Structural report of cobalt ferrite nanoparticles using Williamson-Hall plot with context to the green synthesis

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Abstract. In the present article, cobalt ferrite ($CoFe_2O_4$) nanoparticles were synthesized by using the green synthesis approach. The cobalt ferrite nanoparticles were synthesized by using metal nitrates and black pepper (Piper nigrum) extract as a fuel in the sol-gel method. The green synthesis of cobalt ferrite is ecofriendly, easy to manufacture composite, and inexpensive. The structural properties of the prepared sample were investigated by using the XRD analysis technique. The various structural parameters like lattice constant, crystallite size, d-spacing, etc were calculated from the XRD study. By using the W-H method, the 23.18 nm crystallite size was determined. The structural parameters obtained from the equation and graph were found to be closely the same. The cobalt ferrite nanoparticles prepared by using the green synthesis route were promising material for various applications, especially in a biomedical field like magnetic hyperthermia, magnetic resonance imagining, targeted drug delivery, etc.

1. Introduction

The development of nanosized materials has been becoming interesting for the last decades. The magnetic nanoparticles become more interested in the research field because of their innovative properties which makes them applicable in various applications like magnetic resonance imagining, magnetic hyperthermia, energy storage devices, sensors, mobile communication, magnetic recordings, gyromagnetic devices, information storage, magnetic shielding, etc[1, 2]. Among the various ferrites, spinel ferrites have more attraction in the research field. The spinel ferrite has the general formula MFe_2O_4, where M is a divalent metal ion (M= Zn^{2+}, Co^{2+}, Mn^{2+}, Mg^{2+}, etc.)[3]. Spinel ferrites have a number of applications due to their nanostructure, magnetic properties, and chemical stability. The superparamagnetic spinel ferrite plays a vital role in biomedical applications like magnetic hyperthermia, antibacterial activity, etc. S[4]. Munjal et. Al. prepared oleic acid-coated cobalt ferrite nanoparticles by using the hydrothermal method and checked their magnetic and hyperthermia properties[5]. Raut et. al. prepared Zn doped cobalt ferrite nanoparticles by using the sol-gel auto-combustion method. Also studied their structural, magnetic, morphological properties and reported the particle size of nanoparticles found to be 45-49 nm with increasing Zn concentration in cobalt ferrite[6]. Among the various spinel ferrites, cobalt ferrite is a promising material for different applications due to its moderate saturation magnetization, high coercivity, and large magnetostrictive coefficient. Cobalt ferrite shows both normal and inverse spinel structures. Basically, cobalt ferrite shows inverse spinel structure which can be changed by doping divalent metal ions like Ni, Z, Cd, etc. Due to the high saturation magnetization and high coercivity cobalt ferrite is the hard magnetic material as compared to the other spinel ferrite[7]. To reduce hard magnetism of cobalt ferrite, doping and coating of particles methods are used and making them promising material for various biomedical applications. M. Ali et. al. Synthesised zinc doped cobalt ferrite nanoparticles successfully by sol-gel auto-combustion method and reported the average particle size was increased from 11nm – 28 nm with increasing zinc concentration in cobalt ferrite[8]. S. Sagadevan et. al. prepared Ni-ferrite nanoparticles by chemical co-precipitation method and studied their structural, chemical, morphological properties. Also, concluded that the formation of spinel structure was confirmed from FTIR spectra[9]. P. Coppola et. al. prepared Zn-Co ferrite nanoparticles by using the hydrothermal co-precipitation method. They studied the morphological and structural properties of prepared nanoparticles[10]. The spinel ferrite nanoparticles are synthesized by various wet chemical methods like sol-gel auto-combustion, micro-emulsion, thermal decomposition, mechano-chemical synthesis, mechanical milling, hydrothermal technique, and forced hydrolysis method, etc. Among this sol-gel auto-combustion is broadly used for synthesizing fine-sized and chemically stabled magnetic nanoparticles. Because of sol-gel auto-combustion method has a number of good points like cost-effective, simple to do and reliable[11, 12]. The synthesis parameters like sintering temperature, pH of the solution, surfactants, solvents, organic salts, fuel, etc are affected by the size of particles. The Sol-gel auto-combustion method required organic fuel for combustion but is not environmentally friendly. To overcome this problem nanoparticles synthesized by using a green synthesis approach is one of the best ways for preparation. Green syntheses of nanoparticles also provide advantages over other methods, as they are simple, one step, cost-effective, environmentally friendly, and relatively reproducible and often result in more stable materials[13]. Green nanotechnology is the ideal approach for reducing the negative consequences of nanomaterial manufacturing and application while also lowering the riskiness of nanotechnology. The biological route is an attractive alternative to traditional synthesis methods[14]. Making ferrites the greenway is an attractive choice. Recently there has been a lot of interest in the use of natural plant ingredients and this extract is in the methods of preparation. A. Nadumane et. al. reports an environmentally friendly synthetic strategy to synthesize new nickel ferrite and Mg-doped nickel ferrite photocatalysts under a modified green sol-gel route in which aloe Vera gel acts as a natural template. They open a new window to use this simple greener route to synthesize bi-functional NPs in the area of photocatalysis particularly wastewater treatment and display applications[15]. S. B. Patilet et. al. investigate Sugarcane juice mediated eco-friendly synthesis of visible light active zinc ferrite nanoparticles for degradation of mixed dyes application and antibacterial activities. Author noticed excellent photocatalytic activity in the presence of mixed organic dyes similar to the degradation of individual dyes[16]. M. M. Naiket et. Al. prepared Co-Zn ferrite by combustion method using curd as a green fuel. They conclude that gram-negative Salmonella typhi shows high antibacterial activity with the inhibition zone of Zn-doped $CoFe_2O_4$ (22nm) compared to pure $CoFe_2O_4$ (16nm)[17]. There are, few reports available on green synthesis of ferrite nanoparticles using extract of Aloe Vera, Hibiscus Rosa Sinensis, Sesame seed, Onion, Okra, Seaweed, black pepper, Clove, Cinnamon, Ginger, Cardamom, etc. Different combinations of organic and inorganic reducing agents may be present in the green extract. Further research still has to be done on the improvements in environmentally friendly synthesis methods. It needs to develop systems that are more efficient thus interpretation the environment cleaner and healthier. Using the natural extract for the spinel ferrite nanoparticles synthesis is cost-effective, easy to prepare, environmentally friendly. Black pepper extract is one of the best fuels for the synthesis of nanoparticles by using the sol-gel method and also black pepper is easily available. The present work aims to synthesize the cobalt ferrite nanoparticles by using eco-friendly and clean black pepper extract as a fuel in the sol-gel method. Also, study the effect of green synthesis on the structural properties of cobalt ferrite nanoparticles.

