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Review Of Research

MAGNETIC AND ELECTRIC BEHAVIOUR OF COBALT FERRITE NANOPARTICLES OBTAINED BY USING DIFFERENT CHELATING FUELS IN SOL-GEL TECHNIQUE

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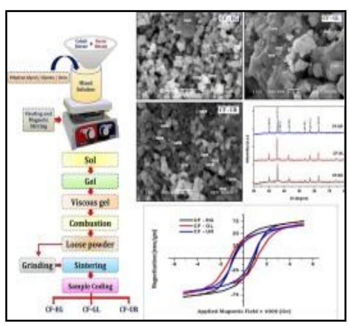
ABSTRACT
By varying the chelating agent as citric acid, L-ascorbic acid and tartaric acid in sol-gel auto-combustion technique, cobalt ferrite nanoparticles were obtained. The prepared $CoFe_2O_4$ powders were then annealed at 500^0C for 4 h for good crystallization. Cubic spinel structure of the samples was confirmed by using X-ray diffraction analysis. The saturation magnetization (M_S), coercivity (H_c) and remanence magnetization (M_r) were obtained from M-H plots recorded at room temperature using pulse field hysteresis loop tracer technique. The observed magnetic parameters of present $CoFe_2O_4$ samples are found to be better as compared to bulk $CoFe_2O_4$ due to the particles size effect. The d.c. electrical resistivity measurements were carried out by using two probe technique in the temperature range 300K to 800K. It can be observed that dielectric constant decreases exponentially with frequency increase indicating that the conduction in present ferrite nano-particles increases with applied ac field.



KEYWORDS: *Saturation magnetization, d.c. resistivity, dielectric constant.*

INTRODUCTION:

In the family of spinel ferrite, cobalt ferrite ($CoFe_2O_4$) is the unique spinel ferrite with inverse spinel structure, in which Co^{2+} ions occupy an octahedral [B] site. The degree of inversion depends on the synthesis method and thermal treatment. High saturation magnetization, high permeability, high electrical resistivity, high Curie temperature, high magneto-crystalline anisotropy etc are the remarkable properties of cobalt ferrite. These properties are useful in many applications including magnetic recording media, antenna rods, permanent magnets etc [1]. The recent literature survey reveals that the structural and magnetic properties of cobalt ferrite nano-particles synthesized by wet chemical methods like sol-gel, hydrothermal, chemical co-precipitation etc have been investigated by number of researchers [2-4]. The wet chemical methods are economic, easy, requires less time and low temperature, produces particles of nanometer dimensions and therefore now a day's commonly used in the synthesis of magnetic nano particles of spinel ferrite. The use of nano-particles has increased in the recent time because of their interesting, unusual and superior properties that are different than that of bulk materials [5]. The magnetic nanoparticles of spinel ferrite are gaining importance in the recent years because of their new applications in the field of medical science, environmental, catalyst and sensors [6, 7].

The present work reports about the synthesis of cobalt ferrite nano-particles using citric acid, L-Ascorbic acid, tartaric acid as a fuel/chelating agent. The effect of fuel variation on magnetic and electric properties of synthesized nano-particles has been investigated.

EXPERIMENTAL:

The magnetic measurements were recorded at room temperature using pulse field hysteresis loop technique. The DC electrical resistivity measurements were carried out in the temperature range 300-600K using two probe techniques. A silver paste was applied on the surfaces of pellet to ensure the good ohmic contact. The dielectric constant measurements were carried out at room temperature as a function of frequency (100Hz – 1MHz) using LCR-Q meter (Model 4192, HP make).

RESULTS AND DISCUSSION:

[1] Magnetic properties:

Magnetic hysteresis loop recorded at room temperature using pulse field hysteresis loop technique of present cobalt ferrite nano particles is shown in Fig. 1. The hysteresis curve exhibit normal ferrimagnetic magnetic behavior. The saturation magnetization (M_S), the coercive field (H_c), remnant magnetization (M_r) values for cobalt ferrite nano particles is given in Table 1. It is observed from Table 1 that the saturation magnetization and coercive field shows higher value which may be due to nanocrystalline nature of the cobalt ferrite sample. These values of magnetic parameters agree well with the reported values [8]. Further, on comparison with bulk cobalt ferrite samples, these values of magnetic parameters are found to be slightly higher. Thus, the smaller crystallite size of the present cobalt ferrite samples results in enhancement of the magnetic properties. The observed magnetic behaviour can also be explained on the basis of Neel's theory of ferrimagnetism [9]. According to this theory, the net magnetic moment can be given by the following relation,

$$n_B^A = M_A - M_B \quad (1)$$

Where, M_B and M_A denotes the net magnetic moment of [B] site and (A) site respectively. Using the cation distribution formula, the magnetic moment at [B] and (A) site was calculated and the calculated magneton number is presented in Table 1. The observed magneton number can be calculated using following relation,

$$n_B^A = \frac{M_S \times \text{Molecular weight}}{5585} \quad (2)$$

The value of observed magneton number is also presented in Table1. It is evident that observed and calculated magneton number (n_B) shows good agreement with each other, indicating the collinear structure of the present sample.

