Structural and Magnetic Properties of Cobalt Ferrite Nanoparticles using Citric Acid as Chelating Agent

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Abstract: Cobalt-ferrite, a spinal ferrite is an attractive material due to the large anisotropy, moderate magnetization, chemical stability and high Curie temperature. In the present work, cobalt ferrite nano particles are synthesized by sol-gel technique using 0.2M cobalt nitrate, 0.2M ferric nitrate and 0.4 M citric acid. Volumetric proportion of metal nitrates (MN) to citric acid (CA) is taken in the ratio of 1:1.4, 1:1.6 and, 1:1.8. From the structural analysis, it is observed that the prepared sample shows poly crystalline nature with prominent peaks along (311) (511) and (440) plane confirming the cubic nature of the spinal ferrites. Micro structural analysis shows the grain size increases from 47 to 104 nm when the MN to CA ratio increases from 1:1.4 to 1:1.8 and the micro structural strain and dislocation density changes accordingly. The decrease in the lattice constant and volume of the cell from 8.314 to 8.302 A° and 5.747 to 5.722 A° reflects the nanosizing effect due to the synthesis process. The increase in the X-ray density from 9.076×10^{-21} to $9.116 \times 10^{-21} g/m^3$ is higher than the bulk cobalt ferrite, is attributed to the formation of pores during the synthesis process and ionic radii. Compositional analysis is carried out by EDS and the functional group was analyzed by FTIR spectroscopy. From SEM analysis the morphology the prepared samples are observed.

Keywords: Metal Nitrates, Citric Acid, XRD, EDS, SEM

I. INTRODUCTION

The interest in the preparation of magnetic materials in nanoscale is evident due to its numerous technological applications and utilization in biosciences. Ferrites are ferromagnetic materials which possess the combined properties of magnetic conductor and electrical insulator. Nanomaterial based on ferrites shows superparamagnetism, enhanced anisotropy and spin canting which leads to the applications such as photocatalysis, adsorption technologies, gas sensor, microwave devices and others [1]. Ferrites are mostly ferromagnetic and non-conducting. They are usually ceramic compounds with spinal structure. Due the unique magnetic properties, Cobalt ferrite nano particles are used in high density magnetic recordings [2] ferrofluids technology, biomedical drug delivery, magnetic resonance imaging, data storage, biosensors, biocompatible magnetic nanoparticles for cancer treatment and magneto-optical devices. Generally nanoparticles of size less than 60nm can be used in biomedical applications and particles of size greater than 60 nm can be used in photo catalytic applications. In order to have good physical and chemical properties with required dimension, different synthesis methods are adopted such as ball milling, ceramic method by firing [3] co precipitation technique [4,5], reverse micelles method [6], hydrothermal method [7,8], using polymeric precursor [9] sol-gel technique [10], micro emulsions method [11], laser ablation technique [12], polyol method [13], sonochemical approaches [14], and aerosol method [15]. In the present work sol-gel technique is used to synthesis cobalt ferrite nanoparticle using cobalt nitrate and ferric nitrate as precursor and citric acid as the chelating agent.

II. EXPERIMENTAL

A. Preparation of Nanoparticles

In the synthesis process analytical grade reagents used, without purification. The precursors are cobalt nitrate, ferric nitrate and citric acid. Citric acid is used as a cross-linker and chelating agent for the reduction of the particle size [16]. A mixture of 0.2M Cobalt nitrate, 0.2M ferric nitrate and 0.4 M citric acid is taken in the volumetric proportion of metal nitrates to citric acid as 1:1.4, 1:1.6 and 1:1.8.Ammonium is used to maintain the pH as 8. The flow chart for the preparation is shown in the fig. 1.
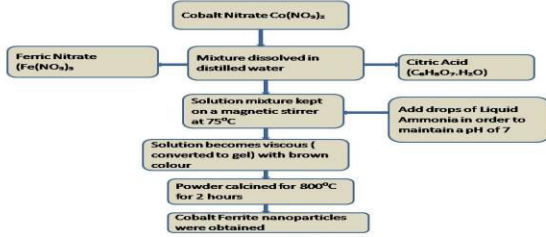
Fig. 1: Synthesis procedure of CoFe Nanoparticles