2. Experimental details

2.1. Chemicals

The Cobalt nitrate [$Co(NO_3)_2{\cdot}6H_2O$] and ferric nitrate [$Fe(NO_3)_2{\cdot}9H_2O$] are used as raw materials for cobalt ferrite synthesis. Ammonia (NH_3) is used to maintain the pH of the solution. All used chemicals are AR-grad.

2.2. Preparation of Black pepper (Piper nigrum) extract

The black pepper extract was prepared by using a fine powder of black pepper. The 9 gm black pepper fine powder is dispersed in 50 ml of DI water and boils the solution for 30 min. after 30 min. the extract was cooled down up to room temperature and filtered. The prepared extract was used for further synthesis procedures.

2.3. Preparation of $CoFe_2O_4$ferrite nanoparticles by sol-gel auto combustion method

Using black pepper (Piper nigrum) extract as a fuel, $CoFe_2O_4$ nanoparticles were synthesized by the sol-gel auto combustion method. The Cobalt nitrate [$Co(NO_3)_2{\cdot}6H_2O$] and ferric nitrate [$Fe(NO_3)_2{\cdot}9H_2O$] with stoichiometric ratio 1:2 dissolved in 500 ml of distilled water. The solution was kept under continuous stirring at 350 rpm for 15 min. The extract of black pepper was added as fuel in the solution to avoid the toxic fuels. The solution was stirred continuously for 15 min. The liquid ammonia was added drop-wise in the solution to maintain the pH at 7. After the maintain pH of the solution, stirred the solution continuously with constant heating 90°C. After 2 hours rises the temperature of the solution up to 120 °C for the conversion of a sol into a gel. After some time gel was converted into viscous gel and combustion gets started and blackish-colored ash was obtained. This ash was grinded for a few hours the obtain a fine powder. The obtained powder was sintered at 600 °C for 5 hours to remove the moisture and other extra content. Used these sintered nanoparticles for further characterizations.

