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Microwave-assisted hydrothermal synthesis and magnetic properties of nanostructured cobalt ferrite

Ana Lúcia Gurgel [a], Antonio Eduardo Martinelli [a, *], Ozivam Lopes de Aquino Conceição [a, 1], Milton Moraes Xavier Jr. [b], Marco Antonio Morales Torres [c], Dulce Maria de Araújo Melo [a]

[a] Materials Science and Engineering Postgraduate Program (PPGCEM), Universidade Federal do Rio Grande do Norte, Av. Salgado Filho 3000, Natal 59078-970, Brazil
[b] Centro de Ciências Exatas e da Terra (CCET), Universidade Federal do Rio Grande do Norte, Natal 59078-970, Brazil
[c] Departamento de Física Teórica e Experimental, Universidade Federal do Rio Grande do Norte, Natal 59078-970, Brazil

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ABSTRACT

Cobalt ferrite is an important magnetic material due to its high saturation magnetization and high energy product BH. $CoFe_2O_4$ nanoparticles can be synthesized by a variety of methods that often demand long synthesis times. Using the microwave-assisted hydrothermal method, single-phase $CoFe_2O_4$ with controlled crystallite size was rapidly obtained. The effect of a preheating step and mineralizing agent, *i.e.*, NH_4OH and KOH, was investigated. Exposure to microwave radiation ranged from 0.5 to 2 h. The formation of $CoFe_2O_4$ was confirmed by X-ray diffraction. The average crystallite size of $CoFe_2O_4$ nanoparticles was estimated between 5.2 nm and 21.3 nm by Rietveld refinement. The crystallite size depended on the preheating step and mineralizing agent used. Transmission electron microscopy images revealed that $CoFe_2O_4$ nanoparticles were nearly spherical when prepared with NH_4OH but cubic and spherical when prepared with KOH. Both, hysteresis curves and Mössbauer spectra at room temperature, showed superparamagnetic behavior for samples with the smaller crystallite size. Samples with larger crystallites consisted of blocked particles and depicted an increase in the M_R/M_{Hmax} ratio and coercive field, H_c. Distinct magnetic properties resulting from variations in the synthesis parameters yield different applications for nanostructured $CoFe_2O_4$.

1. Introduction

The production and magnetic properties of $CoFe_2O_4$ has been continuously studied for different technological applications [1–4]. The average particle size and size distribution homogeneity directly affect the magnetic behavior of $CoFe_2O_4$ [2,5,6]. In the vicinity of the critical region of monodomain particle diameter (~40 nm), larger particles usually determine high coercivity [2]. Hence the importance of the presence of homogeneous nanoparticles of controlled size. There are currently several synthesis methods to produce cobalt ferrite nanoparticles, including ball milling [7], coprecipitation [8], sol-gel [9,10], reaction by modified ion coordination [11] and conventional hydrothermal synthesis [12,13]. Both conventional and microwave-assisted hydrothermal methods have been investigated to produce $CoFe_2O_4$ [12–15]. Studies have reported the production of ferrites with microwave exposure times ranging from few minutes to several hours [14–18]. Their preparation usually involves further thermal treatments, such as calcination. A mineralizing agent may be added to the solution to accelerate the synthesis reaction. Other important control parameters are the preheating and the synthesis temperature. It is possible to produce $CoFe_2O_4$ by hydrothermal synthesis, in the range of ~160–190 °C [19] or even below 160 °C [18,20]. pH must also be adjusted to be at least 12 [20]. The hydrothermal method applied to the synthesis of ceramic materials depicts fast reaction rate and uniform nanoparticle size distribution [21]. In this scenario, the objective of the present study was to evaluate the effect of microwave-assisted hydrothermal parameters on the production of $CoFe_2O_4$ nanoparticles and their magnetic behavior.

* Corresponding author.
E-mail address: martinelli.ufrn@gmail.com (A.E. Martinelli).
[1] In memorian.

