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Synthesis and Characterization of $CoFe_2O_4$ Magnetic Nanoparticles using Sol-Gel Method

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Abstract: In this present work, synthesis and characterization of soft $CoFe_2O_4$ magnetic nanoparticles have been synthesized using sol-gel method. The prepared nanoparticles were characterized by using XRD, SEM, FT-IR, etc. Using XRD, it is confirmed that the samples were cubic structure in nature and the mean crystallite size were 28.41 nm and 14.64 nm respectively. The Morphology and the quantitative analysis of the prepared particles were studied by using SEM and EDS spectrum. The FTIR was used to study the presence of functional groups. Finally, the magnetic properties of the powders have been studied at room temperature from the hysteresis loop measurements using a vibrating sample magnetometer (VSM). From this analysis, the values of the saturation magnetization increase and the coercive field of $CoFe_2O_4$ nanoparticles were found to decrease with increasing degree of Fe substitution.

Keywords: Nanoparticles, Magnetic Properties, Vibrating Sample Magnetometer, FT-IR, Sol gel.

Introduction:

Cobalt ferrites have been the subject of research interest due to its high saturation magnetization and coercivity [1]. The synthesis of magnetic nanoparticles has been intensively developed not only for its great fundamental scientific interest but also for many technological applications in biology, such as extraction of genomic DNA [2]. The excellent magnetic properties of the cobalt ferrite are known to be mainly attributed to the Co ions in a spinal lattice [3]. Shape, or crystalline anisotropy [4], composition [5], coordination [6], density [7], exchange interaction [8], phase or structure [9], Surface effects [10], spin-orbit coupling [11], such as hydrothermal [12], Co precipitation [13], Micro emulsion [14], Forced hydrolysis [15], reduction–oxidation route [16] and sol-gel method. Various synthesis techniques for cobalt ferrites, such as sol–gel [17]. As well known, sol–gel is a simple way to produce ultra fine powders due to their simple synthesis equipment and process [18,19]. Cobalt ferrite materials are known to exhibit very high cubic magneto crystalline anisotropy [20]. Since Co ferrite require higher annealing temperatures (700 °C) [21]. Also, there are some calculations of itinerant ferromagnetism and half-metallicity [22]. The room temperature magnetization in a ±10kOe magnetic field was found to be less than one quarter of that of the bulk material [23]. Many synthetic methods to prepare highly crystalline and uniformly sized magnetic nanoparticles of cobalt ferrite have been reported [24]. A peculiar characteristic of this method is that the heat required to sustain the chemical reaction is provided by the reaction itself and not by an external source [25]. In order to see the role of different synthesis techniques on the growth, structural morphology and magnetic properties of Co-ferrite. Recently, $CoFe_2O_4$ nanocrystals were prepared by sol-gel method using nitrates as metal precursors. As a pH-controller, ethylene glycol as a polymerizing agent [26,27]. In this paper, we report an acetic acid-assisted, sol-gel route using NH_3 as a pH-controller to prepare pure and doped $CoFe_2O_4$ nanoparticles. In this study, the growth of Co ferrite magnetic materials on introduced by a sol-gel method and there are characterized by using an x-ray diffractometer (XRD), a vibrating sample magnetometer (VSM) and as a function of the annealing temperature. Magnetic and structural properties of $CoFe_2O_4$ magnetic materials prepared by the sol-gel method will be presented in this article.

Experimental detail:

