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Structural and Electrical Properties of Cobalt Ferrite Nanoparticles

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Abstract*—Cobalt ferrite nano-powders were obtained by sol-gel auto-combustion method using citric acid as a fuel. The metal nitrate to citric acid ratio was taken as 1:3. The as prepared powder of cobalt ferrite nanoparticles is annealed at 550^{0}C for 4 hrs and the same powder was used for characterization and investigations of structural and electrical properties.The structural characterization of cobalt ferrite nanoparticles were done by X-ray diffraction technique. Micro-structural and morphological studies were carried out by scanning electron microscope technique and energy dispersive spectrum. The average crystallite size obtained by Scherrer's formula is of the order of 34 nm. The grain size and specific surface area of the cobalt ferrite nanoparticles is 34 nm and 55 respectively. The lattice constant determined from XRD data is in the reported range (8.3783 A.U.). The porosity estimated from X- ray density and bulk density shows large value of the order of 47 %. The D.C electrical resistivity was investigated from room temperature to 850 K using two probe technique. The variation of dc electrical resistivity with temperature is explained in this work.

Keywords*— Cobalt ferrite, Nanoparticles, Sol-gel auto-combustion.

I. INTRODUCTION

Ferrites with spinel structure represent the important class of magnetic materials. The combination of magnetic and electrical properties makes ferrite useful in many technological applications. The basic electrical and magnetic properties of ferrite can be modified so as to suit the desire application. The modification in the properties of ferrite can be brought by various ways. One of the important way of modification of properties is to use different synthesis methods by optimizing the synthesis parameters. A number of chemical routes have been used for the synthesis of ferrite nanoparticles. These methods includes sol-gel [1], micro emulsion [2], chemical co-precipitation [3] etc. Among these methods sol-gel method is widely used for the synthesis of nanoparticles of ferrite. The size and the properties of spinel ferrite nanoparticles can be greatly depends on pH, fuel, stirring time and speed, metal nitrates to fuel ratio etc. preparative parameters [4]. The most remarkable size dependent properties of magnetic material is an increase in electrical resistivity, saturation magnetization, coercivity etc. as compared to bulk material as the particle size reduces to nanoscale [5]

Ferrites are ferrimagnetic oxides consisting of ferric oxide and metal oxides. On the basis of crystal structure ferrites are grouped into three classes namely hexagonal ferrite, garnet and spinel ferrite. The spinel ferrites are widely studied because of their numerous applications in several fields.

The spinel ferrite is having the chemical formula MFe_2O_4 (where M- is a divalent metal ions such as Co, Ni, Mn etc.) and possess two sub-lattice namely tetrahedral A and octahedral B sites. The cations of different valence can accommodate in the interstitial sites of spinel ferrites bringing wide variation in the electrical and magnetic properties. The spinel ferrites are very much important magnetic materials due to their combined electrical and magnetic properties. In bulk form spinel ferrite has been investigated for their structural, electrical and magnetic properties by several researchers [6,7].

In the last ten years research on nano-size spinel ferrite has been considerably increased due to their superior properties and applications in new fields like magnetic drug delivery, catalyst, sensors etc [8]. Extensive work on structural and magnetic characterization of spinel ferrite in the form of nano-size has been done by many workers [9, 10]. Among the different spinel ferrites cobalt ferrite ($CoFe_2O_4$) with inverse spinel structure are promising magnetic materials because of their moderate saturation magnetization, high electrical properties, high magneto-crystalline anisotropy, good mechanical properties and chemical stability [5]. In the literature synthesis and investigation of magnetic properties of spinel cobalt ferrite nanoparticles have been carried out by several workers [11, 12]. The large number of researchers has reported magnetic properties of cobalt ferrite nanoparticles with a view to understand magnetism at nano scale and their possible practical applications. However, very less attention has been paid to study the electrical properties of cobalt ferrite nanoparticles. The investigations of electrical properties of cobalt ferrite nanoparticles are important from the point of view of its use in electrical and electronic applications.

