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Structural analysis of nickel doped cobalt ferrite nanoparticles prepared by coprecipitation route

K. Maaz [a,*], S. Karim [a], A. Mashiatullah [a], J. Liu [b], M.D. Hou [b], Y.M. Sun [b], J.L. Duan [b], H.J. Yao [b], D. Mo [b], Y.F. Chen [b,c]

[a] PINSTECH, Post Office Nilore, Islamabad, Pakistan
[b] Institute of Modern Physics, Chinese Academy of Sciences, Lanzhou, PR China
[c] The Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China

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ABSTRACT

Magnetic nanoparticles of nickel substituted cobalt ferrite ($Ni_xCo_{1-x}Fe_2O_4$:$0\leq x\leq 1$) have been synthesized by co-precipitation route. Particles size as estimated by the full width half maximum (FWHM) of the strongest X-ray diffraction (XRD) peak and transmission electron microscopy (TEM) techniques was found in the range 18–28±4 nm. 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 selective area electron diffraction (SAED) analysis confirms the crystalline nature of the prepared nanoparticles. Data collected from the magnetization hysteresis loops of the samples show that the prepared nanoparticles are highly magnetic at room temperature. Both coercivity and saturation magnetization of the samples were found to decrease linearly with increasing Ni-concentration in cobalt ferrite. Superparamagnetic blocking temperature as determined from the zero field cooled (ZFC) magnetization curve shows a decreasing trend with increasing Ni-concentration in cobalt ferrite nanoparticles.

1. Introduction

Ferrite nanoparticles exhibit unique chemical, mechanical, structural and magnetic properties and have a verity 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 (e.g. 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 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 recoding devices), some times relatively high blocking temperature of the nanoparticles is required while for other applications (in biomedical), relatively low blocking temperature is required. So 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 (e.g. 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 (coprecipitation) 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

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[*] Corresponding author. Tel.: +92 321 5029820; fax: +92 51 9290275.
E-mail addresses: maaz@impcas.ac.cn, maaz@phys.qau.edu.pk (K. Maaz).

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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, etc. 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 precipitating 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 (coprecipitation) 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 route. 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.

2. Synthesis and characterization

Salt solutions of 0.4 M iron chloride ($>$99.3%, J.T. Baker) and 0.2 M cobalt and nickel chloride (both 99.99%, Aldrich) were prepared in double distilled de-ionized water and then mixed together. Sodium hydroxide (GR, 28–30%) of 3.0 M was added to the salt solution drop-wise. Few drops of oleic acid (from Albright and Wilson Asia Pvt. Ltd., Singapore) were used as the surfactant. The reaction was performed at 80 °C for 1 h with vigorous stirring. The precipitate prepared was then centrifuged at 2000 rpm to isolate it from the supernatant liquid and dried for 10 h. The dried sample was subsequently annealed at 600 °C for 6 h to get the desired nanoparticles [8]. The size and size distribution was controlled by controlling the nucleation and growth rates during the reaction. Smaller particles were obtained if the nucleation rate was higher than the growth rate. Large pH values (above 12) were used because it controls the process of nucleation (rate) and lowers the particle sizes [9]. Ni-concentration (x) in cobalt ferrite has been controlled by the initial stoichiometric ratios of the reactants. Physical characterization was performed by X-ray diffractometer (Model: X'Pert Philips, Holland), high resolution transmission electron microscopy (HRTEM Model: JEM-3010, JEOL-300 kV) and energy disperse X-ray (EDX) analysis. While magnetic characterization was performed by vibrating sample magnetometer (VSM, Model 7300 Lake Shore, USA) at an applied field up to ±800 kA/m.

