

Effect of Concentration Structural, Magnetic Properties of CoFe_2O_4



Physics

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ABSTRACT

In the present paper, we report the synthesis of cobalt ferrite (CoFe_2O_4) nanoparticles using sol-gel method. The prepared samples were annealed at 700°C for 2 hrs. The average crystallite sizes of the nanoparticles were estimated using Debye-Scherrer's equation and found to be 54.24, 57.46, 28.41, 29.62, 14.64, 26.68, 42.08, nm and 36.64 nm. SEM was used to study morphological variations and EDAX results showed that the compositional mass ratios were relevant as expected from the synthesis. FT-IR confirmed the presence of metal oxide bonds in all the calcined samples. The magnetic properties of the produced powders have been studied using vibrating sample magnetometer (VSM). The saturation magnetization and coercive field are strongly dependent on the various levels of doping concentrations. The saturation magnetization was decreased by increasing the ferrite content and increased by increasing the temperatures from 700°C .

Introduction:

In recent years, researchers have widely studied nano-size materials because of their interesting physical and chemical properties compared to their counterpart bulk materials [1]. Spinel ferrites with nanosized dimensions have drawn considerable scientific and technological interest because of their applications in high-density magnetic recording media, magnetic fluids, catalysts, gas-sensor, high-performance electromagnetic and spintronic devices, etc. [2-5]. In the literature, there are many different preparation techniques to synthesize CoFe_2O_4 nanoparticles such as co-precipitation, hydrothermal, dry and wet-milling and oxidation-reduction [6-8], micro emulsion [9], a new non-aqueous route [10], solvothermal approach [11] and sol-gel technique [12]. Recently, the sol-gel method has been preferred because of many advantages such as good stoichiometry control, short preparation time and inexpensive precursors [13]. And then, produce highly pure, homogeneous and crystalline materials with uniform densities at low processing temperatures [14, 15]. It is a unique combination of a chemical sol-gel process and a combustion process. In this paper, we report an acetic acid-assisted, sol-gel route using NH_3 as a pH-controller to prepare of the Fe doped Co nanoparticles.

In the present work, the doping effect of Fe on CoFe_2O_4 and its structural and magnetic properties have been investigated by using sol-gel method. The structural properties of as-prepared samples were characterized by using X-ray powder diffractometry (XRD). The morphological analysis has been done by using Scanning electron microscopy (SEM) and the chemical composition of the samples were investigated by Energy dispersive spectroscopy (EDAX). The presence of functional groups have been identified by using Fourier transform infrared spectroscopy (FTIR) and the effect of magnetic properties for the synthesized samples with various levels of doping concentrations were studied using vibrating sample magnetometer (VSM).

Experimental detail:

Materials

The chemical reagents used in the work were Cobalt Nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Ferric Nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. All the obtained chemicals were of analytical reagent grade and were used as received without any further purification, and the synthesis process was carried out under an ambient temperature.

Synthesis of CoFe_2O_4 magnetic nanoparticles:

The starting chemicals used in the present study were of ana-

lytical grade Cobalt Nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Ferric Nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and Mixing in 2-Methoxyethanol under constant magnetic stirring for approximately few mins. 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 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.

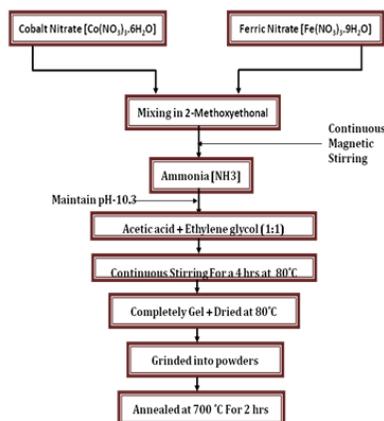


Fig.1. Flow chart showing sol-gel method in synthesis of CoFe_2O_4 Magnetic Nanoparticles

Result and discussion:

XRD studies of synthesized powders:

The XRD pattern of cobalt nanoferrite sintered at 700°C is shown in Fig.1. The miller indices (h k l) help us to identify the obtained powders. The h k l indices of the sample are [2 2 0], [3 1 1], [2 2 2], [4 0 0], and [5 3 1] confirmed the formation of spinel structured cubic cobalt nanoferrites [JCPDS file No: 22-1086]. The average crystallite size of cobalt nanoferrites of the most prominent peak [3 1 1] is calculated by using Debye-Scherrer's formula, [16].