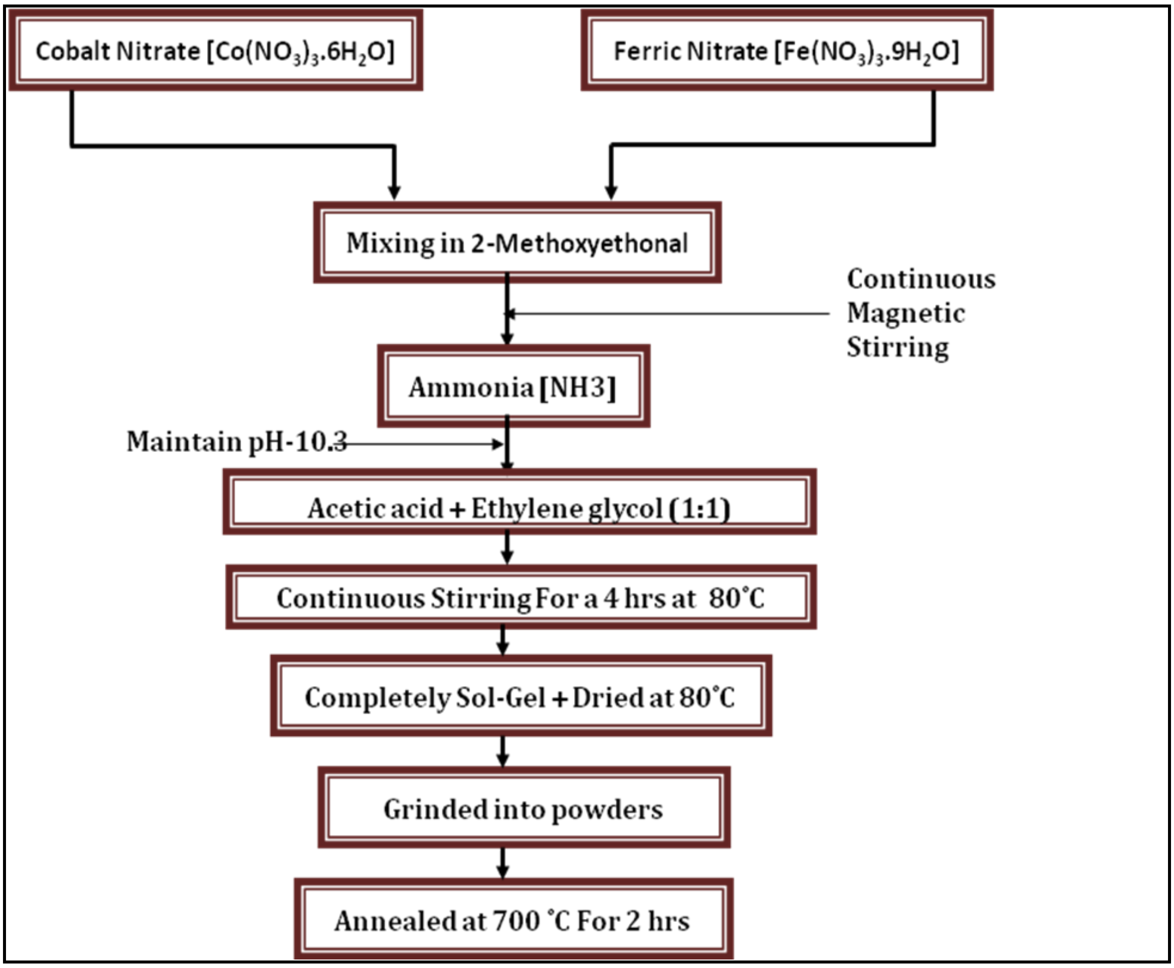
Materials

Cobalt Nitrate $Co(NO_3)_3.6H_2O$ and Ferric Nitrate $Fe(NO_3)_3.9H_2O$ of analytical grade were used to prepare magnetite Nanoparticles and they were obtained from Finar chemicals corporation. The reagents were used without further purification.

Synthesis of $CoFe_2O_4$ magnetic nanoparticles:

The process for synthesizing nearly monodisperse $CoFe_2O_4$ with super paramagnetic behaviour at room temperature was carried out as follows: In a typical synthesis, Cobalt Nitrate $Co(NO_3)_3.6H_2O$ and Ferric Nitrate $Fe(NO_3)_3.9H_2O$ of Co and Mixing in 2-Methoxyethonal under constant magnetic stirring for approximately few mints. Then, NH_3 was added to the precursor solution in order to maintain the pH of the solution to 10.3. Acetic acid and ethylene glycol in 1:1 molar ratio were added to the solution. After continuous stirring For a 4 hours at 80°C, the clear sol was completely turned to a gel. Then, the gel was dried and grinded into powders. After that, the powder was annealed at 700°C for 2 hrs in furnace under air atmosphere. Finally, magnetic nanoparticles in different size were synthesized, as shown in the below flow chart.

