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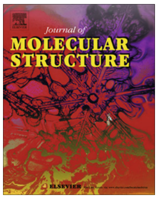

Influence of cobalt on structural and magnetic properties of nickel ferrite nanoparticles

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HIGHLIGHTS

- Nickel ferrite nanoparticles with different composition are synthesized using co-precipitation method.
- The spinel ferrites are improved by the substitutions of Co + 2 ions.
- These nanocrystallites are small enough to achieve suitable signal-to-noise ratio decisive for high density recording media.
- The values of M_s, H_c and M_r are found to be strongly affected by the Co contents.

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ABSTRACT

Improving the magnetic response of nanocrystalline nickel ferrites is the key issue in high density recording media. A series of cobalt substituted nickel ferrite nanoparticles with composition $Ni_{(1-x)}Co_xFe_2O_4$, where $0.0 \leqslant x \leqslant 1.0$, are synthesized using co-precipitation method. The XRD spectra revealed the single phase spinel structure and the average sizes of nanoparticles are estimated to be 16–19 nm. These sizes are small enough to achieve the suitable signal to noise ratio in the high density recording media. The lattice parameter and coercivity shows monotonic increment with the increase of Co contents ascribed to the larger ionic radii of the cobalt ion. The specific saturation magnetization (M_s), remanent magnetization (M_r) and the coercivity (H_c) of the spinel ferrites are further improved by the substitutions of Co^{+2} ions. The values of M_s for $NiFe_2O_4$ and $CoFe_2O_4$ are found to be 43.92 and 78.59 emu/g, respectively and H_c are in the range of 51–778 Oe. The FTIR spectra of the spinel phase calcinated at 600 °C exhibit two prominent fundamental absorption bands in the range of 350–600 cm^{-1} assigned to the intrinsic stretching vibrations of the metal at the tetrahedral and octahedral sites. The role played by the Co ions in improving the structural and magnetic properties are analyzed and understood. Our simple, economic and environmental friendly preparation method may contribute towards the controlled growth of high quality ferrite nanopowders, potential candidates for recording.

1. Introduction

The growth and characterizations of magnetic nanoparticles due to their widespread fundamental and technological importance has received much attention in recent years [1]. Spinel ferrites of $M^{+2}\ Fe_2^{+3}O_4$ (M = Ni, Cu, Zn, Mn) are attractive for numerous applications such as microwave devices [2], recording media [3], magnetic fluids [4], gas sensors [5], high density information storage [6], ferro-fluids [7] and catalysts [8], to cite a few. Several techniques including solid-state reaction [9], high energy ball milling [10], sol–gel [11], hydrothermal synthesis [12], chemical co-precipitation [13], combustion [14], micro-emulsion [15] and microwave hydrothermal [16] are developed to make nickel ferrite nanoparticles.

The unit cell of spinel structured nanoparticles contain 32 oxygen atoms closely packed in the face center cubic lattice in which the metal ions are distributed in two different sub-lattices (interstices) of 8 tetrahedral (A-site) and 16 octahedral (B-site). Co-precipitation method has many advantages over other methods such as the effect of minimal contamination, processing simplicity, low cost, high level of reactivity, easy control of the particle size and the efficiency of more homogeneous mixing of the component materials that lead to the formation of nanocrystallites [17]. The process of conventional solid state reaction involves the mixing of oxides or carbonates with sporadic grinding followed by annealing at high temperatures in the range of 1300–1700 °C [18]. Despite its fabrication simplicity of spinel ferrites it suffers from many drawbacks such as long period of production, high energy consumption, large particle size and the presence of various impurities that lead to inhomogeneous ferrite structures. It is the inhomogeneity that results the formation of voids and thereby weakens the proper transfer of mechanical signal.

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The magnetization in Co doped nickel ferrites strongly depend on the cation distribution of the magnetic Fe^{3+}, Ni^{+2} and Co^{2+} ions among the A and B sites. Bulk cobalt ferrite ($CoFe_2O_4$) is a well-known hard magnetic material that possesses high coercivity (5400 Oe), high chemical stability, good electrical insulation, significant mechanical hardness and moderate saturation magnetization (80.0 emu/g) at room temperature. However, nanosized $CoFe_2O_4$ particles acquire much higher values of coercivity and saturation magnetization [19,20], in which the magnetic properties are particle size and the preparation method dependent. The production of high quality Co substituted Ni ferrites remain challenging. The effect of Co as dopants on the structural properties Ni ferrite nanoparticles and the mechanism behind the enhancement of magnetic response is far from being understood.

Here, we report the effect of cobalt concentration on the structural, magnetic and morphological properties of Co substituted Ni ferrites synthesized using co-precipitation method sintered at 600 °C for 8 h. The mechanism responsible for the improvement of the magnetic and structural properties is analyzed in detail.

2. Experimental

Ferrites having chemical composition $Ni_{(1-x)}Co_{(x)}\,Fe_2O_4$, where $x = 0$, 0.2, 0.4, 0.6, 0.8, 1.0 are prepared by the chemical co-precipitation method using stoichiometric amount of $CO(CH_3COO)_2{\cdot}4H_2O$ (99%, Merck), $Ni(NO_3)_2{\cdot}6H_2O$ (98.5%, Merck), $Fe(NO_3)_3{\cdot}9H_2O$ (98.5%, Merck) and NaOH (99%, Merck) as raw materials. All chemicals of analytical grades are used without further treatment. The solutions of the desired concentrations are prepared in de-ionized water and heated under constant stirring. NaOH solution of 2 M is added drop-wise at 70 °C to form the precipitate. The pH of the aqueous solution is maintained in the range of 12.5–13 during the co-precipitation process. The co-precipitated products are then washed several times with de-ionized water until the pH of the filtered water reached about 7–8. The precipitates are then filtered and dried over-night in the oven at 150 °C to remove the water content. Finally, the pure single phase spinel structures are obtained after annealing the precipitates for 8 h at the rate of heating 5 °C/min.

