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ROLE OF CHELATING AGENT IN THE PREPARATION AND STRUCTURAL CHARACTERIZATION OF COBALT FERRITE NANOPARTICLES SYNTHESIZED VIA SOL-GEL ROUTE

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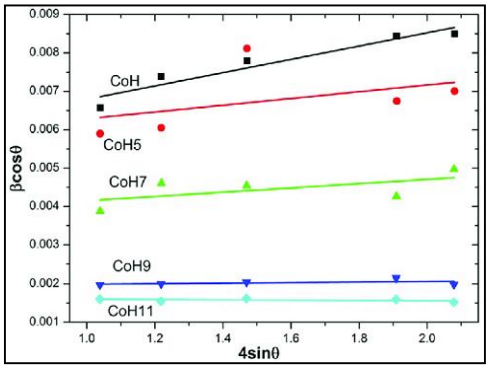
ABSTRACT



Nano – particles of cobalt ferrite were obtained by using sol-gel auto combustion method by varying the chelating agents as L-ascorbic acid, citric acid and tartaric acid. To obtain the exact value of synthesis temperature, TG-DTA analysis was made. TG curves indicate that no further weight loss will be observed above the temperature 600^0C. X-ray diffraction patterns shows the reflections for the planes (220), (311), (400), (511) and (440) which corresponds to the single phase cubic spinel structure. The lattice constant 'a' for all the three fuels is found in the range 8.344 to 8.395 Å. The minimum value of particle size 't' is obtained for the sample CF-CA (38nm) and highest for CF-TA (43nm). The infrared spectroscopy carried out in the frequency range 400 to 1000 cm^{-1} shows two main absorption bands as a common feature of spinel ferrites.

KEYWORDS: *Cobalt ferrite, chelating agent, lattice parameter, infrared spectra* **.**

INTRODUCTION:

The high electrical resistivity, low eddy current and dielectric losses, high saturation magnetization, high permeability, etc are the important electrical and magnetic properties of ferrite. These several properties of ferrite make them useful in numerous applications including antenna rod, transformer core, memory chips, telecommunication, automobile etc. Because of their extremely low eddy current and dielectric losses they are used at high frequency applications (Switch mode power supply, RF transformers, inductors etc) [3]. The properties of ferrites are sensitive to various factors such as method of preparation, preparative conditions and nature of substituent's [4]. The variation in these parameters can lead to a modification in the properties of ferrite. Usually, the ferrites are prepared by ceramic technology using high purity metal oxides. Though, the method has some drawbacks, it is used commonly to produce bulk material. With the advent of nanotechnology, the ferrites have been prepared in nanosize form using different chemical methods. The properties of these nanosized ferrites are found to be very interesting and superior to that of their bulk counterpart [5]. On account of their properties, nanosize ferrites find applications in the field of drug delivery, hyperthermia, sensors, catalyst etc. [6]. In the light of the importance of nanosize ferrite, the research on these materials has been tremendously increased in the recent years. The new synthesis methods have been developed to obtain nanosize particles. Apart from

synthesis methods, synthesis parameters (pH, fuel, annealing temperature) play an important role in governing the properties of nanosize ferrite. Thus, the synthesis methods and synthesis parameters have become the subject of interest to the scientist and technologist as they bring variation in properties.

Among the various synthesis methods, the sol-gel method has some advantages over the others and hence these methods are used on large scale. The sol-gel synthesis produces homogeneous material with nano-size dimensions. In the literature, cobalt ferrite has been synthesized by many techniques and by many workers with a view to understand their structural, electrical, dielectric and magnetic properties [7-9]. In sol-gel method, citric acid as a fuel was commonly used in the synthesis of cobalt ferrite nano-particles [10-12]. In some cases glycine was also used as a fuel for the synthesis of cobalt ferrite nano particles [13]. However, to our knowledge no reports are available in the literature, in which L-Ascorbic acid, tartaric acid was used as a fuel. In comparison with Citric acid and Tartaric acid, L-Ascorbic acid founds to be more effective in the synthesis of cobalt ferrite nano-particles because of it oxidized in nature.