Flow chart for the Sol-Gel method to prepare $CoFe_2O_4$ Magnetic Nanoparticles:



Result and discussion:

A. XRD:

Figure (1) shows the XRD patterns of the $CoFe_2O_4$ nanocrystals obtained at 700°C temperature. The synthesized material structure corresponds with the cubic structure of $CoFe_2O_4$ [JCPDS card No: 22-1086]. The crystalline peaks (2 2 0), (3 1 1), (2 2 2), (4 0 0), and (5 3 1), indexed as cubic $CoFe_2O_4$ [Fd_3m, a=8.391Å]. The crystallite size of the nanoparticles is calculated by Debye-Scherrer formula [28]**:**

$$D = K\lambda / \beta\cos\theta$$

Where K is dimensionless shape factor, y is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) and 0 is the Bragg angle. The mean crystallite sizes of the CoFe2O4 nanoparticles synthesized at 700°C are 28.41 nm and 14.64 nm respectively.

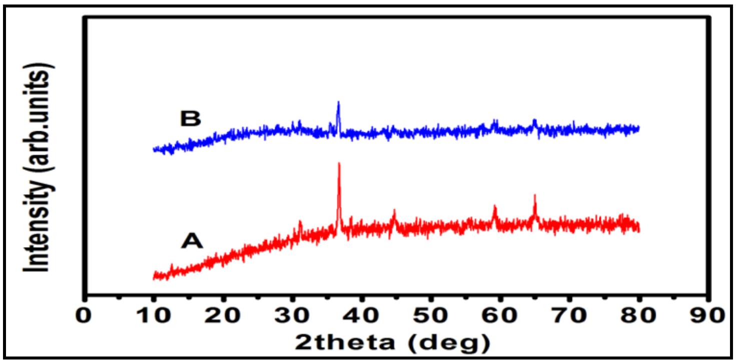


Figure.1: X-ray diffraction pattern of $CoFe_2O_4$ at 700°C annealing temperature: (A) 90+10%, (B) 80+20%

B. SEM:

Figure (2) shows the surface morphology of $CoFe_2O_4$ powder prepared by changing the molar ratio of $CoFe_2O_4$. The typical octahedral morphology is found for the cobalt ferrites calcined at 700°C for 2 hrs. As marked with reed circle in images, few particles with other morphology also are found in the calcined powder, corresponding to the unreacted phase $CoFe_2O_4$ [29].

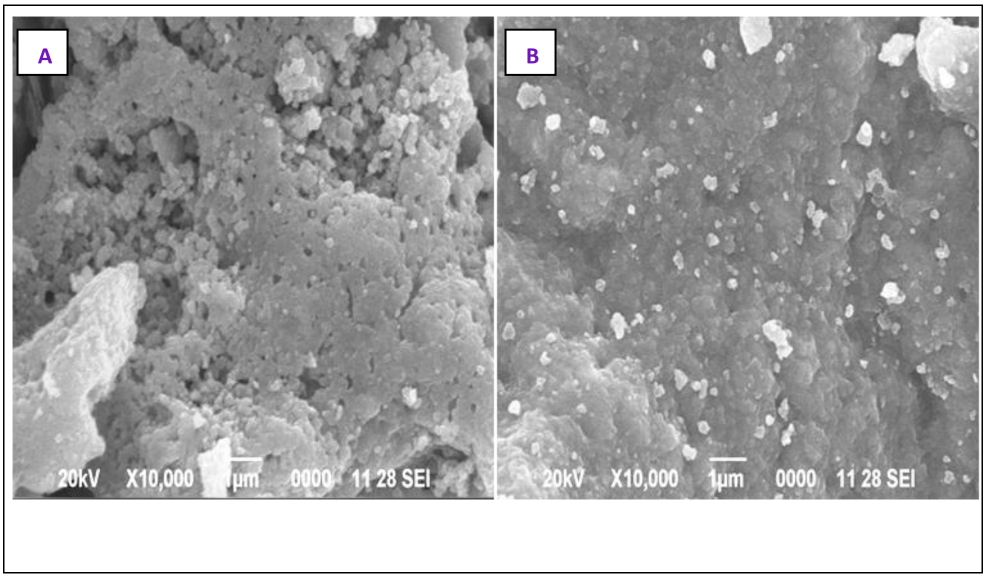


Figure.2: SEM image of the $CoFe_2O_4$ at 700°C annealing temperature: (A) 90+10%, (B) 80+20%

C. EDS:

Figure (3) Shows the Energy dispersive X-ray spectroscopic (EDS) analysis shows that there are elements of Co, Fe, and O in the sample Figure (3), and the atom ratio of Co; Fe; O is , which is close to that of

$CoFe_2O_4$ formula. All of the above analyses confirm that the synthesized sample is $CoFe_2O_4$ without any impurities.