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

Where K is dimensionless shape factor, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) and θ is the Bragg angle. The mean crystallite sizes

of the various percentages of (99+1%, 98+2%, 90+10%, 85+15%, 80+20%, 70+30%, 65+35%, 50+50%) CoFe_2O_4 nanoparticles are 54.24, 57.46, 28.41, 29.62, 14.64, 26.68, 42.08, nm and 36.64 nm respectively.

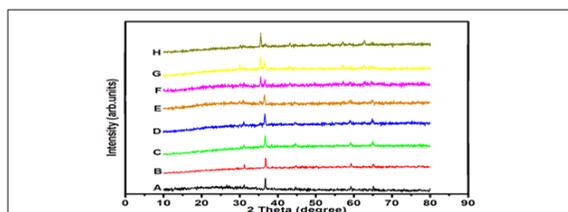


Figure.1: X-ray diffraction pattern of CoFe_2O_4 at 700°C annealing temperature: (A) 99+1%, (B) 98+2%, (C) 90+10%, (D) 85+15%, (E) 80+20%, (F) 70+30%, (G) 65+35%, (H) 50+50%

SEM:

The surface morphology of the eight powders can be observed in the SEM images given in Fig.2. (A-H). Depending upon the doping concentrations, the morphology of the samples also changes. The sample was observed with a smooth surface and also the agglomerations of the samples have been observed. In the case of nanoparticles the agglomeration was usually explained as a common way to minimize their surface energy [17, 18].

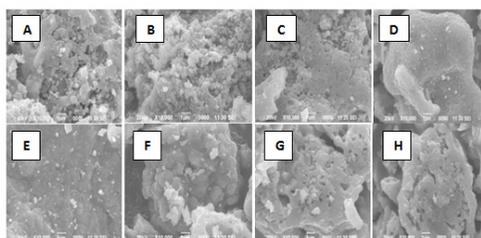


Figure.2: SEM image of the CoFe_2O_4 at 700°C annealing temperature: (A) 99+1%, (B) 98+2%, (C) 90+10%, (D) 85+15%, (E) 80+20%, (F) 70+30%, (G) 65+35%, (H) 50+50%

EDAX:

Fig.3 show the chemical composition of the as prepared samples which was investigated using EDAX spectral analysis. The qualitative elemental analysis obtained from EDAX spectra shows the peak corresponding to the three elements of Co, Fe, and O. This matches well with the stoichiometry of the samples without any impurity.

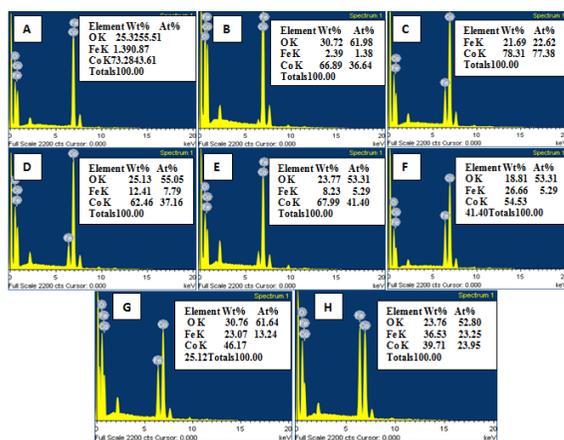


Figure.3: EDAX spectra of the CoFe_2O_4 at 700°C annealing temperature: (A) 99+1%, (B) 98+2%, (C) 90+10%, (D) 85+15%, (E) 80+20%, (F) 70+30%, (G) 65+35%, (H) 50+50%

FTIR: FT-IR analysis is a suitable technique to evaluate the functional groups present in the samples subjected to analysis. Figure.4. Using KBR pellets the Fourier Transform Infrared Spectra of the Fe doped Co nanoparticles were recorded in the range of 4000 to 400 cm^{-1} as shows in Fig.4.(A-H). The IR spectra indicated that two main metal-oxygen bands due to vibrations of the Fe-O and Co-O at the tetrahedral site appear in the fre-

quency range 649-662 cm^{-1} and also their vibrations at the octahedral site in the frequency range 558-568 cm^{-1} [19, 20]. Also, the adsorption broad band at the range of 3418-3456 cm^{-1} represents a stretching mode of -OH groups and H_2O molecules. The weak adsorption bands around at 1018 cm^{-1} due to the asymmetrical stretching vibration of the O-H mode, 1113 cm^{-1} around at stretching vibration of C-O mode, 2918-2928 cm^{-1} around at stretching vibration of C-H mode CH_2 groups as organic sources in the magnetic nanoparticles.