EXPERIMENTAL:

The nano-powders of cobalt ferrite were synthesized by well known sol-gel method using metal nitrates of respective ions and L-Ascorbic acid, as a fuel. Amounts of Co $(NO_3)_2$, Fe $(NO_3)_3$ with molar ratio Co^{2+}/Fe^{3+} = ½ were dissolved completely in de-ionized water. The aqueous solution containing Co^{2+} and Fe^{3+} ions was poured into L-ascorbic acid with the total cations/L-Ascorbic acid molar ratio 1:3 and the initial pH of the solution was measured. To increase the pH up to 7, ammonia hydroxide in aqueous form was added to the mixed solution drop by drop. The mixture was stirred using magnetic stirrer and evaporated at 80^0C to form a gel. The temperature of the gel was further increased to 110^0C for 1-2 hours. The gel burns rapidly and turned into brown loose powder. The obtained powder was annealed at 550^0C and was used for further characterization. Similar procedure was used for synthesis of cobalt ferrite nano-particles using other fuels such as citric acid, tartaric acid. Cobalt ferrite nano-particles synthesized by sol-gel auto-combustion method by using three different chelating- combustion agent citric acid, L-ascorbic acid and tartaric acid were named as CF-CA, CF-LA and CF-TA respectively. The X-ray diffraction technique was employed to confirm the phase purity and nano crystalline nature of the prepared cobalt ferrite nanoparticles. The X-ray diffraction pattern was recorded into 2θ range of 200-800 at room temperature using Cu-Kα radiation. Infra-red spectra of all the samples were taken at room temperature in the wave number 1000- 350cm^{-1}.

RESULTS AND DISCUSSION:

1. Thermo-gravimetric analysis:

A typical TG-DTA plot for as synthesized power of cobalt ferrite nanoparticles prepared by sol-gel auto-combustion technique using Citric acid as a fuel is shown in Fig 1. It was observed that an endothermic reaction with weight loss is observed at around 100^0C, which corresponds to the evaporation of water in the sample. The exothermic peak at the onset temperature of 300^0C in the DTA curve corresponds to the crystallization of cobalt ferrite nanoparticles. From TGA curve a weight loss of 20% was observed over the temperature region 50-550^0C. Above 600^0C no further weight loss was detected indicating that all organic constituents were eliminated.

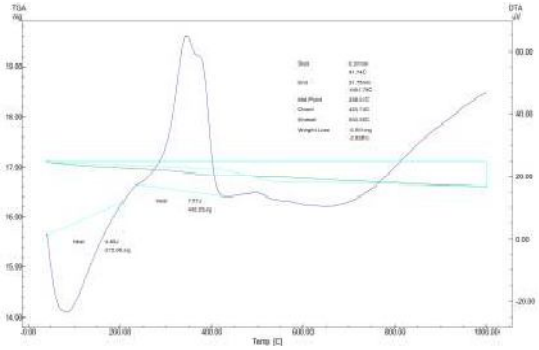


Fig. 1: TGA-DTA Curve for cobalt ferrite nanoparticles prepared by sol-gel auto-combustion technique using Citric acid as a fuel