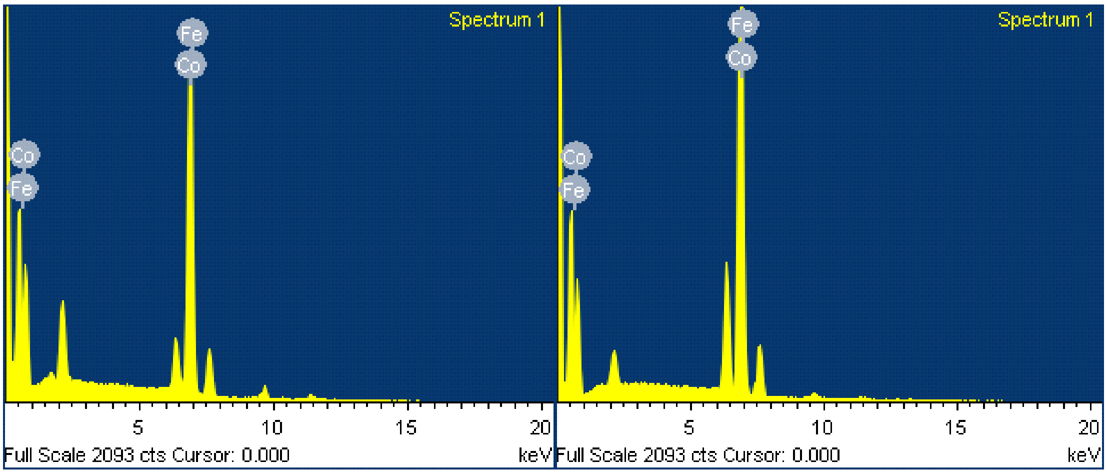


Figure.3: EDS spectra of the $CoFe_2O_4$ at 700°C annealing temperature: (A) 90+10%, (B) 80+20%

D. FT-IR:

Figure (4) Using KBR pellets the Fourier Transform Infrared Spectra of the pure and doped $CoFe_2O_4$ powder was recorded range of 4000 cm^{-1} to 400 cm^{-1} as shows is Figure-4 (a-b). The peak at 564 cm^{-1} corresponds to Fe in the tetrahedral sites while the peak at 656 cm^{-1} is due to the stretching vibration mode associated with the metal-oxygen absorption band. The large absorption band centered at 3432 cm^{-1} can be assigned to the stretches of hydroxyl groups of gallery water molecules and hydrogen-bonded hydroxyl groups in cobalt and iron hydroxide. The peaks at about 2918, 1113 cm^{-1} are due to C-H stretching, C-O bending vibrations. The appearance of a peak at broad band at 562, 654 cm^{-1} is attributed to stretching vibrations of Fe^{3+}-O^{2-} which are observed in all ferrite samples. The broad band at 3424 cm^{-1} can be assigned to vibration mode of chemically bonded hydroxyl groups. The peaks at about 2928, 1107 cm^{-1} are due to C-H stretching, C-O bending vibrations [30]. It was observed in Figure (4).

