



Synthesis and Surfactant Effect on Structural Analysis of Nickel Doped Cobalt Ferrite Nanoparticles by C-precipitation Method

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Abstract

Nanoparticles of nickel substituted cobalt ferrite ($\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$; $0 \leq x \leq 1$) have been synthesized by co-precipitation method. Triton x-100 and oleic acid as surfactants were used. Particles size as estimated by the full width half maximum (FWHM) of the strongest X-ray diffraction (XRD) peak were found 17 and 21nm. Their morphology structure have been determined by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis confirms the presence of Co, Ni, Fe and oxygen as well as the desired phases in the prepared nanoparticles. The results of SEM show that the surfactant played an important role in morphology of nanoparticles.

Keywords: Co-precipitation, Surface Active, X-Ray Diffraction, Scanning Electron Microscopy, Cobalt Ferrite, Nanoparticle and Triton x-100.

Introduction

Ferrite nanoparticles exhibit unique chemical, mechanical, structural and magnetic properties and have a variety of promising technological applications in high-density recording devices, color imaging, ferrofluids, high frequency devices and magnetic refrigerators [1,2]. Cobalt ferrite is a well-known hard magnetic material with relatively high coercivity and saturation magnetization while nickel ferrite is a soft material with low coercivity and saturation magnetization. Many of these (hard and soft magnetic) properties make them very promising candidates for a variety

of applications in biomedical, electronic as well recording technologies [3-6]. From the application point of view, the magnetic character of the nanoparticles depends crucially on size, shape, purity and magnetic stability (such as superparamagnetic blocking effects at particular temperature, etc.) of these nanoparticles. These particles should be single domain, of pure phase, suitable coercivity, moderate magnetization and stable blocking effects. From the application point of view, in recording technologies the superparamagnetic blocking temperature of the particles should be well above the room temperature in

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order to have a stable data recorded in these nanoparticles. In biomedical applications, the nanoparticles are used as drug carriers to the areas of the body where conventional drug delivery systems may not work [7]. For this purpose the nanoparticles used should be magnetically in superparamagnetic unblocked state with relatively low blocking temperature and coercivity.

For practical applications (in recording devices), sometimes relatively high blocking temperature of the nanoparticles is required while for other applications (in biomedical), relatively low blocking temperature is required. Therefore, it is very important to tailor various magnetic properties in these materials according to their requirements. This can be done either by varying the sizes of these nanoparticles or by adjusting the concentrations of soft (such as nickel ferrite) and hard (e.g. cobalt ferrite) magnetic phases in these materials. For this purpose nickel substituted cobalt ferrite nanoparticles have been synthesized by wet chemical (co-precipitation) route.

Conventional techniques for preparation of nanoparticles include sol-gel processing, hot spraying, evaporation condensation, matrix isolation, laser-induced vapor phase reactions and aerosols. Generally, in most types of the nanoparticles prepared by these methods, the control of size and size distribution is difficult to achieve. In order to overcome these

difficulties, nanometer size reactors for the formation of homogeneous nanoparticles of cobalt ferrite are used. To protect the oxidation of these nanoparticles from the atmospheric oxygen and also to stop their agglomeration, the particles are usually coated with some surfactant like oleic acid, and then dispersed in some medium like ethanol, methanol or ammonia. In this method the control of size and size distribution is obtained by controlling the relative rates of nucleation and growth during the synthesis process. Smaller particles are obtained by keeping the nucleation rate larger than the growth rate. This is possible only by the quick addition of the precipitation agent (sodium hydroxide) with the salt solution and performing vigorous stirring during the reaction. The main advantage of this method over the others is that the control of production of ferrite particles is relatively easy and there is no need of extra mechanical or microwave heat treatments.

Another importance of this method (co-precipitation) is that we can obtain the particle size of our interest either by adjusting the relative rates of nucleation and growth or by annealing the sample at higher temperatures. In this paper we present synthesis of nickel substituted cobalt ferrite nanoparticles using co-precipitation method. The structural characterization includes study of crystallinity, desired phases and particle size determination while the magnetic characterization includes

variation of coercivity, saturation magnetization and superparamagnetic blocking temperature as a function of Ni-concentration in cobalt ferrite nanoparticles. However, the reaction in co-precipitation method easily forms aggregates, further influences the luminescent properties of nanoparticles. As we know, surfactants have electrostatic repulsion and steric hindrance. They reduce surface tension of solution, so can hinder the growth of grain and prevent the formation of aggregates, thus effectively improve the morphology and optical properties of nanocrystalline. Chen et al. [8] reported that the variety and amount of surfactants play a key role in controlling of morphology.

Yan et al. [9] reported different morphology of nanoparticles such as sheet, nanorods and microspheres can be obtained by hydrothermal process with different surfactants. In addition, the surfactants not only have the role of template to control the surface morphology of nanocrystallines, but also effectively enhance the luminescent efficiency of ${}^5D_0 \rightarrow {}^7F_2$ [10]. So far, the effects of surfactants on morphology and luminescent properties of $Ni_xCo_{1-x}Fe_2O_4$ were not yet reported.