2. Structural analysis:

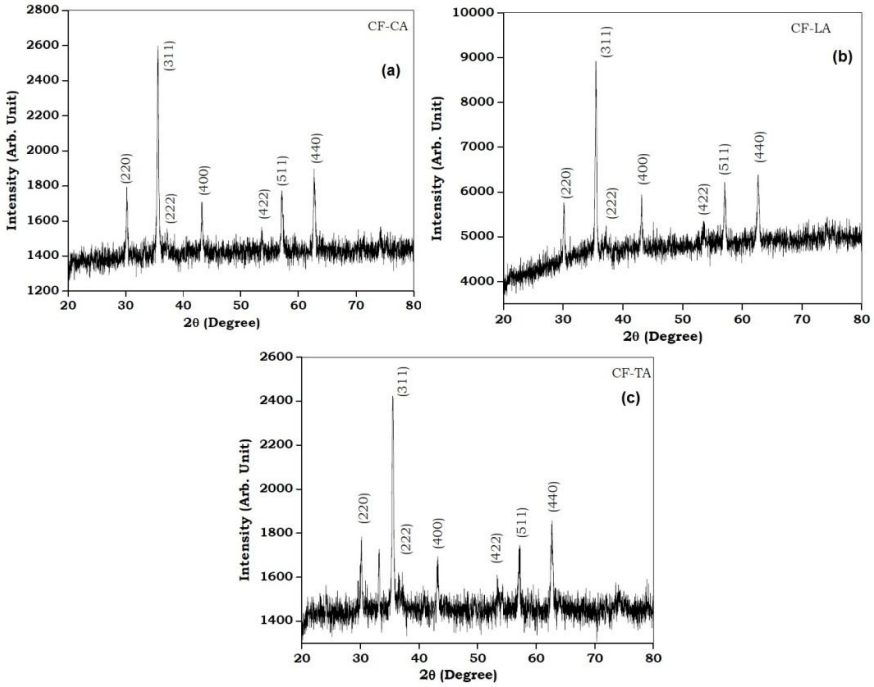


Fig. 2: XRD Pattern of cobalt ferrite nano-particles prepared by sol-gel auto -combustion method using a) Citric acid, b) L-absorbic acid and c) tartaric acid as a fuel

Fig. 2 (a, b, c) represents the X-ray diffraction patterns (XRD) of cobalt ferrite ($CoFe_2O_4$) nano-particles synthesized by sol-gel auto-combustion technique by using different fuels i.e. citric acid, L-ascorbic acid and tartaric acid recorded at room temperature. The X-ray diffraction pattern shows the presence of desired phase of cubic spinel structure; no extra peak of impurity phase was observed in the XRD pattern, confirming the purity of the samples. The reflections (220), (311), (400), (511), (440) belonging to single phase cubic spinel structure are present in the XRD pattern. The reflection (311) is found to be more intense and is used to determine the crystallite size. The crystallite size was determined from the value of full width at half maximum (FWHM) of the most intense reflection (311) [14], using the Scherrer's formula,

$$t = \frac{0.9\lambda}{(w - w_i)\cos\theta_B} \qquad (1)$$

Where, t is the average diameter in nm, w is the half intensity width of the relevant diffraction peaks, w_i represents the half intensity width due to instrumental broadening, λ is the wavelength of X-ray radiation, and θ_B is the Bragg's diffraction angle. The calculated value of crystallite size was given in Table 1 and is in nanometer scale confirming the nanocrystalline nature of the prepared samples. The lattice constant of the present cobalt ferrite nano particles was computed using the inter planar spacing values and the respective (hkl) parameters from the classical formula given in Eq. 2.

$$a = \frac{\lambda\left[h^2 + k^2 + l^2\right]^{1/2}}{2\sin\theta}$$

The value of lattice constant was also given in Table 5.1. The lattice constant of the present cobalt ferrite nano-particles is found to be in the reported range. The lattice constant is slightly greater than that of bulk cobalt ferrite [15], this is attributed to the particle/crystallite size. The X-ray density 'dx' was calculated using the values of lattice constant and molecular weight. Table 1 gives the values of X-ray density. For the

sake of comparison the values of crystallite size, lattice constant and X-ray density of cobalt ferrite synthesized by sol-gel method using different fuel is given.

Table 1: lattice parameter 'a', X-ray density (d_X), bulk density (d_B), percentage porosity (P), crystalline size 't', absorption bands (ν_1 and ν_2) and force constants (K_0, K_t) of cobalt ferrite for different chelating agents.

