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Synthesis and Microstructural Characterization of Pure Cobalt Ferrite for D.C. Electrical Study

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Abstract—*Cobalt ferrite ($CoFe_2O_4$) is a well-known magnetic material with high coercivity and moderate magnetization. It possesses excellent chemical stability and good mechanical hardness. It is a promising candidate for sensors and actuators application, dynamic sealing, magnetic drug targeting, electronic devices and has a vast scope in materials research for technological applications. Cobalt ferrite nanoparticles at ambient temperature were effectively synthesized via a simple co-precipitation process. The crystal structure and morphology of the sample was determined by XRD and SEM. The XRD spectrum confirms that the synthesized nanoparticles are formed with the ideal spinel structure. The average crystallite size was determined using the Modified Scherrer (54nm) and Williamson-Hall methods (49nm). SEM observation showed that the $CoFe_2O_4$ nanoparticles are aggregated in near spherical structures. The bonding and optical properties were characterized by FTIR and UV–Vis spectroscopy. Compared to other absorption bands reported in literature, this material shows a very wide absorption band between 350 and 600 cm-1 wavenumber in FTIR test. More than one peak is observed in UV-Vis spectrum with calculated direct band gaps of 4.1 eV and 4.9 eV. This is again at variance with other reports in literature. These anomalous results indicate that while the phase structure is ideal spinel, the coordination of cations in the unit cell may be different here. Electrical DC conductivity was studied for cobalt ferrite nanoparticles against temperature, which again showed some interesting results different from those reported in literature. This combination of anomalous properties in a perfectly spinel phase of this ferrite needs a deeper analysis of structure and properties of cobalt ferrites in general against the methods of synthesis.*

Keywords: *Cobalt ferrite; magnetic nanoparticles; dc electrical study; spinel structure.*

1. INTRODUCTION

Magnetic ferrites with spinel structure have acquired the attention of the global market and many researchers due to their fascinating and strikingly unusual electromagnetic properties. Their ease of preparation and the stability under varied conditions have signified their use in the technological industry. The changes that are brought about in the physical, chemical, electrical and magnetic properties by altering particle size have inspired many researchers around the world to fabricate these materials with new properties. The magnetic, electrical and magneto-optical properties of the pure and doped cobalt ferrites have embarked them to be the most widely used ferrite systems in the fabrication of magnetic recording devices and magnetic fluids. Among the different spinel ferrites, cobalt ferrite ($CoFe_2O_4$) with inverse spinel structure are most suitable magnetic materials because of their high magneto-crystalline anisotropy, moderate saturation magnetization, high curie temperature, good electrical properties, good mechanical properties and chemical stability [1-5]. All these properties and features of cobalt ferrite make it a suitable material for sensors and actuators, shaft seal, spacecraft propulsion, electronic devices, data storage, magnetic drug targeting, biosensors, and magnetic refrigeration, materials research, optics, art and make an exceptionally good core material for power transformers in electrical and electronic industry, recording heads, antenna rods, loading coils and telecommunication applications. [6-12]

Interpretation of the measurements of ferrites to the nanometer scale can be accomplished through a wide mixed range of techniques, both physical and chemical. The physical techniques are "top-down" systems in which powders of bulk precursor materials (of high purity) are changed into nano-crystalline ferrites by a mechanical, mechano-chemical or laser assisted process. Conversely, solution-based chemical techniques are "bottom-up" systems where nanoparticles are synthesized via chemical reactions between sub-nanometer reactive species, such as atoms or molecules. [9-11]

Although the physical methods are simple and versatile, enabling the preparation of a wide variety of ferrite nanopowders in large quantities and with a relatively low cost, their reliability is often questionable due to the contamination of the products (especially in the mechanical milling processes) and the limited control of the morphology of the resulting nanosized materials. The wet chemical synthetic routes have proven to be much more advantageous for the preparation of transition metal ferrites than the physical methods since they provide a better control over the size, size distribution, shape, and degree of aggregation of the nanocrystals formed. The chemical co-precipitation is the most widely used method due to its high yield and simplicity in producing ultrafine magnetic nanocrystals. [12-15]

Ferrites are mixed oxides with general formula AB_2O_4, where A is a metal ion of divalent nature and B is the trivalent ferric ion. They have a spinel-type structure similar to that of the mineral "spinel", $MgAl_2O_4$. In a typical spinel lattice, the voluminous oxide ions (r_o^{2-} =124 pm) adopt a cubic close-packed arrangement, thereby forming two different types of sites, *i.e.*, tetrahedral (A) and octahedral (B).

