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Structural, magnetic and dielectric properties of nanocrystalline cobalt ferrite by wet hydroxyl chemical route

T. Boobalan [a], N. Suriyanarayanan [b,*], S. Pavithradevi [a]

[a] Park College of Engineering and Technology, Coimbatore 641659, India
[b] Government College of Technology, Coimbatore 641013, India

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ABSTRACT

Nanopowders of $CoFe_2O_4$ are synthesized via wet chemical co-precipitation processing at pH 8. The synthesized nanoferrite powders are annealed at various temperatures (350 °C, 700 °C and 1050 °C) and are characterized. X-ray diffraction (XRD) patterns indicate the crystalline nature of $CoFe_2O_4$ nanopowders. Transmission electron microscope (TEM) investigations show, anisotropic shapes like cubic, hexagonal and spherical morphology of nanoparticles with average particle size 38–85 nm. Dielectric constant decreases as the frequency increases. Low value of dielectric loss at higher frequencies suggests the material is suitable for high frequency applications. AC conductivity increases with frequency. The saturation magnetization (M_s), remanant magnetism (M_R) and coercivity (H_C) increases with applied field.

1. Introduction

Cobalt ferrite is a cubic spinel ferrite with interesting magnetic properties useful in many technological applications [1–4]. Much attention has recently been devoted to the controlled preparation of nanosized ferrites [5,6] because of their potential applications in high density magnetic recording [7], electronic devices [8,9] and medicines [10,11]. Such particles have been the object of the intensive fundamental research to explore the size, composition and surface related effects on the magnetic properties [5,6,12–15]. The tunabilty of the particle size and composition allows fine modification of the magnetic properties.

Nanosized Cobalt ferrites have been prepared using a variety of physical methods, including mechanochemical [16], post-laser deposition [17], combustion [18] and thermal decomposition [19]. Wet chemical methods are particularly interesting for their versatility, low-preparation temperature and potential for production scale up. Cobalt ferrite nanoparticles have been obtained by sonochemical [20], hydrothermal [21,22], sol–gel [23], co-precipitation [24,25] and micelle microemulsion [26,27] approaches. It is also possible to stabilize these particles in organic [28] and inorganic [23] polymeric matrices.

Various common methods for the preparation of ferrites have tendency of becoming impure while grinding, poor compositional control and chemical inhomogeneity, which could be overcome by wet chemical co-precipitation processing [24,25].This technique results in better homogeneity of the ferrite nanoparticles. Almost single phase crystalline structure is obtained by this method. The prepared $CoFe_2O_4$ samples show high value of coercivity and moderate saturation magnetization. Such nanoferrites are used in medical field especially in hyperthermia, magnetic resonance imaging (MRI), magnetic separation and drug delivery of cobalt ferrite nanoparticles [29].

2. Experimental

2.1. Sample preparation

Nanocrystalline $CoFe_2O_4$ is prepared by wet chemical co-precipitation processing at pH 8. The chemicals used are of high purity of A.R. grade cobalt chloride, ferric chloride. Each material is weighed and are carefully

* Corresponding author. Tel.: +91 2432221 (0422).
E-mail addresses: madurasuri2210@yahoo.com, nsuri22@gmail.com (N. Suriyanarayanan).

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dissolved into 500 ml doubly distilled water according to the formula of CO_x [Fe_{2x} O_4]. Then, the solution is mixed together by constant stirring for 6 h. The precipitate is carried out by adding NaOH solution drop wise continuously till the pH reaches 8. The precipitate is washed several times with distilled water until the washings are free from impurities. The product is dried on a hot plate at 120 °C to so that the water content is evaporated and eventually converted to black powder. The resultant dried product is powdered in an agate mortar.

The chemical reactions proceed as follows.

$$CoCl_2+2Fecl_3+4NaOH+2H_2O \rightarrow CoFe_2O_4 \cdot 2H_2O+4Nacl +4HCl \quad (1)$$

Synthesized $CoFe_2O_4$ samples are annealed at different temperatures 350 °C, 700 °C and 1050 °C respectively for 3 h. Phase purity of the powder is confirmed by XRD studies using PW3701 Philips diffractometer. The powder morphology is studied using a JEOL model 1200 EX transmission electron microscope (TEM). Selected powders are characterized for FTIR by SHIMADZU. Magnetic measurements like retentivity, coercivity, and saturation magnetization are performed using vibrating sample magnetometer (VSM 7407) at room temperature. Sintered disc shaped samples with silver electrodes are subjected to the measurements of dielectric constant and dielectric loss using HP4194 analyzer at room temperature.

