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Study of structural and optical properties of Nd doped cobalt ferrite

Physics

KEYWORDS:Mixed nano-ferrites, Co-precipitation, Doping, Rare-earth metal ions

Sunil Rohilla	Department of Applied Physics, TIT&S Engg. College, Birla Coloney Bhiwani-127021,India
Pinki Rani	Department of Physics, Bansathali University, Bansthali- , Rajasthan, India
Navneet Kumari	Department of Physics, Mewar University Gangrar, Chittorgarh- 312901 (Rajasthan), India

ABSTRACT

- Neodymium (Nd) doped cobalt ferrite ($CoFe_2O_4$) were successfully prepared by coprecipitation technique using metallic chlorides and metal cyanides as precursors. Subsequently mixed ferrites were annealed at 300^{0}C for 2h. The samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Ultraviolet visible spectroscopy (UV-Vis). The structural and optical properties of mixed nano ferrites were investigated. Crystallite size was estimated using XRD data and it was found in range of 25-32 nm. Structural studies suggest that mixed ferrite could be used as high density magnetic recording, permanent magnets, magnetic fluids, catalysis, photo-magnetic materials.

INTRODUCTION

Recently research in nanoscience has focused attention of researchers in the direction of rare earth doped nanocrystals due to their use in electromagnetic application. Nano-crystalline ferrites containing rare earth metals have interesting technological and physical applications [1]. Normally properties of ferrites depend on method of preparation [2]. But intrinsic properties of fer-rites like resistivity, dielectric losses, conductivity and magnetic properties are controlled by chemical composition and type of doped metal cations [3,4]. Several cations, such as Ti^{3+}, Cr^{3+}, Pb^{3+}, La^{3+}, Gd^{3+}, Er^{3+}, and Ce^{3+} have been investigated and discussed [5–11]. These substitutions greatly affect the magnetic, electrical, and structural properties of the ferrites. Doping of rare earth metal ions into cobalt ferrite leads to structural distortion that induces strains in the material which indicate improved crystallinity of the sample and to affect the electrical and magnetic properties significantly. The rare earth doped cobalt ferrites found an application in high frequency devices and power supply due to high resistivity and low dielectric losses [12], [13]. Cobalt ferrite has become an ingredient in the formation of metallic/magnetic nanocomposites due to the observations of a wide range of magnetic, electric and other novel properties in its derivatives [14-15]. Many researcher and research group have been reported on ferrites to modify the magnetic properties via doping rare earth metals ions [16]. In present study on synthesis and characterization of Nd doped cobalt ferrites has been made to enhance its structural, electronic, dielectric, optical and magnetic properties that might play important role in high efficiency device applications.

Experimental Details

Nd dopped cobalt ferrite was prepared using high purity reagents: Potassium ferry cyanide ($K_3[Fe(CN)_6]$; Aldrich 99.99%), cobalt chloride ($CoCl_2$; Aldrich 99.99%), Neodymium(III) nitrate hexahydrate ($Nd(NO_3)_3 \cdot 6H_2O$; Aldrich 99.99%), and deionized water. Firstly $Fe_4[Co(CN)_6]_3.16H_2O$ nanosuspension is prepared by the method given in literature [17]. In this suspension .0125M of $Nd(NO_3)_3 \cdot 6H_2O$ is added drop wise with vigorous stirring for 3h at a speed of 6000 rpm. The temperature of the system was kept constant at 57^{0}C in a water jacketed reaction vessel using circulating thermostatic bath. The resultant solution was then filtered and washed many times with dionised water. The filtrate was then dryed at 75^{0}C in a vaccume oven at a pressure of 100mmHg for 3 h. The samples were ground to very fine powder. The powder material so obtained was sinterted in a muffle furnace (KSL 1600X, MTI) in air at temperature 300^{0}C with uniform heating rate of 2^{0}C/ minutes for different time durations