The aim of the present work is to synthesize cobalt ferrite nanoparticles by sol-gel auto-combustion method and to investigate the structural and electrical properties. The sol-gel auto-combustion method requires low temperature and less time, produces homogenous particles of uniform size. The porosity of the spinel ferrite produced by sol-gel auto-combustion method is high which leads to increases in the resistivity. To our best of knowledge, systematic investigations of structural and electrical properties of cobalt ferrite nano-particle prepared by sol gel auto combustion technique is not presented in the literature.

In the present work, we report the structural and electrical properties of cobalt ferrite (CoFe2O4) nanoparticles.

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II. EXPERIMENTAL TECHNIQUE

All the reagents used for the synthesis of cobalt ferrite nanoparticles were analytical grade and used as received without further purification. The stoichiometric amounts of cobalt ferrite $Co(No_3)_2.6H_2O$ (6.2021 g) and ferric nitrate $(Fe(NO_3)_3.9H_2O)$ (17.2191 g) were dissolved in deionized water under magnetic stirring. Then citric acid $(C_6H_8O_7.H_2O)$ (13.4347 g) was mixed in the metal nitrate solution to chalet Co^{2+} and Fe^{3+} ions in the solution. The molar ratio of citric acid to total moles of nitrates was maintained at 1:3. A small amount of ammonia was added drop-wise into the solution to adjust pH value to about 7 and stabilize the nitrate-citrate solution. The neutralities solution was evaporated to dryness by heating at 90^0C on a hot plate with continuous stirring until it becomes viscous and finally formed a very viscous gel. The temperature is further raised up to 120^0C so that the ignition of the gel starts. The dried gel burnt completely in a self propagating combustion manner to form a lose powder. Finally the as burnt powders were annealed at temperature 550^0C for 4 hrs with a heating rate of 50^0C per minute to obtain the spinel phase.

. The structural characterization was carried out by the X-ray diffraction. XRD data were taken at room temperature using Cu-Kα (λ= 1.5406Å). Scanning electron micrograph and energy dispersive spectrum were carried

D.C. electrical resistivity was measured by two probe method. A small constant voltage was applied across the sample and the current through the sample was measured with respect to temperature. Temperature of the sample in the form of pellet was measured with chromel-alumel thermocouple.

III. RESULTS AND DISCUSSIONS

A. Structural Properties

Figure 1 shows the powder X-ray diffraction pattern (XRD) of cobalt ferrite nano-particles. A careful examination of XRD pattern reveals the appearance of slightly broader peaks signifying the low crystallite size of the prepared samples. All the peak belongs to cubic spinel structure and the analysis of XRD pattern prove the formation of single phase samples. The average crystallite size was calculated using the Scherrer's formula [13] from the broadening of XRD peak corresponding to most intense (311) peak of the XRD pattern. The crystallite size obtained from XRD data is 27 nm. The lattice constant 'a' was calculated using the relation

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} \qquad (1)$$

where h, k, l are the Miller indices of the crystal planes and d_{hkl} is the inter planer spacing. The lattice constant obtained from XRD data is in reported range.

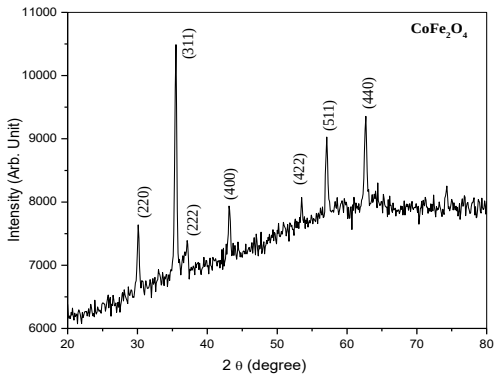

Fig.1 X-ray diffraction pattern for $CoFe_2O_4$ nanoparticles.