In this work $Ni_xCo_{1-x}Fe_2O_4$ using Triton x-100 and oleic acid at 50°C and pH=11 as surfactants are prepared by co-precipitation method and the effect of surfactants on morphology of nanoparticles is also reported. The morphology properties of there are investigated in detail. The morphological

characterization of $Fe_2Co_2O_4$ spinel prepared by a co-precipitation method was studied without Nickel and Surfactant [11]. Also, it is considered that using Surfactants effect on morphology of nanoparticles [12].

Experimental

Synthesis of $Ni_xCo_{1-x}Fe_2O_4$

$Ni_xCo_{1-x}Fe_2O_4$ ($0 \leq X \leq 1$) was prepared by co-precipitation method. All starting materials were of analytical purity and were obtained from Merck Company Triton x-100 ($C_{14}H_{22}O(C_2H_4O)_n$) is the most material that used as a nonionic Surfactant. First, stoichiometric amounts of $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, oleic acid and Triton x-100 were dissolved in distilled water under magnetic stirring and heating at 50°C with molar ratio ($0 \leq X \leq 1:1-x:2:0.1$) respectively, then the clear solution obtained was dropped into the ammonium hydroxide precipitator with different surfactants Triton x-100 and oleic acid at a speed of 5 ml/min under continuous stirring and white precipitation generated. The white precursor was obtained after aging, filtration, washing, drying. Finally, the precursor was put into a furnace for precalcination at 500°C for 2h, and then calcined at 800°C for 4 h in air, dark brown product were obtained.

Characterization

The morphology of nanoparticles was performed by (SEM Philips XL 30) scanning

electron microscope. The crystal structure was characterized by X-ray diffraction (Model: XPERT-MPD, Philips) with Cu K α radiation over the 2θ rang of $10-70^\circ$ with a step width of $8^\circ/\text{min}$, the accelerating voltage and emission current were 40 kV and 30 mA, respectively. All measurements were performed at room temperature.

Result and discussion

Effect of triton x-100 and oleic acid on morphology of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$

Figure 1 shows the SEM images of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ prepared with different surfactants by co-precipitation method. It can be seen that

the morphology of nanocrystalline changes dramatically depending on the surfactants. The size of nanocrystalline with Triton x-100 is smaller than that of nanocrystalline with other surfactant. Nonionic surfactant Triton x-100 is not ionized in water and has good stability, which leads to a better morphology of nanocrystalline than that of nanocrystalline prepared with other ionic surfactant. As for Triton x-100 series, molecular weight has great influence on the morphology. Therefore, the nanocrystalline prepared with Triton x-100 exhibits smaller, uniform, and spherical particles.

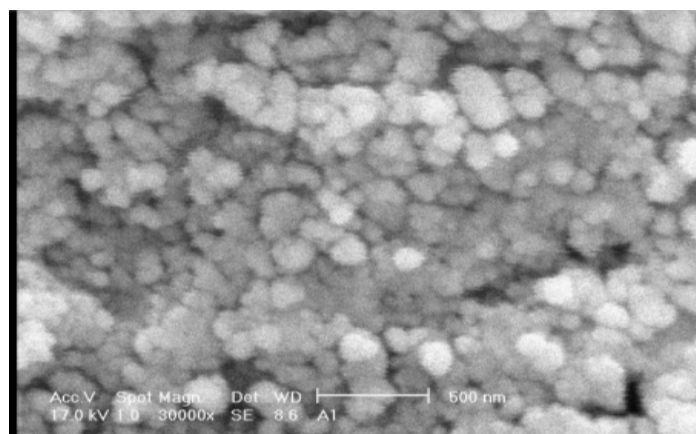


Figure 1. Morphology of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ with Triton x-100.

The SEM images of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ prepared with oleic acid is shown in Figure 2.

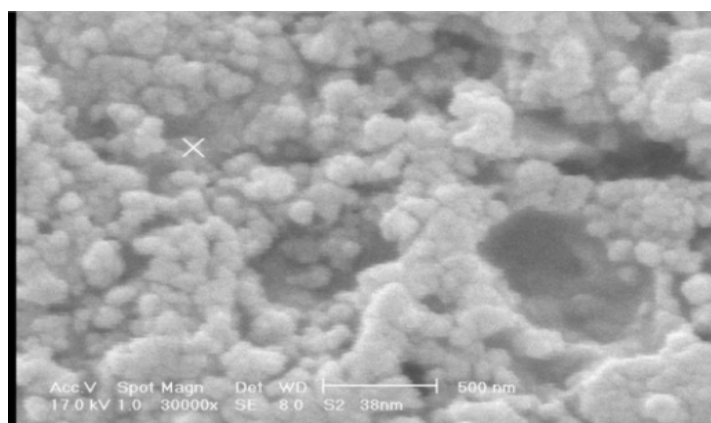


Figure 2. Morphology of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ with oleic acid.

