Magnetic nanofilms prepared by Langmuir-Blodgett nanoarchitectonics using Co and Co-Y ferrite nanoparticles

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Abstract

The magnetic properties of nanofilms prepared by Langmuir-Blodgett nanoarchitectonics with CoFe_{2-x}Y_xO₄ (x=0; 0.2) nanoparticles (NPs), are studied. Magnetization measurements M(H) of the nanofilms and the NPs were performed, with maximum applied magnetic fields of \pm 5 T at different temperatures from 5 K to 300 K, as well as zero-field-cooling, field-cooling curves (ZFC-FC).

In the nanofilms, saturation magnetization as a function of temperature, Ms(T), and ZFC-FC curves exhibit a sharp increase below 50 K, which is attributed to the existence of a disordered spin shell in the NPs forming the nanofilms, where superficial effects are more relevant than in compacted NPs. The Ms(T) curves were fitted with the modified Bloch's law plus an additional term corresponding to surface spins. Freezing temperatures of (6 ± 1) K for the nanofilm prepared with CoFe₂O₄ and (14 ± 3) K for the one made with CoFe₂O₄ were obtained, indicating that the contribution of freezing spins to Ms(T) is negligible above approximately 5 T_f .

Coercivities are higher for the NPs with yttrium substitution due to their smaller size and *Ms* reduction as a consequence of yttrium inclusion in the spinel lattice. Both NPs and nanofilms follow the modified Kneller's law, with the exponent greater than 0.5, indicating the presence of magnetic dipolar interactions.

At room temperature, the effective magnetic anisotropy (K_{eff}) of the nanofilm prepared with CoFe_{1.8}Y_{0.2}O₄ NPs (4.2 x 10⁵ J/m³) is smaller than K_{eff} for the nanofilm made of CoFe₂O₄ NPs (5.6 x 10⁵ J/m³). Nonetheless, K_{eff} values for both nanofilms are relatively large, making these nanoarchitectures promising for different applications.

Keywords: Co ferrite; Co-Y doped NPs; Magnetic nanofilms; Langmuir-Blodgett technique.

1. Introduction

Spinel ferrites keep receiving the attention of scientists due to their thermal and chemical stability, tunable magnetic properties and excellent cost/benefit ratio that make them suitable for numerous applications including magnetic storage devices, transformers, magnetic resonance imaging (MRI), and sensors [1, 2]. Particularly, cobalt ferrite (CoFe₂O₄) nanoparticles (NPs) have been the focus of several studies for their distinctive characteristics, including large magnetocrystalline anisotropy and coercivity, mechanical robustness, and substantial magnetostrictive coefficient as well as а considerable mechanical hardness [3]. For these reasons, cobalt ferrite NPs have been synthesized by different methods as coprecipitation [1], thermal decomposition [3], combustion [4] and sol-gel [5].

The magnetic properties of cobalt ferrite NPs are influenced by different factors such as particle size, chemical composition, crystalline structure, morphology, cationic distribution, and intergranular interactions. Among these factors, grain and particle size and their distributions are some of the most important factors governing the nanomaterial magnetic properties [6]. For example, Nlebedim et al. showed that it is the particle size distribution in Co ferrite which determines the magnetostictive properties [7]. Furthermore, D. Peddis et al. have shown that depending on the grain size, Co ferrite NPs display particular magnetic characteristics such as spin glass-like behavior, and higher or lower saturation magnetization [8]. Also, depending on the size of the nanoparticles, the material can present high or low coercivity [9] and superparamagnetism [10]. However, further studies are essential to elucidate the influence of grain size, distribution, and intergranular interactions on the magnetic properties of Co ferrite NPs.

Although manipulating the size and shape of pure Co ferrite NPs enables tailoring their properties for particular applications, substituting elements in ferrite structures can also improve the magnetic characteristics of these materials [11, 12]. In this sense, doping the CoFe₂O₄ spinel ferrite with rare earth ions $(Y^{3+}, Gd^{3+}, Ho^{3+}, Sm^{3+}, Nd^{3+})$ allows manipulating magnetic coupling, as reflected by the decrease in Curie temperature [13,14]. Because rareearth elements have larger ionic radii compared to iron, the substitution produces alterations in the cell symmetry that leads to structural disorder and lattice stress. Consequently, the substitution not only affects the structural properties of the material, such as the cell parameter, average crystallite, and grain size, but also influences the dielectric, microwave absorption, magnetic and magnetostrictive properties of substituted materials [14]. In addition, doping different materials with Y^{3+} has proved to be beneficial in different catalytic reactions. Yttriumdoped ferrites present a good performance as photocatalysts to degrade harmful organic pollutants [15], as catalysts for the synthesis of several triazoles and coumarin derivatives [16], as an electrocatalyst for highly sensitive detection of mesotrione herbicide [17], and as a new material to generate photocatalytic water splitting with a significant H₂ evolution rate [18].

In the past few years, considerable attention has been paid to the fabrication of extensive 2D arrays of magnetic NPs with good chemical and mechanical stability, having in mind their potential utilization in various fields including high-density magnetic storage media, magneto-optical devices, electronic logic devices, and sensors [19]. Among the variety of methods proposed for the 2D assembly of nanoparticles, the Langmuir-Blodgett (LB) technique can be considered as part of the emerging nanoarchitectonics [20] used to produce several nanostructured materials. Particularly, the LB technique stands out as the most versatile for film deposition due to the precise control that can be achieved over the thickness and uniformity of the deposited layer [20-23]. The LB technique allows creating highly ordered thin films by transferring monolayers of materials to a substrate from a Langmuir film, which is spread over a liquid surface. The transfer of the monolayer is carried out at constant surface pressure and substrate insertion speed, which guarantees the creation of homogeneous films. Parameters such as surface pressure, deposition rate, and the number of depositions can be adjusted to finely tune the properties of the LB films. LB nanoarchitectonics seems superior to casting methods, which are simpler and often used for producing thicker films; however, the uniformity and precision in thickness are less controlled, leading to variations in the physical-chemical properties across the film. Furthermore, in the LB technique, the process

naturally aligns molecules or particles during deposition, resulting in a better orientation of the material, whereas film casting produces disordered structures.

The most significant challenge of this technique is the fabrication of LB films at a large scale. The Roll-to-Roll LB methodology was developed to overcome this difficulty, where the substrate is a film guided from a start roll into the subphase. As the film rises from the subphase through the interface, it gets coated with the particles or molecules being used. The substrate then continues onto a collecting roll, which gathers the coated film. An automated movable barrier ensures the particle packing density reaches the desired value, resulting in a high-quality coating [26].

Several achievements have been made in assembling magnetic nanoparticles using the LB technique [24-25]. However, to the best of our knowledge, a complete magnetic characterization comparing the behavior of yttrium-doped cobalt ferrite nanoparticles with that of films made with these same structures has never been performed. The present work aims to synthesize nanoparticles of Co and CoY ferrites by the low-temperature citrate selfcombustion method, and use the so-obtained material to prepare nanofilms by the LB technique. Our previous studies have been focused on investigating the magnetic response at room temperature of Co ferrite and Y-doped Co ferrite NPs. Here, we analyze the temperature dependent magnetic properties of Co ferrite and Y-doped Co ferrite nanoparticles and nanofilms, finding a spin freezing effect present only in the films.

2. Materials and methods

2.1 Synthesis of Co-ferrite and CoY-ferrite nanoparticles

Cobalt ferrite $CoFe_2O_4$ and yttrium-doped cobalt ferrite $CoFe_{1.8}Y_{0.2}O_4$ were prepared by the selfcombustion method, as described elsewhere [4]. Briefly, to synthesize Co ferrite NPs, different proportions of iron nitrates and cobalt oxalates were weighed according to the required stoichiometric proportion and diluted in water ([Fe(III)]+[Co(II)] = 1 M). A 3 M citric acid solution (50 ml) was added to each metal solution (50 ml) and heated at 40°C for approximately 30 min with continuous stirring. Then, a highly viscous gel formed after evaporation of the solution while heating at T < 200 °C, until ignition in a self-propagated process. The obtained residue was then calcined at 800 °C for 2 h. This process is schematized in Scheme 1 (a). Yttriumdoped cobalt ferrite (CoFe_{1.8}Y_{0.2}O₄) was obtained in a similar way, using stoichiometric proportions of yttrium nitrate solution in 3 M citric acid. Table S1 in the Supplementary Information shows the number of moles of all reagents used to prepare both ferrites. The resulting CoFe₂O₄ and CoFe_{1.8}Y_{0.2}O₄ NPs were labeled Co-P and CoY-P, respectively.

