Synthesis and Characterization of Cobalt doped Nickel - Ferrites Nanocrystalline by Co-precipitation Method

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Abstract— Improving the magnetic response of nanocrystallite 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 x= (0.0, 0.2 and 1.0), are synthesized using co-precipitation method. These synthesized compounds are characterized by X-ray diffraction (XRD), field emission scan electron microscopy (FESEM), Fourier transformed infrared (FTIR) spectrum, energy dispersive X-ray diffraction (EDX) and TGA-DTA. 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 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.

Index Terms— Nickel ferrite; Nanostructures; XRD; FESEM; EDX..

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1 INTRODUCTION

In recent years, nanomaterials fabrication and their uses are emerging as a critical technology having applications in many industrial sectors [1, 2]. Among these materials, spinel ferrite structure of MFe_2O_4, where M represents the Ni, Mn and Zn has been extensively studied due to electric, magnetic, chemical and mechanical properties. They currently used in wide application areas, such as microwave devices, memory cores, low energy inductors, transformer cores, deflection-yokes, loading coils, choke coils, electro-magnetic interference (EMI), high-density magnetic recording and many other applications [3, 4]. Nano-scale ferrites have led to production of modern magnetic materials because of their extraordinary magnetic property mainly in the radio frequency region. Many novel methods are used to synthesize ferrite nanoparticles, such as microwave-assisted flash combustion technique [5], solid state method [6, 7], sol-gel method [8], ball milling process [9], spray pyrolysis [10] and citrate method [11]. The solid state ceramic method for the preparation of ferrites has certain limitations such as long heating time and high temperature. This method also suffers from other disadvantages like chemical inhomogeneity, coarser particle size of the resulting material, impurity insertion during processing and losing of certain elements that leading to the formation of chemically inhomogeneous materials. The co-precipitation method has received considerable interest because it can offer simplicity, it is economic, and it is suitable for large-scale production with the good control of size and homogeneity [12]. In this paper, ferrite materials have been successfully synthesized by co-precipitation method. These ferrite materials are characterized using X-ray diffraction (XRD), Fourier transform spectrometer (FT-IR), field emission scanning electron microscope (FESEM), energy dispersive X-ray diffraction (EDX), TGA-DTA and vibration samples micrometer (VSM) techniques. 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.

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2 EXPERIMENTAL

Ferrites nanomaterials with composition $Ni_{1-x}Co_xFe_2O_4$ (x= 0.0, 0.2 and 1.0) are synthesized by chemical co-precipitation method. The chemicals used for synthesis ferrite samples are stoichiometric molar amounts of nickel(II) nitrate [$Ni(NO_3)_2.6H_2O$)] (98%, Aldrich), cobalt(II) acetate ([$Co(CH_3COO)_2.4H_2O$] (98% Merck) and ferric nitrate [$Fe(NO_3)_3.9H_2O$)] (98.5% Merck). Ferric nitrate, nickel nitrate and cobalt acetates are dissolving in de-ionized water with constant magnetic stirring. The (1.5M) of NaOH solution is used as a precipitation agent. When the solution temperature reached 90 °C, NaOH solution is added wisely drop by drop of the complex solution to kept the pH of the solution around 13. Then the precipitates are washed several times with de-ionized water until the pH solution become natural (pH = 7~8). The precipitates of product are dried at 200 °C in oven overnight in order to remove the water contents than grinded to find powder and calcined at 600 °C temperature in electric furnace for 8 h with heating rate of 5 °C per/min to obtain the spinel ferrite phase.

3 Results and Discussions

The crystal structure and phase purity of the samples are characterized by XRD. The XRD spectra for the samples are shown in Fig. 1. The X-ray diffraction patterns of the different chemical compositions $Ni_{1-x}Co_xFe_2O_4$ (x = 0.0, 0.2 and 1.0) product at 600 °C for 8 h show a pure-phase with a cubic spinel structure $NiFe_2O_4$ (JCPDS card no 10-0325), CoFe2O4(JCPDS card no 22-1080) and Co doped nickel ferrite (JCPDS card no 40-1191). All the samples exhibit a poly-oriented structure with several peaks characteristic of other crystallite planes (220, 311, 222, 400, 422, 511 and 440), which explain the single phase cubic spinel structure of $Ni_{1-x}Co_x Fe_2O_4$. The sizes of the nanocrystallites are estimated from the XRD spectra using Debye–Scherrer's equation.

$$D= K\lambda/\beta Cos\theta \qquad (1)$$

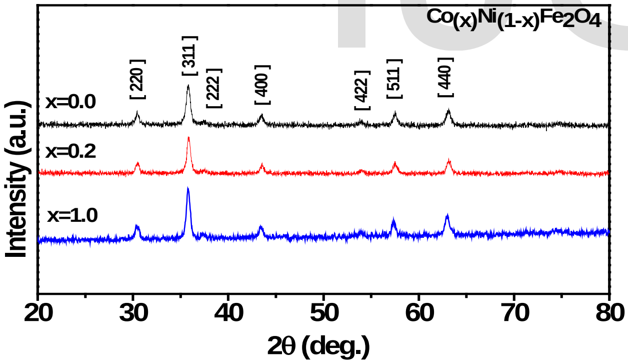

Fig. 1 XRD pattern of $Ni_{1-x}Co_xFe_2O_4$ nanoparticles after calcination at 600 °C.

