Synthesis and Characterization of CoFe₂O4 Nanoparticles Prepared by Sol-Gel Method

Rihab Jabbar *[a], **Sabah H. Sabeh** [b], **Awham M. Hameed** [c]

[a] Applied Science Department, University of Technology, Baghdad, Iraq, rihabjabbar@yahoo.com

[b] Science Department, University of Technology, Baghdad, Iraq, sabahhabeeb@gmail.com

[c] Science Department, University of Technology, Baghdad, Iraq, awham_m@yahoo.com

*Corresponding author.

K E Y W O R D S

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A B S T R A C T

Cobalt Ferrite (CoFe2O4) nanoparticles (NPs) were prepared by Sol-Gel precipitation method. Two samples were synthesized and sintered with different sintering temperatures; sample A at 400 °C and sample B at 800 °C for two hours. The prepared samples were characterized by XRD, FTIR, SEM, and AFM, Compressive test and Micro-hardness. The result showed as the sintering temperatures increased, the crystallite size increased from 10.07 nm to 15.14 nm. FTIR spectra showed two strong absorption bands in the range of 800 - 400 cm-1, confirmed formation of spinel ferrites NPs. SEM and AFM micrographs showed that the samples have an approximately spherical shape. The mechanical properties of CoFe2O4 NPs were not widely studied. Therefore, in this work, the mechanical properties (Compressive strength and Micro-hardness) of prepared material studied as an important contribution for researchers to focus on mechanical properties of CoFe2O4 NPs. Where the mechanical result showed that both the compressive strength was increased (from 4.42 to 10.57 N/mm2) and Micro-hardness (from 10.33 to 174.4 N/mm2) with increasing sintering temperature.

1. Introduction

Nano sized spinel ferrite particles have attracted more attentiveness in the last few years because of their properties; therefore, it is used in many applications in high-density magnetic recording, magnetic fluids, gas sensors, etc. [1]. Preparation method, chemical composition, heat treatment have a strong affected on the magnetic and dielectric properties of the Cobalt Ferrite NPs [2]. Moreover the ferrite nanoparticles, Cobalt Ferrite has been extensively studied due to their properties include large magnetic anisotropy, high coactivity value up to (5.4 kOe), moderate saturation magnetization (80 emu g^{-1}), excellent chemical stability, and a mechanical hardness, that makes it an important candidate for many applications [3-5]. Bulk $CoFe_2O_4$ has an inverse spinel structure in which ideally half of the trivalent ferric anions (Fe^{+3}) are