3. Results and discussion

The X-ray diffraction patterns of $NiFe_2O_4$, $Ni_{0.5}Co_{0.5}Fe_2O_4$ and $CoFe_2O_4$ annealed at 600 °C for 6 h show the crystallinity of the final product as given in Fig. 1(a–c), respectively. All the peaks in the pattern correspond to the cubic $NiFe_2O_4$ and $CoFe_2O_4$ phases according to the standard JCPD cards (742081 for $NiFe_2O_4$ and 791744 for $CoFe_2O_4$). In Fig. 1(a) the peaks at 32° and 45° correspond to NiO as an impurity in $NiFe_2O_4$ that is an antiferromagnetic in nature. The formation of NiO is possible because of the two reasons, either due to the access oxygen that can cause the formation of intermediate products (NiO) instead of ferrites or due to the broken oxygen bonds at the surface causing incomplete exchange bonds resulting in the formation of nickel oxide. It is to be noted that in case of $Ni_{0.5}Co_{0.5}Fe_2O_4$ and $CoFe_2O_4$ [see Fig. 1(b and c)] the oxides peaks at 32° and 45° are not present. This indicates that these unwanted impurities (oxides) are not present in case of $Ni_{0.5}Co_{0.5}Fe_2O_4$ and $CoFe_2O_4$. From the XRD line broadening of the strongest (3 1 1) peak using Scherrer's formula [10] the crystallite sizes of all the prepared samples were obtained in the range (18–28$\pm$4 nm). This was also confirmed from the TEM results of the respective samples. The size distribution has been calculated from the TEM images only for the particles that are well separated from each other; however for agglomerated particles the size distribution is difficult to estimate. The size distribution in our samples has been found to be around $\sim\pm$4 nm. The size and size distribution of the particles have been controlled by controlling the nucleation and growth rates during the reaction. Smaller particles were obtained if the nucleation rate was higher than the growth rate. However, the size can also be controlled by annealing temperature of the sample [8].

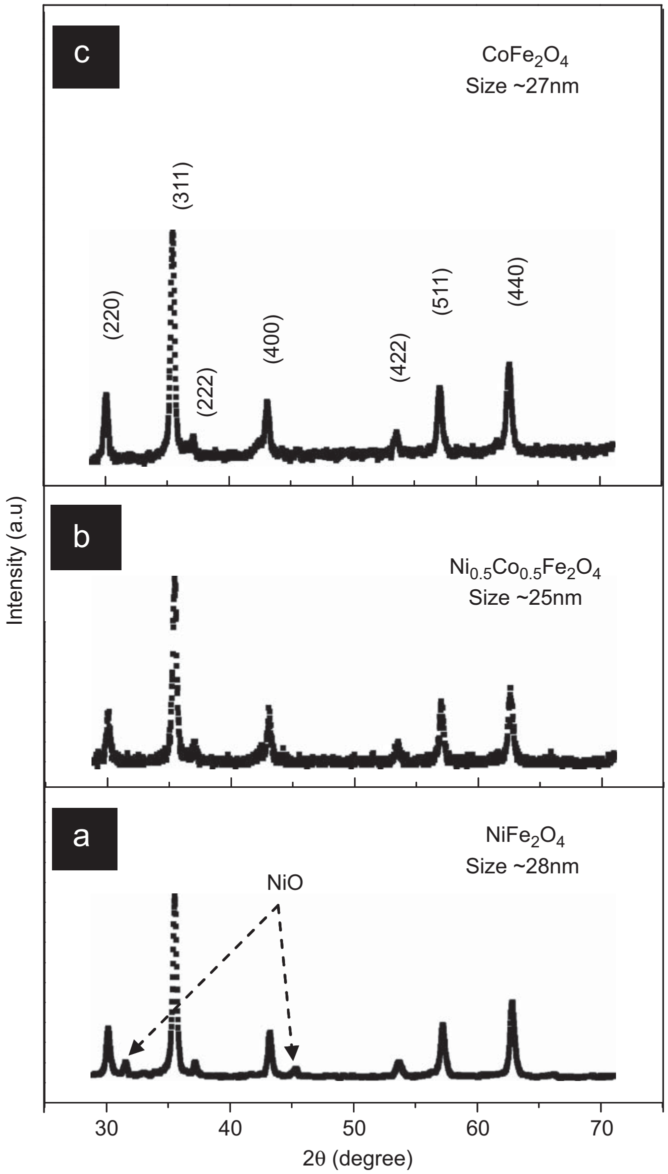

Fig. 1. XRD pattern of (a) $NiFe_2O_4$, (b) $Ni_{0.5}Co_{0.5}Fe_2O_4$ and (c) $CoFe_2O_4$ nanoparticles with crystallite sizes of $\sim$28$\pm$4, $\sim$25$\pm$4 and $\sim$27$\pm$4 nm respectively.