Effect of Triton x-100 and oleic acid on the crystal structure of $Ni_xCo_{1-x}Fe_2O_4$

Figure 3 is the XRD pattern of $Ni_xCo_{1-x}Fe_2O_4$ prepared with different amount of Triton x-100. The pattern showed that all reflection peaks corresponded to the standard file. The approximate Crystallite sizes of the nanoparticles with Triton x-100 can be calculated by the Scherrer's equation [13],

$$D = 0.89\lambda / \beta \cos\Theta$$

Where D is the average crystallite size, λ ($=0.15405$ nm) is the Cu K α wavelength, β is the full width at half maximum (FWHM) and Θ represents Bragg angle. The XRD peaks are used to calculate the mean size of the nanoparticles that are about 17nm. Also, the particle size, obtained by SEM images is bigger than the calculated crystallite sizes by XRD.

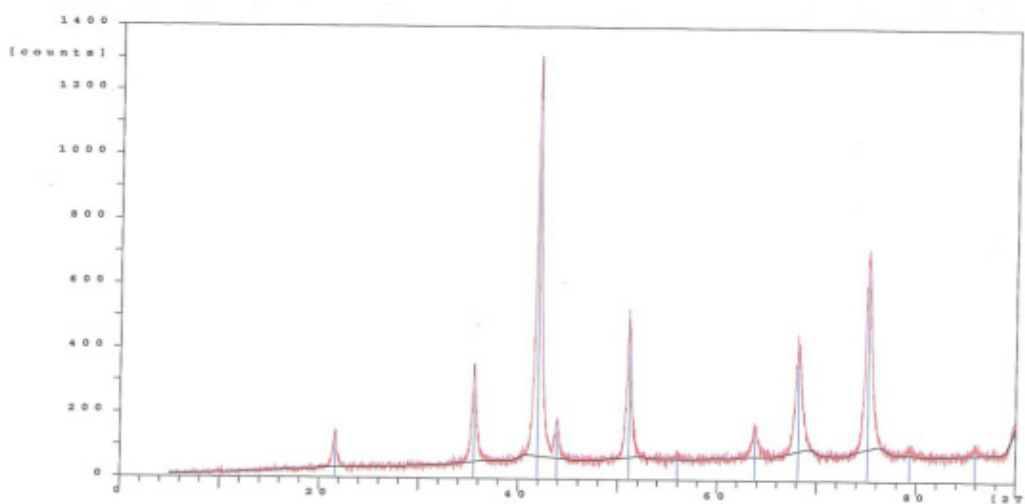


Figure 3. XRD pattern of $Ni_xCo_{1-x}Fe_2O_4$ prepared with Triton x-100.

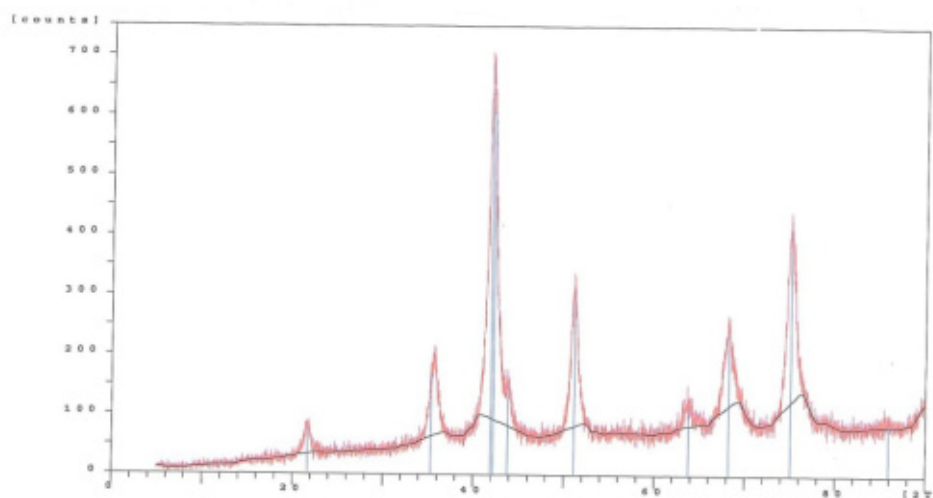


Figure 4. XRD pattern of $Ni_xCo_{1-x}Fe_2O_4$ prepared with oleic acid.

XRD pattern of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ with oleic acid is about 21nm.

acid is shown in Figure 4. The approximate nanocrystalline sizes of the particles with oleic acid can be calculated by Scherrer's equation

is about 21nm.

Therefore, the effect of surface active material on nanoparticles sizes were studied and shown in Table 1.

Table 1. The effect of surface active on particle sizes.

$\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$	Nanoparticle size with Oleic acid (nm)	Nanoparticle size with Triton x-100 (nm)
X=0.2	21	17
X=0.4	27	20
X=0.6	35	27
X=0.8	54	32

Conclusion

$\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($0 \leq X \leq 1$) were prepared by coprecipitation method with Triton x-100 and oleic acid as surfactants. The $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ prepared with Triton x-100 has narrowest particle size than oleic acid. Just different between two Triton x-100 and oleic acid is considered in nanoparticle sizes. When Triton x-100 is used as surfactant, nanocrystalline sizes is smaller than the oleic acid as surfactant. In conclusion, the results of SEM showed that the surfactants played an important role in morphology of nanoparticle.

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