

Dielectric Behavior of the Cobalt ferrite Nanoparticles Synthesized by the Sol-gel Auto-Combustion Method

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Abstract: Magnetic nanoparticles of pure cobalt ferrite (CoFe_2O_4) were prepared by sol-gel auto-combustion method at sufficiently low temperature. Glycine was used as a chelating agent. X-ray diffraction (XRD), technique was used to characterize the prepared cobalt ferrite nanoparticles. The crystallite size estimated from Scherrer formula is of the order of 38 nm. The structural parameters obtained from XRD data are in good agreement with reported data. The dielectric properties as a function of frequency were investigated.

INTRODUCTION

Ferrites are magnetic ceramics of great importance in many technological applications on account of their various electrical, dielectric and magnetic properties. The properties of ferrite are dependent on synthesis methods, synthesis parameters, type and nature of substituent and distribution of cations over the available sites [1, 2]. These materials finds applications in the field of antenna rods, transformer cores, permanent magnet, data storage etc. [3, 4] Owing to their Nemours applications ferrites are being studied from last six to seven decades with a view to understand and improve their properties for suitable applications. Many efforts have been taken by researchers to study the structural, electrical and magnetic properties of ferrites [5-10]. In early decades they have been synthesized by commonly used ceramic technique. However, in the last decade ferrites have been synthesized by various chemical methods with intension to obtain nanoparticles of ferrite which finds applications in the drug delivery, ferro-fluids, catalyst, sensors [11-14].

In the family of ferrites, cobalt ferrite with spinel structure have attracted scientists and technologists because, cobalt ferrite is a hard magnetic material with high coercivity, moderate magnetization, high Curie temperature, and excellent chemical stability. The high electrical resistivity and negligible eddy current losses make the cobalt ferrite useful in high frequency applications. The cobalt ferrite has cubic inverse spinel structure with Co^{2+} ions occupying half of the octahedral [B] sites whereas Fe^{3+} ions occupy all

tetrahedral (A) sites and half of the octahedral [B] sites [8]. In addition to these remarkable features the cobalt ferrite exhibits large magneto crystalline anisotropy along with (100) crystallographic direction and large magneto-striction in bulk form.

A review of literature shows that very limited work has been done on infrared and cation distribution studies of nanocrystalline cobalt ferrite. The important electrical and magnetic properties of ferrites are related to the distribution of cations among the available octahedral [B] and tetrahedral sites (A) in spinel structure, therefore control of cation distribution provides a mean to tailor their properties for desired applications. In view of this, the study of cation distribution is of particular interest in understanding the structural, magnetic and electrical properties of cobalt ferrite nanoparticles. The cation distribution depends on method of preparation, valence of electrons, electronic configuration etc. parameters [15]. The changes in the particle size can also influence the magnetic properties arising due to change in the cation distribution [16]. In this study, we report the synthesis of cobalt ferrite using sol-gel auto combustion technique and their structural, infrared and dielectric properties.

EXPERIMENTAL DETAILS

Synthesis of cobalt ferrite nano particles

Cobalt ferrite (CoFe_2O_4) with nano size particles was synthesized by a sol-gel auto combustion technique. The precursors used in the synthesis were cobalt nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and ferric nitrate

[Fe(NO₃).9H₂O], Glycine [C₂H₅NO₂] was added as the fuel. All the reagents used for the synthesis of cobalt ferrite nanoparticles were of an analytical grade and used as received without further purification. The detailed procedure followed in the synthesis is reported by [17].

RESULTS AND DISCUSSION

X-ray diffraction

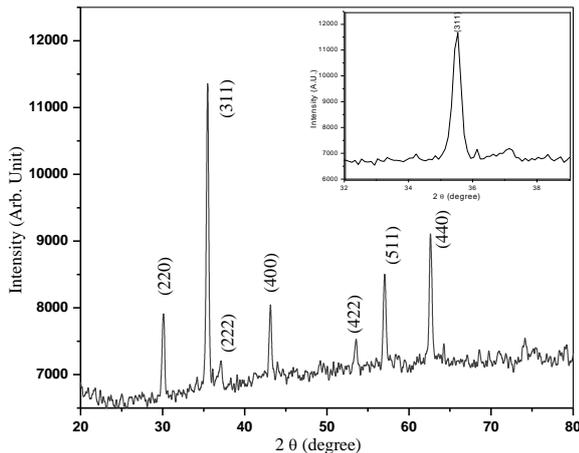


Figure 1: Powder X-ray diffraction (XRD) pattern of sintered cobalt ferrite powder (Inset shows the most intense peak).

