

## Influence of heat treatment on the crystallite size, structural, elastic, and magnetic properties of cobalt ferrite nanoparticles

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**ABSTRACT:** Cobalt ferrite structure besides their magnetic characteristics was studied. The citrate nitrate combustion process was utilized to prepare cobalt ferrite nanoparticles. For all prepared samples, the x-ray diffraction analysis (XRD) illustrated the single phase structure. The crystal structure has been refined using the MAUD software with the Rietveld profile method. Particle size was largely affected by the thermal processing. The formation of nanoparticles with a spherical shape has been confirmed using HRTEM technique. The magnetic nature of CoFe<sub>2</sub>O<sub>4</sub> nanoparticles causes a degree of agglomeration which decreases the quality of the TEM images. The two characteristic bands of ferrite have been observed by FTIR analysis. The M-H curve, for the prepared nanoferrites, provided details about magnetic parameters like MS and H<sub>c</sub>. The reduced particle size significantly reduces the saturation of magnetization, where it decreased from 99 emu/g for Co ferrite sample treated at 600°C (90 nm) to 55 emu/g for as prepared Co ferrite sample (12 nm).

**KEYWORDS** Co nanoferrite, XRD, VSM, TEM, FTIR

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### I. INTRODUCTION

The generic formula for nanocrystalline spinel ferrites, which is a magnetic material, is AB<sub>2</sub>O<sub>4</sub>; where A and B are tetrahedral and octahedral metals [1]. With appropriate divalent or trivalent cation substitution into the spinel structure, their physical features can be easily tailored [2, 3]. Spinel ferrites have received revived attention in today's technological society thanks to their promising physical properties [4]. Co-ferrite (CoFe<sub>2</sub>O<sub>4</sub>) is often regarded as an exhausting magnetic substance with pleasant physical and chemical stability owing to its high coercivity besides magnetization. The ferrites CoFe<sub>2</sub>O<sub>4</sub> are widely used in versatile applications [5,6]; Thanks to their high strength hardness and high magnetization saturation. In addition, the highly advanced cobalt ferrite permeability in a wide range of frequencies makes it a very economical material as a microwave magnetic filter [7], radar digital recording systems [8, 9], ferro-fluids, and magnetic refrigeration systems [10–12]. CoFe<sub>2</sub>O<sub>4</sub> was prepared in this paper using a combustion method, which investigates the impact of preparation conditions for the particle size (D). This mission is done utilizing XRD, HRTEM, FTIR, and VSM techniques.

## II. EXPERIMENTAL DETAILS

### 2.1 Sample Preparation

Citrate combustion approach was used to produce nanocrystalline powders CoFe<sub>2</sub>O<sub>4</sub> [13]. Metals nitrates (Iron (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and cobalt (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>·7H<sub>2</sub>O) [99.7% Win lab, UK] and distilled water were used to prepare the nanoparticles. Half of the prepared powder was then sintered at 600°C for 5 hours.

### 2.2 Materials Characterization

The product powder of nanoparticles was characterized by XRD, HRTEM, FTIR, and VSM techniques using the identical instruments in the preceding paper [14]. The crystal structure has been refined using the MAUD software with the Rietveld profile method [15], where the particle size and lattice constant (a) are established.

## III. RESULTS AND DISCUSSION

### 3.1 X-ray Measurements

Figure 1 displays XRD patterns of the prepared nanoferrites. The as-prepared sample did not subject to any heat treatment after preparation. The XRD model of the sample as prepared is associated with a broad diffraction peak; these broad peaks are the signature of the reduced particle size (12 nm). For the sample heated at 600°C, sharper diffraction peaks were observed and hence a higher particle size is obtained (90 nm). The maximum diffraction observed can be indexed to the cubic spinel ferrite phase (Fd-3m space group). Using the Maud software, XRD patterns were fitted and analyzed to calculate the sample's lattice parameter (a) besides its particle size (D). Furthermore, a broadening of the X-ray line utilizing the Scherer equation was calculated to obtain the average crystallite sizes of various ferrites:

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

The values of a and (D) are tabulated in Table 1. The lattice parameter of the as prepared and that heated to 600°C were increased from 8,291 Å to 8,389 Å. The inverse structure of the CoFe<sub>2</sub>O<sub>4</sub> spinel contains all Co<sup>2+</sup> ions at the octahedral sites. However, by decreasing the particle size the degree of inversion tends to decrease. In this case, a partial inverse CoFe<sub>2</sub>O<sub>4</sub> is obtained. The ionic radius of Co<sup>2+</sup> ions in the tetrahedral environment is 0.38 Å which is smaller than the ionic radius of Co<sup>2+</sup> ions (high spin state) in the octahedral environment (0.745 Å) [17]. Hence, the decrease of inversion for the as-prepared sample (12 nm) is accompanied by an increase in Co<sup>2+</sup> ions in the tetrahedral environment, and accordingly, a smaller lattice parameter (a) is observed.