2.3. Characterization tools

The $CoFe_2O_4$ nanoparticles were characterized by using an X-ray diffractometer (Bruker) with Cu Kα radiation (λ=1.54 Å) was used to record the XRD patterns in a 2θ range of 20-80°. The analysis determines various structural parameters and phase purity of the sample.

3. Results and discussion

3.1. X-ray diffraction (XRD) studies

The various structural parameters of prepared $CoFe_2O_4$ were calculated from Bragg's diffraction angles shown in **table 1.** The lattice parameter value of prepared cobalt ferrite nanoparticles has been calculated both ways. The lattice parameter for each Bragg's diffraction angle is shown in table 1. The observed planes having (hkl) values (220), (311), (222), (400), (422), (511) and (440) indicated the formation of cubic spinel structure with Fd-3m space group. No, the additional plane was observed in the XRD pattern which gives the purity of the prepared sample. The lattice parameter was calculated from each observed plane by using the following **equation 1**. The calculated values of lattice parameters are shown in **table 1**.

$$\sin^2\theta = (\lambda^2/a^2)(h^2 + k^2 + l^2) \quad (1)$$

Where, θ in the Bragg's angle, a is lattice constant, h, k and l are the Miller indices and λ is the X-ray wavelength. The average lattice constant (a_{ave}) was found to be 8.3755 Å shown in **table 2**. Also, the lattice parameter was calculated graphically shown in **figure 1**. The 1/d-spacing versus square root of the (h^2+k^2+l^2) graph was plotted. By using the best linear fitting procedure slop of the line was obtained which gives the lattice constant (a_{grf}) value. From **figure 1**, the slope of the straight line was found to be 8.3810 Å which is tabulated in **table 2**. There is a very small difference was found in the calculated value of the lattice constant and the graphically obtained value of the lattice constant. The various methods are available for obtaining clear information about microstructure. Warren-Averbach method, Williamsons Hall method, etc. are some methods are used to investigate the microstructure information. The Williamson-Hall plot method is a promising method for structural parameters analysis because of its easiness and simple calculations. The W-H plot for the prepared sample was drawn by using **equation 2**. The present W-H plot is based on a uniform deformation model (UDM).

$$\beta\cos\theta = \frac{k\lambda}{D} + 4\varepsilon \text{Sin}\theta \quad (2)$$

The UDM takes into account uniform strain as well as crystallographic orientation, which is seen in nanocrystals due to crystal defects. The overall broadening has been expressed as given in the equation based on strain and size of a particular peak with hkl value. The straight-line observed in the W-H plot gives the intrinsic strain and crystallite size of the sample. The intercept on the y-axis gives the crystallite size and the slope of the straight line gives the intrinsic strain. The obtained straight line equation gives the 0.00598 y-intercept value. By using the y-intercept value crystallite size was found to be 23.18 nm tabulated in table 2. The lattice parameter and crystallite size were well matched with previous literature [18-20].

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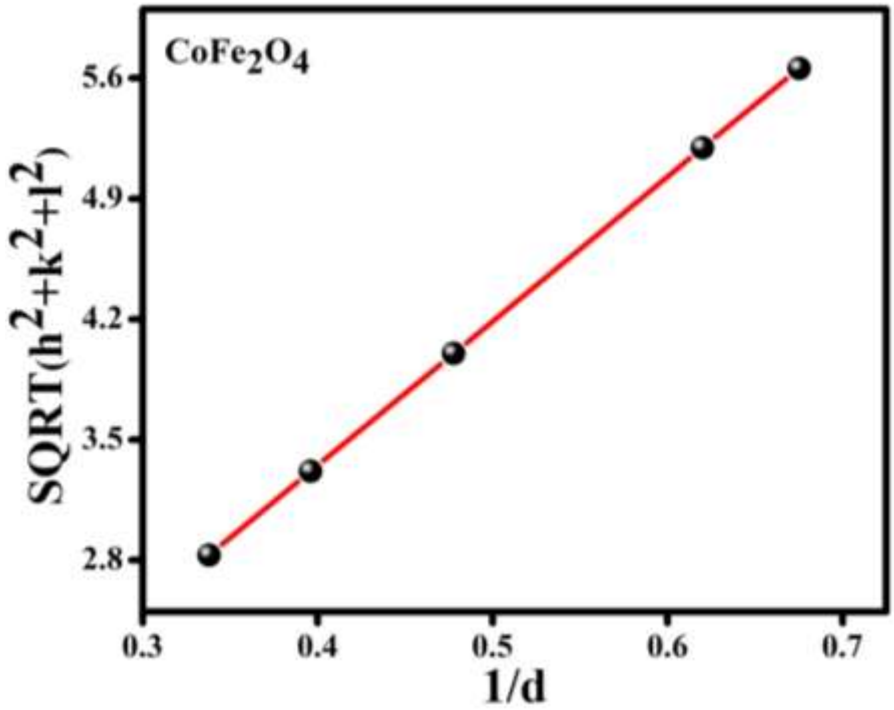