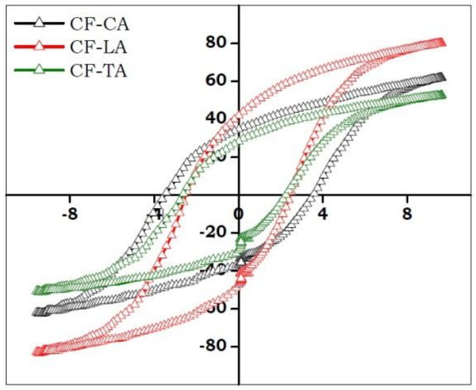


Fig. 1: M-H plots of cobalt ferrite nano-particles prepared by sol-gel auto-combustion technique by using different fuels

[2] d. c. electrical resistivity:

The d.c. electrical resistivity measurements were carried out on pressed pellet of 10 mm diameter and 3 mm thickness of synthesized ferrites using two probe techniques. The pellets were prepared using hydraulic press by applying a pressure of 5 tons. The dc resistivity was calculated from resistance measurement and pellet dimensions. Fig. 2 shows the variation of dc electrical resistivity as a function of inverse of temperature. It can be observed from Fig. 2 that the resistivity decreases with increase in temperature indicating the semiconducting nature of the samples. Using the resistivity plot (Fig.2) and the relation

$$\rho = \rho_0 \exp\left(E_a / kT\right) \quad (3)$$

where, ρ_0 is the resistivity at infinitely high temperature, k is the Boltzman constant, E_a is the activation energy.

The activation energy values are presented in Table 1. The electrical conductivity has been attributed to electron hopping between the two valence state of iron ($Fe^{2+} \leftrightarrow Fe^{3+}$) on octahedral site. The electron hopping depends on sintering time, sintering atmosphere, synthesis method etc. The electrical conduction in this ferrite can be explained on the basis of Verwey mechanism of electron hopping between two valence states distributed randomly on equivalent lattice site [10].

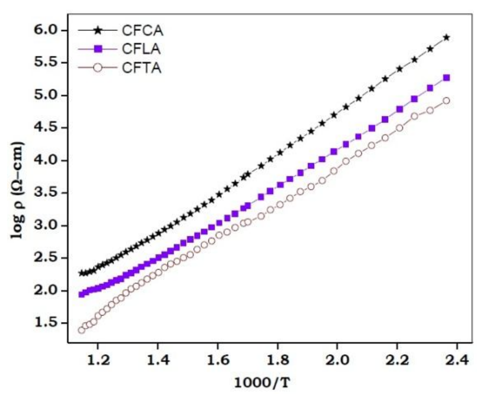


Fig. 2: Variation of DC electrical resistivity with temperature of cobalt ferrite nanoparticles prepared by using sol-gel auto-combustion technique.

[3] Dielectric properties:

Fig. 3 shows the variation of dielectric constant (ε') as a function of applied frequency (f) at room temperature. It can be observed that dielectric constant decreases exponentially with frequency increase indicating that the conduction in present ferrite nano-particles increases with applied ac field. At low frequency, the dielectric constant decreases much rapidly showing usual dielectric dispersion. At high frequency, the decrease in dielectric constant is very slow (almost remain constant). This variation can be explained on the basis of space charge polarization model of Maxwell-Wagnar [11] type of interfacial polarization in accordance with Koops phenomenological theory [12].

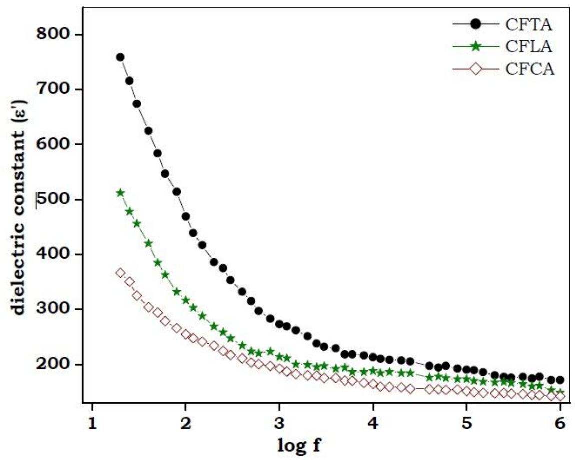


Fig. 3: Variation of dielectric constant (ε') with frequency of cobalt ferrite nanoparticles prepared by sol-gel auto-combustion technique using different fuels.