3. Results and discussions

3.1. Phase identification

Fig. 1 shows the XRD patterns of synthesized $CoFe_2O_4$ nanoparticles. All the peaks correspond to $CoFe_2O_4$ phase which show the formation of cobalt ferrite structure. Increase in annealing temperature leads to a gradual growth of the crystallite size and no additional phases are detected. The reflections from the XRD patterns depicts the characteristic peaks (220), (400), (511), (440) of cobalt ferrite structure with preferred orientation along (311) plane and it well agrees with the JCPDS (#22-1086) data. As the annealing temperature increases, the preferred orientation along (311) plane also increases and almost single phase cubic spinel structure is obtained which has a space group of Fd3m.The small peaks in XRD pattern indicate the existence of fine nanocrystalline cobalt ferrite nanoparticles [30,31].

The average grain size of the samples are calculated using the Debye–Scherrer formula

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (2)$$

where λ is the X ray wavelength, θ is the Bragg's angle and β is the full width of the diffraction line at the half maximum intensity. The average crystallite size is found to be in the range of 40–76 nm. The particle size increases as the annealing temperature increases. The increase in particle size is due to the agglomeration of particles and as the annealing temperature increases, more Fe^{2+} ions are formed with a significant decrease in Fe^{3+} ions. Fe^{2+} ions have larger ionic radius (0.77 Å) than Fe^{3+} ions (0.63 Å) [32].

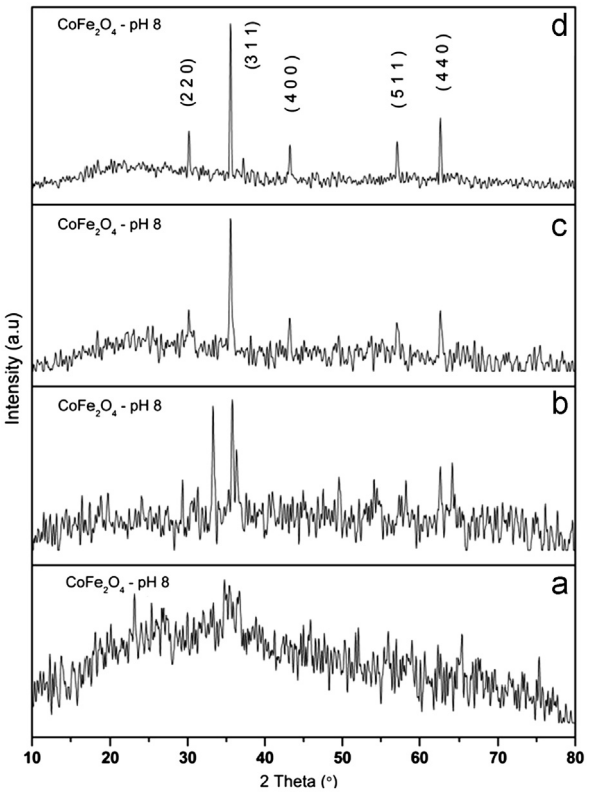

Fig. 1. XRD of $CoFe_2O_4$ as prepared and annealed at different temperatures, (a) as prepared, b.350 °C, (c) 700 °C, and (d) 1050 °C.

3.2. FTIR analysis

Fig. 2 shows the FTIR spectra of $CoFe_2O_4$ nanoparticles annealed at 1050 °C recorded between 3500 cm^{-1} and 400 cm^{-1}. The O–H stretching vibrations interacting through H bonds are observed at 3186 cm^{-1}, 2345 cm^{-1}, 2923 cm^{-1} and the absorption band present at about 1630 cm^{-1} is due to the bending of the absorbed water molecules. The intensities of absorption band at 1026 $cm^{-1}$and 918 cm^{-1} are the characteristic of cobalt ferrite system and this may be due to the residual FeOOH. The absorption bands present at about 594 cm^{-1}, and 401 cm^{-1} are due to the stretching vibrations of metal oxide in octahedral group complex CO^{2+}–O^{2-} and Fe^{3+}–O^{2-} tetrahedral group complex of the cobalt ferrite phase respectively which proves the existence of spinel ferrite [33,34].

3.3. Morphology and microstructure

Fig. 3(a,b) shows the TEM images of $CoFe_2O_4$ nanoparticles annealed at 700 °C and 1050 °C. Most of the particles present in the TEM images are seen to be anisotropic shapes like cubic, hexagonal, spherical with average particle size 38–85 nm, and it is in good agreement with XRD results. In certain regions of the TEM micrograph, dark areas are noticed due to congregation of nanoparticles. This occurs