



Effect of Mn and Ni codoping on ion dynamics of nanocrystalline cobalt ferrite: A structure property correlation study



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ABSTRACT

Effect of Mn and Ni codoping on structure, optical and electrical properties of cobalt ferrite nanoparticles prepared by coprecipitation route have been investigated in detail. DSC-TGA, XRD and HRTEM studies have been explored to confirm the phase purity and structure. Most possible cation distribution as estimated by Rietveld analysis suggests the formation of mixed spinel ferrite phase by the migration of Co^{2+} ions from B site to A site and hence Fe^{3+} ions from A site to B site in different amounts due to the doping of Mn and Ni ions. UV–vis study reveals a red shift for Mn and Mn–Ni co-doped samples while a blue shift was observed in case of Ni doping. Conductivity spectra follows the double power law and the modulus spectroscopy study indicates the coexistence of two incomplete relaxation processes in the system that arises due to the co-contribution from both grain and grain boundary which were thoroughly confirmed by complex impedance analysis. Improvement in the dielectric properties in the materials due to doping could be beneficial for device applications.

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1. Introduction

Magnetic nanoparticles, particularly spinel ferrite nanoparticles have been studied extensively due to their remarkable properties such as high saturation magnetization, large permeability at high frequency, and high electrical resistivity. Due to low eddy current losses, there exist no other materials with such wide-ranging properties suitable for electronic applications in terms of power generation, conditioning, and conversion [1–3]. Cobalt ferrite (CFO) possesses excellent chemical stability, good mechanical hardness, and a large positive first-order crystalline anisotropy constant, making it a promising candidate for magneto-optical recording media. In addition to precise control of the composition and structure of CoFe_2O_4 , its practical application will require the capability to control particle size at nanoscale [4–6]. Doping of different ions in place of Fe in the system can also sometimes tailor the physical and chemical properties that could be due to the changes occurred in the microstructural configuration [7–9].

While doped with other transition metal ions i.e. Mn, Ni, Zn etc cobalt ferrite nanoparticles some structural changes than its bulk counterpart which ultimately leads to interesting changes in some

properties like saturation magnetization, remnant magnetization, electrical conductivity etc. [10,11]. These changes depend on the valence state of cations and their distribution between the two interstitial sites of spinel ferrites. CFO in bulk form normally exhibit inverse spinel structure with one half of Fe^{3+} ions in the A sites and the remaining half of Fe^{3+} ions along with Co^{2+} ions in the B sites and AB pair (Fe–Fe) has a strong superexchange (antiferromagnetic) interaction [7,9]. It was reported that the cationic distribution for cobalt ferrite nanoparticles is different from bulk cobalt ferrite [12]. Nano-dimensional cobalt ferrite mostly remains in mixed spinel state depending on the preparatory conditions [13]. The general formula can be represented as $(\text{Me}_\delta\text{Fe}_{1-\delta})_T(\text{Me}_{1-\delta}\text{Fe}_{1+\delta})_O$ where Me stands for any divalent metal and δ is the degree of inversion (defined as the fraction of tetrahedral sites occupied by Fe^{3+} ions) for the mixed spinel state. Since ions in two sites are antiferromagnetically ordered, the resultant magnetism observed in ferrites is due to the unbalanced magnetization of sub lattices A and B [14]. Since the cationic distribution among the lattice sites is strongly dependent on the materials preparation [14], it is important to determine the cation sites occupancies as well as the structural parameters in order to tailor the materials performance.

Different authors have reported the behaviors of Mn and Ni doped cobalt ferrite nanoparticles separately prepared under different conditions which showed some changes in properties [15,16]. However it is meaningful to investigate the effects of their

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codoping for suitable tuning of the properties in more precise way. In this work we report the effect of codoping on structural, optical and electrical properties of cobalt ferrite nanoparticles having compositions $\text{CoXFe}_{1.9}\text{O}_4$ ($X = \text{Fe}_{0.1}, \text{Mn}_{0.1}, \text{Ni}_{0.1}$ and $\text{Mn}_{0.05}\text{Ni}_{0.05}$) which are abbreviated hereafter as CFO, CFMO, CFNO and CFMNO, respectively.

2. Experimental

2.1. Sample preparation

The pure, Mn and Ni doped cobalt ferrite nanoparticles were prepared by mixing reagent grade chemicals procured from MERCK. Proportionate amounts of ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$), nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and NaOH (98 %) were used. The nitrates were dissolved in de-ionized water to get a solution. Nitrate solutions were mixed together and stirred for one hour. NaOH solution was added for precipitation. The precipitate was washed several times with distilled water followed by acetone and dried at room temperature. Dried powders were annealed at 773 K for 30 min to precipitate the nanoparticles. A code name has been used hereafter as listed in Table 1.