B. Characterisation

In the The samples were subjected to Powder X-ray diffraction analysis using Shimadzu XRD 6000 diffractometer with CuKα radiation wavelength of 1.541 Å. The crystalline size (D) were calculated using the Scherrer formula [19] from the full- width half maximum (FWHM)(β) for the most intense peak (311)

$$D= (k \lambda) / (\beta \cos\theta) \text{ A}°$$

In general, diffraction peak from a lattice plane is labeled as Miller indices (h, k, l) and these indices are related to inter-atomic spacing or 'd' spacing. For Cubic crystals, the lattice parameter 'a' is calculated for prominent peak (311) using the relation [19]

$$a = d_{hkl} /(h^2 + k^2 + l^2)^{1/2} \text{ A}°$$

The strain (ε) is calculated from the relation with β

$$\varepsilon = \beta \cos\theta / 4$$

The dislocation density (ρ) is defined as the length of dislocation lines per unit volume of the crystal, was calculated from the formula

$$\rho=1/D^2 \text{ lines /cm}^3$$

The theoretical X-ray density,(ρx) was calculated as [20]

$$\rho_x =8M/Na^3 \text{ g/cm}^3$$

Where *M* is the molecular weight of the sample and *A* is the Avogadro's number $(6.022 \times 10^{23} \text{mol}^{-1})$ and 'a' is the lattice parameter

The X-ray diffraction data is further used to calculate the tetrahedral and octahedral ionic radii (rA, rB) sites, the bond lengths on tetrahedral (A-O) and octahedral (B-O) sites of cubic spinel structure by using Standely's equations.

$$r_A =(u-¼)a\sqrt{3}- r(O^{-2}) \text{ A}°$$
$$r_B =(^5/_8 -u)a- r(O^{-2}) \text{ A}°$$
$$A-O=(u-¼)a\sqrt{3} \text{ A}°$$
$$B-O=(^5/_8 -u)a \text{ A}°$$

where *a* is the lattice constant; r(O⁻²) is the radius of oxygen ion (1.35 Å); u is the oxygen ion parameter, for ideal spinel ferrite u=3/8.

Hopping lengths in tetrahedral sites (LA) and in octahedral sites (LB) which is nothing but the distance between the magnetic ions is calculated by the following equation

$$L_A=a(\sqrt{3}/_4) \text{A}°$$
$$L_B=a(\sqrt{2}/_4) \text{A}°$$

The samples were subjected to Powder X-ray diffraction analysis using Shimadzu XRD 6000 diffractometer with CuKα radiation wavelength of 1.541 Å. The functional group were analysed by FTIR using Perkin-Elmer spectrometer by KBr pellet technique in the range of 4000-400 cm⁻¹. The morphology and elemental analysis of the prepared samples were assessed by Scanning Electron microscopy with EDAX using JEOL (JSM 6390of the prepared samples were assessed by Scanning Electron microscopy with EDAX using JEOL (JSM 6390).
agent

III. RESULTS AND DISCUSSIONS

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A. Structural Analysis

The Structural studies are carried out by XRD. Observation shows that, the samples show improved crystallinity when the volume of the citric acid is increased. The observed peaks (111),(220),(311), (400),(511),(446) and (533) matches well with the JCPDS data of cobalt ferrite nanoparticle [17]. Figure 2 shows that the powder XRD pattern of the synthesized samples.
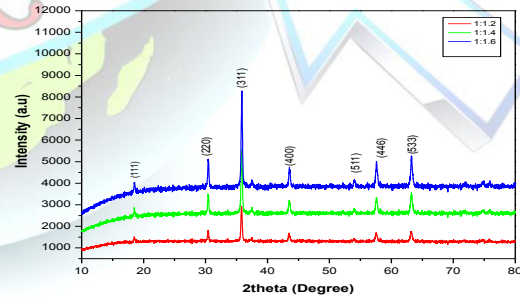