2. EXPERIMENTAL METHOD

2.1 Materials

All the materials used were of reagent grade and were further used without purification. Double distilled, de-ionized water was used as solvent. Ferric nitrate ($Fe\ (NO_3)_3.9H_2O$, >98% pure), cobalt nitrate ($Co\ (NO_3)_2.6H_2O$, >99% pure) and ammonia solution (25% w/v) of HPLC grade were used. Oleic acid of HPLC grade was used as a surfactant.

2.2 Procedure

Equal volumes of 2M ferric nitrate solution and 1M cobalt nitrate solution were prepared in double distilled, de-ionized water and stirred after mixing, on a magnetic stirrer for fifteen minutes. To avoid the production of impurities, the metal salts solution was prepared in de-ionized distilled water. 4M ammonia solution was prepared and slowly added to the above salt solution drop wise. The pH of the solution was constantly monitored as the ammonia solution was added. The above contents were constantly stirred using a magnetic stirrer until a pH level of 9-10 was reached. A pre-calculated fixed quantity of oleic acid was added to the solution as a surfactant and coating material. The liquid precipitate was then heated to a temperature of 80ºC and stirred for one hour. The product was then cooled to room temperature. To get particles free from ammonia, nitrogen or salt compounds, the precipitate was then washed twice with distilled water and then to remove the excess surfactant from the solution it was washed with ethanol. To separate the supernatant liquid, the beaker contents were then centrifuged for twenty minutes at 5000 rpm. The supernatant liquid was removed, and the remaining contents were centrifuged again till thick black precipitate was left. The precipitate was then dried overnight at 70 ºC. The acquired sample was then ground into a fine powder and annealed at 1000 ºC for four hours.

3. CHARACTERIZATION RESULTS

3.1 XRD Analysis

The X-Ray Diffraction (XRD) of the sample was performed using X-Ray Diffractometer (RIGAKU SMART LAB) with monochromatic Cu-K_α, radiations of wavelength 1.5418 Å at 40 KV and 30 mA. For the fixed composition, the synthesized cobalt ferrite powder has no extra phase. Fig. 1 shows the XRD pattern of $CoFe_2O_4$. These patterns confirm the formation of cubic spinel lattice (space group Fd-3m) which matches well with JCPDS No. 22-1086. [16]

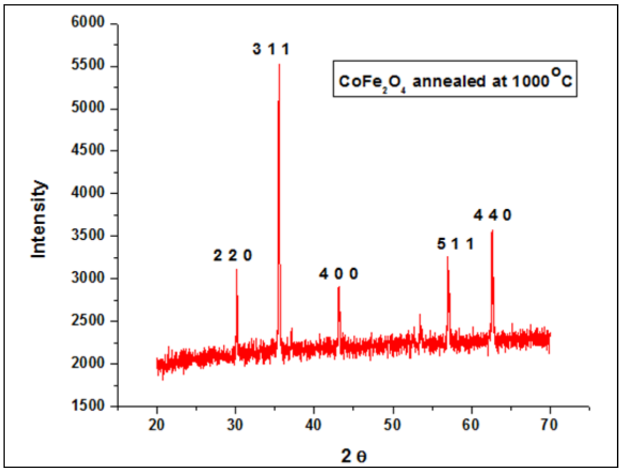

Fig. 1: XRD of $CoFe_2O_4$

The Modified Scherrer (Fig. 2) and Williamson-Hall (Fig. 3) plots were also drawn and average crystallite sizes as calculated were 54 nm and 49 nm, respectively with a lattice strain of 0.00111 in the latter case.