Table 1: Saturation magnetization (M_S), remnant magnetization (M_r), Coercivity (H_C), magneton number 'n_B' and activation energy (E_a) for cobalt ferrite prepared by sol-gel auto-combustion technique by using different fuels

Sample	M_S (emu/gm	M_r (emu/gm)	M_r/M_S	H_C (Oe)	n_B	Activation energy (eV)		
						E_P	E_f	Δ E
CF-CA	62.04	60.92	0.98	3520	2.61	1.231	0.806	0.424
VF-LA	80.21	69.27	0.86	2444	3.37	1.082	0.769	0.313
CF-TA	52.84	42.58	0.81	2167	2.22	0.864	0.662	0.203

The large value of dielectric constant at lower frequency is due to the predominance Fe^{2+} ions, interfacial dislocation; oxygen vacancies grain boundaries defects etc. The maximum values of dielectric constant are due to availability of space charge polarization at the grain boundaries [13]. The variation of dielectric loss tangent (tan δ) with frequency is shown in Fig 4. It is evident from Fig. 4 that like dielectric constant the dielectric loss tangent also decreases exponentially. The dispersion at lower frequency region may be due to the existence of resonance between applied frequency as hopping frequency of charge carriers [14] and also due to domain wall resonance [15,16]. The dielectric loss tangent in ferrite is a measure of lag in the polarization with respect to the alternating field.

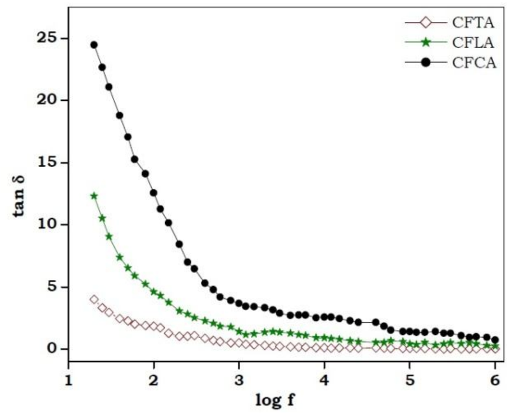


Fig. 4: Variation of dielectric loss tangent (tan δ) with frequency of cobalt ferrite nanoparticles prepared by sol-gel auto-combustion technique using different fuels.

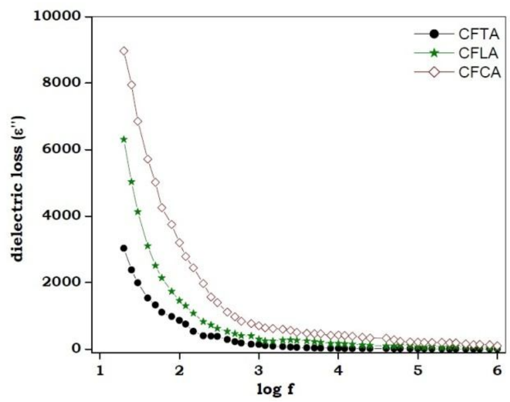


Fig. 5: Variation of dielectric loss (ε'') with frequency of cobalt ferrite nanoparticles prepared by sol-gel auto-combustion technique using different fuels.

Variation in dielectric loss factor (ε'') with logarithm of frequency is shown in Fig 5. It is clear from Fig. 5 that the dielectric loss decreases as the frequency increases like dielectric constant the dielectric loss tangent. The values of dielectric constant (ε'), dielectric loss (ε'') and dielectric loss tangent (tan δ) at room temperature for cobalt ferrite prepared by sol-gel auto-combustion technique by using different fuels are tabulated in Table 2.

Table 2: Room temperature dielectric constant (ε′), dielectric loss (ε″) and dielectric loss tangent (tan δ) for cobalt ferrite prepared by sol-gel auto-combustion technique by using different fuels

Sample	f = 100 Hz			f = 1 MHz		
	ε′	ε″	tan δ	ε′	ε″	tan δ
CF-CA	350	7935	22.67	141	104.3	0.74
VF-LA	478	5033	10.53	148	37	0.25
CF-TA	569	3471	6.1	162	6.48	0.04

CONCLUSIONS:

The magnetic parameters like Ms, Hc, shows enhancement in their values compared to bulk cobalt ferrite. The observed and calculated magneton number agrees close to each other. The comparison of the structural data and magnetic data obtained from ceramic method and sol-gel method exhibit significant difference which contributes to crystallite size effect. Further the comparison of the structural and magnetic data obtained by sol-gel method but with different fuel used namely citric acid, L-ascorbic acid and tartaric shows slight variation in their values. The best results are obtained for the cobalt ferrite nano particles, obtained by L-ascorbic acid assisted sol-gel method.

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