Fig. 2 Structural analysis of cobalt ferrite nanoparticle with different MN:CA ratio

TABLE 1: MICROSTRUCTURAL PARAMETERS OF COBALT FERRITE NANOPARTICLES

MN:CA	2theta (deg.)	Lattice constants (A°)	Grain Size (nm)	Dislocation Density (10^{14}m)	Microstrain (10^{-6}m)
1:1.4	36.024	8.314	47	44.46	0.02466
1:1.6	36.095	8.306	65	185.16	0.0185
1:6.8	36.16	8.302	104	112.22	0.0122

MN:CA	a (A°)	cell volume ($x10^{-28}$m)	tetrahedral ion radii (r_A) ($x10^{-11}$m)	octahedral ion radii (r_B) ($x10^{-11}$m)
1:2	8.26	5.747	4.501	7.286
1:3	8.25	5.731	4.484	7.266
1:4	8.23	5.722	4.474	7.255

MN:CA	L_A (Å)	L_B(Å)	A-O (Å)	B-O (Å)	X-ray density ($x10^{-21}$m)
1:2	3.117	2.939	1.800	2.078	9.076
1:3	3.114	2.936	1.798	2.076	9.102
1:4	3.113	2.935	1.797	2.075	9.116

Micro structural parameters of cobalt ferrite nanoparticles are shown in the Table 1. It is noted that the grain size increase from 65 to 104 nmasthe ratio of MN:CA increases from 1:1.4 to 1:1.8 . The variation in the dislocation density and the strain reflect the same. The lattice constant was found to decrease from 8.314 to 8.302 A° when MN: CA increases from 1:1.4 to 1:1.8 which is close to 8.373Å, the value for bulk. The calculated volume of the cell is less compared to the bulk value (590.99A°) is attributed to the nano sizing effect in cobalt ferrite [18] X-ray density found to be increases with decrease in the lattice constant and similar type of observations are noted for Mg-Zn ferrite system prepared at different molar concentrations [19]. Also the value of the X-ray density is higher than their bulk value is due to the formation of pores during the synthesis process and due to the ionic radii [20]. The mean ionic radius of tetrahedral site A (r_A) is found to decrease slowly with the

octahedral site B (r_B). This type of observations is noted by other investigators for their Co-Zn system [21].The hopping length L_A and L_B increases gradually with the composition and the bond length A-O and B-O were found to decrease which reflects the decrease in lattice constant.

B. Functional Group Analysis

In the present study 0.3M Cobalt Nitrate, 0.3M Ferric Nitrate and 0.4M Citric acid is used to prepare cobalt ferrite nanoparticle by sol-gel technique, by taking different composition of FT-IR spectra of $CoFe_2O_4$ nanoparticles are shown in figure 3. It is noted that the characteristic higher frequency band corresponding to the vibration of bond between oxygen and tetrahedral metal ion $M_{tetra \leftrightarrow O}$ is observed at 562cm^{-1} and however the characteristic lower band corresponding to the vibration of bond between oxygen and $M_{octa \leftrightarrow O}$. ion to be found at 374 cm^{-1}is not observed [22].The peak observed at around 1637 cm^{-1} corresponds to H-OH bending of water molecule which confirms the water compound of cobalt and ion nitrate hexahydrate left in the system. The broad band observed at 3446cm^{-1}corresponds to the stretching vibrations of free and absorbed water on the surface of the nanoparticle [23] is found around the peak at 1050 cm^{-1}
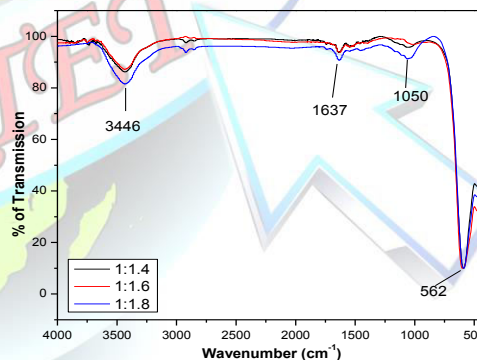