positioned on tetrahedral (A-site) and the other half Fe^{+3} cations and all divalent cobalt cations (Co^{+2}) on octahedral (B-site). An inverse spinel unit cell is made up of eight face-centered cubic (FCC) cells of oxygen ions in the arrangement (8). Accordingly, $CoFe_2O_4$ has also 8 sublattices (molecules) in its unit cell with 32 anions and 24 cations, which are ideally distributed at room temperature [6]. Due to the great properties of $CoFe_2O_4$, it is used in many applications such as catalysts, Ferro fluid, drug delivery, magnetic resonance imaging (MRI), magnetic separation, biosensors and hyperthermia and gas sensors [7]. Nanoparticles Cobalt Ferrite can by synthesis by many chemical and/or physical methods include; Sol-Gel auto-combustion, co-precipitation, high energy milling, etc. [8]. Amongst chemical synthesis methods, the Sol-Gel method widely used due to their advantages over other preparation methods. These advantages include; low cost, simple, high purity, good stoichiometric control, and narrow size distribution [9]. Nanoparticles prepared by different physical and chemical methods found wide applications in many fields including the medical, electronic, and environment. [10] prepared Cobalt Ferrite nanoparticles by the Sol-Gel method and study the effect of four different sintering temperatures on the structural and magnetic properties of the $CoFe_2O_4$. The results showed that the crystallite size and saturation magnetization were found to increase with sintering temperatures. [11] found the same results with a different range of the sintering temperatures (500°C to 1100°C). [12] synthesized nano-crystalline Cobalt Ferrite by Sol-Gel auto combustion method." It was found that the particle size and magnetic properties of the as-prepared ferrite samples showed a strong dependence on the annealing temperature. [13] synthesized of $CoFe_2O_4$ nanoparticles via a Sol-Gel combustion method. X-ray diffraction pattern shows that the $CoFe_2O_4$ powder is in a single phase and well crystallized in the cubic spinel structure, and the grain size in the range of 20-70 nm. [14] synthesized $CoFe_2O_4$ nanoparticles via a Sol-Gel method. They found that the particle size and saturation magnetization increase with the increase of sintering temperature. [15] synthesized silver nanoparticles were prepared from two natural sources; pomegranate peel extract and cochineal dye by solution-phase method. The crystalline size ranged between (27.8 – 36 nm). [16] prepared cubic zirconium oxide nano-crystals by thermal decomposition method. Results showed that synthesized ZrO_2 nanoparticles have a cubic structure. [17] prepared Silver Vanadium Oxide via a facile sonochemical route. SEM, TEM, and XRD results showed that AgO nanoparticles were formed onto $AgVO_3$ nanorods in the presence of ethanol, cyclohexanol, dimethylsulfoxide (DMSO). [18] synthesized Mercury Selenide (HgSe) nanoparticles by a sonochemical method. It was found that morphology, particle size and phase of the products could be greatly affected by type of capping agent, ultrasonic power, reaction time and temperature. [19] reported preparation and characterization of spherical silica nanoparticles synthesized via a sonochemical a method based on a modified Stöber process. Results showed that the average particles size ranged between (100 – 300 nm).

The mechanical properties of the nanoparticles in general was not widely studied, especially Cobalt Ferrite nanoparticles. Therefore, in this work, $CoFe_2O_4$ nanoparticles will prepare via Sol-Gel precipitation. Investigations on the crystallite size, morphology, in addition to mechanical properties have been studied with X-ray diffraction (XRD), Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), and the mechanical properties studied with Compressive test and Micro-hardness.

2. Experimental

I. Synthesis

$CoFe_2O_4$ nanoparticles were synthesized by the Sol-Gel method. A stoichiometric ratio of Ferric Chloride "$FeCl_3$" (8 gm) and Cobalt Chloride "$CoCl_2.6H_2O$" (6 gm) provided from (BDH) with purity above 97 %) were dissolved separately in (50 ml) of distilled water using a magnetic stirrer. Then, (2M) Sodium Hydroxide (NaOH) solution prepared by dissolved (8 gm) of NaOH in (100 ml) of distilled water. Then, added into mixture slowly like a drop with continuous stirring for 90 min. Then, the mixture was heated to (100 ±5 °C) for two hours with continuous stirring, the solution converts gradually to wet gel with black color then the wet gel converted completely to powder. The obtained powder was washed fives time with ethanol and distilled water to remove Sodium Chloride (NaCl) and any other impurities. The prepared powder was sintered at (400 °C for A-sample and 800 °C for B-sample) for two hours using furnace type Nabertherm GmbH – Germany.

II. Characterization Studies

The structural properties of prepared $CoFe_2O_4$ nanoparticles were investigated by X-ray diffraction using Philips PW 1050 X-ray diffractometer of $\lambda = 1.5$ A° from Cu-kα. The crystallite size (D), lattice constant (a), X-ray density (ρX) and specific surface area (S) were calculated. The chemical compounded in

samples was observed by FTIR type (SHIMADZU) with wavelength in range (400 – 4000 cm^{-1}). The surface morphology was investigated by (SEM) type (INSPECT S50 (FEI) -Netherlands) and Atomic force microscope (AFM) type (CSPM-AA3000 Japan) while the mechanical properties was carried out on pellet with (1cm) in diameter prepared by pressed (1 gm) by hydraulic piston by force equal to (1 ton) for 2 minutes.