The X-ray density (d_x) was calculated using the relation,

$$d_x = \frac{8M}{Na^3} \qquad (2)$$

where, M is molecular weight, N is Avogadro's number and a is the lattice constant. The X-ray density is found to be of the order of 5.2996 gm/cm^3.The bulk density of cobalt ferrite nano particles was measured from the Archimedes principle. The value of bulk density is of the order of 3.594 gm/cm^3. The percentage porosity (%P) was calculated from X-ray density and bulk density values. The porosity of cobalt ferrite nanoparticle is of the order of 47 %, which is quite greater than that of bulk $CoFe_2O_4$ [14]. The increase in porosity is due to preparation condition [15]. The values of lattice constant, unit cell volume, molecular weight, X-ray density, bulk density and porosity of cobalt ferrite nano particles are given in Table I. All the structural data of prepared cobalt ferrite nanoparticles is in reported range.

Figure. 2 depicts the scanning electron micrographs (SEM) of cobalt ferrite nano particles. It is observed from SEM image that it exhibits coral like features indicative of nano crystalline nature of the samples. Using the SEM image grain size was calculated and the average value is given in Table II.

Table. I Lattice constant (a), X-ray density (d_x),bulk density (d_{exp}),porosity (%p), particle size (T) for $CoFe_2O_4$ nanoparticles.

Parameter	a(Å)	d_x (gm/cm^3)	d_{exp} (gm/cm^3)	% P	T (nm)
Value	8.387	5.299	3.594	47	27

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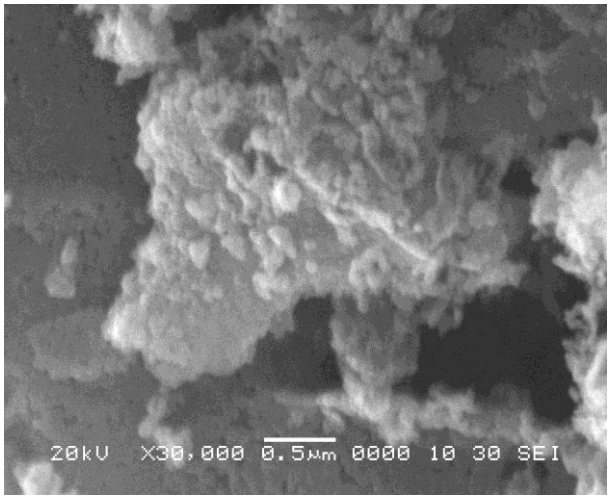

Fig.2.Scanning electron micrograph of $CoFe_2O_4$.

Table: II
Grain Size (G), Specific surface area (S), percentage of cobalt (Co), ferric (Fe) and oxygen (O) of cobalt ferrite nanoparticles obatained from SEM and EDS

Sr. No.	Parameter	Value
1	Grain size(G)	34 nm
2	Surface area (S)	55 m^2/g
3	Co	28.67%
4	Fe	57.34%
5	O	13.99%

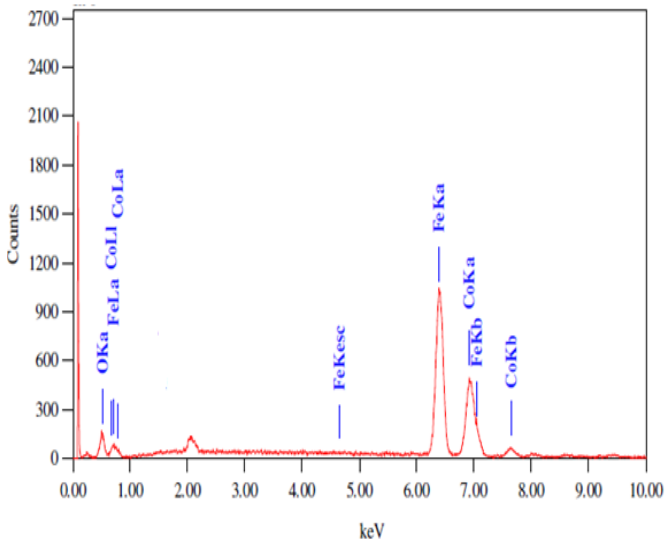

Fig.3. EDS Spectrum of CoFe2O4 nanoparticles.