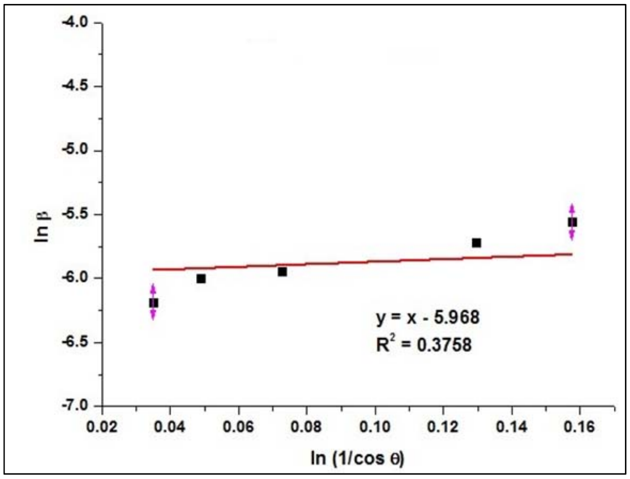

Fig. 2: Modified Scherrer plot of $CoFe_2O_4$

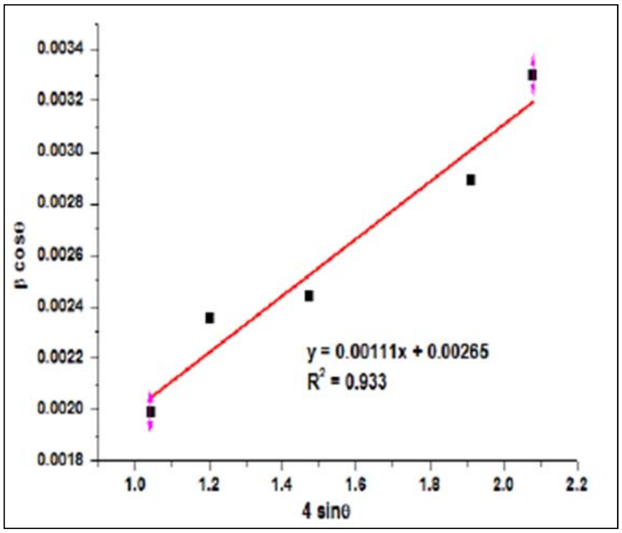

Fig. 3: Williamson-Hall plot of $CoFe_2O_4$

3.2 SEM Analysis

The microstructure of prepared sample was evaluated using JSM-6010PLUS_LA with accelerating voltage from 0.5-20 kV. Typical SEM image of the $CoFe_2O_4$ sample annealed at 1000°C for 4 hours is shown in Fig. 4. The image shows that the particles have almost uniform distribution and some of them are in agglomerated form. It can be seen that there is no sign of contamination in the samples. The particles are almost spherical in shape and agglomeration may be attributed to the magnetic nature of the particles.

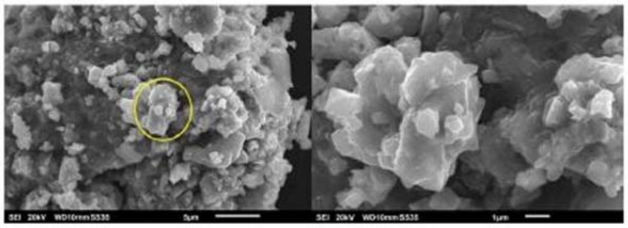

Fig. 4 SEM image of CoFe2O4 nanoparticles annealed at 1000^{0}C

3.3 FTIR Analysis

Perkin Elmer Frontier FTIR Spectrometer with KBr detector and KBr beam splitter was used for FTIR analysis. Spectrum was obtained with wave number ranging from 400 cm^{-1} to 4500 cm^{-1}. Typical FT-IR spectrum for sample annealed at 1000°C for four hours is shown in Fig. 5. The spectrum indicates the presence of absorption bands in the range of 300 to 800 cm^{-1} which is a common feature of the spinel ferrite. The higher frequency absorption band (ν_1) lies in the range of 500 to 600 cm^{-1} and is fixed for vibration of the tetrahedral metal complex which consists of a bond between the oxide ion and the tetrahedral site metal ion ($O\text{-}M_{Tet}$), while the lower frequency absorption band (ν_2) lies in the range of 400 to 490 cm^{-1} and is fixed for vibration of the octahedral metal complex which consists of a bond between the oxide ion and the octahedral site metal ion ($O\text{-}M_{Oct}$). The occurrence of higher frequency band is caused by stretching vibration within bonds between molecules/ions, while the lower frequency band is due to the bending vibration. These band positions are in good agreement with the characteristic infrared absorption bands of cobalt ferrite nanocrystals. [17]