The so-obtained nanoparticles were further modified with stearic acid (SA) following the procedure described in a previous paper [27, 28], which is depicted in Scheme 1 (b). In brief, 0.15 g of $CoFe_2O_4$ NPs or $CoFe_{1.8}Y_{0.2}O_4$ NPs were first dispersed in a mixed solution of absolute ethanol (25 ml) and stearic acid (0.075 g). The resulting solutions were sonicated at 80 °C for 1 h and then the mixtures were washed 5 times to remove the free SA; finally, they were dried at 60 °C for 24 h.



Transfer of films to the substrate

Scheme 1. (a) Synthesis of Co-ferrite and CoY-ferrite nanoparticles, (b) coating of NPs with stearic acid, and (c) preparation of Co-ferrite and CoY-ferrite films.

2.2 Preparation of Co-ferrite and CoY-ferrite nanofilms

In order to deposit SA-modified Co-P and CoY-P on glass substrates, the Langmuir-Blodgett method was employed. Using a mixture of chloroformmethanol as solvent, 5 mg/ml of NPs solutions were prepared. Then, 300 μ l of each suspension were spread at the air/water (Milli-Q, 18.2 M Ω , Millipore) interface form in the Langmuir Balance using a micro-syringe. The pressure-area isotherms of Co-P and CoY-P films were monitored with a Wilhelmy plate equipped on a KSV Mini-trough a (36.4 cm x 7.5 cm, KSV model 2000). Compression of the films was performed at a rate of 10 mm/min after the solvent evaporated (~20 min). The formed nanofilms were transferred onto a glass substrate at a pressure of 40 mN/m at a speed of 3 mm/min through a process of immersion and emersion of the substrate from the subphase, as illustrated in Scheme 1 (c). To ensure complete coverage, the substrates were twice immersed and emerged from the subphase. Previous to the deposition, the glass substrate was washed several times with acetone, ethanol, and Milli-Q

water and then treated with hexane. The film samples were named Co-F and CoY-F, corresponding to deposits of $CoFe_2O_4$ NPs and $CoFe_{1.8}Y_{0.2}O_4$ NPs, respectively.

2.3 Experimental Techniques

Samples Co-P and CoY-P, as well as Co-F and CoY-F were characterized by different techniques. The crystalline structure was analyzed by X-ray powder diffraction (XRD) with a PANalitycal X'Pert Pro diffractometer using Bragg-Brentano geometry, operated at 40 kV, 40 mA and Cu Ka radiation (λ = 1.5418 Å). The morphology of the nanoparticles and the thickness of the films were determined in a Sigma Zeiss Field Emission Scanning Electron Microscope (FE-SEM) and an Force Microscope Atomic (AFM) Agilent Technologies 5500. AFM measurements were performed in tapping mode at atmospheric pressure and room temperature by using rotated monolithic silicon probes coated with an aluminum reflex film (Budget Sensors TAP150-Al-G, Nominal spring constant 5 N m⁻¹, resonance frequency of 150 kHz, nominal radius < 10 nm). Transmission electron microscopy (TEM) was performed in a Hitachi 7800 microscope with an accelerating voltage of 100 kV. X-ray Photoelectron Spectroscopy (XPS) spectra were obtained using a K-Alpha X-ray photoelectron spectroscope (Thermo-Fisher Scientific Co.) with a monochromatic Al-Ka X-ray source. The acquisition time was 7 min and several scans were averaged, with an energy step size of 0.5 eV for survey scans and 0.05 eV for high resolution spectra. The surface area of the nanoparticles was determined by the N_2 absorption method using a BET ASAP 2020 Plus.

Magnetic characterization of the samples was conducted in a Cryogenic Ltd. vibrating sample magnetometer in a temperature range from 4 K to 300 K and maximum applied fields of ± 5 T. For the magnetic measurements, the NPs were compacted in pellets as thin disks while the films were measured applying the magnetic field parallel and perpendicular to the substrate surface. The glass was also measured in order to subtract its contribution from the magnetic measurements.

3. Results

3.1 Characterization of the nanoparticles

Figure 1 (a) is a SEM image of as-synthesized Co ferrite NPs, where rather spheroidal particles can be observed. Several similar images allowed us to determine a mean diameter of (84 ± 2) nm and a dispersion of (44 ± 1) nm, as shown in the size distribution displayed in Figure 1 (b). On the other hand, as-prepared yttrium-doped Co ferrite NPs are smaller than the previous ones, displaying a faceted structure (see Figure 1 (d)) and a narrow size distribution with a mean particle size of (43 ± 2) nm and a dispersion of (22 ± 1) nm, as shown in the histogram of Figure 1 (e). This result indicates that yttrium inclusion drastically reduces the particle sizes, as previously reported for similar samples [4], and it is also effective in reducing the size dispersion.

The crystalline structure of the nanoparticles was verified by XRD, as shown in Figure 1 (c) and 1 (f) CoFe_{1.8}Y_{0.2}O₄ for $CoFe_2O_4$ and powders, respectively. The peak positions and relative intensities, corresponding to reflections (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (3 3 3), (4 4 0), (5 3 1), (6 2 0), (5 3 3) and (6 2 2), match well with the standard pattern of the cubic spinel structure (JCPDS-PDF 22-1086). No secondary phases are detected in any of the powders. Rietveld refinements of Co-P and CoY-P X-ray diffraction patterns were performed, using the software XPert HighScore Plus (Malvern Panalytical) and they are presented in Figure S1 (a) and S1 (b) of the Supplementary Information. The lattice parameter given by the refinements is a = 8.3718(4) Å for Co-P and a =8.3574(6) Å for CoY-P. These values agree well with similar NPs of the same ferrites prepared by self-combustion [4]. The average crystallite sizes were calculated with the Scherrer formula, giving (80 ± 5) nm and (25 ± 5) nm for CoFe₂O₄ and CoFe_{1.8}Y_{0.2}O₄ NPs respectively. These values confirm that yttrium incorporation to the lattice decreases the grain size, as well as the particle size, as it was determined by SEM. Similar results were obtained by Meng et al. for $CoFe_{(2-x)}Y_xO_4$ (x = 0, 0.1, 0.3, 0.5) ferrites; these authors found that increasing Y doping leads to smaller crystal grains, indicating that Y hinders the grains growth [29].



Figure 1. SEM image, histogram and XRD pattern of (a), (b), (c) Co ferrite NPs and (d), (e), (f) Co-Y ferrite NPs.

The surface area of Co and Co-Y ferrite NPs was measured using the BET method, finding values of $(2.8 \pm 0.1) \text{ m}^2/\text{g}$ and $(7.92 \pm 0.04) \text{ m}^2/\text{g}$, respectively. These areas agree with the mean sizes determined for both kinds of NPs, since CoY ferrite NPs are smaller therefore a larger surface area is expected. Figure S2 in the Supplementary Information shows the corresponding isothermal curves.

In order to successfully prepare magnetic films using the LB technique with the obtained NPs, they should be highly hydrophobic. For this reason, the first step was modifying the nanoparticle's surface with stearic acid (SA), as mentioned in Section 2.1.

TEM images of the modified NPs are shown in Figure 2, where it is possible to confirm that the size and morphology of both samples are unaltered after the coating. Comparing the histograms in Figure 2 with those of Figure 1 it is also noticed that after SA modification, the size dispersions have been reduced from (44 ± 1) nm to (10 ± 2) nm in Co ferrite NPs,

and from (22 ± 1) nm to (12 ± 2) nm in Co-Y ferrite NPs.

X-ray photoelectron spectroscopy (XPS) measurements were carried out to investigate the electronic state and cation distribution of the NPs before and after SA coating. Figure S3 in the Supplementary Information displays the survey spectra of Co and Co-Y ferrites before and after modification. No other elements are detected, confirming the purity of the samples. A detailed analysis of the survey spectra as well as the high resolution XPS spectra of Co, Fe, Y, C and O (shown in Figures S4 through S8) are included in the Supplementary Information. It is possible to conclude that the spinel phase remains unaltered after SA coating and that the NPs modification has been successful.