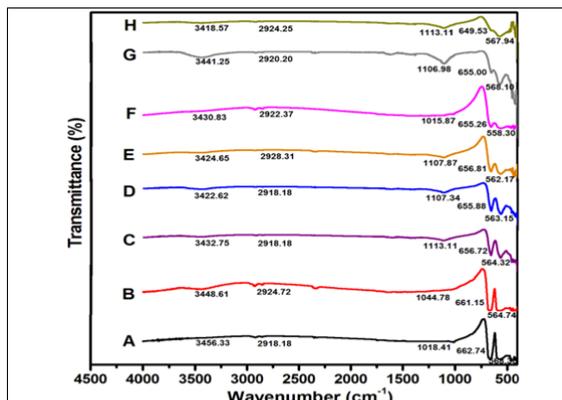


Figure.4: FTIR spectra of CoFe_2O_4 at 700°C annealing temperature: (A) 99+1%, (B) 98+2%, (C) 90+10%, (D) 85+15%, (E) 80+20%, (F) 70+30%, (G) 65+35%, (H) 50+50%

VSM:

The magnetic properties of the samples of CoFe_2O_4 nanoparticles (A-H) were measured at room temperature using VSM in an external magnetic field ranging from $\pm 10\text{kOe}$, as shown in Fig.5. Figure 5 shows the room temperature hysteresis loops of samples A-H. It can be observed that all the samples from (A-H) revealed typical ferromagnetic behavior. The ferromagnetic behavior of the prepared nanocrystals is clearly shows significant hysteresis, and the value of Saturation magnetization (M_s), Remanent magnetization (M_r), and Coercivity (H_c). 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 [21]. From the figure 5, it is noted that sample A has low saturation magnetization value of 0.34, 0.29, 3.12, 8.62, 14.17, 24.61, 32.69, 44.78 emu gm^{-1} with remanent magnetization and Coercivity values of 0.01, 0.00, 1.58, 4.49, 7.51, 12.56, 16.36, 22.86 emu gm^{-1} and 292.81, 60.75, 1402.88, 1379.55, 1273.79, 1151.67, 985.05, 891.95 Oe, respectively. From the figure 5, it is seen that the M_s Values of sample-A (0.34 emu gm^{-1}) is smaller as compared to M_s Values of sample-H (44.78 emu gm^{-1}) at an applied field of $\pm 10\text{kOe}$ 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-H has relatively lower Coercivity compared with that of sample-A, which can be considered as a further improvement of the magnetic properties.

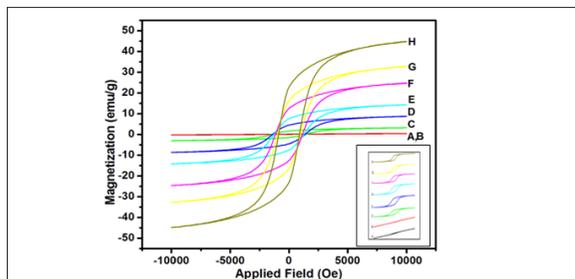


Figure 5: Room temperature hysteresis loops of CoFe₂O₄ at 700°C annealing temperature: (A) 99+1%, (B) 98+2%, (C) 90+10%, (D) 85+15%, (E) 80+20%, (F) 70+30%, (G) 65+35%, (H) 50+50%

Table I. Magnetic Parameters at Room Temperature

Percentage (%)	Saturation Magnetization M _s (emu/g)	Remanance Magnetization M _r (emu/g)	Coercivity H _c (O _e)
CoFe ₂ O ₄ A (99+1%)	0.34229	0.01365	292.8103
CoFe ₂ O ₄ B (98+2%)	0.29725	0.00204	60.75602
CoFe ₂ O ₄ C (90+10%)	3.12308	1.579333	1402.881
CoFe ₂ O ₄ D (85+15%)	8.62544	4.487169	1379.546
CoFe ₂ O ₄ E (80+20%)	14.17865	7.512399	1273.786
CoFe ₂ O ₄ F (70+30%)	24.61363	12.55942	1151.668
CoFe ₂ O ₄ G (60+40%)	32.69414	16.36315	985.0466
CoFe ₂ O ₄ H (50+50%)	44.78799	22.85830	891.9522

CONCLUSION:

CoFe₂O₄ nanoparticles were successfully 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 54.24, 57.46, 28.41, 29.62, 14.64, 26.68, 42.08, nm and 36.64 nm respectively. The SEM studies showed a total coverage of substrate surface with smooth surface of morphologies. The EDAX shows the presence of Co, Fe, and O. FT-IR spectroscopy methods confirmed the presence of Co-O and Fe-O stretching vibrations in the synthesized cobalt ferrite nanoparticles. The prepared samples exhibit ferromagnetism nature of all samples at room temperature with clear hysteresis loops.

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