3. Results and Discussion

I. Structural Analysis

The XRD patterns of CoFe$_2$O$_4$ nanoparticles sintered at 400 °C and 800 °C are shown in Figure 1. The obtained pattern compared with standard data (JCPDS PDF card No. 22-1086) which confirmed the formation of Cobalt Ferrite NPs. The crystallite size (D) of the samples was calculated from the bordering peak of XRD pattern using the Scherrer relation [20]:

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \qquad (1)$$

The lattice constant (a) was estimated from outstanding peak (311) used Bragg's relation:

$$a = d_{hkl}\sqrt{h2 + k2 + l2} \qquad (2)$$

The X-ray density (ρx) estimate using the following equation:

$$\rho x = \frac{8M}{Na3} \qquad (3)$$

Where (M) is the molecular weight, (N) is Avogadro's number and (a) is the lattice constant.
Specific surface area (surface area per unit mass) can be calculated by the following relation [20].

$$S = \frac{6000}{D\,\rho X} \qquad (4)$$

The porosity for all the samples was calculated using the following formula [21]:

$$P = 1 - \frac{\rho m}{\rho x} \qquad (5)$$

Crystallite size (D), lattice constant (a), X-ray density, Specific surface area (S) and porosity (P) of the prepared samples tabulated in the Table 1. XRD results indicated that the CoFe$_2$O$_4$ has cubic spinal structure also it can be seen that the crystallite size was increased with increasing sintering temperatures this in agreement with Sheena X. et al. [10], Raghvendra et al. [11] and Lunhong et al. [12]. Many reports showed that the sintering process mostly lowering lattice defect and strain, however, this technique is the reason behind the coalescence of smaller grains, causing an increase of average grain size for the nanoparticles [22].

Figures 2a and 2b showed FTIR spectra of Cobalt Ferrite nanoparticles annealed at 400 °C and 800 °C respectively. FTIR spectrum of the CoFe$_2$O$_4$ nanoparticles showed weak bands at (3404.47, 3419.90 cm^{-1}) for sample A and (3425.69, 3576.14 cm^{-1}) for sample B which were assigned to the stretching vibrations of (OH) group on the surface of nanoparticles. CO$_2$ absorption observed at (1516.10, 1556.61, 1639.55, 1699.34 cm^{-1} for A) and (1510.31, 1562.39, 1658.84 cm^{-1} for B). The aliphatic and aromatic C–H bond stretching is assigned around (2316.58 – 2877.99 cm^{-1}). C-H stretching band observed at 2877.89 for A-sample and (3030 cm^{-1}) for B-sample. The bands at 1057.03 cm^{-1} for A sample is assigned to the formation of Co-substituted spinel ferrites [23]. Figure (2 a), the band spotted at 499.85 cm^{-1} attributed to octahedral group complexes, while the band 592.17 cm^{-1} attributed to the tetrahedral group complexes. In Figure (2b), the bands observed at 443.64m 484.15 cm^{-1} attributed to the tetrahedral group complexes, while bands at 582.52, 592.17 cm^{-1} assigned to the tetrahedral group complexes. This confirms the formation of Cobalt Ferrite with cubic spinal structure. Due to the strong relationship between the structural properties of Cobalt Ferrite nanoparticles with their magnetic and dielectric properties, it is recommended to study magnetic and dielectric properties with the sintering temperatures and their correlation with the structural properties.
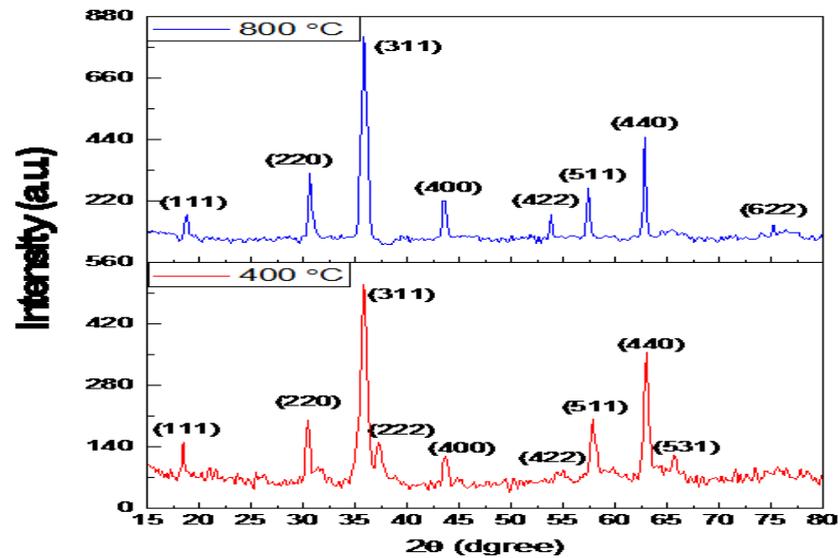
Figure 1: XRD patterns of CoFe$_2$O$_4$ sintered at 400 °C, (b) 800 °C