Characterization of sample

Complementary methods were used to characterize annealed samples. In order to determine the crystallite size and lattice constant, XRD patterns of samples were recorded by an X-ray diffractometer (X' Pert Pro) using Cu-k radiation of wavelength 1.54 Å at 50kV and 40 ma diffractometer. The divergence of scanning beam on the source slide was controlled with the help of 0.15mm slit. The specimens were scanned in the range 20^0 to 80^0. Fourier transform infrared spectrometer has been used to study the IR properties of ferrite in the Mid-IR range, 4000-400 cm^{-1} using Perkin-Elmer instrument. Absorption spectra of the samples were studied with the help of Lambda 750 (Perkin Elmer) spectrophotometer in the wavelength range of 200–800 nm

Results and discussion

XRD: X-ray crystallography is a tool used for identifying the atomic and molecular structure of crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. Fig.1(a) shows the XRD pattern of as prepared Nd dopped cobalt ferrite. This figure show diffraction peaks at 2 ~ 17.21^0 (2 0 0), 24.42^0 (2 2 0), 34.79^0 (4 0 0), 39.13^0 (4 2 0), 65.26^0 (6 4 0). In this sample at these angles peaks are obtained for cobalt iron cyanide hydrate having face centered cubic lattice and space group F43m(216) [JCPDS file no. 860502].

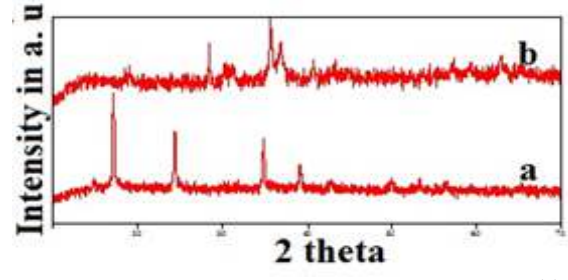


Figure 1: XRD pattern of Nd dopped $CoFe_2O_4$ powder for (a) as-prepared, (b) at 300^{0}C

Fig.1(b) shows the XRD pattern of Nd dopped cobalt ferrite annealed at 300^{0}C.

This figure shows diffraction peaks at 2θ ~ 18.88^0 (1 1 1), 28.44^0 (1 1 0), 30.22^0 (2 2 0), 31.27^0 (2 2 0), 35.61^0 (3 1 1), 36.91^0 (3 1 1), 40.64^0 (2 0 0), 43.27^0 (4 0 0), 57.21^0 (5 1 1), 62.78^0 (4 4 0). In this sample at 2θ ~ 18.88^0, 30.22^0, 35.61^0, 43.27^0, 57.21^0, 62.78^0 cobalt ferrite shows face centered cubic lattice having space group Fd3m(227) [JCPDS file no. 221086]. At 2θ ~ 28.44^0, 40.64^0 peaks are obtained for Nd_2O_3 having body cen-

tered cubic lattice and space group-Im3m (229) [JCPDS file no. 831356].

FTIR: Fourier transform infrared spectroscopy is a technique which enables us to identify the organic, inorganic materials and specially the presence of impurity phase in natural or synthesized materials. The FTIR spectrum of the as-prepared Nd dopped cobalt ferrite is shown in Fig. 2(a).

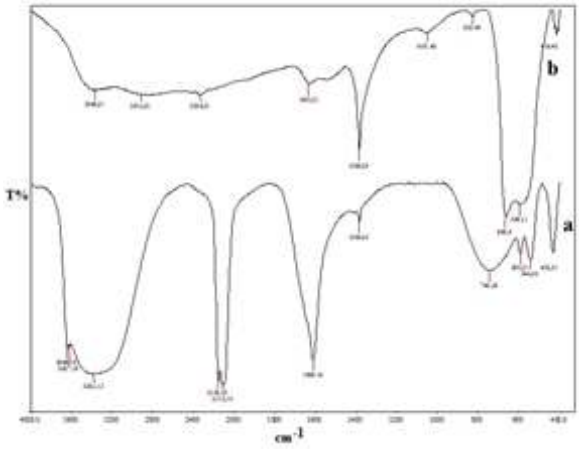


Figure 2: FTIR spectra of Nd dopped $CoFe_2O_4$ powder for (a) as-prepared, (b) at 300^{0}C