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 $Ni_{1-x}Co_xFe_2O_4$ nanocrystallites and are found the range of 16–19 nm (Table 1). The lattice parameters have been computed using the d-spacing values and respective (h k l) parameters from the classical formula given in equation (2), which is illustrated in (Table 1)

$$a = d\,(h^2+k^2+l^2)^{1/2} \qquad (2)$$

TABLE 1
THE HIGH FREQUENCY WAVE, AVERAGE PARTICLE SIZE, CALCULATED PARTICLE SIZE BY XRD, LATTICE CONSTANT AND LENGTH JUMP OF THE SAMPLES.

Composition	ν_1(cm^{-1})	D_{XRD} (nm)	Lattice const.'a' (Å)	Length Jump L (Å)
$NiFe_2O_4$	595	16	8.330	2.9450
$Ni_{0.8}Co_{0.2}Fe_2O_4$	597	19	8.335	2.9468
$CoFe_2O_4$	592	17	8.361	2.9560

The lattice constant has been affected by the cationic stoichiometry. The lattice parameters are found to increase almost linear by increase of Co content. The slow linear increase in lattice constant can be explained by the basic of the ionic radii. The ionic radius of Ni^{2+} (0.69 Å) replacement by slight larger Co^{2+} ions with an ionic radius of (0.74 Å) in the system $Ni_{1-x}Co_xFe_2O_4$. The values of lattice parameter exhibit an almost linear dependence, thus obeying Vegard's law [13]. Lattice constant and crystallites size of these nanoparticles are summarized in Table 1.

The room temperature FTIR spectra of $Ni_{1-x}Co_xFe_2O_4$ recorded in the wave-number range of 350–4000 cm^{-1} are shown in Fig. 2. The assignments for the absorption bands are summarized in Table 1. Following Waldron [17], the ferrites are described 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 sub-lattices designated as tetrahedral (A-site) and octahedral (B-site) positions with respect to the geometrical configuration of the oxygen nearest neighbors. The one with the higher wave number, v1 observed in the range of 580–600 cm^{-1} corresponds to the intrinsic stretching vibrations of the metal at the tetrahedral site (Mtetra ↔ O).

While the lower wave number one,v_2 which is usually observed around 375–450 cm^{-1} is attributed to the octahedral-metal stretching (Mocta↔O) [18, 19]. The appearance of much weaker absorption bands around 1100–1300 cm^{-1}, 1400–1700 cm^{-1}, 2850–3000 cm^{-1} and 3400 cm^{-1} are assigned to the vibrations of NO_3^- ions, carboxyl group COO $^-$, the stretching of the C–H bands and hydrogen bonded O–H groups, respectively [20, 21]. The noticeable change in the band positions are resulted from the difference in the distance of Fe^{3+} –O^{2-} ions associated with the octahedral and tetrahedral complexes. Interestingly, the characteristic band v_1 shows a shift towards lower and higher frequency region with increasing Co substitution contents (Table 1).

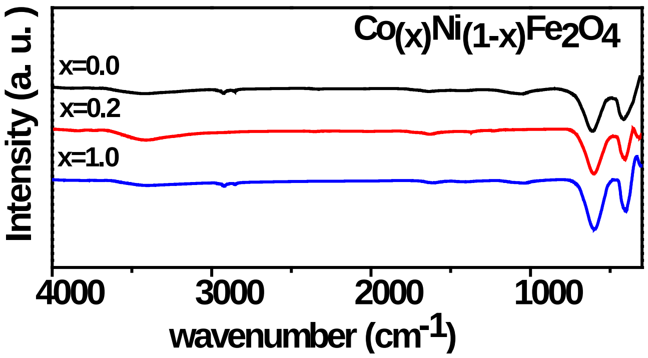

Fig. 2. FT-IR spectra of $Ni_{1-x}Co_xFe_2O_4$ nanoparticles after calcination at 600 °C.

Fig. 3. illustrates The FESEM micrographs of nearly spherical shaped Co ferrites nanoparticles with grain size below 20 nm. In addition to this, although these smaller crystallites are distributed regularly over the entire region displaying fine grain growth, a clear boundary between neighboring crystallites can yet be observed with occasional agglomeration due to the interactions of magnetic nanoparticles.

