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### Calcination Treated Hydrothermal Method to Produce Fine Crystalline $\text{CoFe}_2\text{O}_4$ Nano-Particles

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#### ABSTRACT

Cobalt ferrite nano-powder have been obtained through a hydrothermal method with 2:1 molar ratio of Fe:Co without using any surfactant. X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were used to consider the structural and morphological properties of  $\text{CoFe}_2\text{O}_4$  nano-particles. Also, EDAX spectroscopy applied to evaluate the chemical composition. Results demonstrated that 15 hr hydrothermal processing was enough. In the hydrothermal period of reaction more than 15 hr (21 hr)  $\text{Fe}_2\text{O}_3$  sub-phase was identified which this could be due to instability of  $\text{CoFe}_2\text{O}_4$  at supercritical condition. The average particle size and the percentage of crystallinity for single phase sample were calculated 34.7 nm and 98%, respectively.

**Keyword:** Nano-powder; Hydrothermal; Cobalt Ferrite; Crystallinity; Sub-phase.

#### 1. INTRODUCTION

In the Last decades, synthesis of bimetallic spinel ferrites has attracted attention [1]. Among this magnetic materials, cobalt ferrite with high coercivity, high magnetocrystalline anisotropy, large magneto-optical coefficient [2], moderate saturation magnetization, high chemical stability [3], supported wide range of applications. From spinel ferrites,  $\text{CoF}_2\text{O}_4$ ,  $\text{MnFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$  have been investigated as potential T2 “contrast agents [4]”. Magnetic properties of  $\text{CoFe}_2\text{O}_4$  subjected this to be applied in magnetic resonance imaging (MRI) as contrast agents [5]. In additional, the ferrites were shown a good photo catalytic activity in

UV-Visible range and antimicrobial activity in combination with other metals such as Ag. Cobalt ferrite was shown effective reduction of  $\text{CO}_2$  to methanol [6].

Various synthesis methods have been developed to produce ferrite nano-particles such as Solvothermal [7-10], Microwave [11, 12], Coprecipitation [13, 14], Hydrolysis [15], Complexometry [16], Liquid-phase method [17], and Auto-combustion [18-20]. Among these methods, hydrothermal synthesis requires neither sophisticated processing nor high processing temperature [10].

The main purpose of this work was to investigate a

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simple hydrothermal route to produce a good crystalline, small size and uniform shape cobalt ferrite nano-particle without using any surfactant, stabilizer or capping agents as additive or high pressure and temperature conditions.

This method is very attractive for higher scale and continuous product [21, 22]. In this work, fine  $\text{CoFe}_2\text{O}_4$  nano-particles have been synthesized with a simple hydrothermal technique. Characterization of nano-particles showed decomposition of  $\text{CoFe}_2\text{O}_4$  to sub-phases after 21 hr reaction time.

## 2. EXPERIMENTAL

### 2.1. Materials

Iron (III) nitrate nona-hydrate (Merck 99-101%), cobalt (II) nitrate hexa-hydrate (Merck 99%) and Sodium hydroxide (NaOH) used as chemical agents. All solutions prepared with deionized water.

### 2.2. Synthesize of $\text{CoFe}_2\text{O}_4$

Nano-particles synthesis without any surfactant or need to pressure monitoring carried out as follow: cobalt and iron solutions prepared by dissolving of 1.21 g cobalt nitrate in 250 mL deionized water and 3.36 g iron nitrate in 250 mL deionized water, respectively. 500 mL of NaOH (4M) used as precipitant agent and based on the nucleation theory [23, 24], pH maintained above 11.5 with an aqueous 4 M solution of NaOH. Metal solutions were mixed and immediately added to the boiling NaOH solution under stirring. The solution mixed and heated for

4 hours at 80 °C and then transferred to a simple autoclave, sealed and heated for 15 and 21 hours at 180 °C. After hydrothermal reaction time, autoclave took out and remained until cooled to room temperature. Solid product collected on a filter and washed with absolute ethanol and water several times to remove any unreacted materials. Obtained powders prepared by 15 and 21 hr hydrothermal reaction dried with an electrical oven at 80 °C for 4 hours and then calcined in 600 °C for 2 hours and were denoted as S1 and S2, respectively.