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2. Material and methods

Cobalt ferrite ($CoFe_2O_4$) was synthesized by using 0.794 g of $Co(NO_3)_2 \cdot 6H_2O$, 2.206 g of $Fe(NO_3)_3 \cdot 9H_2O$, and two mineralizing agents, *i.e.*, NH_4OH (Sigma Aldrich) solution at 28.30% and KOH (Fluka Analytical) solution at 45%. The metal salts and alkaline reagents were mixed for 25 min in 100 mL of distilled water at a given temperature. Then, the resulting solutions were moved to a Teflon autoclave and placed in a microwave hydrothermal reactor HMO100 INOVTEC (f = 2.45 GHz, 900 W) where they were heated at 10 °C/min up to 140 °C and treated for periods ranging from 0.5 h to 2.0 h. Then, the samples were cooled down to room temperature, washed with water and ethanol several times until pH = 7 was reached and, finally, dried in an oven at 100 °C for 5 h. The sample series were labelled as A and P when prepared with NH_4OH or KOH, respectively. Samples labelled as A1 and P1 were preheated at different temperatures, before microwaving, contrary to samples A2 and P2. The temperatures and pre-heating conditions are shown in Table 1 along with the resulting crystallite sizes.

The resulting powders were characterized by x-ray diffraction (XRD) using a Rigaku diffractometer with Cu Kα radiation. The patterns were refined using the Rietveld method to estimate their corresponding crystallite sizes. The isothermal hysteresis measurements at 300 K were recorded by using a Vibrating Sample Magnetometer (VSM) from Lakeshore, model 7400. The low temperature magnetization measurements were recorded in a Physical Properties Measurement System (PPMS) from Quantum Design, model Dynacool. The 300 K ^{57}Fe Mössbauer spectra were recorded using a spectrometer from SEECO equipped with a gamma radioactive source of ^{57}Co:Rh with activity of 25 mCi. Transmission electron microscopy (TEM) images were obtained by using a JEOL JEM-2100 system.

3. Results and discussion

The XRD analysis showed that both series of samples presented single phase $CoFe_2O_4$ (Fig. 1). For series A, the Rietveld refinements revealed an average crystallite size that depended on the pre-heating temperature prior to the microwave treatment (Table 1). Samples A1-0.5 h and A1-2 h were preheated at ~92–95 °C for 25 min and they depicted crystallite sizes of ~5 nm. On the other hand, samples preheated at lower temperatures (A1-1.0 h and A1-1.5 h) showed larger crystallites sizes ranging from 11 nm to 12 nm. The preheating temperature has an important effect on the size of crystallites and magnetic properties, contrary to the effect of the exposure time to microwaves. Further indication of this effect can be seen for sample A2-0.5h, which was only thermal treated in the microwave oven at 140 °C and showed a crystallite size of 12.1 nm. The impact of the microwave heating on the particle size is greater

Table 1
Synthesis parameters and corresponding average crystallite size.

Agent	Microwave time (h)	Pre-heating temperature (°C)	Average crystallite size (nm)
NH_4OH	A1-0.5	92	5.2
	A1-1.0	53	11.3
	A1-1.5	64	12.4
	A1-2.0	95	5.7
	A2-0.5	–	12.1
KOH	P1-0.5	73	20.7
	P1-1.5	68	21.3
	P1-2.0	68	19.6
	P2-0.5	–	19.1