### 3.2 HRTEM analysis

Figure 2 shows the HRTEM image of the prepared CoFe<sub>2</sub>O<sub>4</sub> sample. These micrographs suggest spherical nanoscale particles in the range from 3 to 8 nm. The magnetic nature of CoFe<sub>2</sub>O<sub>4</sub> nanoparticles causes a degree of agglomeration which decreases the quality of the TEM images.

### 3.3 FTIR Spectroscopy

FTIR curves of both CoFe<sub>2</sub>O<sub>4</sub> samples are shown in Figure 3. The spectrum was recorded in frequency span 200 to 4000 cm<sup>-1</sup> at RT (303K). The vibration frequencies of the two samples are tabulated in Table 1. Spinel ferrites are usually branded with two frequency vibrational bands; ν<sub>1</sub> near 500–600 cm<sup>-1</sup> which is connected to the Fe<sup>3+</sup>–O<sup>2-</sup> at the tetrahedral site (A) and ν<sub>2</sub> near 350 – 450 cm<sup>-1</sup> that is attributed to the Fe<sup>3+</sup>–O<sup>2-</sup> and Co<sup>2+</sup>–O<sup>2-</sup> complexes at octahedral (B) site [18]. The value of vibrational frequency ν<sub>1</sub> is higher than the value of ν<sub>2</sub>, which shows that the tetrahedral complexes have a normal vibration mode which is higher than the corresponding octahedral location. This can occur because of the tetrahedral site's shorter bond length than the octahedral site [19]. In the residual modes of the water molecules (H-O-H), symmetric deformation of the carboxyl group (COOH) and the asymmetric detention vibrator of the adsorbed NO<sub>3</sub> produced as a nitrate group residue following sample combustion, the vibrational vibration frequency bands near 3510 cm<sup>-1</sup>, 1613 cm<sup>-1</sup>, 1359 cm<sup>-1</sup>,

and 1115  $\text{cm}^{-1}$  [20]. Due to the slight change in the lattice parameter ( $a$ ) and accordingly, in the tetrahedral and octahedral bond lengths, small changes were observed for both samples of the vibrational frequency  $\nu_1$  and  $\nu_2$ .

### 3.4 magnetic properties

The VSM measurements of  $\text{CoFe}_2\text{O}_4$  samples at room temperature were performed in the field range of  $\pm 20$  kOe). Figure 4 illustrates the hysteresis loop of the two samples. The magnetic parameters; saturation magnetization ( $M_s$ ) and coercivity ( $H_c$ ) are described in Table 1. The particle size depends heavily on both  $M_s$  and  $H_c$ . The reduced particle size significantly reduces the saturation of magnetization, where it decreased from 99  $\text{emu/g}$  for Co ferrite sample treated at 600 $^\circ\text{C}$  (90 nm) to 55  $\text{emu/g}$  for as prepared Co ferrite sample (12 nm). Such decrease in The  $\text{NiFe}_2\text{O}_4$  nano samples was previously magnetized with the saturation of magnetization [21]. The nanoparticle surface is commonly consists of certain distorted spins, which produce spin repulsion in their core to line up their directions to the applied field, and thus, with the reduction in particle size,  $M_s$  declines. The observed magnetic moment ( $\eta_{\text{Bobs}}$ ) per formula unit in Bohr magneton ( $\mu_B$ ) is determined by the relation listed in the Ref. [22]. According to Néel's theory, the magnetic moment of complete inverse Co ferrite should be exact 3  $\mu_B$  [21]. As indicated in table 1, the as-prepared sample has an observed magnetic moment significantly lower than 3  $\mu_B$ . The Co ferrite sample, on the other hand, has a magnetic moment with a particle size of 90 nm that is much higher than the expected 3  $\mu_B$ . The coercivity in the multi-domain region tends to increase with the decrease of particle size [21].

**Table1.** The lattice constant ( $a$ ), particle size ( $D$ ), tetrahedral and octahedral vibrational frequencies ( $\nu_1$  and  $\nu_2$ ), Saturation magnetization ( $M_s$ ), and Coercivity ( $H_c$ ) of different  $\text{CoFe}_2\text{O}_4$  nanoparticles samples.