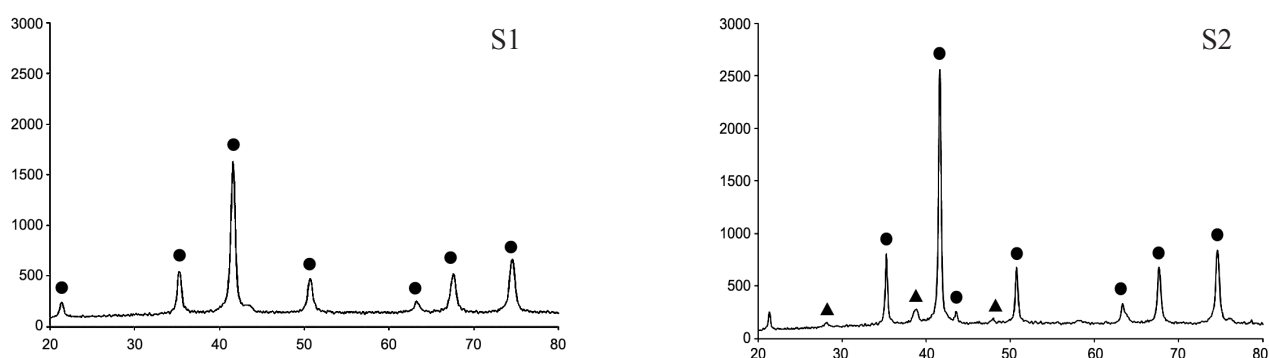
### 2.3. Characterization process

X-ray diffraction (XRD) pattern was recorded by a "Philips X'pert", using  $\text{Cu K}\alpha$  radiation at 40 kv and 30 mA. A "Philips XL-30" scanning electron microscope was used to characterize the morphologies and microstructures of the samples.

## 3. RESULTS AND DISCUSSION

X-ray powder diffraction patterns of calcined nano-powders have been shown in Figure 1. All the peaks in plot of S1 were well matched with JCPDS (No. 22-1086) card, so this sample was single phase and only contain  $\text{CoFe}_2\text{O}_4$  as shown in Figure 1-S1. The unmatched peaks seen in S2 X-ray plot (Figure 1-S2) return to  $\text{Fe}_2\text{O}_3$  presents as sub-phase. The average crystallite sizes calculated by using Scherrer's formula (Eq. 1) from 2theta positions from 20 to 80:

$$d = 0.9\lambda / \beta \cos \theta \quad (\text{Eq. 1})$$



**Figure 1:** X-ray diffraction pattern of  $\text{CoFe}_2\text{O}_4$  synthesized in 15 hr hydrothermal (S1) and in 21 hr hydrothermal (S2) (black Circle (●) means  $\text{CoFe}_2\text{O}_4$  phase and black triangle (▲) means  $\text{Fe}_2\text{O}_3$  sub-phase).

**Table 1:** Qualitative and quantitative extracted data from X-ray diffraction.

S.	Composition	Crystalline structure	Mean particle size of $\text{CoFe}_2\text{O}_4$ (nm)	Crystalline percent of $\text{CoFe}_2\text{O}_4$ (%)	Lattice parameter (Å)	Unit cell volume (Å) <sup>3</sup>
S1	$\text{CoFe}_2\text{O}_4$	Cubic spinel	14	98	8.36	583.27
S2	$\text{CoFe}_2\text{O}_4$	Cubic spinel	22	86.07	8.35	585.18
	$\text{Fe}_2\text{O}_3$	Rhombohedral	Not calculated	Not calculated	Not calculated	Not calculated

Where  $d$  is the grain size,  $\beta$  is half-intensity width of the relevant diffraction;  $\lambda$  is X-ray wavelength and  $\theta$  is the diffraction angle.

The increase of particle size by increasing reaction time was obtained and approved by calculation from X-ray data and shows good crystalline percent about 98% for S1 from ratio of net area to total area.