Figure 2. TEM images and size histograms of (a), (b) Co-P and (c), (d) CoY-P after SA coating.

3.2 Pressure-area isotherm study with Co-P and CoY-P

Surface pressure-area isotherms of samples Co-P and CoY-P were measured to select the optimal conditions for depositing the films with the LB technique (Figure S9 in the Supplementary Information).

Before barrier compression, Co-P and CoY-P are initially in the gas phase: they are fully dispersed and do not interact. The isotherm corresponding to sample CoY-P exhibits a gaseous, liquid and solid phase as well as a well-defined collapse point. As the area is reduced, the surface pressure in this almost isotherm remains constant up to approximately 120 cm², which is characteristic of the gas phase in Langmuir-Blodgett films. Then, the surface pressure of the isotherm starts to increase, indicating the beginning of the so-called liquid phase and the formation of nanoparticle domains. Upon reaching the area value 85 cm^2 (solid phase region), the slope becomes steeper, indicating even closer nanoparticle packing and formation of large domains of organized CoY-P. However, the compression of the film beyond 80 cm² causes molecular disorder and a phenomenon commonly called collapse. On the other hand, in the Co-P isotherm a gas phase can be observed up to 140 cm^2 , but the beginning of the liquid phase is not delimited. As the film is continuously compressed, the surface pressure begins to gradually increase up to a value of approximately 40 cm^2 where the slope is steepest, indicating the region of the solid phase as a result of greater packing of the Co-P.

Based on the surface pressure-area isotherms recorded for samples Co-P and CoY-P, the pressure of 40 mN/m was selected as optimal for the film deposition on a hydrophobic glass —dashed line in Figure S9 of the Supplementary Information—because at this pressure the nanoparticles are mostly packed. In this way, multiple layers were deposited, with a maximum transfer ratio ranging between 1.4 and 0.3 for Co-P and between 1.6 and 0.4 for CoY-P, during both inward and outward movements of the substrates.

3.3 Characterization of Co-F and CoY-F nanofilms

Figure 3 shows the morphological characterization of the nanofilms obtained by transferring the NPs to the glass substrates.



(b)

a)

Figure 3. SEM and AFM images and cross-sectional line profile of the nanofilms Co-F (a), (b), (c) and CoY-F (d), (e), (f).

SEM images of the nanofilms Co-F (Figure 3 (a)) and CoY-F (Figure 3 (d)) show dense arrays of nanoparticles and suggest an efficient transfer at the air-water interface onto the hydrophobic substrates. The data shown are representative of the structures observed on the whole substrate surfaces, i.e., a continuous NPs layer is formed. Bright areas in SEM images indicate that the NPs are well compacted, which agrees with the high transfer ratio for Co (~1.4) obtained and Co-Y (~1.6) nanoparticles. Furthermore, the surface pressure at which the NPs are transferred to the substrates remains constant at 40 mN/m.

On the other hand, AFM measurements at the film boundaries allowed us to obtain the topography and cross-section line profile from samples Co-F (Figure 3 (b), (c)) and CoY-F (Figure 3 (e), (f)). It can be seen that small aggregates form in both films, corroborating SEM results. In addition, the cross-section line profiles extracted from Figure 3 (c) and Figure 3 (e) (corresponding to samples Co-F and CoY-F, respectively), confirm that the films consist of multiple layers of nanoparticles and allow to estimate their thicknesses, being approximately 160 nm and 140 nm for samples Co-F and CoY-F, respectively.

3.4 Magnetic properties

Magnetic measurements were performed in samples Co-P, CoY-P, (after compacting the NPs in thin disk-shaped pellets) Co-F and CoY-F (nanofilms). The results obtained for the nanofilms are displayed after subtracting the paramagnetic contribution from the glass substrate.

Figure 4 (a), (b), (c) and (d) depict magnetic hysteresis loops measured at different temperatures in the range 5-300 K for samples Co-P, CoY-P, Co-F respectively. and CoY-F, The expected ferrimagnetic behavior can be observed in all samples with considerable values of remanence (Mr)and coercivity (Hc). The M vs. H curves do not saturate even at the highest applied field of 5 T, as a result of а paramagnetic/superparamagnetic contribution (probably arising from the smaller particles) which is more noticeable at temperatures below 150 K. For this reason, saturation magnetization M_S was calculated as the y-intercept of M vs 1/H when plotting the M(H) data measured at the highest fields (H > 4 T). Furthermore, M vs. H curves for Co-P (Figure 4 (a)) and CoY-P (Figure 4 (b)) clearly indicate that M_S decreases with the vttrium incorporation while Hc increases, as it was reported before for similar samples at room temperature [4]; here we verify that this tendency is maintained in the whole temperature range.

The decrease of M_S with Y³⁺ incorporation to the spinel lattice is associated with two factors: (1) Magnetic interactions between A-A, B-B and A-B sites in the spinel structure and interaction of magnetic ions with the external applied field, which determine the net magnetic moment of the material;

and (2) being a non-magnetic ion, Y^{3+} does not take part in the exchange interaction with its nearest neighbors. As a consequence, the net magnetization is reduced upon Y^{3+} incorporation. According to the well-known Stoner-Wohlfarth model, the increase in *Hc* from samples Co-P to CoY-P is a consequence of the particle size reduction and a decrease in magnetization, since Hc $\propto 1/Ms$ [30].

Figure 4. Hysteresis loops obtained at different temperatures of (a) Co-P, (b) CoY-P, (c) Co-F and (d) CoY-F.

An interesting feature observed in sample Co-P is that below 150 K the M(H) loops display a waspwaisted shape, while the other samples do not show this behavior. According to the literature, waspwaisted M(H) curves are observed when any (or some) of the following features occur: (i) bimagnetic exchange spring magnet systems composed of two different magnetic phases (soft and hard) [31]; (ii) more than one population of magnetic particles with different average sizes and coercivity values; (iii) magnetically soft material with oxidized surfaces; and/or (iv) spin reorientation leading to alteration in the magnetic structure [1,2,6,32].

In our samples, XRD allowed determining the presence of a single crystalline phase, so we can rule out (i) as a possibility. We propose that the wasp-waisted hysteresis curves of sample Co-P occur due to a quite wide NP size distribution (see Figure 1 (b)). A similar behavior was found by Chithra et al.

for CoFe₂O₄ nanoparticles with a multi-modal size population [6]. At low temperatures, the particles decouple from their neighbors, which can account for the wasp-waisted shape observed in the M(H)hysteresis curves. The wasp-waisted behavior disappears as the dispersion in particle size decreases, being this a possible explanation that this feature is not observed in the nanofilm prepared with these NPs. As it was shown in the histograms of Figure 1(b) and Figure 2(b), the size dispersion is reduced upon SA coating. Hc values at different temperatures for all the samples are plotted in Figure 5 where a large, monotonic increase in Hc with decreasing temperature can be observed. At a given temperature, coercivity values Hc increase in CoY-P with respect to Co-P, and become even higher in CoY-F. The increase in Hc is related to the particle size decrease, and it is a consequence of a decrease in magnetization because of Y doping [30, 31].

Figure 5. Coercivity as a function of temperature data, corresponding to nanoparticles and nanofilms of (a) Co and (b) CoY ferrites. Red solid lines are fitting curves according to Eq. (1).

As it can be seen from comparing Figure 5 (a) with Figure 5 (b), Hc is higher in samples with yttrium than in samples without yttrium (for both NPs and nanofilms), reaching quite high values at low temperatures. In all the studied samples, Hc(T) follows the modified Kneller's law [6,33,34]:

$$Hc(T) = Hc(0)(1 - \frac{T}{T_{P}})^{\beta}$$
 (1)

where Hc(0) is the coercivity at T = 0 K and T_B is the blocking temperature.

The fact that Hc(T) follows Eq. (1) with β >0.5 (in every case) is in agreement with predictions for a collection of nanoparticles with magnetic dipolar interaction [34]. The obtained fitting parameters using Eq. (1) are shown in Table 1.

Table 1. Fitting parameters to $H_C(T)$ data with Eq. (1). $H_C(0)$ is the coercivity at T = 0 K, T_B is the blocking temperature and β is the exponent.

