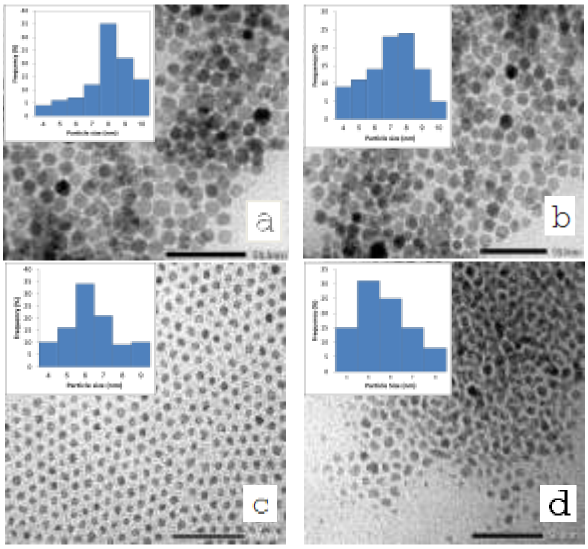

Fig. 3 TEM images of samples heated at:
(a) 180, (b) 160, (c) 140 and (d) 120 °C

The average crystallite size of heated $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite nanoparticles also were analyzed by software TEM image J and shown in table 3.

Table 3: Average crystallite sizes of samples heated and analyzed by software TEM image J

Samples	Average crystallite size (nm)
Heated at 180°C/6h	8 ± 1
Heated at 160°C/6h	7 ± 1
Heated at 140°C/6h	6.5 ± 1
Heated at 120°C/6h	6 ± 2

Comparing the average crystallite size of of heated samples determined by Scherrer formula and analyzed by software TEM image J (tables 2 and 3) shows very good agreement.

It has also demonstrated that increase of heating temperature from 120 up to 180°C leads to increasing the average crystallite size of ferrite from 6 to 8 nm. This may be explained by the growth of crystallite nanoparticles of ferrites with temperature.

3.3 Magnetic properties

Magnetic properties of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite nanoparticles were measured by vibrating sample magnetometer (VSM). Figures 4 shows magnetization curve of nanoferrite samples crystallized at 120, 140, 160 and 180°C.

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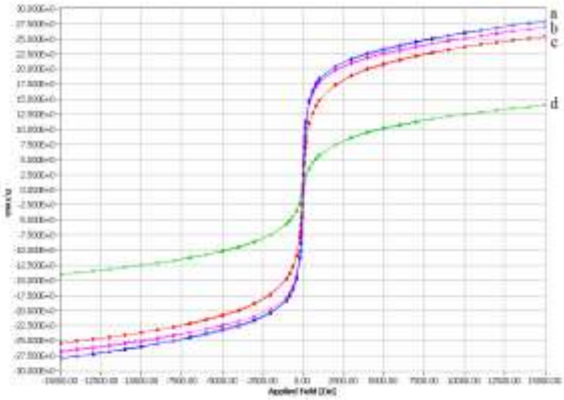

Fig. 4 Magnetization curves of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite crystallized at: (a) 180; (b) 160, (c) 140 and (d) 120^{o}C

Measured magnetic properties of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite nanoparticles are coercive force (H_c), remanence (M_r) and saturation magnetization (M_s) given in table 4. It has shown that all heated samples having zero coercive force H_c and remanence M_r are of superparamagnetic nature.

Superparamagnetic nature of ferrite may be attributed by their small crystalline size [3, 4]. As mentioned above, crystallite size of SPM is around a few to 10 nanometers. With such a small crystallite size, the crystalline nanoparticles have greater thermal energy than magnetic anisotropic energy and the magnetic moment of nanoparticles fluctuates like in paramagnetic materials [3, 4].

Table 4. Magnetic properties of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite samples crystallized at 120, 140, 160 and 180^{o}C

Samples	M_r (emu/g)	M_s (emu/g)	H_c (Oe)
Crystallized at 180^{o}C	≈ 0	27.12	≈ 0
Crystallized at 160^{o}C	≈ 0	26.81	≈ 0
Crystallized at 140^{o}C	≈ 0	25.39	≈ 0
Crystallized at 120^{o}C	≈ 0	14.20	≈ 0

In addition, tables 2, 3 and 4 also show that when the crystallization temperature dropped from 180 down to 120^{o}C, the crystallite size decreased from 8 to 6 nm and corresponding saturation magnetization decreased from 27.12 down to 14.20 emu/g. The more heating temperature is reduced, the smaller is crystallite size of ferrite and the lower saturation magnetization observed. This is explained by the growth of crystalline nanoparticles of ferrite as temperature increased and the proportionality of magnetic energy to crystal volume

4. Conclusions

Successfully are synthesized superparamagnetic nanoparticles of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite by chemical co-precipitation, modifying with oleic acid and hydrothermal heating at low temperatures (120÷180 ^{o}C) for 6h in autoclave. The lowest temperature for complete ferritization is 140°C. The superparamagnetic nanoparticles of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ ferrite have crystallite size of nearly (6÷8) nm, zero coercive force H_c and remanence M_r and saturation magnetization M_s of about (14÷27) emu/g.

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