The EDS spectrum of the cobalt ferrite sample is shown in figure 3. It is evident from the Fig.3 that Co: Fe ratio is 1:2 indicating that the stoichiometric proportion is maintained. Table II shows the composition of cobalt ferrite observed by the EDS spectrum.

B. Electrical Properties

The electrical behavior of cobalt ferrite nanoparticles was studied by measuring dc resistivity as a function of temperature using two probe technique. Temperature variation of dc resistivity is shown in Fig. 4 It is evident from figure 4 that the plot of log ρ versus 1000/T exhibit the similar nature to that of bulk cobalt ferrite. It can be further observed from Fig.4 that resistivity decreases with increase in temperature indicating the semiconducting nature of the samples and obeys the Arrhenius relation

$$\rho = \rho_0 e^{\left(\Delta E / kT\right)} \quad (3)$$

where, ρ_0 is resistivity at room temperature, k is the Boltzman constant (8.617×10^{-5} eV K^{-1}), ΔE is the activation energy and T is the absolute temperature.

The resistivity plot shows two regions high temperature region (ferrimagnetic) and low temperature region (paramagnetic) separated at a particular temperature which may correspond to Curie temperature of cobalt ferrite. A change in slope is contributed to change in conduction mechanism or phase transition from ferrimagnetic to paramagnetic. The conduction mechanism can be explained on the basis of Verwey model [16]. According to Verwey, the conduction mechanism in ferrite occurs mainly due to hopping of Fe^{2+} and Fe^{3+} ions in the octahedral [B] site.

It is well known that hopping probability depends upon the separation between ions and the activation energy. The activation energy can be determined from slope of the linear plots of dc electrical resistivity (Fig. 4) and the Arrhenius relation [Eq. 3]. The calculated values of activation energy is of the order of 0.172 eV. The activation energy of material is associated with mobility of charge carrier. The charge carriers are located with ions or vacant site and conduction takes place through hopping process.

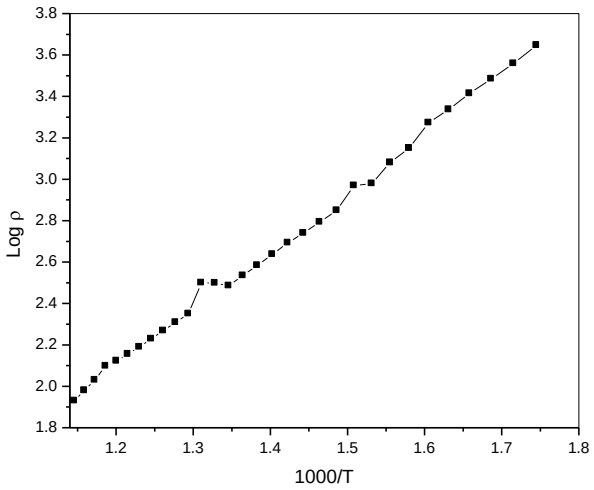

Fig.4. Temperature variation of dc resistivity of nanocrystalline cobalt ferrite

IV. CONCLUSIONS

On the basis of experimental results we can conclude the following :

- Cobalt ferrite nanoparticles have been successfully synthesized at a sufficiently low temperature by sol gel auto combustion technique.
- The single phase nature of the samples (CoFe2O4) was confirmed from X-ray diffraction data.

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- The particle size was calculated from the most intense peak (311) using Schrerrer formula and is in the range of 27 nm.
- The structural data of the present cobalt ferrite is in the reported range, EDS spectrum reveals the presence of Co2+, Fe3+ and O2- ions in proper proportions.
- The D.C. electrical resistivity decreases with increase in temperature obeying Arrhenius plot.
- The activation energy calculated from D.C electrical resistivity versus temperature is of the order of 0.172 eV.

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