Enhanced electrical properties in Nd doped cobalt ferrite nano-particles

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Abstract. Spinel ferrites are important class of compounds which has variety of electrical, magnetic and catalytic applications. A small amount of rare earth element causes modification in structural, electrical and magnetic properties of ferrite materials for practical applications. Neodymium doped cobalt ferrites with composition CoNd₆Fe₂₄O₃₄ where x is 0.1 has been synthesized by sol-gel method. Sol-gel method was preferred because it has good control over stoichiometry, crystallite size and particle size distribution. Characterization was done by using X-Ray Diffraction (XRD) technique for structural analysis and crystal structure was found to be spinel. Particles like morphology was observed in micrographs obtained by Scanning Electron Microscopy (SEM). Thermal analysis of sample has been done which includes Thermogravimetric analysis (TGA) and Differential Scanning calorimetry (DSC). Fourier transform infra-red spectroscopy (FT-IR) of samples was also performed. DC resistivity as a function of temperature has been studied and its shows direct dependence on temperature and inverse dependence on the concentration of Nd dopant. The studied material is a potential candidate for resistive random access memory application.

1. Introduction
Ferrites are material of interest due to unique combination of their electrical and magnetic properties. Nano particles of spinel ferrites are widely used in different application that include microwave devices, biomedical applications and magnetic storage information [1]. Spinel ferrites can be represented by a general formula AB₂O₄ A and B are metal cations that are distributed upon tetrahedral (A) and octahedral (B) interstitials sites that is formed by face centered cubic arrangement of oxygen anions. In the cubic unit cell, to maintain charge neutrality, only 8 out of 64 available tetrahedral A sites and 16 out of 32 available octahedral B sites are occupied. In terms of the cation distribution among these tetrahedral A sites and octahedral B sites, the spinel structure can be normal, inverse, or partially inverse Cobalt ferrites has a special place among all other spinel ferrites due to having unique properties. CoFe₂O₄ has high cubic magneto crystalline anisotropy, high coercivity, and moderate saturation magnetization and high chemical stability [2]. In many applications DC resistivity of cobalt ferrites plays important role and desired resistivity can be controlled by addition of a dopant element. Effect of neodymium (rare earth) dopant on electrical resistivity was thoroughly studied in present research work. The results were compared with results of already reported pure cobalt ferrites.
2. Experiment

2.1. Synthesis

CoNdₓFe₂₋ₓO₄ with x=0.1 was synthesized by simplified sol-gel method. The stoichiometric amount of Cobalt Nitrate Hexa Hydrate (Co(NO₃)₂·6H₂O), Iron Nitrate Nona Hydrate (Fe(NO₃)₃·9H₂O), and Nd₂O₃ were taken. Reagents were of analytical grade and were used without further purification. All precursors were individually mixed into a beaker containing ethylene glycol. The ratio of precursors to ethylene glycol was 1:14 in order for homogeneous mixing of precursors. This solution was heated at 80°C until a wet gel was formed. The gel was then dried at near 250°C which results into burning of the gel. This formed product was then further grinded and a fine powder was obtained. This powder was weighed on a weighing balance. The formed powder sample was then pelletized into a disk shaped pellet using a hydraulic pressure and maintaining a pressure of 1000 psi. The pellet has 13mm diameter with thickness of 2mm and then it was sintered at 550±5 °C for 2 hours. This pellet was then used for DC electrical analysis.

2.2. Characterizations

Nd doped cobalt ferrites sample was characterized by X-ray diffraction (XRD) technique using Cu Kα (λ= 1.5406 Å) radiations in 2θ range 20-80° for structural analysis. Crystallite size D(311) was measured by using Scherrer’s formula [3]. Lattice constant a was measured by equation (1)

\[ a = d_{hkl} \sqrt{h^2 + k^2 + l^2} \]  

Where hkl are miller indices and d_{hkl} is interplanar distance. The Fourier transform infrared (FTIR) absorption spectra was recorded in wave number range of 400-800 cm⁻¹. Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) were used for thermal analysis. DC electrical resistivity as a function of temperature was found by using two-probe method. The sample was heated inside a sample. Temperature range was kept from 40-450°C.

3. Results and discussions

3.1. X-ray diffraction (XRD) analysis

X-ray diffraction of the sintered sample shown in Figure 1 confirmed the formation of face centered cubic (FCC) spinel crystalline structure. X-0.1 showed an increased in lattice constant as compared to pure cobalt ferrites [4]. This was due to larger ionic radii of Nd³⁺ ions (0.983 Å) as compared to Fe³⁺ ions (0.645 Å). Crystallite size was found to be 29 nm. The lattice constant (a), crystallite size (D(311)), measured density ρ_m, X-ray density ρ_x and porosity P of x-0.00 and x-0.10 are tabulated in Table 1.