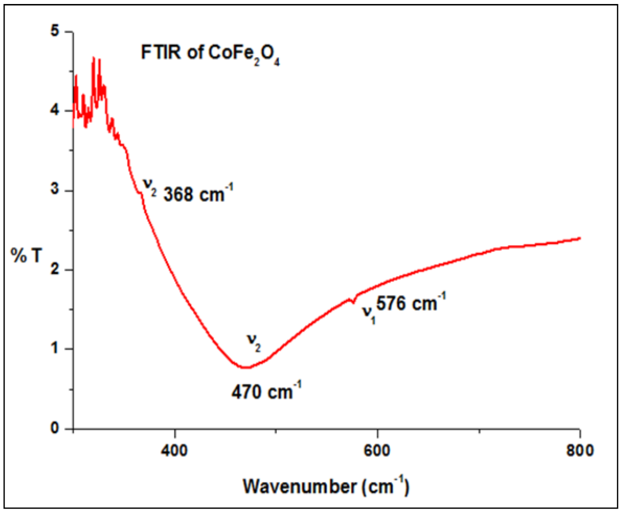

Fig. 5: FTIR spectra of $CoFe_2O_4$ sample annealed at 1000 ^oC for 4 hours

3.4 UV-Vis Analysis

The UV–visible spectrum was obtained with a Perkin Elmer spectrophotometer. UV-Visible absorption spectrum of $CoFe_2O_4$ nanoparticles is shown in Fig. 6. From Fig. it has been observed that there is a tail in the absorption spectrum of pure $CoFe_2O_4$ nanoparticles in the visible region. However, in the UV range no such tail has been observed. Further, the absorption spectroscopy plays an important role for the determination of band gap which can be calculated from Tauc's relation,

$$\alpha h\nu = A\,(h\nu - Eg)^n$$

where, E_g is the energy gap, constant A, is different for different transitions, ($h\nu$) is energy of incident photon and n is a constant value, which is equal to 2 for indirect band gap semiconducting materials. [18]

Fig. 7 shows the plot of $(\alpha h\nu)^2$ versus ($h\nu$). It has been observed from Fig. 7 that the direct band gap value for pure $CoFe_2O_4$ nanoparticles is 4.1 eV.