Parameter	Co-P	Co-F	СоУ-Р	CoY-F
$H_{C}(0)$ [T]	1.1±0.1	1.3±0.1	1.7±0.1	1.6±0.1
T_B [K]	317±20	319±20	305±20	313±20
β	0.8±0.1	0.7±0.1	0.7±0.1	0.7±0.1

Blocking temperature T_B values are similar for all the samples, and no significant differences were found either between samples with and without yttrium or between particles and films.

The saturation magnetization temperature dependence Ms(T) of the studied NPs and nanofilms obtained from the hysteresis loops recorded at various temperatures, are shown in Figure 6.

Comparison of Co-P and Co-F is displayed in Figure 6 (a), while CoY-P and CoY-F are compared in Figure 6 (b). As it can be seen, both determinations are similar for particles and films at high temperatures but differ below \sim 50K. It is worth mentioning again that the magnetic contribution from the glass substrate has been subtracted from the films' magnetic measurements.

Figure 6. Saturation magnetization as a function of temperature corresponding to nanoparticles and nanofilms of (a) Co and (b) CoY ferrites. Red solid lines correspond to fittings with Eq. (2) (used to fit Co-P and CoY-P data) and green solid lines are the fittings with Eq. (3) (used for the nanofilms Co-F and CoY-F).

In complex systems below the Curie temperature, the temperature dependence of the saturation magnetization can be described by the expression [35]:

$$M_S(T) = M_S(0) \left[1 - \left(\frac{T}{T_C}\right)^{\alpha} \right]$$
(2)

where Ms(0) is the saturation magnetization at 0 K, *Tc* is the Curie temperature and α is an exponent which for bulk ordered magnetic systems takes the value of 1.5, but it is larger when finite size effects are important. This equation fits quite well the data for the nanoparticles Co-P and CoY-P, as it is shown in Figure 6 (a) and 6 (b) (open circles). However, both nanofilms Co-F and CoY-F exhibit a sharp increase in *Ms* below 50 K, which is usually attributed to frozen surface spins [31-37], and could not be fitted with this expression alone. In fact, a term related to frozen spins contribution was needed to achieve the best fit to the data in the case of the nanofilms:

$$M_{S}(T) = M_{S}(0) \left[1 - \left(\frac{T}{T_{c}}\right)^{\alpha} \right] + A e^{\left(-\frac{T}{T_{f}}\right)} \quad (3)$$

where *A* and T_f (the freezing temperature) are experimental parameters that depend on the nanoparticle size [33-36]. Figure 6 displays the resulting fitting curves and Table 2 lists the fitting parameters obtained for both nanofilms. The exponents α for all samples are not 1.5 as predicted for bulk ferromagnets but instead they are close to 2, due to a reduction in the ferrites particle size [34]. The value of T_f (6±1) K for Co-F and (14±3) K for CoY-F indicate that the contribution of frozen spins to Ms(T) is negligible above approximately 5 T_f , in agreement with Chakrabarti et al. [35].

In magnetic NPs, the saturation magnetization is usually lower than in its respective bulk material due to surface effects. The reduced saturation magnetization of magnetic NPs (compared to their bulk counterpart) can be explained by a spins core/shell structure in which the core is composed of ordered spins while the shell, of thickness t, has disordered spins that fluctuate randomly [37, 38]. Assuming the shell thickness t is constant, the magnetization of the particles can be expressed as [37]:

$$Ms = Ms(0)\left(1 - \frac{6t}{d}\right) \tag{4}$$

where d is the crystallite size obtained from the Scherrer formula. The shell thicknesses calculated for our samples are informed in Table 2. As it can be

seen, this layer is larger when the particles are in a 2D array than when they are grouped in a compact pellet, because surface effects are more relevant in the films.

Table 2. Fitting parameters to $M_s(T)$ data using Eq. (2) (for NPs) and Eq. (3) (for the films). $M_s(0)$ is the saturation magnetization at 0 K, Tc is the Curie temperature, α is the exponent and T_f is the freezing temperature. Shell thickness *t*, calculated with Eq. (4) is also listed for each sample.

Parameter	Со-Р	Co-F	CoY-P	CoY-F	
<i>M</i> s(0) [emu/g]	104±1	100±1	69.1±0.3	68.7±0.4	
Tc [K]	720±100	750±60	650±80	670±70	
α	1.9±0.3	2.0±0.2	2.5±0.3	2.5±0.3	
A	-	30±3	-	10±1	
T_{f}	-	6±1	-	14±3	
<i>t</i> [nm]	2.7	3.5	1.1	1.6	

In order to further investigate this behavior, zero field cooling (ZFC) and field cooling (FC) magnetization curves were measured at different cooling fields. Figure 7 shows the curves obtained for samples Co-P, CoY-P, (NPs compacted in thin disk-shaped pellets) Co-F and CoY-F (nanofilms). The ZFC-FC curves obtained for both Co-P and CoY-P (Figure 7 (a) and (b), respectively) show the characteristic behavior of ferrimagnetic NPs, with blocking temperatures at around 300 K (in agreement with the $T_{\rm B}$ values from Table 1) and irreversible temperatures T_{irr} (the point where the ZFC and FC curves split, indicating the onset of an irreversible behavior), which depend on the cooling field and on the particle size [39]. Samples Co and Co-Y have similar T_{irr} , regardless whether they are compacted NPs or dispersed as a film. On the other hand, the ZFC-FC curves for the nanofilms Co-F and CoY-F display a steep increase in magnetic moment, which is proportional to the applied field, in both the ZFC and FC curves at temperatures below 50 K. This

effect is in agreement with M(H) hysteresis loops measured at T < 50 K and it can be explained by the presence of uncompensated frozen spins at the surface of the nanoparticles, as it has also been reported by other authors [40]. This feature becomes more important when the nanoparticles are forming a 2D film, in which surface effects are more noticeable than in compacted pellets. Therefore, we interpret the increase of magnetic moment at low temperatures in the nanofilms as coming from the surface spins, which are more important in 2D structures than in bulk materials. The surface spins misalign with the spins of the ordered core, and the former freeze along the applied field direction at lower temperatures. In addition, as the nanofilm preparation includes a process at a water/air interface, it is expected that both the largest and the smallest NPs are expelled from the interface to the sub-face, being the nanofilm formed with NPs of sizes very close to the distribution mean value.

Figure 7. ZFC and FC magnetic moment curves at different applied fields of samples (a) Co-P, (b) CoY-P, (c) Co-F and (d) CoY-F. In (c) and (d), the glass contribution has been subtracted from the data.

To obtain information about the effective magnetic anisotropy of the films, the hysteresis loops of samples Co-F and CoY-F were measured with the applied field in both in-plane (IP) and outof-plane (OoP) directions, at room-temperature. The hysteresis loops are shown in Figures 8 (a) and 8 (b), for samples Co-F and CoY-F, respectively. The saturation magnetization in both cases is the same when the film is measured in both directions, but in the IP direction the magnetization reaches higher values than in OoP direction at low fields, indicating that there is an easy plane of magnetization along the film's surface. Higher coercivity values are also measured when the field is applied along the film's surface (IP direction), confirming the previous statement. Similar results were obtained for cobalt ferrite thin films deposited on MgO [11]. The characteristic values of the hysteresis loops at room temperature are summarized in Table 3.

Figure 8. Hysteresis loops measured at room temperature with the magnetic field applied IP and OoP for (a) Co-F and (b) CoY-F. The inset in (b) schematizes the IP and OoP directions.

The effective magnetic anisotropy constant (K_{eff}) can be determined using various methods, such as pendulum, torque magnetometry, torsion magnetization curves, and magnetic resonance. Specifically, the determination of K_{eff} from magnetization curves can be carried out using the area method, which involves measuring the area in the first quadrant which is enclosed between the magnetization curves measured along a hard and an easy direction [26]. This area represents the energy that is needed to move the magnetization from an easy direction (or plane) to a hard one.