2.2. Sample characterization

DSC-TGA measurements were carried out in SDT Q600 V20.5 Build 15 model. X-ray diffractograms of the samples were recorded by X Pert Pro X-ray diffractometer (PANLYTICAL, Almelo, The Netherlands) using nickel-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5414 \text{ \AA}$) in 2θ range from 20 to 90°. The Transmission electron microscopy (TEM) analyses for all the samples were carried out using a JEOL-200FX microscope operated at 200 kV. For TEM study the samples were ground in an agate mortar, dispersed in ethanol by sonication and cast one drop on a carbon coated copper grid. The optical absorption spectra of the samples were recorded at room temperature in the range 200–800 nm using a double beam Hitachi spectrophotometer (model U3410). Electrical measurements were carried out in the frequency range 20 Hz to 2 MHz at different temperatures between from 323 K to 478 K using Agilent high precision LCR meter (Model E4980A). For electrical study prepared powders were pressed into pellet form which was painted on either side with silver paste to ensure good electric contacts. A.C. electrical conductivity as well as the dielectric parameters such as dielectric constant, electrical modulus and loss tangent were measured and analyzed.

3. Results and discussions

3.1. DSC-TGA analysis

DSC and TGA curves of synthesized CFO samples are shown in Fig. 1. The TGA curve exhibits weight loss in two distinct steps and the DSC curve presents one exothermic peak over the temperature range of 25–700 °C. The first weight loss in the range of 25–175 °C, which is accompanied by an endothermic broad peak started around 150 °C in the DSC curve, arises due to the loss of residual

Table 1
Samples abbreviation.

Sample abbreviation	Sample formulation
CFO	CoFe_2O_4
CFMO	$\text{CoFe}_{1.9}\text{Mn}_{0.1}\text{O}_4$
CFNO	$\text{CoFe}_{1.9}\text{Ni}_{0.1}\text{O}_4$
CFMNO	$\text{CoFe}_{1.9}\text{Mn}_{0.05}\text{Ni}_{0.05}\text{O}_4$

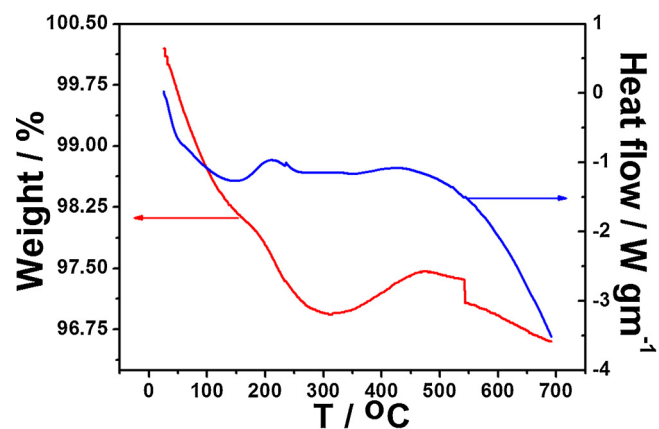


Fig. 1. DSC-TGA curve of CFO sample.

moisture in the powder. The second weight loss around 200 °C is associated with the combustion of nitrates and the oxidation of carbon from the sample to form carbon dioxide. No weight loss was observed above 300 °C, implying the presence of stable phase of cobalt ferrite nanoparticles in this temperature range [17].

3.2. TEM analysis

To reveal the microstructure and phase information of all the prepared samples, TEM/HRTEM study was carried out. The typical TEM images of CFMO sample are shown in Fig. 2. The image reveals that the sample in the form of nanoparticles, and nearly spherical in shape. The particle sizes have been estimated independently by fitting the experimental data measured from TEM micrograph (Fig. 2(a)), with a lognormal size distribution following a standard procedure. The average size of the sample as estimated from the TEM image were found to be around 11.02 nm (Table 2a). The corresponding particle size distribution histogram is shown in Fig. 2(b) which follows the log-normal distribution function described by [18]:

$$P(y) = \frac{1}{ys(2\pi)^{1/2}} \exp\left[-\frac{\ln(y/y_0)^2}{2s^2}\right] \quad (1)$$

where y is the diameter of the particles, y_0 is the most probable diameter and s is a parameter determining the width of the distribution.

We have extracted information concerning the crystalline phases from the selected area diffraction (SAED) pattern and lattice fringes acquired using HRTEM for the samples. The SAED pattern from a finely dispersed region of CFNO sample is presented in Fig. 2(c). It clearly shows that the rings are made up of discrete spots indicating the highly crystalline nature of the nanoparticles. We have measured the diameters for each circle to estimate the lattice spacing and compared them with JCPDS (card no # 221086) data for CoFe_2O_4 . The good agreement between these two data sets indicates the precipitation of cobalt ferrite phase. Also a cross checking of phase formation has been performed from the lattice fringes of high-resolution image (HRTEM) presented in Fig. 2(d). The distances between two adjacent planes estimated from the lattice fringes correspond to the plane (311) of cobalt ferrite.

3.3. X-Ray analysis and Rietveld refinement

The X-Ray diffraction patterns with Rietveld refinement fitting of all the samples are shown in Fig. 3. It is observed that all the peaks are matched well with the standard data (JCPDS card no # 221086) which indicates the growth of pure single phase cobalt

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