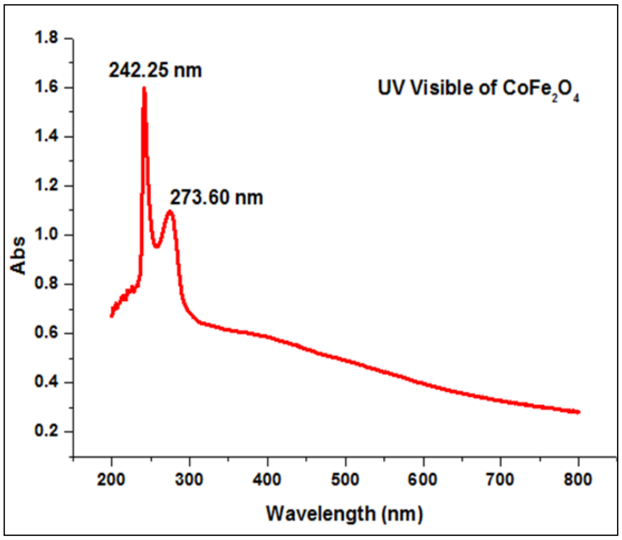

Fig. 6: UV-Vis spectrum of $CoFe_2O_4$ nanoparticles

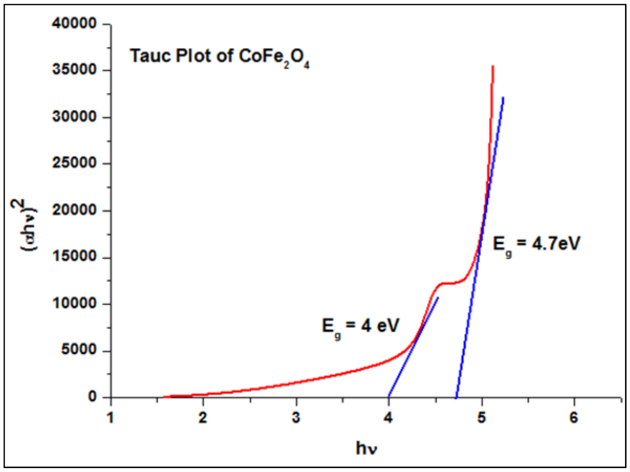

Fig. 7 Tauc plot for direct band gap of $CoFe_2O_4$ nanoparticles

Table 1 Comparison of reported band gap values [27-30]

SYNTHESIS METHOD	REPORTED BANDGAP VALUES	REFERENCE
Co-precipitation	(direct) 3.85 eV	S. Singh et al.
PLD (thin film)	(direct) 2.5 to 2.6eV	A.V.Ravindra, P. Padhan
PLD (thin film)	(direct) 1.95 eV (indirect) 1.42 eV	Himcinschi et al.
PLD (thin film)	(direct) 2.74 eV (indirect) 1.18 eV	Holinsworth et al.
Electrostatic spray (thin film)	(direct) 2.57 eV	Rajendra S. Gaikwad et al.
Solvo-thermal	(direct) 1.81 eV	Asokarajan R., Neyvasagam K., Milton Franklin Benial

4. D.C. ELECTRICAL CONDUCTIVITY OF $COFE_2O_4$

The electrical response of the sample to D.C. voltage has been investigated to identify and better understand the conduction mechanism in this material. In this experiment we measured the resistivity of cobalt ferrite sample as a function of temperature, from about 50 ºC upto about 500 ºC, using a cryostat with a heating stage. The system measures D.C. resistance at different temperatures. The sample is generally disk shaped bulk material of regular area. Silver/gold coating is performed on both sides of the disks to make contacts. DC voltage of different level is applied and output current is read simultaneously at different temperatures.

Fig. 8 reveals that D.C. conductivity increases with increase in temperature and obeys the well-known Arrhenius equation for semiconducting materials, i.e.

$$\sigma_{dc} = \sigma_o \exp(-E_{dc}/kT)$$

where σ_o is the pre-exponential factor, which depends on composition, mobility of diffusing ions, etc. and E_{dc} is the D.C. activation energy. The activation energy for the conduction mechanism / process was calculated from the slope of the straight line portion (Fig. 9). The value of activation energy is found to be E_{dc} = 0.305eV and the value of conductivity varies from 10^{-9} S/cm to 10^{-6} S/cm with increase in temperature. [19-21]

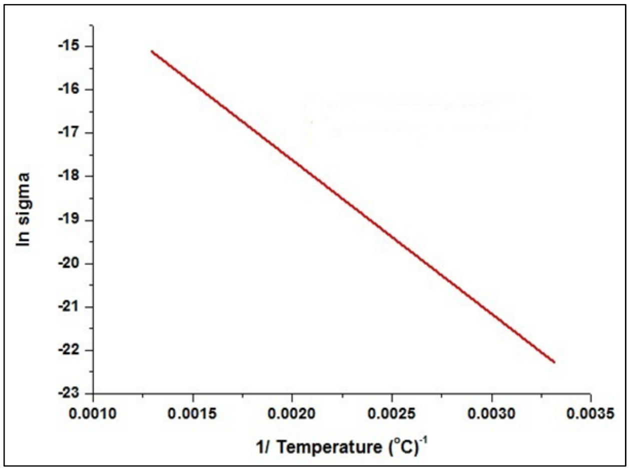

Fig. 8 DC conductivity variation with temperature of CoFe2O4 nanoparticles (linear fit)