In this study, the area method was employed to calculate K_{eff} values, using the graphs shown in

Figures 8(a) and 8(b). The obtained results were K_{eff} = 5.9 × 10⁵ J/m³ for Co-F and K_{eff} = 4.2 × 10⁵ J/m³ for CoY-F. These values are higher than K_{eff} = 2.9 x 10⁵ J/m³ obtained by S. Regmi et al. for thin films of cobalt ferrite (CoFe₂O₄) [41]. On the other hand, K_{eff} is higher for Co-F than for CoY-F, which is attributed to the difference in M_S . In CoY-F, M_S decreases due to the incorporation of Y³⁺ into the lattice, as previously demonstrated. Nevertheless, the effective anisotropy values obtained for both nanofilms at room temperature are relatively large, which predicts applications in which an external magnetic field may be used to tune the system's outcome.

Table 3. Magnetic parameters at room temperature corresponding to the nanofilms: saturation magnetization M_s , remanent magnetization M_R , coercive field H_c and effective magnetic anisotropy K_{eff} .

0	/	0		•	0	17 -55	
	M_S	M_R [± 1 emu/g]		<i>Hc</i> [± 1 mT]			
Sample	$\begin{bmatrix} \pm & 3 \\ emu/g \end{bmatrix}$	IP	OoP	IP	OoP	K_{eff} [J/m ³]	
Co-F	84	43	22	123	57	5.9 x 10 ⁵	
CoY-F	59	25	8	150	30	$4.2 \ge 10^5$	

4. Conclusion

Two magnetic nanofilms were successfully prepared by Langmuir-Blodgett nanoarchitectonics using cobalt ferrite NPs, and yttrium-doped cobalt ferrite NPs on glass substrates. Magnetic properties of the as-prepared nanofilms and NPs were investigated in the temperature range 5 K to 300 K. A wasp-waisted behavior is observed in the M(H) curves at low temperatures for Co ferrite NPs as a result of a wide size distribution, in contrast with the other samples.

Hc is higher in Co-Y ferrite than in Co ferrite, due to the difference in particle size and *Ms* reduction as a consequence of Y inclusion in the spinel lattice. Both samples of nanoparticles and nanofilms follow the modified Kneller's law with an exponent β >0.5, indicating that magnetic dipolar interactions are present.

In both kinds of nanofilms, Ms(T) curves exhibit a sharp increase in Ms below 50 K which is attributed to a core/shell spin configuration, in which the shell contains misaligned spins that freeze at low temperatures. The ZFC and FC curves of the nanofilms confirm this hypothesis, as they show a steep increase in the magnetization at low temperatures which increases with increasing the applied field. This effect is only observed in the films (not in the compacted NPs of the same composition), since surface effects are more important in 2D structures than in bulk materials.

The hysteresis loops of the nanofilms Co-F and CoY-F measured with the applied field IP and OoP indicate that there is a magnetization easy plane, as expected in 2D structures. While CoY-F displays larger IP coercivities than Co-F, its effective magnetic anisotropy at room temperature ($K_{eff}^{CoY-F} = 4.2 \times 10^5 \text{ J/m}^3$) is smaller than K_{eff} for Co-F ($K_{eff}^{Co-F} = 5.6 \times 10^5 \text{ J/m}^3$). This rather unintuitive behavior is a result of the decrease in saturation magnetization due to size reduction upon yttrium inclusion. Nonetheless, K_{eff} values for both nanofilms are relatively large, making these nanoarchitectures promising for different applications in which an external magnetic field may be used to control the system's response.

This work presents a complete structural and magnetic characterization comparing the behavior of Co and Co-Y ferrite nanoparticles with that of nanofilms made with the same particles using LB nanoarchitectonics. These films expand the field of application of Co and Co-Y ferrite NPs, since they could be implemented in devices for fuel cells, magnetic and magneto-optical sensors, advanced magnetic memories, or optoelectronic devices.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Viviana B. Daboin: Data curation; Formal analysis; Investigation; Methodology; Validation; Visualization; Writing – original draft.

Julieta S. Riva: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Supervision; Validation; Visualization; Writing – original draft; Writing – review & editing. **Paula G. Bercoff**: Conceptualization; Formal analysis; Funding acquisition; Investigation; Methodology; Project administration; Supervision; Validation; Visualization; Writing – review & editing.

Data availability

The data that support the findings of this paper are available from the corresponding author, upon reasonable request.

References

- A. Nairan, M. Khan, U. Khan, M. Iqbal, S. Riaz, S. Naseem, Temperature-Dependent Magnetic Response of Antiferromagnetic Doping in Cobalt Ferrite Nanostructures, *Nanomaterials* 73 (2016) 2-13. doi:10.3390/nano6040073.
- [2] T. Dippong, E.A. Leve, F. Goga, O. Cadar, Influence of Mn²⁺ substitution with Co²⁺ on structural, morphological and coloristic properties of MnFe₂O₄/SiO₂ nanocomposites, *Mater. Charact.* 172 (2021) 110835. doi: 10.1016/j.matchar.2020.110835
- [3] D. Tomar, P. Jeevanandam, Synthesis of CoFe₂O₄ Nanoparticles via Thermal Decomposition of Co-Fe Bimetallic Glycolates: Effect of Using Different Cobalt Precursors on Their Morphology and Magnetic Properties. J. Supercond. Nov. Magn. 36 (2023) 1717-1735. https://doi.org/10.1007/s10948-023-06614-4.
- [4] I. Haïk Dunn, S.E. Jacobo, P.G. Bercoff, Structural and magnetic influence of yttriumfor-iron substitution in cobalt ferrite, *J. All. Comp.* 691 (2017) 130-137, http://dx.doi.org/10.1016/j.jallcom.2016.08.223
- [5] T. Dippong, E.A. Levei, O. Cadar, F. Goga, G. Borodi, L. Barbu-Tudoran, Thermal behavior of CoxFe_{3-x}O₄/SiO₂ nanocomposites obtained by a modified sol-gel method, *J. Therm. Ana.l Calorim.* 128 (2017) 39–52. https://doi.org/10.1007/s10973-016-5930-8
- [6] M. Chithra, C.N. Anumol, B. Sahu, S.C. Sahoo, Exchange spring like magnetic behavior in cobalt ferrite nanoparticles, *J. Magn. Magn. Mater.* 401 (2016) 1–82. http://dx.doi.org/10.1016/j.jmmm.2015.10.007.
- [7] I.C. Nlebedim, D.C. Jiles, Dependence of the magnetostrictive properties of cobalt ferrite on the initial powder particle size distribution, *J. Appl. Phys.* 115 (2014) 17A928. http://dx.doi.org/10.1063/1.4867343.
- [8] D. Peddis, C. Cannas, G. Piccaluga, E. Agostinelli, D. Fiorani, Spin-glass-like freezing and enhanced magnetization in ultra-small CoFe₂O₄ nanoparticles, *Nanotechnology* 21

14

(2010) 125705. http://dx.doi.org/10.1088/0957-4484/21/12/125705.

- [9] A.S. Ponce, E.F. Chagas, R.J. Prado, C.H.M. Fernandes, A.J. Terezo, E. Baggio Saitovitch, High coercivity induced by mechanical milling in cobalt ferrite powders, J. Magn. Magn. Mater. 344 (2013) 182–187. http://dx.doi.org/ 10.1016/j.jmmm.2013.05.056.
- [10] Q. Song, Z. John Zhang, Correlation between spin-orbital coupling and the superparamagnetic properties in magnetite and cobalt ferrite spinel nanocrystals, J. Phys. Chem. B. 110 (2006) http://dx.doi.org/10.1021/ 11205–11209. ip0605770.
- [11] F. Eskandari, S.B. Porter, M. Venkatesan, P. Kameli, K. Rode, J.M.D. Coey, Magnetization and anisotropy of cobalt ferrite thin films, Phys. Rev. Mater. 074413. 1 (2017)https://doi.org/10.1103/PhysRevMaterials.1.074 413.
- [12] T. Dippong, O. Cadar, E.A. Levei, Effect of Transition Metal Doping on the Structural, Morphological, and Magnetic Properties of NiFe₂O₄, *Materials* 15(9) (2022) 2996. doi: 10.3390/ma15092996.
- [13] L. Zhao, H. Yang, X. Zhao, L. Yu, Y. Cui, S. Feng, Magnetic properties of CoFe₂O₄ ferrite doped with rare earth ion, Mater. Lett. 60 (2006)1–6. https://doi.org/10.1016/j.matlet.2005.07.017.