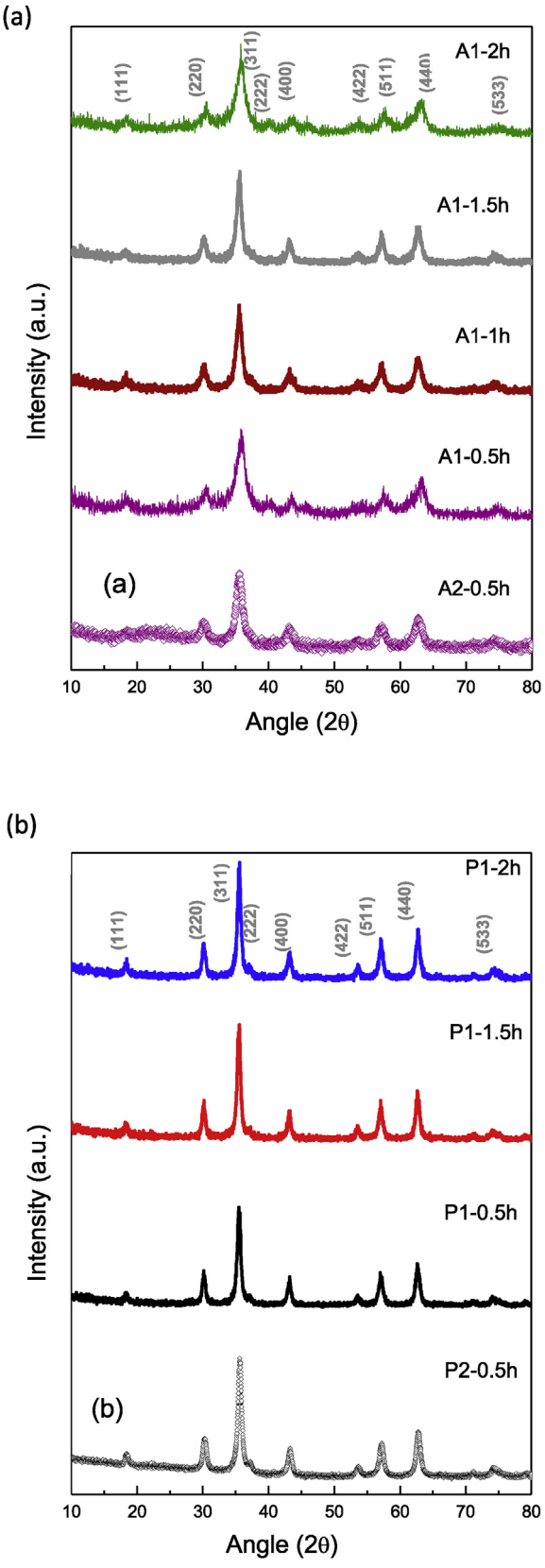

Fig. 1. X-ray diffractograms of (a) series A; and (b) series P.