Sample	'a' (Å)	'd_X' (gm/cm^3)	'd_B' (gm/cm^3)	'P' (%)	't' (nm)	'ν_1' (cm^{-1})	'ν_2' (cm^{-1})	$K_0\times10^5$ (dynes/cm)	$K_t\times10^5$ (dynes/cm)
CF-CA	8.363	5.329	3.445	35	38	574	352	2.40	0.90
VF-LA	8.344	5.365	3.773	30	42	598	416	2.61	1.27
CF-TA	8.395	5.268	3.897	26	43	578	398	2.44	1.15

It is found from Table 1 that cobalt ferrite prepared with L-ascorbic acid (CF-LA) as a fuel shows better crystalline size. L-ascorbic acid is found to be effective fuel in synthesizing cobalt ferrite nano-particles as it provides more donors for oxidation reaction compared to other fuels (citric acid, dextrose etc.). The X-ray density (d_x) was calculated using the values of interplaner spacing (d) and lattice constant (a) and the values are given in Table 1. It can be observed from Table 1 that X-ray density is in reported range. For L-ascorbic acid the X-ray density is found to be more as compared to other fuels. The bulk density (d_B) of all the samples was determined using Archimedes principle [16] and their values are presented in Table 1. The percentage porosity (P) was evaluated using the values of X-ray density and bulk density. The observed porosity varies in the range 25-35%. The minimum porosity was observed for tartaric acid and the maximum porosity was observed for citric acid.

3. Infrared spectroscopy:

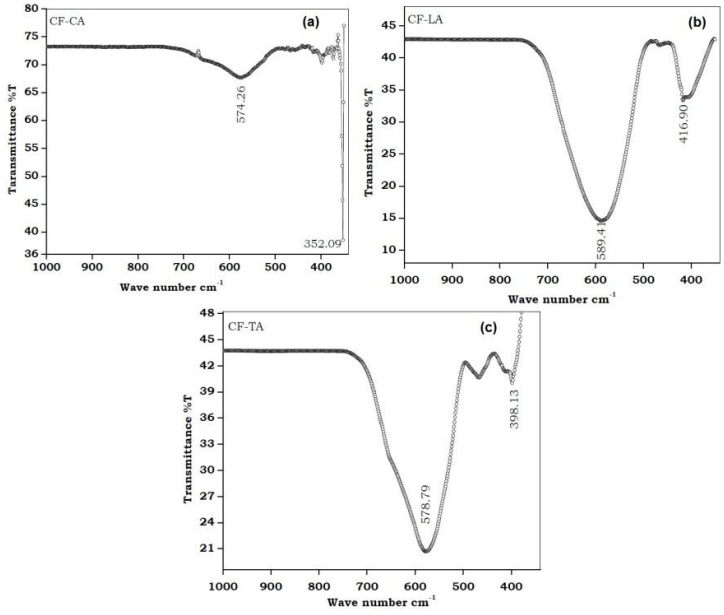


Fig. 3: Infrared spectra of cobalt ferrite prepared by using sol-gel technique by using a) citric acid, b) L-absorbic acid and c) tartaric acid

Infra-red absorption spectra were recorded in the wave number range 1000 to 350cm^{-1} at room temperature and is shown in Fig. 3 (a, b and c) The spectra show to broad absorption bands, as a common feature of ferrite samples. The high frequency band is located around 600cm^{-1} and the low frequency band located at 400 cm^{-1}. The high frequency band ν_1 is assigned to the intrinsic vibration of metal ions complexes at the tetrahedral sites (M_{th} - O) and the low frequency band ν_2 corresponds to octahedral metal stretching (M_{oh}-O) of the spinel lattice [17]. The observed absorption bands are in good agreements with those

reported for other spinel ferrite nano particles [18, 19]. Using the values of ν_1 and ν_2 the force constant K_t and K_0 have been evaluated and their values are presented in Table 1. The force constant K_t and K_0 are also in good agreement with that reported in the literature [19].

CONCLUSIONS:

The synthesis of cobalt ferrite nano particles was successfully achieved through sol-gel method, assisted by L-Ascorbic acid. The nanocrystalline nature was confirmed through crystallite size and grain size. The analysis of X-ray diffraction data and pattern confirms the formation of single phase cubic spinel structure. The structural parameters obtained from XRD data are in the reported range. The IR spectrum exhibits two major absorption bands near 600 cm^{-1} and 400 cm^{-1} indicates the characteristics features of spinel ferrite nano particles.

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