[14] G. Bulai, L. Diamandescu, I. Dumitru, S.

Gurlui, M. Feder, O.F. Caltun, Effect of rare earth substitution in cobalt ferrite bulk materials, J. Magn. Magn. Mater. 390 (2015) 123-131.

http://dx.doi.org/10.1016/j.jmmm.2015.04.089.

- [15] R. Sharma, Komal, V. Kumar, S. Bansal, S. Singhal. Boosting the catalytic performance of pristine $CoFe_2O_4$ with yttrium (Y^{3+}) inclusion in the spinel structure, Mater. Res. Bull. 90 (2017) 94-103. https://doi.org/10.1016/j.materresbull.2017.01.0 49.
- [16] N. Moeini, A. Alemi, Z. Rezvani, Synthesis of Yttrium-Doped Copper Ferrite Spinel Nanoparticles by Means of a Solid-State Reaction: An Efficient Nanocatalyst for Click and Pechmann Reactions, ChemistrySelect. 7 (2022)e202200275. https://doi.org/10.1002/slct.202200275
- [17] U. Rajaji, S. Chinnapaiyan, S.M. Chen, M. Govindasamy, J. Ilton de Oliveira Filho, W. Khushaim, V. Mani, Design and Fabrication of Yttrium Ferrite Garnet-Embedded Graphitic Carbon Nitride: A Sensitive Electrocatalyst for Smartphone-Enabled Point-of-Care Pesticide (Mesotrione) Analysis in Food Samples, ACS

Appl. Mater. Interfaces 13 (2021) 24865-24876. https://doi.org/10.1021/acsami.1c04597.

[18] T. Ahmada, I.H. Lonea, S.G. Ansari, J. Ahmed, T. Ahamad, S.M. Alshehric, Multifunctional properties and applications of yttrium ferrite nanoparticles prepared by citrate precursor route, Materials & Design 126 (2017) 331-338.

https://doi.org/10.1016/j.matdes.2017.04.034.

[19] A. Thampi, K. Babu, S. Verma, Large scale solvothermal synthesis and a strategy to obtain stable Langmuir-Blodgett film of CoFe₂O₄ nanoparticles, J. Alloys Compd. 564 (2013) 143-150.

https://doi.org/10.1016/j.jallcom.2013.02.139.

- [20] K. Ariga, Chemistry of Materials Nanoarchitectonics for **Two-Dimensional** Films: Langmuir–Blodgett, Layer-by-Layer Assembly, and Newcomers, Chem. Mater. 35 (2023)5233-5254. https://doi.org/10.1021/acs.chemmater.3c01291
- [21] O.N. Oliveira Jr., L. Caseli, K. Ariga, The Past and the Future of Langmuir and Langmuir-Blodgett Films, Chem. Rev. 122 (2022) 6459-6513.

https://doi.org/10.1021/acs.chemrev.1c00754

- [22] K. Ariga, Don't Forget Langmuir-Blodgett Films 2020: Interfacial Nanoarchitectonics with Molecules, Materials, and Living Objects, Langmuir (2020)7158-7180. 36 https://doi.org/10.1021/acs.langmuir.0c01044
- [23] W. Gu, Q. Li, R. Wang, L. Zhang, Z. Liu, T. Jiao, Recent Progress in the Applications of Langmuir–Blodgett Film Technology, **Nanomaterials** 14 1039. (2024)https://doi.org/10.3390/nano14121039.
- [24] C. Liu, Y. Shan, Y. Zhu, K. Chen, Magnetic monolayer film of oleic acid-stabilized Fe₃O₄ particles fabricated via Langmuir-Blodgett technique, Thin Solid Films 518 (2009) 324-327.

https://doi.org/10.1016/j.pmatsci.2017.04.006.

- [25] H. Machida, N. Kikuchib, T. Ohashia, A. Fujimori, Analysis of soft and hard nanoparticle alternating multilayers for the development of theory for long-period stacking order structure prepared by Langmuir-Blodgett method, Thin Solid **Films** 709 (2020)138235. https://doi.org/10.1016/j.tsf.2020.138235.
- [26] G. Zhavnerko, G. Marletta, Developing Langmuir-Blodgett strategies towards practical devices, Mater. Sci. Eng. B 169 (2010) 43-48. https://doi.org/10.1016/j.mseb.2009.12.005
- [27] V.B. Daboin, S.N. Moya Betancourt, E.D. Farias, J.S. Riva, P.G. Bercoff, Enhancement of the electrochemical oxygen evolution reaction

15

by light and external magnetic fields, using hybrid electrodes made by Langmuir–Blodgett, *Electrochim. Acta* 480 (2024) 143910. https://doi.org/10.1016/j.electacta.2024.143910.

- [28] J.D. Zuluaga, S. Sánchez, L.F. Ramos, F.I. Beltrán, L. da-Silva, E. Ramírez, S. Vázquez, S. Flores, J. Méndez, M. Valera, E.N. Cabrera, A novel method for the modification of magnetite nanoparticles for the enhancement of its dispersibility in hydrophobic media, *J. Magn. Magn. Mater.* 514 (2020) 167-169. https://doi.org/10.1016/j.jmmm.2020.167169.
- [29] X. Meng, H. L, J. Chen, L. Mei, K. Wang, X. Li, Mössbauer study of cobalt ferrite nanocrystals substituted with rare-earth Y³⁺ ions, *J. Magn. Magn. Mater.* 321 (2009) 1155– 1158.

https://doi.org/10.1016/j.jmmm.2008.10.041

- [30] Cullity, B.D. and Graham, C.D. Introduction to Magnetic Materials. 2nd ed. Hoboken, NJ: Wiley-IEEE Press, (2009).
- [31] M. Tadica, I. Milosevicb, S. Kraljc, D. Hanzelc, T. Barudzijaa, L. Motted, D. Makovecc, Surface-induced reversal of a phase transformation for the synthesis of ε -Fe₂O₃ nanoparticles with high coercivity, *Acta Mater*. 188 (2020) 16-22. doi: 10.1016/j.actamat.2020.01.058
- [32] T.M. de Lima Alves, B. Ferreira Amorim, M.A. Morales Torres, C.Gomes Bezerra, S.N. de Medeiros, P.L. Gastelois, L.E. Fernandez Outon, W.A. de Almeida Macedo, Waspwaisted behavior in magnetic hysteresis curves of CoFe₂O₄ nanopowder at a low temperature: experimental evidence and theoretical approach, *RSC Adv.* 7 (2017) 22187–22196. https://doi.org/10.1039/C6RA28727A.
- [33] N.S.E. Osman, T. Moyo, Temperature Dependence of Coercivity and Magnetization of Sr_{1/3}Mn_{1/3}Co_{1/3}Fe₂O₄ Ferrite Nanoparticles, J. Supercond. Nov. Magn. 29 (2016) 361–366 https://doi.org/10.1007/s10948-015-3227-y.
- [34] E. Mosiniewicz-Szablewska, A.R. Clavijo, APOR Castilho, L.G. Paterno, M.A. Pereira-da-Silva, J. Więckowski, M.A.G. Soler, P.C.

Morais, Magnetic studies of layer-by-layer assembled polyvinyl alcohol/iron oxide nanofilms, *Phys. Chem. Chem. Phys.* 20 (2018) 26696-26709.

https://doi.org/10.1039/C8CP05404E.