Fig. 1 1/d Vs. SQRT (h^2+K^2+l^2) pattern of $CoFe_2O_4$ nanoparticles

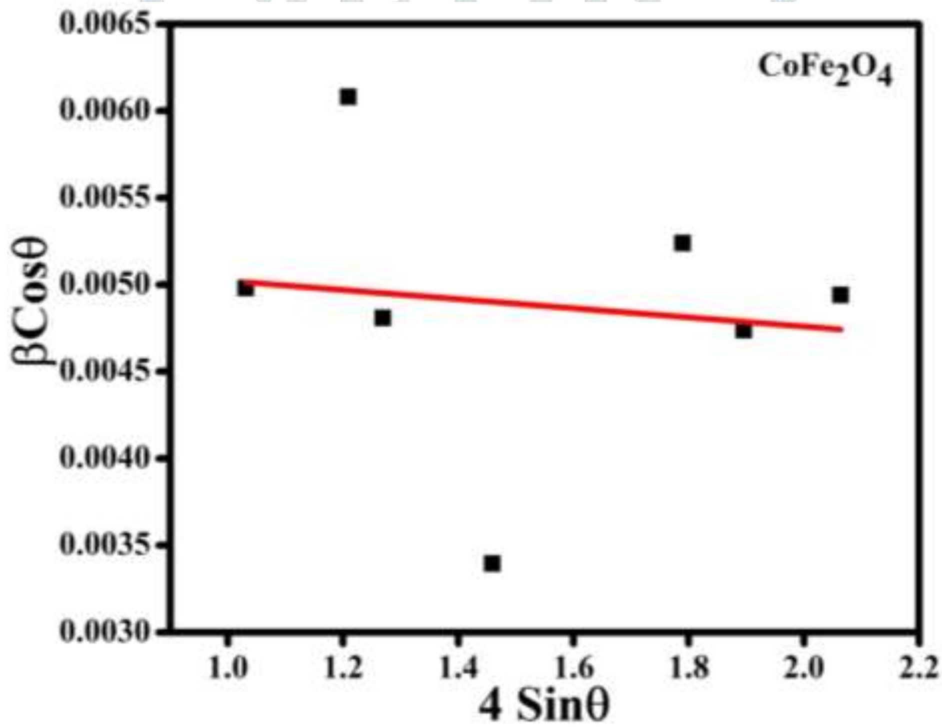

Fig. 2 Williamson – Hall plot of $CoFe_2O_4$ nanoparticles

Table 1: Bragg's angle (2θ), plane (hkl), d-spacing, lattice constant 'a' (Å)

2θ	Sinθ	2Sinθ	d	h	k	l	a
30.17	0.2603	0.5206	2.958	2	2	0	8.3686
35.50	0.3049	0.6099	2.5254	3	1	1	8.3759
43.17	0.3679	0.7359	2.0932	4	0	0	8.3728
57.03	0.4774	0.9548	1.6131	5	1	1	8.3822
62.66	0.5200	1.0400	1.4810	4	4	0	8.37787

Table 1: lattice constant 'a_{ave}' (Å), lattice constant 'a_{grf}' (Å) and crystallite size't' (nm)

Parameter	a_{ave}	a_{grf}	t
value	8.3755	8.3810	23.18

Conclusions

The cobalt ferrite nanoparticles were successfully prepared by using the sol-gel auto combustion method. The black pepper (Piper nigrum) extract as a fuel in this method. The (hkl) planes obtained from the XRD pattern confirm the formation of the spinel ferrite structure. The average crystallite size calculated from the W-H plot was found to be 23.18 nm. The lattice parameter values were calculated by using an equation and also a graph. The 8.3810Å and 8.3755Å lattice parameter values were obtained from 1/d Vs SQRT ($h^2+k^2+l^2$) and equation 1 respectively**.** The lattice parameter value was found to be nearly the same calculated from both types. The black pepper extract is suitable for the preparation of cobalt ferrite nanoparticles using the sol-gel auto combustion method.

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