Sample	$a$ ( $\text{\AA}$ )	$D$ (nm)	$\nu_1$ ( $\text{cm}^{-1}$ )	$\nu_2$ ( $\text{cm}^{-1}$ )	$M_s$ ( $\text{emu/g}$ )	$H_c$ (G)	$\eta_{\text{Bobs}}$ ( $\mu_B$ )
$\text{CoFe}_2\text{O}_4$ As-prepared	8.291	12	565	368	55.338	1839.6	2.32
$\text{CoFe}_2\text{O}_4$ (600 $^\circ\text{C}$ )	8.389	90	580	375	99.239	1316.6	4.17

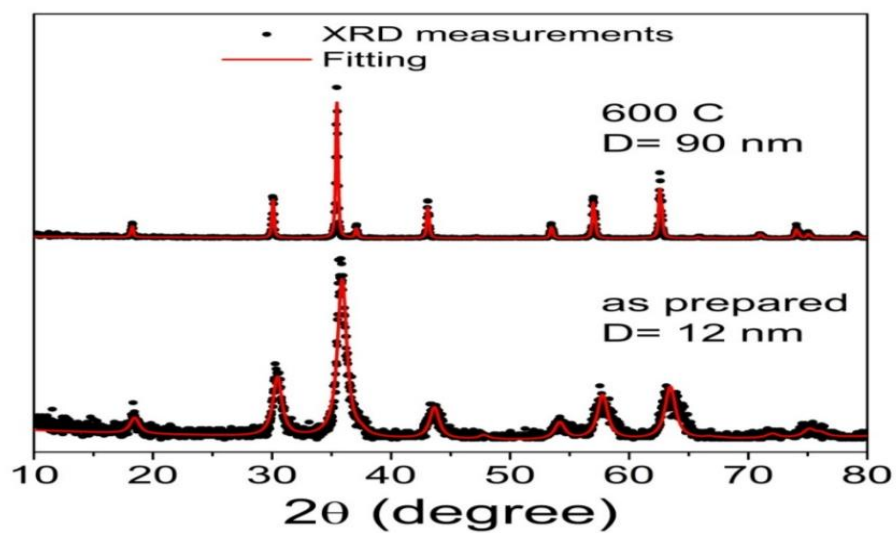


Figure 1 XRD patterns of different CoFe<sub>2</sub>O<sub>4</sub> samples and the average particle size (D) are indicated for each sample.