Figure 1 represents the room temperature X-ray diffraction (XRD) pattern of sintered cobalt ferrite nanoparticles. All the peaks in the XRD pattern were indexed by using Bragg's law. The reflections observed in XRD pattern of sintered sample are slightly broader. The broader peaks in the XRD pattern suggest the nano crystalline nature of the samples. All the reflections in the XRD pattern belongs to cubic spinel structure, space group Fd_{3m}. XRD pattern showed the formation of single phase cubic spinel structure.

The lattice constant was determined from X-ray data analysis with an accuracy of $\pm 0.002 \text{ \AA}$ using the formula,

$$\frac{\lambda^2}{4a^2} = \frac{\sin^2\theta}{(h^2 + k^2 + l^2)} \quad \dots\dots\dots(1)$$

Where, 'a' is lattice constant, (h k l) represents the Miller indices and λ is the wavelength of X-rays used and ' θ ' is the glancing angle. The crystallite size was determined from the full width at half maximum (FWHM) of the strongest reflection (311) and by using the Scherrer's formula [18],

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

Where, D is the crystallite size (nm) β is full width at half maximum of the (311) strongest diffraction peak, λ is wavelength of the X- ray radiation. (CuK α = 0.154 nm), θ is the diffraction angle. The crystallite size obtained from Scherrer's formula is of the order of 38 nm.

The X-ray density was calculated from lattice parameter (a) using the formula,

$$\rho_{\text{XRD}} = \frac{8M}{N_A a^3} \quad \dots\dots\dots(3)$$

Where, M is molecular weight and N_A is the Avogadro's number. The values of lattice constant (a), X-ray density (ρ) and crystallite size (t) are given in Table 1. All the values reported in Table 1 are comparable to those reported for similar compounds [19]. The bulk density (d_B) of sintered cobalt ferrite sample was measured using Archimedes principle [20] and the value is given Table 1.

From the X-ray density and bulk density values, porosity (P %) was calculated using the relation

$$P = 1 - \frac{\rho_B}{\rho_X} \quad \dots\dots\dots(4)$$

Where ρ_B is the physical density, ρ_X is the x-ray density and is given in Table 1. It is observed from Table 1 that porosity shows higher value which is attributed to synthesis conditions.

TABLE 1: Structural parameters of cobalt ferrite nanoparticles

Parameter	Value
Lattice constant (a \AA)	8.381
Crystallite Size (D nm)	38
X-ray density ($d_x \text{ g/cm}^3$)	5.295
Bulk density ($d_B \text{ g/cm}^3$)	3.01
Porosity (P %)	43.12

Dielectric Measurements

Fig 2 shows the variation of the dielectric constant (ϵ') as a function of frequency (100 Hz - 1 MHz) at room temperature. It is observed from Fig. 2 that the dielectric constant shows dispersion with frequency. It is also seen from Fig. 2 that the values of dielectric constant are high at low frequency and then decreases rapidly with the

increase in frequency. Finally, the dielectric constant attains a constant value at high frequency. This behaviour of dielectric constant with frequency is the general trend and is observed for all the ferrite samples [21, 22]. The observed dielectric dispersion is attributed to space charge polarization produced inside the material due to the presence of inhomogeneous dielectric structure. Electron hopping between Fe^{2+} and Fe^{3+} present at crystallographically equivalent sites i.e. octahedral sites can also cause dielectric dispersion. This is known as the hopping mechanism of the electron transfer. The electron hopping between Fe^{2+} to Fe^{3+} ions at octahedral sites can not follow the alteration of ac electrical field at higher frequencies. The electrons have to pass through the well conducting grains and the poorly conducting grain boundaries. As the grain boundaries have the large resistance the electrons pile up there and produce large space charge polarization. Therefore, the dielectric constant has large values in low frequency range. Further increase in the frequency electron changes their direction of motion rapidly, which hinders the electrons inside the dielectric material and accumulation of charge at the grain boundaries decreases. This decreases the space charge polarization and therefore the values of the dielectric constant are also reduced [23]. Our results are analogous with the other well-known spinel ferrite and are in accordance with the Koop's theory [24, 25].