Fig. 3: Functional group analysis of cobalt ferrite nanoparticle with different MN:CA ratio

C. Morphoogical Analysis

The scanning electron microscopic images of the synthesized samples are shown in figure 4. It is evident that the SEM images show uniform distribution of grain with agglomeration in the nanometric region confirming the crystalline nature of the particle. It is also noted that at higher MN to CA ratio, pores are noted which is due to the gas evolved during the synthesis process at higher temperature.
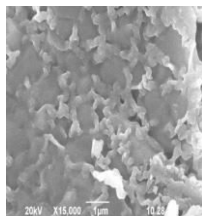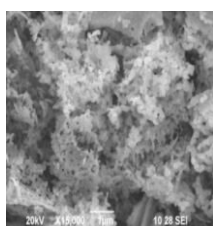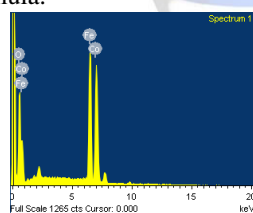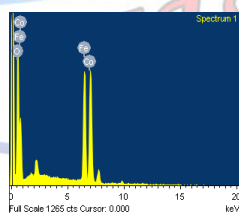
(b)CA:MN=1:1.4
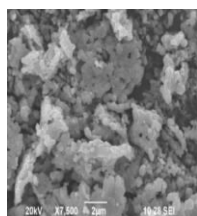
(b)CA:MN: 1:1.6

(c)CA:MN: 1:1.8

Fig. 4: Morphological analysis of cobalt ferrite nanoparticle with different MN:CA ratio
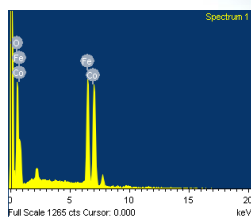
D. Compositional Analysis

Figure 4 shows compositional analysis by Energy dispersive X-ray spectroscopic (EDS) analysis. The analysis indicates the synthesized sample is $CoFe_2O_4$ without any impurities and the atomic ratio of Co:Fe:O is close to that of $CoFe_2O_4$ formula.

(a) CA:MN: 1:1.4

(b) CA:MN: 1:1.6

(b) CA:MN: 1:1.8

Fig. 5: Compositional analysis of cobalt ferrite nanoparticle with different MN:CA ratio

TABLE 2: COMPOSITIONAL ANALYSIS OF COBALT FERRITE NANOPARTICLE

Composition	Atomic Percentage Weight %		
	O (K)	Fe (K)	Co (K)
1:1.4	49.44	26.03	24.54
1:1.6	60.44	18.99	20.56
1:1.8	57.11	21.65	21.24

IV. CONCLUSION

Cobalt ferrite nanoparticles are synthesized by sol-gel technique using MN: CA in the ratio of 1:1.4, 1:1.6 and 1.1:8. The prepared samples show cubic ferrite phase with the planes matching with the JCPDS dada. Microstructural analysis shows the grain size increases from 47 to 104nm when the MN:CA ratio increases from 1:1.4 to 1:1.8. The decrease in the lattice constant and volume of the cell from 8.314 to 8.302 Å and 5.747 to 5.722 Å reflects the nanosizing effect due to the synthesis process. The increase in the X-ray density from 9.076×10^{-21} to $9.116 \times 10^{-21} g/m^3$ is higher than the bulk cobalt ferrite, is attributed to the formation of pores during the synthesis process and ionic radii. Compositional analyses indicates the impurity free $CoFe_2O_4$ and the atomic ratio of Co:Fe:O is close to that of $CoFe_2O_4$ formula. SEM analysis shows higher the MN to CA ratio, pores are noted which is due to the gas evolved during the synthesis process at higher temperature.

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