The structural characterization is performed at room temperature using powder X-ray diffractometer (XRD, D8 Advanced) with Cu-Kα radiations (1.54178 Å) at 40 kV and 10 mA. The scanning range of 2θ from 20° to 80° and a slow speed of scanning ~2°/min with a resolution of 0.011 is employed. The Scherrer equation is used to determine the sizes of ferrite nanoparticles. Fourier transformed infrared (FTIR) spectra are recorded using Perkin Elmer 5DX FTIR after mixing 1 mg of ferrite sample with 100 mg of potassium bromide (KBr). The contents are crushed well in the mortar with a pestle for 5 min until a fine mixture is resulted, which is further used to make pellets in a die of diameter 10 mm. A pressure of about 4–5 ton is applied for 2 min to make the pellets via a hand press machine. The room magnetic properties are measured employing vibrating sample magnetometer (VSM, Lake Shore 7303-9309 VSM). Each sample is calcined for 8 h at 600 °C prior to the measurement.

3. Results and discussion

Fig. 1 shows the XRD spectra of all the synthesized cobalt substituted nickel ferrites with concentrations ranging from 0.0–1.0. The structure and phase purity of the as prepared product were confirmed by analyzing the powder X-ray diffraction patterns. The diffraction patterns of all the compositions confirm the formation of single phased cubic spinel structure of $NiFe_2O_4$ ($x = 0.0$) (JCPDS No. 10.0325) and for pure $CoFe_2O_4$ ($x = 1.0$) (JCPDS No. 22.1086). The lattice constant 'a' is determined from the XRD data by using powder-x-software [21]. All the samples exhibit a poly-oriented structure with several peaks characteristic of the crystalline planes 220, 311, 222, 400, 422, 511, and 440 corresponding to the single cubic phase of $Ni_{(1-x)}Co_{(x)}Fe_2O_4$. The broadening of the X-ray diffraction peaks for as-prepared sample is attributed to the nanocrystalline particle size [21]. The absence of any additional peaks related to impurities indicates the high purity of our nickel–cobalt ferrite samples. The sizes of the nanocrystallies are estimated from the XRD spectra using Debye–Scherrer's equation [22,23].

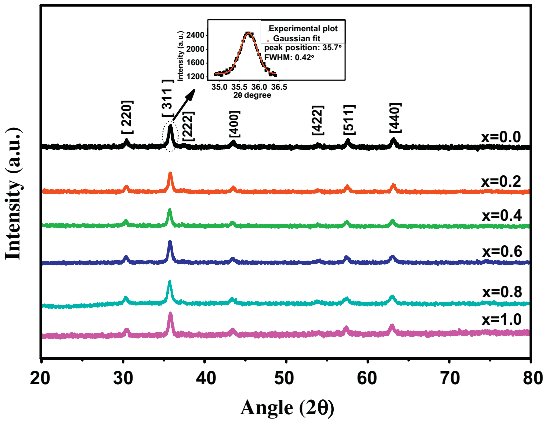

Fig. 1. XRD spectra for $Ni_{(1-x)}Co_{(x)}Fe_2O_4$ with the Gaussian fit of the peak (311) (inset).

$$D = K\lambda/\beta\cos\theta \tag{1}$$

where λ is the wavelength of the X-ray radiation, K is a constant taken as 0.89, β is full width at half maximum (FWHM) of line broadening and θ is the angle of diffraction. The most intense peak (311) are used to estimate the sizes of $Ni_{(1-x)}Co_{(x)}Fe_2O_4$ nanocrystallites and are found the range of 17–19 nm (Table 1). Our nanoparticles are much smaller compared to those reported earlier (25–30 nm and 18–23 nm) [24,25]. These nanocrystallites are small enough to achieve suitable signal-to-noise ratio detrimental for high density recording media.

The lattice constant (a), cell volume (V) and the density are calculated from the XRD spectra using the following relations:

$$a = [d^2(h^2 + k^2 + l^2)]^{1/2} \tag{2}$$

$$V = a^3 \tag{3}$$

$$d_x = \frac{8M}{Na^3} \tag{4}$$

where M is the molecular weight and N is the Avogadro number.

Fig. 2 represents the influence of cationic stoichiometry on the lattice parameters which shows monotonic increment obeying Vegard's law for increasing Co content [26]. This is due the smaller ionic radius of Ni^{+2} (0.69 Å) compared to that of Co^{2+} (0.74 Å). The lattice parameter is calculated as $a = 8.345$, which is found to be in agreement with JCPDS value. The density of X-rays calculated from the XRD pattern is summarized in Table 1. The density of X-ray decreases with the increase of lattice constant as expected.

The room temperature FTIR spectra recorded in the wave-number range of 350–4000 cm^{-1} are shown in Fig. 3. The assignments for the absorption bands are summarized in Table 1. Following Waldron [27], we describe ferrites as continuously bonded crystals in which the atoms are bonded to all nearest neighbors by equivalent strength of ionic, covalent or van der Waals interactions. In ferrites the metal ions occupy two different