

# Effect of the thermal treatment on the magnetic and structural properties of cobalt ferrite particles



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## ABSTRACT

We herein report a study on the sol-gel synthesis of  $\text{CoFe}_2\text{O}_4$  and the effect of thermal treatment on the product outcome. Xerogels treated at 750, 800 and 850 °C had their structural and magnetic properties thoroughly studied, in order to correlate their synthesis conditions to the positions in which the cations are inserted in the spinel structure. X-ray diffractograms exhibit reflections representative of the spinel structure and demonstrate that the thermal treatment does not affect the lattice parameters of the material. Mossbauer spectroscopy studies indicate a very low inversion degree in the synthesized spinels, which is very unusual for  $\text{CoFe}_2\text{O}_4$ . A maximum in coercivity of 1405.2 Oersted was achieved for the sample treated at 800 °C.

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## 1. Introduction

Insulating magnetic materials are in ever increasing demand due to their ability to suppress certain losses, most notably the hysteresis loss [1]. Spinel ferrites ( $\text{MFe}_2\text{O}_4$ ) have hereof been in the spotlight of many research groups for their applicability in modern electric devices, [2] such as sensors [3], memories [4] and in the medical field [5]. Owing to their high coercivity, moderate saturation magnetization, [6] mechanical hardness and excellent chemical stability, [7,8] these materials are nowadays highly popular for applications in magnetic and magneto-optical devices. Cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) is a member of the class of spinel ferrites which has been widely used for information storage applications due to its highly desirable characteristics [9]. Its large magneto-crystalline anisotropy and facile synthesis, coupled to the aforementioned features of ferrites, make this material an ideal candidate for cutting-edge applications in industry [10]. Under ambient conditions, most ferrites crystallize in the spinel space group ( $Fd\bar{3}m$ ,  $n^\circ 227$ ). This family of compounds presents the formulation  $A^{2+}B_2^{3+}O_4^{2-}$ , with the anions arranged in an fcc structure, whilst the divalent and trivalent cations occupy 1/8 of the tetrahedral and half of the octahedral sites, respectively [11]. In inverse spinels, the interstitial occupancy is inverted, with the trivalent cation filling the available tetrahedral sites, while the octahedral interstices are populated by the divalent and remaining trivalent ions [12]. This

inversion process is usually explained in terms of crystal field stabilization energies (CSFE) [13]. The interplay between the distinct preferences of each cation for tetrahedral or octahedral arrangements is one of the factors governing the final configuration of ferrite crystals. Cobalt ferrite, however, displays a mixed structure, with an intermediate character between normal and inverse spinel, albeit with a clear tendency towards the inverse structure; i.e. in the structure  $\text{Co}_{1-x}\text{Fe}_x(\text{Co}_x\text{Fe}_{2-x})\text{O}_4$ , where  $x$  is the inversion degree which ranges from 0 to 1, the variable tends to values close to unity [14]. This degree of mixing is not fixed and can be steered towards each end of the spectrum by the conditions utilized during synthesis. Configurational entropy reaches a maximum with a  $A_{1/3}B_{2/3}(A_{2/3}B_{4/3})\text{O}_4$ , the most random possible distribution [15]. Nevertheless, kinetic contributions have been demonstrated to influence the final structure more profoundly. Different cooling rates after thermal treatment have previously shown to have a dramatic role in the degree of inversion displayed by  $\text{CoFe}_2\text{O}_4$  [16]. Given the ferrimagnetic behavior of cobalt ferrite, its net magnetism is strongly influenced by the positioning of its cations. Therefore, the cationic arrangement inside the lattice plays a pivotal role in the determination of the macroscopic magnetism displayed by  $\text{CoFe}_2\text{O}_4$  [17]. Cobalt ferrite can be synthesized via a wide range of methods. Co-precipitation [18], polyol [19] and solid state methods [20] have already demonstrated to be viable pathways for the production of this material. Nonetheless, one of the most versatile methods for ferrite production is the sol-gel method. This procedure allows for a great control of the various synthetic parameters, which thus translates into a more direct

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manipulation of the desired product [21,22].

This work aimed to synthesize  $\text{CoFe}_2\text{O}_4$  nanoparticles via the sol-gel method and to analyze the effects of the synthesis parameters on the outcome of the process. Furthermore, we intended to thoroughly characterize the thus-obtained particles, in order to correlate the synthesis parameters to the occupancy of the lattice sites and ultimately to the magnetic behavior of this material.