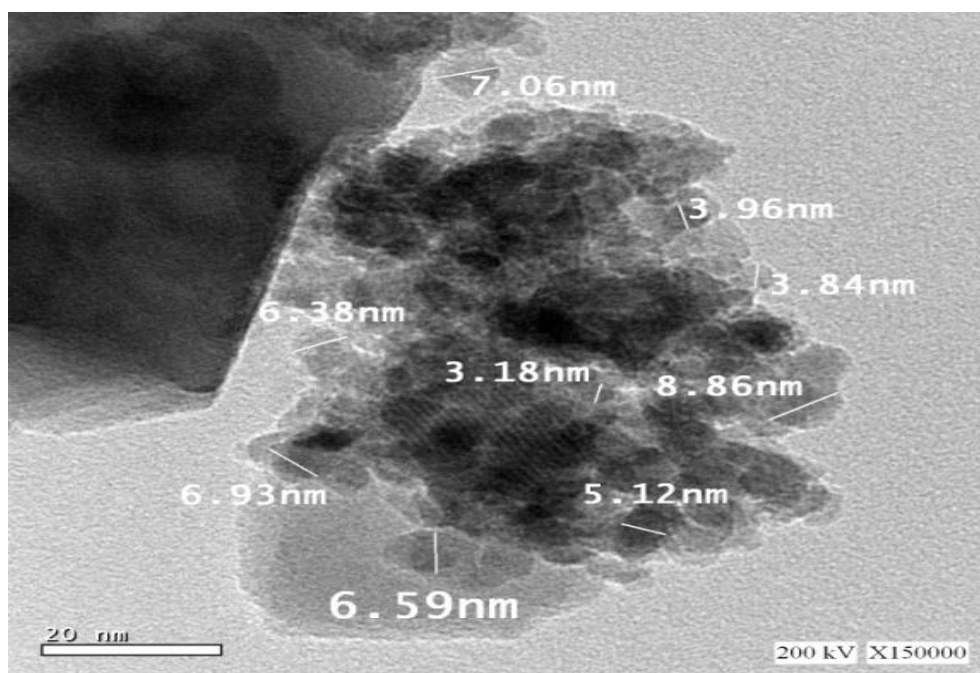


Figure 2 HRTEM micrographs for CoFe<sub>2</sub>O<sub>4</sub> as prepared sample

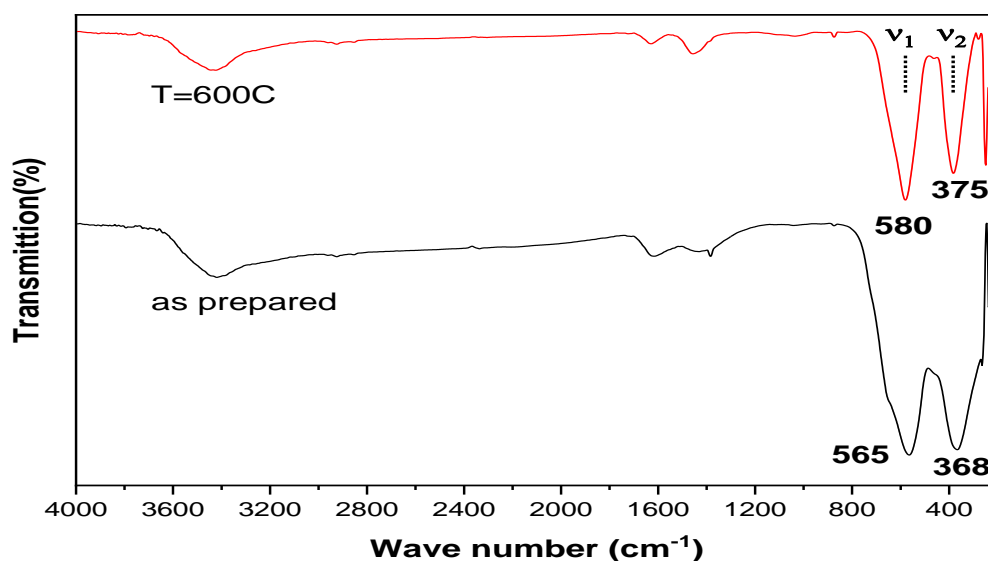


Figure 3: FTIR spectra measurements of CoFe<sub>2</sub>O<sub>4</sub> with different heat treatment.

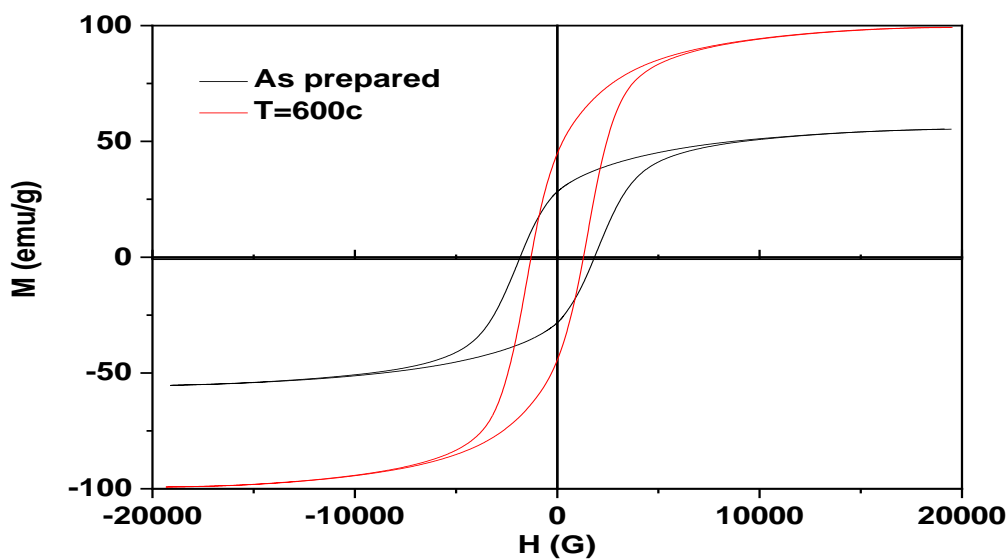


Figure 4: VSM measurements of CoFe<sub>2</sub>O<sub>4</sub> with different heat treatment.

#### V –CONCLUION

An effective method of Citrate – nitrate combustion of nanoparticles of Co ferrite was used. Different heat processing leads to various particle sizes, which have been confirmed by radiation diffraction measurement and electron microscopy at high resolution. The prepared sample is almost 12 nm in size while the sample heated at 600oC is almost 90 nm in size. The lattice parameter (a) has been determined using XRD patterns where a small shift can be seen for various Co ferrite samples. In two vibrational frequency bands (around 370 cm<sup>-1</sup> and 570

cm-1) observed in the Fourier Transform Infrared Spectroscopy, the A and B- sublattices signatures were clearly traced. The vibrating sample magnetometer measurements have provided saturation magnetization ( $M_s$ ) and coercivity ( $H_c$ ) showed a clear dependence on the particle size.

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