In this spectrum, absorption band at 3381 cm^{-1} is the characteristics of stretching vibration of OH which shows the presence of water in the sample. Peak around 1609 cm^{-1} shows bending vibration modes of H-O-H/C=N [18]. The peak at 593 cm^{-1} may be assigned to Fe-CN-Co bending mode [19]. The absorption around 2115 cm^{-1} which is the most strong peak of FTIR spectrum shows the stretching mode of CN for the PB like compounds $[M_K^A[M^B(CN)_6]_L.xH_2O$ {(K, L) = (1,1) (4,3) (3,2) (2,1)} in which cyanide forms bridges between M^A and M^B cations [20]. The presence of bluish green precipitate (on dissolving $K_3[Fe(CN)_6]$ with dilute mineral acid $CoCl_2$) along with 2080 cm^{-1} peak of FTIR spectrum confirms the formation of cobalt iron cyanide hydrate. Fig.2(b) shows the FTIR spectrum of Nd dopped cobalt ferrite heat treated at 300^{0}C. There are two characteristics bands of spinal structure which are high frequency band υ_1 (around 600cm^{-1}) and low frequency band υ_2 (around 400 cm^{-1}). υ_1 represents the A-site lies at 596 cm^{-1} and the band υ_2 corresponds to B-site at 416 cm^{-1}. Bands are at υ_1 and υ_2 are due to change in bond length of Fe^{3+}-O^{2-} at tetrahedral and octahedral site. The shifts in the bands are due to the perturbation occurring in the Fe^{3+}-O^{2-} band by Nd^{3+} substitution. Band at 666 cm^{-1} is assigned to the neodymium oxide (Nd_2O_3). The peak at 825 cm^{-1} shows the stretching of Nd-O [21]. The peaks at 1384 cm^{-1} and 1633 cm^{-1} are attributed to stretching the symmetric and asymmetric stretching vibration of CO_2 group. The peak obtained at 2336 cm^{-1} is assigned to the aliphatic/aromatic C-H bond stretching. The peak obtained at 3366 cm^{-1} is attribute to stretching vibration of hydroxyl group.

UV-Vis SPECTROSCOPY

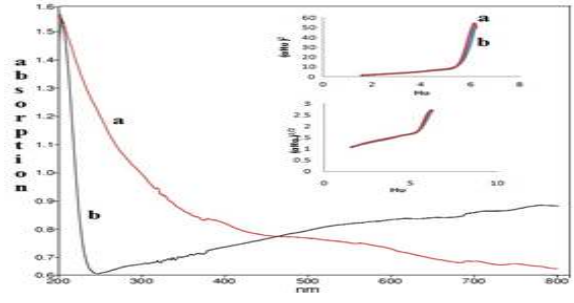


Figure 3: UV-vis spectra of Nd dopped $CoFe_2O_4$ powder for (a) as-prepared, (b) at 300^{0}C

The band gap energy of samples has been calculated using the relation between the incident photon energy (hυ) and the absorption coefficient (**α**) which is given by the equation: $(\alpha h\upsilon)^{1/n} = A(h\upsilon - Eg)$, where α is a constant and Eg is the band gap energy of the material and the exponent n depends on the type of transition [22]. Direct band gap of the samples (using n = ½) were calculated by plotting $(\alpha h\upsilon)^2$ verses hυ and then extrapolating the straight portion of the curve on hυ axis at α = 0. It is found that blue shift has been occurred due to well known quantum size effect [23]. The possible reason for red shift in band-gap energy with annealing temperature could be aggregation effects, strongest interaction of rare earth oxide in solid state.

CONCLUSIONS

Spinel structured Nd dopped cobalt ferrite was successfully obtained by coprecipitation method. Results illustrate that structural evolution of spinal ferrite depends on the annealing temperature and preparation method. XRD study reveals the size of nanocrystallite is in the range of 25-30 nm. FTIR bands observed near 400 cm^{-1} and 600 cm^{-1} revealed the typical features of spinel structure. FTIR data supports the XRD. The study suggested the possible use of these nano-ferrites in high frequency devices applications and high density recording media.

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