Table 1: XRD parameters of CoFe$_2$O$_4$, Specific surface area and porosity

Annealing Temperature (°C)	Crystallite size D (nm)	lattice parameter a (nm)	X-ray density ρ_x (g/cm^3)	Specific surface area (m^2/g)	Porosity
400	10.07	0.8187	5.6809	104.88	0.6557
800	15.14	0.8183	5.6884	69.66	0.4989

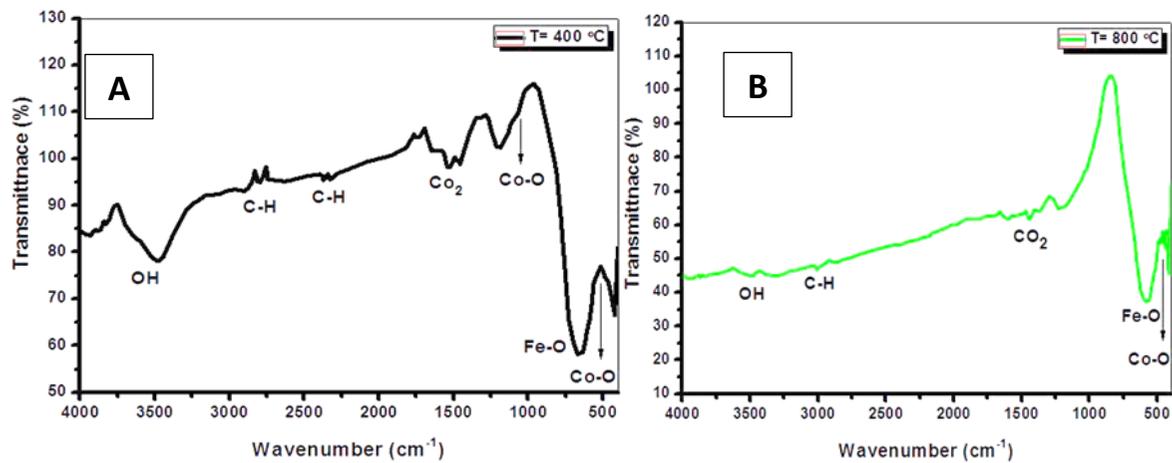**Figure 2:(A) FTIR of CoFe$_2$O$_4$ annealed at 400 °C and (B) FTIR of CoFe$_2$O$_4$ annealed at 800 °C**
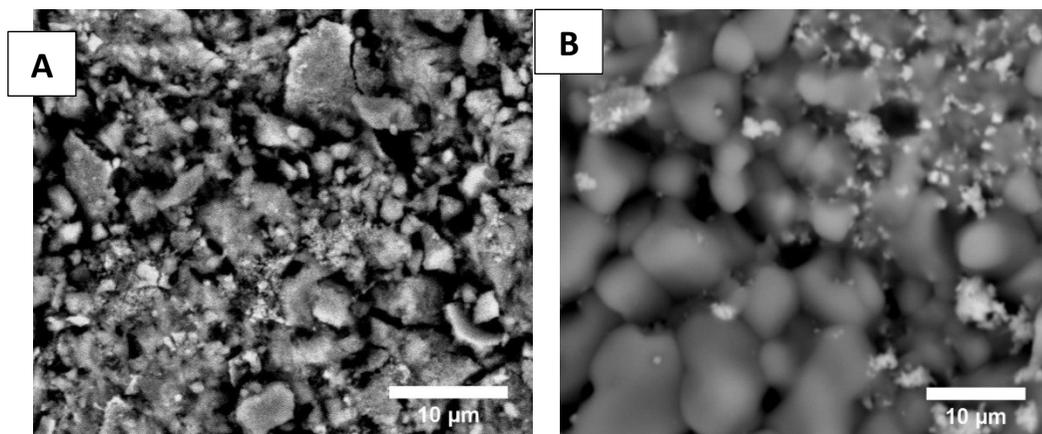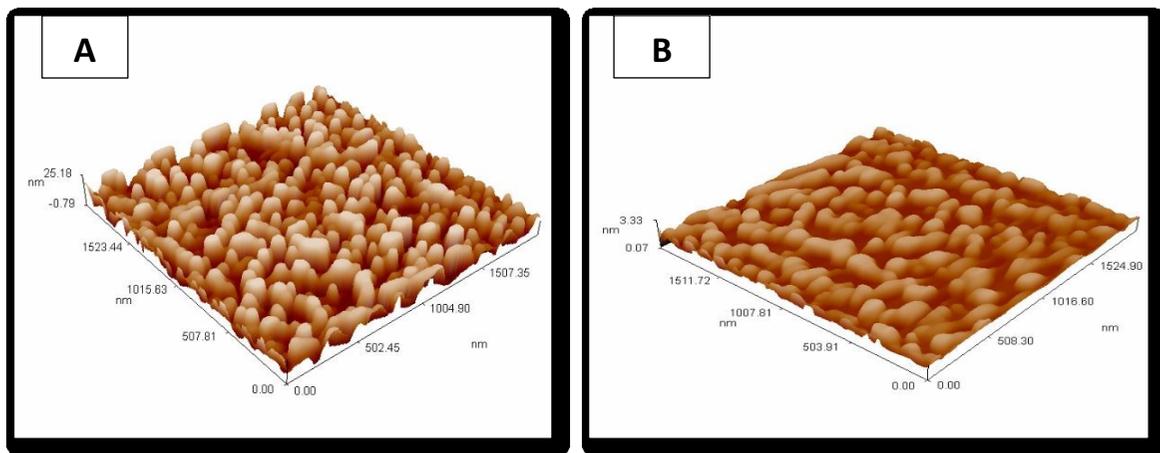

Figure 3: SEM images of samples annealed at (A) 400 °C and (B) 800 °C

Figure 4: 3D AFM images of CoFe$_2$O$_4$ at different annealing temperature (A) 400 °C and (B) 800 °C

II. Morphological study

Figure 3 showed SEM micrograph of CoFe2O4 samples sintered at (A= 400 °C) and (B = 800 °C). The images showed that A-sample has flat shape while B-sample has a spherical shape, also it showed both samples were agglomerate which is the property of nanoparticles [24].

Figure 4 showed the three dimensional AFM images of which annealed at different temperature (A) 400 °C and (B) 800 °C. It is clear that the particles have a spherical shape. The average grain size found to be increase while surface roughness and root mean square decreased with increasing the sintering temperatures as shown in the Table 2.