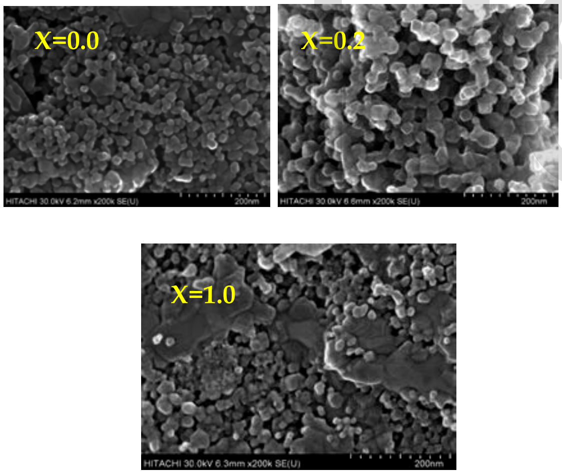

Fig. 3. FESEM micrograph of $Ni_{1-x}Co_xFe_2O_4$ nanoparticles after calcination at 600 °C.

Fig. 4 shows the energy dispersive X-ray (EDX) spectra of the $Ni_{0.8}Co_{0.2}Fe_2O_4$ sample confirm the presence of iron in addition to the cobalt, the nickel, carbon and the oxygen. The occurrences of peaks confirm the existence of nanoparticles composed purely of ferrite samples as observed in the FESEM images Fig. 3.

Fig. 5. shows TGA-DTA curves of the powder precursor recorded under N2 atmosphere with a heating rate 10 °C min^{-1}. The curve shows that the multistep continuous weight loss occurs from room temperature to 400 °C. These weight loss appeared as exothermic peaks at 53°C and 257 °C, the exothermic peak at 53°C is attributed to the desorption of water physically absorbed on the surface of the powder and another exothermic peak is due to thermal decomposition of precursor. The endothermic process happens nearly 400 °C, which corresponds to the formation and transition of crystalline spinel phase. The exothermic and endothermic regions in the DTA pattern are consistent with the change regions in the TG pattern. The TG curve shows no further weight loss above 600 °C, confirming the formation of the stable cobalt-nickel ferrite

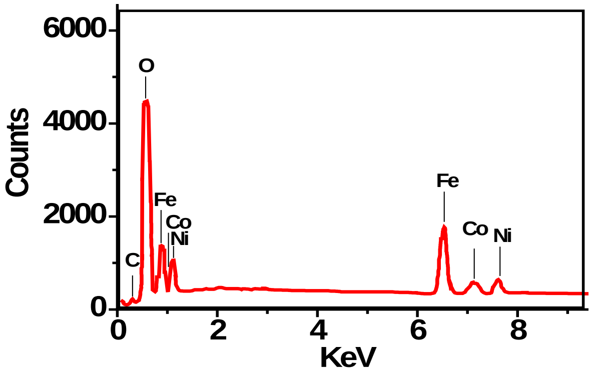

Fig. 4. EDX spectra of $Ni_{0.8}Co_{0.2}Fe_2O_4$ nanoparticles after calcination at 600 °C.

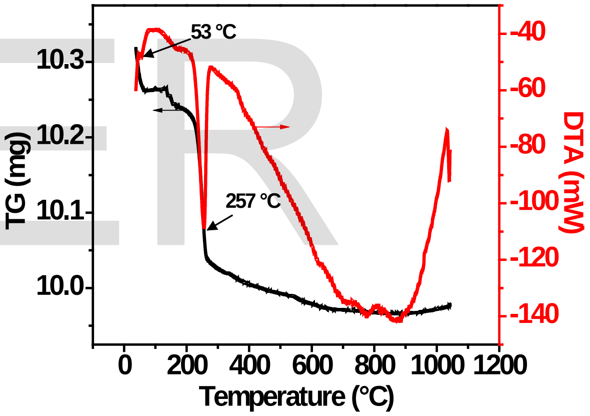

Fig. 5. DTA/TG curves for as-received $Ni_{0.8}Co_{0.2}Fe_2O_4$ powder.

4 CONCLUSION

The chemical co-precipitation method have been employed to fabricate the cobalt substituted nickel spinel ferrite nanoparticles at 600 °C for 8 h. XRD pattern of the ferrite samples reveal the formation of the cubic spinel phase. The average crystalline size for ferrite nanoparticles material has single cubic spinel structure with the range between 16 and 19 nm as determined by the X-ray diffraction. FESEM images confirm the nanocrystalline nature of the synthesized products. FT-IR measurement for the ferrite powders shows two characteristic bands in the range 500-600 cm-1 and 385-450 cm-1, which could be attributed to the tetrahedral and octahedral complexes respectively. The co-precipitation is found to be simple and economic method to produce high-quality ferrite nanosized powder with narrow size distribution.

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