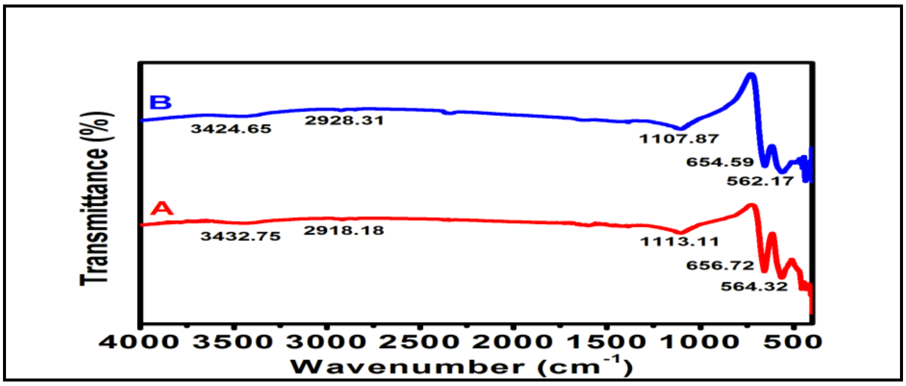


Figure.4: FTIR spectra of $CoFe_2O_4$ at 700°C annealing temperature: (A) 90+10%, (B) 80+20%

E. Magnetic Study:

Magnetic characterization of the samples was performed by VSM at room temperature with a maximum applied field of ±10kOe. Figure 5 shows the room temperature hysteresis loops of samples A and B. It can be observed that both formulations reveal typical ferromagnetic behavior. The ferromagnetic behavior of the prepared nanocrystals is clearly shown by coercivity (H_c), saturation magnetization (M_s) and remanence magnetization (M_r). The saturation magnetization is the maximum induced magnetic moment that can be obtained in a magnetic field, beyond this field no further increase in magnetization occurs. High saturation magnetization magnetic materials are required for further high-frequency inductors [31].

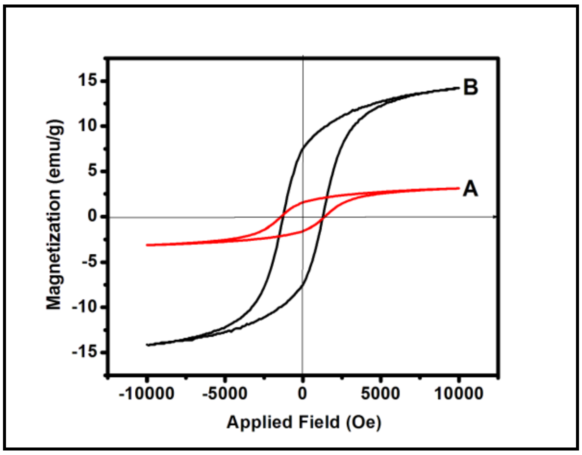


Figure.5: Room temperature hysteresis loops of $CoFe_2O_4$ at 700°C annealing temperature: (A) 90+10%, (B) 80+20%

Table I. Magnetic Parameters at Room Temperature

Preparation technique	Annealed temperature (°C)	Sample	Percentage (%)	Saturation Magnetization M_s (emu /g)	Remanence Magnetization M_R (emu /g)	Coercivity H_c (O_e)
Sol-gel	700°C	$CoFe_2O_4$-A	90+10%	3.123083	1.579333	1402.881
Sol-gel	700°C	$CoFe_2O_4$-B	80+20%	14.17865	7.512399	1273.860

From the figure 5, it is noted that sample A has low saturation magnetization value of 3.12 emu gm^{-1} with remanence magnetization and coercivity values of 1.579333 emu gm^{-1} and 1402.881 Oe, respectively. From the figure 5, it is seen that the M_s values of sample A (3.12 emu gm^{-1}) is smaller as compared to M_s values of sample B (14.18 emu gm^{-1}) at an applied field of ±10kOe at 700°C**.** These magnetic parameters are small compared to that of the bulk $CoFe_2O_4$. This decrease in the M_s value could be mainly attributed to the small particle surface effect (spin canting) that becomes more dominant as the particles are smaller. From the above table, it is confirmed that the sample B has relatively lower coercivity compared with that of sample A, which can be considered as a further improvement of the magnetic properties.

Conclusions:

$CoFe_2O_4$ nanoparticles were successfully synthesized prepared by sol-gel method combined with annealing temperature at 700°C. XRD patterns confirm the cubic structure phase presence of the prepared sample and the mean crystallite size are 28.41 nm and 14.64 nm respectively. The SEM studies showed a total coverage of substrate surface with smooth surface of typical octahedral morphologies. The EDS shows the presence of Co, Fe, and O. The prepared samples exhibit ferromagnetism nature of all samples at room temperature with clear hysteresis loops.

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