![Figure 1. XRD pattern of the sample CoNdₓFe₂₋ₓO₄ (x-0.10)](image-url)
Table 1. A comparison of crystallite size $D_{(311)}$, Lattice constant ($a$), measured density ($\rho_m$), x-ray density ($\rho_x$), porosity (P) and DC resistivity ($\rho$) for the sample CoNd$_x$Fe$_{2-x}$O$_4$ (x=0.00 and x=0.10)

| Parameters | X=0.00 | X=0.10 |
|------------|--------|--------|
| $D_{(311)}$ (nm) | 12 | 29 |
| $a$ (Å) | 8.36(1) | 8.39(2) |
| $\rho_m$ g/cm$^3$ | 3.278 | 2.091 |
| $\rho_x$ g/cm$^3$ | 5.351 | 5.490 |
| P (%) | 38.7 | 61.7 |
| $\rho$ (Ω.cm) at 300 °C | $2.88 \times 10^4$ | $4.30 \times 10^5$ |

3.2. FTIR spectra analysis

FTIR spectra of x-0.10 is shown in Figure 2. Two prominent bands were observed in the FTIR spectra. The infrared bands in solids are usually due to vibrations of ions in the crystal lattice. The absorption band ($\nu_1$) in the range of 400-450 cm$^{-1}$. This corresponds to octahedral-metal stretching. The second absorption band ($\nu_2$) was observed in the 550-600 cm$^{-1}$ range. This corresponds to tetrahedral-metal stretching [5]. The formation of spinel structure was confirmed by the presence of characteristics absorption bands in the FTIR spectrum.

3.3. Thermogravimetric analysis (TGA)/ Differential scanning calorimetry (DSC)

TGA/DSC curve for x-0.10 is shown in Figure 3. The first weight loss was observed at 100°C which corresponds to the removal of moisture. The second weight loss was observed at ~550°C which is due to the removal of by-products that were nitrates in present case and the final weight loss was due to removal of trapped gases within the sample at ~800°C. The crystallization peak was observed at 500°C, after that no further transition was observed for this sample.
3.4. DC electrical properties
The measured DC electrical resistivity of Nd doped cobalt ferrites shown in Figure 4 with \( x=0.10 \) was found to be \( 5.45 \times 10^9 \, \Omega \cdot \text{cm} \) at \( 40^\circ \text{C} \). It was observed that electrical resistivity got increased markedly with addition of Nd as compared to \( x=0.00 \)[6]. Since the conduction in ferrites is considered as the electron hopping between \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) at B (octahedral) sites. So the lower \( \text{Fe}^{2+} \) ions content decreases the conduction and an increase in resistivity. There are many other factors which also influence DC electrical resistivity. There are the microstructural factors that includes grain size, porosity and grain boundaries. Activation energy was also found from linear plots of DC resistivity. Table I give a comparison of DC electrical resistivity and activation energy of pure and doped sample. It was also observed that Nd doped cobalt ferrites has increased activation energy as compared to pure cobalt ferrites. The sample showed activation energy greater than 0.4 eV which attribute to polaron hopping mechanism in cobalt ferrites [4].

![Figure 3. TGA/DSC curves for the sample CoNd\(_x\)Fe\(_{2-x}\)O\(_4\) (x=0.10).](image1)

![Figure 4. Variation in DC resistivity with temperature for the sample CoNd\(_x\)Fe\(_{2-x}\)O\(_4\) (x=0.10)](image2)

4. Conclusions
Neodymium doped cobalt ferrites having composition \( \text{CoFe}\(_{2-x}\)Nd\(_x\)O\(_4\) \) where \( x=0.10 \) was successfully synthesized by simplified sol-gel method. XRD confirmed the phase purity with lattice constant of 8.39(2) Å with spinel cubic structure (Fd-3m space group). Neodymium doping has resulted in an increase in lattice constant. Crystallite size was measured by using Scherrer formula. It has value of 29 nm confirming the formation of nanocrystallites. Fourier transform infra-red (FTIR) spectroscopy also
confirmed the spinel structure of ferrites. SEM revealed particle like morphology. Thermogravimetric analyses confirmed the thermal stability of the sample in the studied temperature range. DC electrical resistivity (ρ) as a function of temperature showed semiconductor like behavior. Replacement of Fe ions by Nd has caused the higher resistivity than that of undoped sample. Thus electrical properties of cobalt ferrites could be tailored by choice of neodymium ion concentration and hence make it suitable for many technological applications.

5. References

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