Appearing a shift (from standard peaks) to the right position is clearly visible in both spectra. That's probably corresponded to a decrease in lattice parameter due to occurrence of some strain or elimination of some lattice defects and strains [25]. For investigation of this guess the lattice parameters were calculated by Bragg's formula (Eq. 2) and report in Table 1.

$$a = (h^2 + k^2 + l^2)^{1/2} \quad (\text{Eq. 2})$$

Where  $h$ ,  $k$ , and  $l$  is Miller indices and  $a$  is the lattice parameter.

As seen from calculated data, lattice parameters were in good agreement with 8.39 Å, lattice parameters for bulk  $\text{CoFe}_2\text{O}_4$ , but in review of some same literatures [26] that no-one faced with this shift phenomena in their XRD plots. At last, also equipment error's factor may be involved in this case.

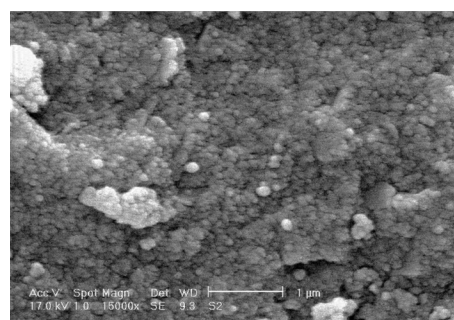
Peak intensity decrease seen in Figure 1-S1. It seems in contrast with increasing in crystallinity in sample

**Table 2:** EDAX ZAF (Standard less) Element Normalized for S1 and S2.

S.	Element	Wt (%)	At (%)
S1	FeK	62.00	63.26
	CoK	38.00	36.74
S2	FeK	61.72	62.98
	CoK	38.28	37.02

S1 reported in Table 1 but considering the presents of sub-phase justified.

Yanez-Vilar et al. [8] reports the synthesis of single phase  $\text{CoFe}_2\text{O}_4$  in solvothermal conditions (by hexanole and benzyl alcohol) in 180 °C for 24 and 48 hours. Also Zaho and coworkers [10], studied the reaction time (from 10 to 360 min) and concluded that in hydrothermal method, period of reaction has little influence on the size and morphology of particles but any data presented in their paper prove this claim. In this work we observed that if reaction time increases to 21 h, the sub-phase  $\text{Fe}_2\text{O}_3$  is formed. This means that  $\text{CoFe}_2\text{O}_4$  prepared in in the hydrothermal procedure (15 hour) is unstable and decompose to  $\text{Fe}_2\text{O}_3$ .  $\text{Co}^{2+}$  ions in qualitative analysis have not been observed because this ion in washing step with water and alcohol is dissolved and removed from the product. Presents of Co and Fe confirm by EDAX data series that abstracted in Table 2. The SEM images of S1 and S2 presented in Figures 2 and 3, respectively. Both sample images shows the uniform spherical morphology. The value of particle size obtained from SEM images for S1 and S2 samples are 29 and 34 nm, respectively, which this result confirms the crystallite size calculated from X-ray peaks by Scherrer's equation. The SEM images for both samples shows that the particles

**Figure 2:** SEM imaging of S1 (15 hr hydrothermal sample).

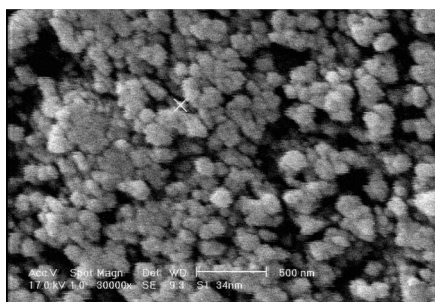


Figure 3: SEM imaging of S2 (21 hr hydrothermal sample).

dispersed uniformly, but agglomerated to some extent due to the interaction between magnetic nanoparticles.

#### 4. CONCLUSIONS

Cobalt ferrite nano-particles were produced successfully with hydrothermal route using the sodium hydroxide as precipitant agent. Results could be drawn as follows: X-ray pattern's shows the presents of the sub-phase in 21 hr hydrothermal processing. We guess that obtained  $\text{CoFe}_2\text{O}_4$  after 15 hr hydrothermal condition was instable and a slight disintegrate to  $\text{Fe}_2\text{O}_3$  carried out. The obtained  $\text{CoFe}_2\text{O}_4$  nano-particles in 15 and 21 hours hydrothermal process, was fine in size about 14 and 22 nm for main phase, respectively.

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