## 2. Material and methods

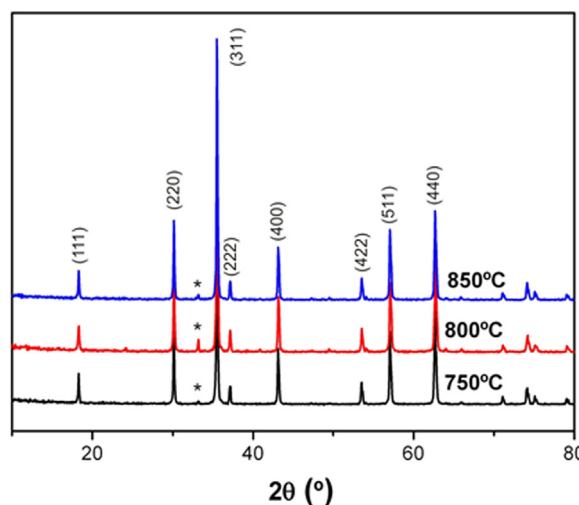
Cobalt ferrite with nominal stoichiometry  $\text{CoFe}_2\text{O}_4$  was prepared by a sol-gel method using citric acid as a complexant. Analytical grade  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and citric acid in a molar ratio of 1:2:3 were dissolved in 20 mL of deionized water for the production of 10 mmol of product. The solution was heated to 85 °C for 1.5 h under magnetic stirring until a dark red gel was formed. The gel was dried at 110 °C for 12 h, transferred to an alumina crucible and further treated at 750, 800 or 850 °C for 4 h. The as-obtained black powder was then subjected to characterization. The crystal structure of the samples was characterized by an X-ray diffractometer (XRD, Philips, X'pert MPD) equipped with a  $\text{Cu-K}\alpha$  source. SEM studies were performed in a JEOL JSM 6060 scanning electron microscope operating at 15 kV. The nanoparticles were previously sputtered with Au in order to enhance their electrical conductivity. For the assessment of their surface area, the samples underwent a desorption pre-treatment of 24 h at 110 °C in a muffle oven and further 2 h at 300 °C under reduced pressure. The measurements were performed in a Nova 1000e device (Quantachrome) using  $\text{N}_2$  as adsorbate at a temperature of  $-195.8$  °C. BET theory was applied to the isotherms for the retrieval of surface data. Raman studies were performed in an inVia Renishaw Raman spectrometer equipped with a 532 nm laser. Magnetic hysteresis curves were achieved in a vibrating sample magnetometer (Model EZ9, Microsense). Hyperfine studies were performed through  $^{57}\text{Fe}$  Mössbauer spectroscopy in transmission mode. Measurements were carried out at room temperature using a  $^{57}\text{Co}$  source and the spectra were adjusted based on the discrete Gaussian line for each hyperfine site.

## 3. Results and discussion

The X-ray diffraction studies of the three samples show that the synthesized powders present the spinel phase as major component (JCPDS 22–1086). The diffractograms of the synthesized ferrites are displayed in Fig. 3.1, with the corresponding reflections indexed to the  $Fd\bar{3}m$  space group (227). The samples treated at 750, 800 and 850 °C present lattice parameters a of 8.3765(7), 8.3709(6) and 8.3760(9), respectively. These values are compatible with standards for the unit cell of cobalt ferrite and rather similar among themselves, indicating that the different thermal treatments applied on the xerogel do not strongly affect the crystalline structure of the products. Nonetheless, the sample that underwent thermal treatment at the intermediate temperature shows a slight deviation towards a more compact unit cell.

A second constituent was also detected in the diffractograms. This minor phase was indexed to hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ,  $R\bar{3}c$ ). The sample treated at 800 °C presents the highest ratio of ferrite/hematite peaks, indicating either a larger fraction of the secondary phase or a lower crystalline character of the major phase. The Scherrer equation applied to the 311 reflection yields a lower limit for crystallite size of 42.1, 39.5 and 42.3 nm for the samples treated at 750, 800 and 850 °C.

The results of nitrogen adsorption isotherms are displayed in Table 3.1, along with an approximate aggregate diameter,



**Fig. 3.1.** Diffractograms of the samples treated at 750 (black), 800 (red) and 850 °C (blue line). All datasets were normalized to their most intense reflection (311). A secondary phase is indicated by an asterisk (\*). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 3.1**  
Specific area and average aggregate size of the cobalt ferrite samples.

| Temperature (°C) | Specific area ( $\text{m}^2 \text{g}^{-1}$ ) | Average aggregate size (nm) |
|------------------|--|-----------------------------|
| 750              | 4.884  | 231                         |
| 800              | 3.409  | 332                         |
| 850              | 4.226  | 265                         |

considering these to be spherical in shape. BET theory yields 4.884, 3.409 and  $4.226 \text{ m}^2 \text{g}^{-1}$  for the samples treated at 750, 800 and 850 °C. The specific areas are rather low, as expected of a magnetic material, where aggregation cannot be avoided in the absence of separation processes. Nevertheless, the sample treated at the intermediate temperature presents an anomalous behavior. Increasing temperature usually works towards diminishing the available surface due to increased atomic diffusion. This decrease, however, did not occur when increasing the treatment temperature from 800 to 850 °C.

SEM images of the sample treated at 750 °C are exhibited in Fig. 3.2. Its morphology is mostly composed of heterogeneous, highly-agglomerated flattened grains. The extent of aggregation among particles explains the low specific area obtained from the  $\text{N}_2$  isotherms.

Increasing the thermal treatment to 800 °C does not significantly affect the morphology of the ferrite, as can be seen in Fig. 3.3. The SEM images are quite similar to those previously shown. The particles are visibly larger, though, which explains the decrease in specific area observed through the adsorption isotherms.

The thermal treatment at 850 °C for 4 h brings on marked modifications to the overall configuration of the ferrite particles. While the morphology of some areas of the sample remains agglomerated and heterogeneous, some analyzed regions exhibit spherical, detached particles. The latter morphology can be explained in terms of the Ostwald ripening [23]. In this process, larger particles effectively absorb the smaller ones, decreasing the specific area of the material and therefore its net surface energy. A higher treatment temperature increases the atomic mobility inside the material, which precipitates the diffusion of atoms into the large grains, i.e. the latter grow at the expense of the smaller particles. The homogeneity observed at the right of Fig. 3.4 is also a

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