The variation of dielectric loss tangent ($\tan \delta$) with increase in frequency for cobalt ferrite nano particles is shown in Figure 3. It is evident from Figure 3 that $\tan \delta$ decreases with increase in frequency because the jumping frequency of charge carriers can not follow the frequency of the applied field after certain frequency. In spinel ferrite dielectric loss arises from two mechanism electron hopping and charge defect dipoles. The dielectric loss in the low frequency region may be due to charge defect dipole. The dielectric loss at higher frequency originate from the response of the defect dipoles to the field are formed due to change in cation states such as $\text{Fe}^{3+}/\text{Fe}^{2+}$ during the sintering process [26].

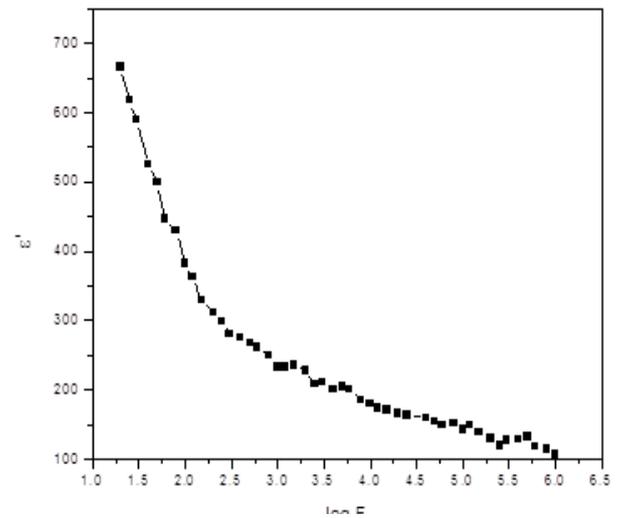


Figure 2: Variation of dielectric constant (ϵ') with frequency of cobalt ferrite nanoparticles

Variation of dielectric loss tangent with frequency:

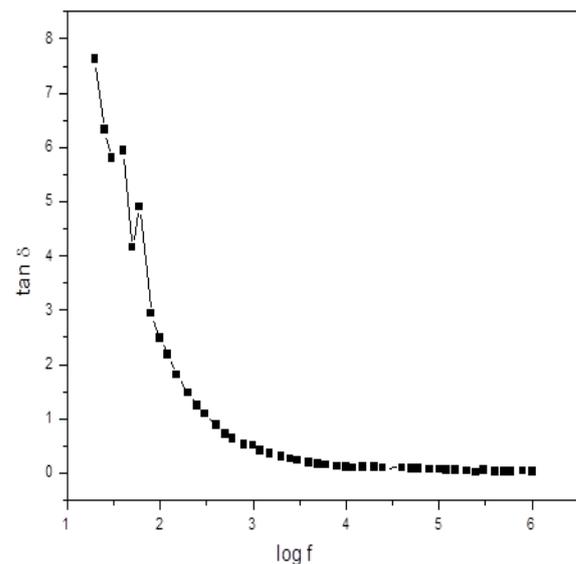


Figure 3: Variation of dielectric loss tangent ($\tan \delta$) with frequency of cobalt ferrite nanoparticles

CONCLUSIONS

The nanocrystalline cobalt ferrite was successfully prepared by sol-gel auto-combustion technique using glycine as a fuel. The X-ray diffraction results showed the formation of single phase cubic spinel structure. The crystallite size, lattice constant and X-ray density are in the reported range. The bulk density is quite low compared to X-ray density and hence porosity is increased. The dielectric constant decreases with increase in frequency

and follows exponential nature. The values of dielectric constant are low compared to bulk cobalt ferrite. The dielectric loss tangent decreases exponentially with increase in frequency.

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