II. Mechanical properties

Linear shrinkage (longitudinal) is a measure of the change in the length of the dimensions of the specimen after drying and sintering processes also it determined the shape and size of the final product.
Linear shrinkage (longitudinal) describes the sensitivity of the specimen towards our burning process and is calculated by the following relationship:

$$L.S. \% = \frac{Lo-L}{Lo} \times 100 \% \qquad (6)$$

Volumetric shrinkage is calculated in the same style of relationship (6)

$$V.S. = \frac{Vo-V}{Vo} \times 100\% \qquad (7)$$

Density is also known as the relationship between the mass (weight) of material are the size and is given by [25]:

$$Density \ (gm/ \ cm^3) = \frac{Mass \ (gm)}{Volume \ (cm3)} \qquad (8)$$

Table 3 shows the linear, volume shrinkage and density of CoFe$_2$O$_4$ with different annealing temperatures. It is clear that the linear and volume shrinkage increased with increasing the sintering temperature. This due to decrease in the porosity and gaps, voids when the temperature increasing, because the linear shrinkage and volume shrinkage is affected by two factors including the particle
size and the melting temperature of some grains that leads to create leak of the viscous liquid that works to collect the grains together, close the pores and increase the density.

Compressive strength of the body is known as the ability to resist loads that are applied to it. It is calculated from the following relationship [25]:

$$\sigma f = F/A \qquad (9)$$

When the load is applied to the diameter of the specimen, the (Indirect Tensile Strength) is calculated from the relationship:

$$\sigma f = 2F/ \pi hd \qquad (10)$$

Where: σf = the resistance strength (Compressive strength), F = the maximum load after the specimen starts failure, d = the diameter of the specimen, and h = the thickness of the specimen.

Table 2: Average grain size, surface roughness, and Root mean square of CoFe₂O₄ by AFM

Annealing Temperature (°C)	Grain size (nm)	Roughness (nm)	Root mean square (nm)
400	85.93	5.49	6.32
800	118.93	0.393	0.444

Table 3: Density, Linear shrinkage and volume shrinkage of CoFe₂O₄

Annealing Temperature(°C)	Linear shrinkage	Volume shrinkage	Density (g/cm³)
400	0.0048	0.0146	1.95
800	0.1285	0.3412	2.85

Hardness defines the resistance of the material to penetration. There are many methods to measure the hardness, but it is very appropriate to use the Vickers Test for brittle material like ferrite. Vickers hardness relationship:

$$HV = 1.844 \, F/d^2 \qquad\qquad (11)$$

Where: F = the magnitude of the applied load (N).

d = the average of the diameter (arithmetic average of the diagonal polygon quadrilateral) (m).

Vickers hardness method was developed by using a very small microscopic indenter known as (Micro-Hardness Test). This type is commonly used in product material due to the presence of fine pores which cannot estimate the impact on the hardness therefore, this method is used [26,27].

From Table (4), it is noticed that both of the compressive strength and hardness of CoFe₂O₄ NPs were increased with increasing the sintering temperature from 400 °C to 800 °C due to a decrease in the apparent porosity and then increase in force of bonding and the density of samples where the porosity decreased from 0.65 to 0.49 for samples sintering at 400 °C and 800 °C, respectively [28].

Table 4: Compression strength and Microhardness of CoFe₂O₄

Annealing Temperature (°C)	Compression (N/mm²)	Microhardness (N/mm²)	Shore D Hardness
400	4.42	10.33	34.56
800	10.57	147.4	40.43

4. Conclusions

CoFe₂O₄ nanoparticles were prepared successfully by the Sol-Gel method, this makes the Sol-Gel technique an inexpensive and simple method used to prepared material with narrow crystallite size. FTIR is a useful technique to know the compounds found in the prepared sample that cannot observe by XRD diffraction, FTIR spectra was confirmed the formation of cubic spinal structure of CoFe₂O₄ NPs. SEM and AFM images confirmed grain growth of NPs with increased sintering temperature. Porosity found to decrease and as a result the density of the samples increased with increase in the sintering temperatures. Both the compressive strength and hardness increase with increase the sintering temperature due to the decrease in the defect, porosity and improvement of the crystal structure. This work pushed the researchers to investigation the mechanical properties of the nanoparticles specially Cobalt Ferrite nanoparticles.

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