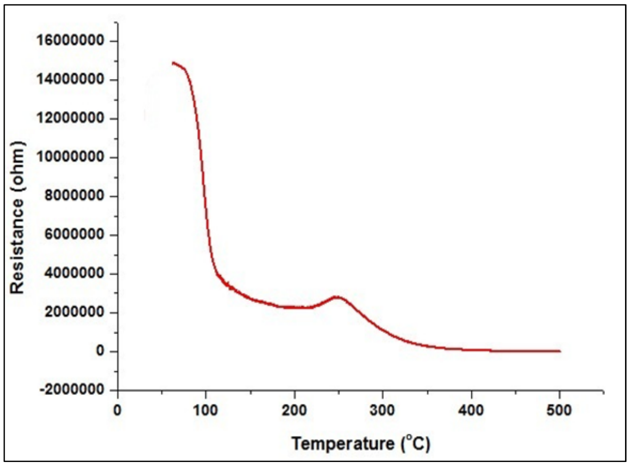

Fig. 9a Variation plot of Resistance vs. Temperature

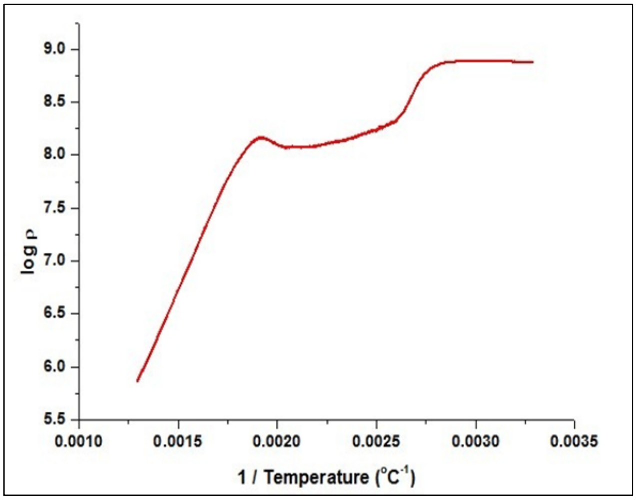

Fig. 9b Variation plot of Log ρ vs. Temperature

Cobalt ferrites are known to be semiconducting material, and this is confirmed by the increasing of conductivity with temperature for the tested sample (Fig. 8). Charge carrier in cobalt ferrites can be Co^{2+}, Co^{3+}, Fe^{2+}, Fe^{3+} and may all occupy octahedral sites. The electrical conductivity in ferrites can be explained on the basis of exchange of electrons between ions of the same element that are present in more than one valence state distributed randomly over equivalent crystallographic lattice sites [22]. It is well known that the change in slope is attributed to the Curie temperature or to a change in the conduction mechanism [23-25]. At the Curie temperature, the samples transform from an ordered ferrimagnetic state to a disordered paramagnetic state with a marked increase in conductivity. The observed break at 520K may be due to a phase transition from ferrimagnetic to paramagnetic nature. [26]

5. CONCLUSION

Cobalt ferrite nanoparticles were successfully synthesized via chemical co-precipitation method at ambient temperature. The XRD confirms that the highest intensity peak was at $2\Theta = 35.48^0$, which corresponds to the reflection plane (3 1 1). The average particle sizes calculated by the Scherrer and Williamson-Hall methods are 54 nm and 49 nm respectively. SEM results reveal that particles have agglomerated in near spherical structures and agglomeration may be attributed to the magnetic nature of the particles. FTIR studies for cobalt ferrite nanoparticles show a very wide absorption band between 350 and 600 cm^{-1}. ν_1 (vibration of the tetrahedral metal complex) lies in the range of 500 to 600 cm^{-1}, while ν_2 (vibration of the octahedral metal complex) lies in the range of 400 to 490 cm^{-1}. More than one peak is observed in UV-Vis spectrum with calculated direct band gaps of 4.1 and 4.9 eV. These anomalous results indicate that while the phase structure is ideal spinel; the coordination of cations, grain size and synthesis method can all affect the band gap. Finally, the electrical DC resistivity study showed a decrease in value with increasing temperature thereby proving its semiconducting nature. It is also observed that the cobalt ferrite nanoparticles undergo a phase transition around 520 K, corresponding to its curie temperature.

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7. COMPLIANCE WITH ETHICAL STANDARDS

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Conflict of Interest.

The authors declare that they have no conflict of interest.

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