- [35] N.D. Chaudhari, R.C. Kambale, D.N. Bhosale, S.S. Suryavanshi, S.R. Sawant, Thermal hysteresis and domain states in Ni–Zn ferrites synthesized by oxalate precursor method, *J. Magn. Magn. Mater.* 322 (2010) 1999-2005. https://doi.org/10.1016/j.jmmm.2010.01.022.
- [36] R. Aquino, J. Depeyrot, M.H. Sousa, F.A. Tourinho, E. Dubois, R. Perzynski, Magnetization temperature dependence and freezing of surface spins in magnetic fluids based on ferrite nanoparticles, *Phys. Rev. B* 72 (2005) 184435. https://doi.org/10.1103/PhysRevB.72.184435.
- [37] M. Dalal, P.K. Chakrabarti, Core-shell spin model of magnetization in Li-Zn-Co ferrite, J. Magn. Magn. Mater. 564 (2022) 170157. https://doi.org/10.1016/j.jmmm.2022.170157.
- [38] M. Zheng, X.C. Wu, B.S. Zou, Y.J. Wang, Magnetic properties of nanosized MnFe₂O₄ particles, *J. Magn. Magn. Mater.* 183 (1998) 152-156.
- [39] I.J. Bruvera, P. Mendoza Zelis, M.P. Calatayud, G.F. Goya, F.H. Sanchez. Determination of the blocking temperature of magnetic nanoparticles: The good, the bad, and the ugly, *J. Appl. Phys.* 118 (2015) 184304. http://dx.doi.org/10.1063/1.4935484.
- [40] D. Binns, M.J. Maher, Q.A. Pankhurst, D. Kechrakos, K.N. Trohidou, Magnetic behavior of nanostructured films assembled from preformed Fe clusters embedded in Ag, *Phys. Rev. B* 66 (2002) 184413. https://doi.org/10.1103/PhysRevB.66.184413.
- [41] S. Regmi, Z. Li, S. KC, R. Mahat, A. Rastogi, Ranjan Datta, A. Gupta, Structural and magnetic properties of CoFe₂O₄ thin films grown on isostructural lattice-matched substrates, *Appl. Phys. Lett.* 121 (2022) 102401. https://doi.org/10.1063/5.0107242

Supplementary Information

1. Synthesis of Co-ferrite and CoY-ferrite nanoparticles

Table S1. Moles of all reagents used to prepare the ferrites.

	Precursors amount [mmol]						
Compound	Fe(NO ₃) ₃ CoC ₂ O ₄ Y(NO ₃) ₃ C ₆ H ₈ O ₇						
CoFe ₂ O ₄	33	16.5	-	150			
CoFe _{1.8} Y _{0.2} O ₄	23	16.5	10	150			

2. NPs characterization by X-ray diffraction

The crystal structure of the NPs was identified by X-ray powder diffraction (XRD) with a PANalitycal X'Pert Pro diffractometer using Bragg-Brentano geometry, operated at 40 kV, 40 mA, Cu K α radiation (λ = 1.5418 Å) and with a step size of 0.02°, from 20° to 100°. X-ray diffraction patterns of Co-P and CoY-P are presented in **Figure S1(a)** and **S1(b)** as well as the Rietveld refinements obtained using the software XPert HighScore Plus (Malvern Panalytical).

Figure S1. Rietveld refinement analysis of XRD patterns: (a) Co-P and (b) CoY-P

In both samples, the peak positions corresponding to reflections $(2\ 2\ 0)$, $(3\ 1\ 1)$, $(2\ 2\ 2)$, $(4\ 0\ 0)$, $(4\ 2\ 2)$, $(3\ 3\ 3)$, $(4\ 4\ 0)$, $(5\ 3\ 1)$, $(6\ 2\ 0)$, $(5\ 3\ 3)$ and $(6\ 2\ 2)$, match with the standard diffraction peaks of the cubic spinel structure, which is characteristic of cobalt ferrite (JCPDS-PDF 22-1086) and are shown in Figure 1 (c) and (f) of the main text.

The lattice parameters obtained from the refinements are a = 8.3718(4) for Co-P and a = 8.3574(6) for CoY-P. These values agree with those by other authors, as shown in **Table S2**.

ĺ		a [Å]	a [Å]	a [Å]	a [Å]			
		This work	Ref. a	Ref. b	Ref. c			
ĺ	CoFe ₂ O ₄	8.3718(4)	8.37176(4)	8.4011	8.3454			
ĺ	CoFe _{1.8} Y _{0.2} O ₄	8.3574(6)	8.35744(6)	8.4119	8.3548			

Table S2. Lattice parameters for Co and CoY ferrites.

Ref. a. I. Haïk Dunn, S. E. Jacobo, P. G. Bercoff. Structural and magnetic influence of yttrium-for-iron substitution in cobalt ferrite, *J. All. Comp.* 691 (2017) 130-137. http://dx.doi.org/10.1016/j.jallcom.2016.08.223.

Ref. b. S. Chakrabartya, A. Duttaa, M. Pal. Effect of yttrium doping on structure, magnetic and electrical properties of nanocrystalline cobalt ferrite. *J. Magn. Magn. Mat.* 461 (2018) 69–75. https://doi.org/10.1016/j.jmmm.2018.04.051Get rights and content.

Ref. c. T. K. C. Nguyen, A. T. Nguyen. Structural, optical and magnetic properties of Y-doped CoFe₂O₄ nanoparticles prepared by a simple coprecipitation method. *J Mater Sci: Mater Electron.* 34 (2023) 448. https://doi.org/10.1007/s10854-023-09914-6

3. NPs characterization by BET

4.

The surface area of Co and CoY ferrite NPs was measured using the BET method, finding values of (2.8 \pm 0.1) m²/g and (7.92 \pm 0.04) m²/g, respectively. These values agree with the mean sizes determined for both kinds of NPs, since CoY ferrite NPs are smaller therefore a larger surface area is expected. **Figure S2** shows the isothermal curves used to determine the NPs areas.

Figure S2. BET analysis for Co and CoY ferrite NPs by using N₂ adsorption-desorption isotherms.

5. NPs characterization by XPS

The survey spectra of the four samples (Co and CoY ferrite NPs before and after stearic acid (SA) coating) are shown in Figure S3.

Figure S3. XPS survey spectra of Co-ferrite and CoY-ferrite with and without SA coating.

The peaks of iron, cobalt, oxygen and carbon, are visible in the spectra of bare and coated NPs. A peak corresponding to yttrium is also present in the spectra corresponding to CoY ferrite. The binding energies (BE) of the samples were calibrated by taking the C1s peak as reference (284.8 eV). No other elements are detected, confirming the purity of the samples.

Figure S4 shows the high resolution XPS spectra of Co 2p for bare and SA-coated **Co** and **CoY ferrite NPs**. The two peaks which are centered at 179.9 eV and 795.4 eV correspond to two spin–orbit doublets characteristic of Co $2p_{3/2}$ and Co $2p_{1/2}$, respectively. Sequentially, the peaks at 786 eV and 802 eV correspond to satellite peaks. The Co $2p_{3/2}$ peak is deconvoluted into two peaks centered at 779.9 eV and 795 eV which are associated to Co²⁺ ions at octahedral and tetrahedral sites, respectively, of the spinel structure [Ref. d, e, f and g]. The percentage of Co²⁺ ions in the octahedral and tetrahedral sites are found to be 58.70% and 41.30% for **Co ferrite**, and 53.08 % in the octahedral and 46.92 % for tetrahedral sites for **CoY ferrite**, as calculated from the area of deconvoluted peaks [Ref. d, e, f and g]. XPS peaks for Co $2p_{3/2}$ and Co $2p_{1/2}$ in **CoY ferrite** are slightly higher compared to the **Co ferrite** because of doping with yttrium.

Figure S4. High-resolution spectra of Cobalt 2p for Co (a) and CoY (b) ferrites with and without SA coating.

It is remarkable that the signal of cobalt is attenuated in the case of coated NPs, especially in the case of CoY-ferrite, which is consistent with the smaller size of these particles. This attenuation is related to the presence of SA on the NPs surface. Furthermore, the positions of the peaks remain almost unchanged (see Table S3) indicating that the coating does not affect the ferrite structure.

In the same way, the Fe 2p spectra have two main peaks at ~710 eV and ~724 eV corresponding to Fe $2p_{1/2}$ and Fe $2p_{3/2}$, respectively, as shown in **Figure S5**. The Fe $2p_{3/2}$ band has two deconvoluted peaks with binding energies of 710.24 eV and 712.72 eV, which suggest the presence of Fe³⁺ ions located at octahedral and tetrahedral positions [Ref. d, e, f and g]. The percentage of Fe³⁺ ions in the octahedral and tetrahedral sites obtained from the area under the curve of the fitted peaks are 68.20% and 31.80%, respectively for **Co ferrite**, and 57.24% and 42.76%, respectively for **CoY ferrite**.

Also in this case, as mentioned for cobalt, the signal intensity is attenuated in coated NPs, especially in CoY-ferrite, and the peaks positions remain unchanged after SA modification, which is explained by the same considerations as before.

Figure S5. High-resolution spectra of Fe 2p for **Co ferrite** (a) and **CoY ferrite** (b) with and without SA coating.

The decrease in the fraction of Co^{2+} and Fe^{3+} in the octahedral sites in CoY ferrite can be explained by the incorporation of Y^{3+} into the structure. It has been reported that Y^{3+} preferentially replaces Fe^{3+} in the octahedral sites, which generates stresses in the crystal lattice [Ref. a]. To compensate for this effect, a fraction of Co^{2+} migrates from octahedral to tetrahedral sites, modifying the cation distribution and contributing to a slight shrinkage of the unit cell. This behavior is consistent with previous studies on spinels doped with rare-earth cations, where it has been observed that cation redistribution is a structural mechanism associated with the incorporation of Y^{3+} , rather than the generation of vacancies in the octahedral sites [Ref. i, j and k].

Figure S6 shows the XPS spectra of yttrium for bare and SA-coated CoY ferrite nanoparticles. These spectra show a peak that can be deconvoluted into two peaks corresponding to BE of ~158 eV and ~160 eV, which are assigned to Y $3d_{5/2}$ (Y-O bonds) and Y $3d_{3/2}$ (Y³⁺) respectively [Ref. h.]. As observed for the other elements, the signal intensity is reduced in coated NPs, which confirms that the coating has been successful and it does not modify the spinel structure, since the peaks positions are the same in coated and bare NPs.

Figure S6. High-resolution spectra of Yttrium for CoY ferrite with and without SA coating.

Figure S7 shows the high-resolution spectra of C 1s, where the peak at a BE value of 284.8 eV is attributed to aliphatic (C–C) and C–H bonds, which are adsorbed on the nanoparticles during the decomposition of the fuel (citrate). Moreover, the intensity of the carbon peak is higher in the case of SA-coated NPs, confirming the presence of the organic coating agent in both ferrites.

Figure S7. High-resolution spectra of Carbon 1s for **Co ferrite** (a) and **CoY ferrite** (b) with and without SA coating.

The O 1s peak appears at 529.5 eV (**Figure S8**) and presents three deconvoluted peaks. The O 1s peak has chemical bonding with Co, Fe and in some cases Y. The deconvoluted peaks centered at 529.5 eV and 531.56 eV are assigned to the M-O-M, (M = metals) and C-O signals respectively, coming from acid groups from the stearic acid, citrate residues or CO₂ on the surface of the nanoparticles [Refs. d, e, f and g].

Figure S8. High-resolution spectra of Oxygen 1S for **Co ferrite** (a) and **CoY ferrite** (b) with and without SA coating.

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	Co-	Ferrite	Co-Ferrite-SA		CoY-Ferrite		CoY-Ferrite-SA	
Assignment	BE	Area	BE	Area	BE	Area	BE	Area
Assignment	(eV)	(CPS.eV)	(eV)	(CPS.eV)	(eV)	(CPS.eV)	(eV)	(CPS.eV)
Y-O					157.67	8487.01	157.59	3231.90
Y (III)					159.78	4580.12	159.68	1773.23
C-C	284.64	4661.36	284.75	10916.47	284.77	4041.01	284.80	9138.60
C-0	285.62	1085.33	286.83	232.01	286.24	942.50	285.43	6427.95
C=O	287.91	572.89	288.58	417.03	289.09	1726.57	288.66	527.13
M-O	529.50	53743.68	529.85	62492.54	529.52	29717.68	529.50	12643.39
C-O	531.56	16281.52	531.95	9578.35	530.87	29229.71	531.36	6910.05
Fe (III) oct.	710.24	44852.22	710.36	40468.80	710.20	24228.88	710.22	7070.24
Fe (III) tetr.	712.72	20911.71	712.84	20603.42	712.51	18096.89	712.39	4361.60
Fe (III) sat.	717.56	41384.90	717.78	41095.38	717.53	37899.14	717.81	1934.38
Fe (III) sat.	731.47	12010.62	731.56	12675.49	732.05	4971.21	732.56	1054.32
Co (II) oct.	779.34	22579.95	779.80	26006.14	779.52	15314.56	779.57	5391.04
Co (II) tetr.	781.21	15887.21	782.32	15396.49	781.27	13535.45	781.55	3719.06
Co (II) sat.	785.48	34679.88	786.42	28403.47	785.90	22615.75	786.10	3687.95
Co (II) sat.	802.05	1435.25	802.16	9500.21	802.12	6378.61	802.13	1900.13

Table S3. Results of the XPS curve fitting analysis of Co ferrite and CoY ferrite with and without SA coating.

Ref. d. S. Patil, S. Meti, P.S. Kanavi, R.F. Bhajantri, M. Anandalli, R. Mondal, S. Karmakar, M. Muhiuddin, M.R. Rahman, B.C. Kumar, B.G. Hegde. A study on solubility of bismuth cations in nickel cobalt ferrite nanoparticles and their influence on dielectric and magnetic properties. *Mater. Sci. Eng. B.* 296(11) (**2023**) 116570. https://doi.org/10.1016/j.mseb.2023.116570.

Ref. e. M. M. El-Masry, M. El-Shahat, R. Ramadan, R. M. Abdelhameed. Selective photocatalytic reduction of nitroarenes into amines based on cobalt/copper ferrite and cobalt-doped copper ferrite nano-photocatalyst. *J. Mater. Sci.: Mater. Electron.* 32(8) (2021) 18408–18424. DOI: 10.1007/s10854-021-06387-3

Ref. f. R.S. Yadav, I. Kuřitka, J. Vilcakova, J. Havlica, J. Masilko, L. Kalina, J. Tkacz, J. Švec, V. Enev, M. Hajdúchová. Impact of grain size and structural changes on magnetic, dielectric, electrical, impedance and modulus spectroscopic characteristics of CoFe2O4 nanoparticles synthesized by honey mediated sol-gel combustion method. *Adv. Nat. Sci.: Nanosci. Nanotechnol.* 8(4) (2017) 045002. DOI: 10.1088/2043-6254/aa853a.

Ref. g. Y. Kumar, A. Sharma, M.A. Ahmed, S.S. Mali, C.K. Hong, P.M. Shirage. Morphology-controlled synthesis and enhanced energy product (BH) max of CoFe₂O₄. *New J Chem.* 42(19) (2018) 15793-15802. https://doi.org/10.1039/C8NJ02177E

Ref. h. U. Rajaji, S. Chinnapaiyan, S.M. Chen, M. Govindasamy, J.I. de Oliveira Filho, W. Khushaim, V. Mani, Design and Fabrication of Yttrium Ferrite Garnet-Embedded Graphitic Carbon Nitride: A Sensitive Electrocatalyst for Smartphone-Enabled Point-of-Care Pesticide (Mesotrione) Analysis in Food Samples. *ACS Appl. Mater. Interfaces* 13 (**2021**) 24865-24876. doi: 10.1021/acsami.1c04597.

Ref. i. X. Meng, H. L, J. Chen, L. Mei, K. Wang, X. Li, Mössbauer study of cobalt ferrite nanocrystals substituted with rare-earth Y³⁺ ions, *J. Magn. Magn. Mater.* 321 (2009) 1155–1158. https://doi.org/10.1016/j.jmmm.2008.10.041

Ref. j. S. Kumari, V. Kumar, P. Kumar, M. Kar, L. Kumar, Structural and magnetic properties of nanocrystalline yttrium substituted cobalt ferrite synthesized by the citrate precursor technique, *Adv. Powder Technol.* 26 (2015) 213e223. https://doi.org/10.1016/j.apt.2014.10.002

Ref. k. X. Zhao, W. Wng, Y. Zhang, S. Wu, F. Li, J. Ping Liu, Synthesis and characterization of gadolinium doped cobalt ferrite nanoparticles with enhanced adsorption capability for Congo Red, Chem. Eng. J. 250 (2014) 164e174. https://doi.org/10.1016/j.cej.2014.03.113

6. Pressure-area isotherm study with Co-P and CoY-P

Surface pressure-area isotherms of samples Co-P and CoY-P were measured to select the optimal conditions for depositing the films with the LB technique. The gray and blue lines **in Figure S9** are the isotherms obtained for Co-P and CoY-P samples, respectively.

Figure S9. Surface pressure versus area isotherm of Co-P (gray line) and CoY-P (blue line) on a water subphase.