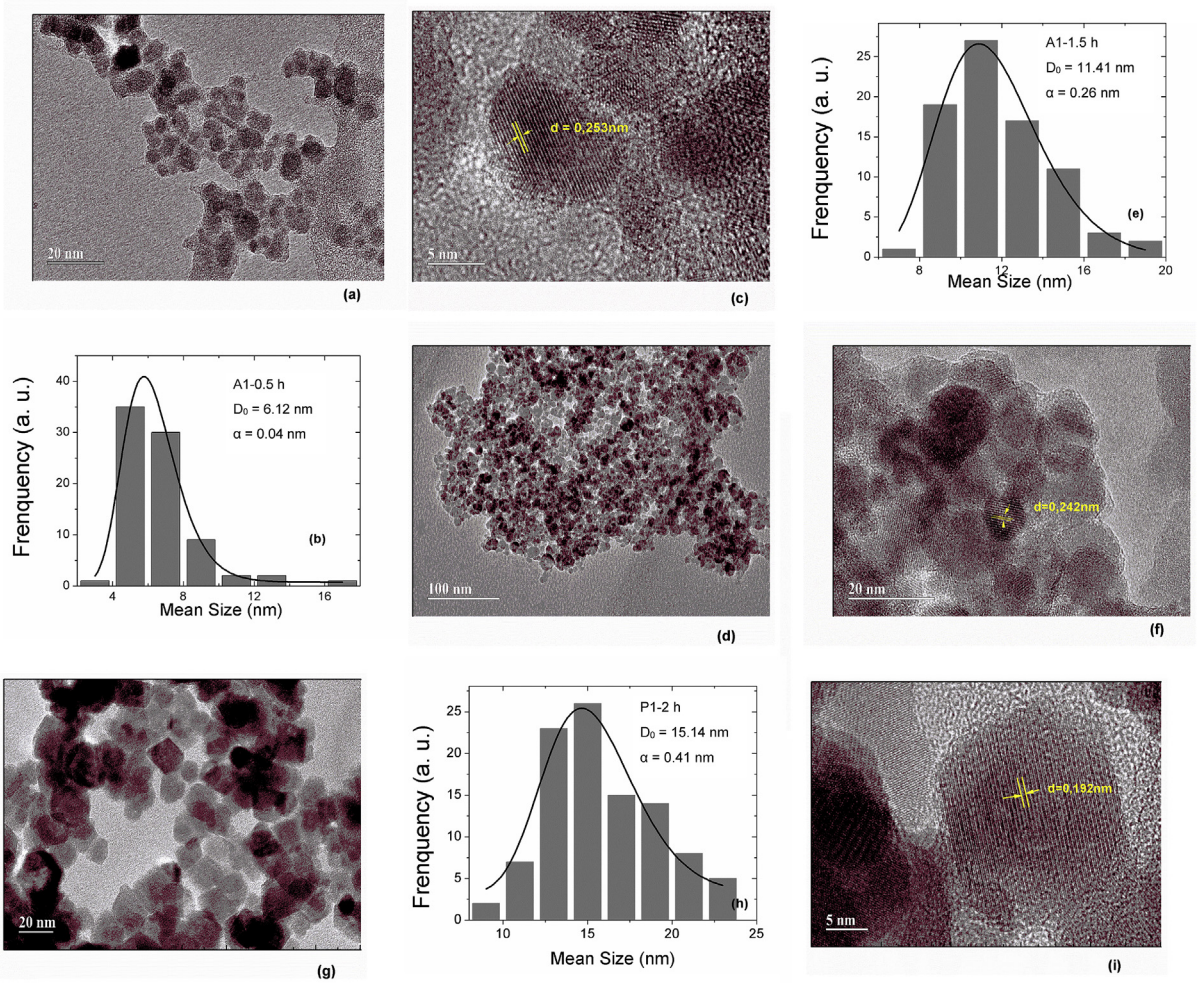

Fig. 2. TEM images, corresponding particle size distribution and interplanar distance of (a, b, c) sample A1-0.5h; (d, e, f) sample A1-1.5h; and (g, h, i) sample P1-2h.

when there is not preheating, thus, resulting in larger particle sizes. These results suggest that cobalt ferrite forms at 140 °C for times as short as 30 min, as suggested by Kuznetsova et al. [18].

Samples A were synthesized using NH_4OH, which is a weak base with low dissociation of OH^-, which may inhibit particle growth [22], therefore, resulting in smaller particle sizes. The pH measured during synthesis of series A was 10, which is in good agreement with values reported elsewhere for the synthesis of $CoFe_2O_4$ using NH_4OH [23]. For series P, corresponding to samples synthesized using KOH, the average crystallite size was around 20 nm, regardless of preheating and time exposed to microwaves (Table 1). The average crystallite size of samples P is likely associated to the fact that KOH is a strong base [23]. The average pH measured in the synthesis of series P was 13, which is also in good agreement with data reported for the synthesis of $CoFe_2O_4$ using KOH [20].

It should be emphasized that the weak base NH_4OH has a boiling point of 35 °C, lower than that of the KOH solution. The NH_4OH aqueous solution containing the metal cations remained up to 25 min at 95 °C in an open Becker. Thus, some evaporation of $NH_{3(g)}$ and water occurred, therefore, affecting the final pH = 10. Since samples A1-0.5h and A1-2h, preheated at 92 °C and 95 °C during 25 min, have smaller particles sizes, *i.e.*, 5.2 nm and 5.7 nm (larger particles size were obtained with lower preheating temperatures), it can be concluded that the evaporation of NH_4OH has a pronounced effect in samples prepared at higher temperatures. On the other hand, samples prepared with KOH and similar preheating treatments showed particles sizes in the range from 19.1 nm to 21.3 nm. In these cases, evaporation of the alkaline reagent is negligible, and the larger particle size is mostly related to the stronger base, *i.e.*, KOH.

TEM imagens of samples A1-0.5h, A1-1.5h and P1-2h are presented in Fig. 2. The samples A1-0.5h and A1-1.5h consist of sphere-like particles (Fig. 2a) and (Fig. 2d), respectively. According to the Sturges relationship,

$$C = 1 + 3.322 * \log(N) \quad (1)$$

where N is the number of particles and C is the number of classes [24], the average particle size for sample A1-0.5h is of 6.12 nm and A1-1.5h is of 11.4 nm. The number of particles examined was 80, in both cases. Fig. 2c shows fringes related to atomic planes with an interplanar distance of d = 0.253 nm and ascribed to (311) $CoFe_2O_4$ planes. Fig. 2f shows fringes related to atomic planes with an interplanar distance of d = 0.242 nm and ascribed to (222). The TEM image for sample P1-2h presents sphere and cube-like particles, (Fig. 2g). The average particle size is 15.1 nm, and the number of particles considered was 100. A high magnification image with a particle exhibiting fringes related to interplanar distance of d = 0.192 nm is shown in Fig. 2i. These fringes correspond to planes

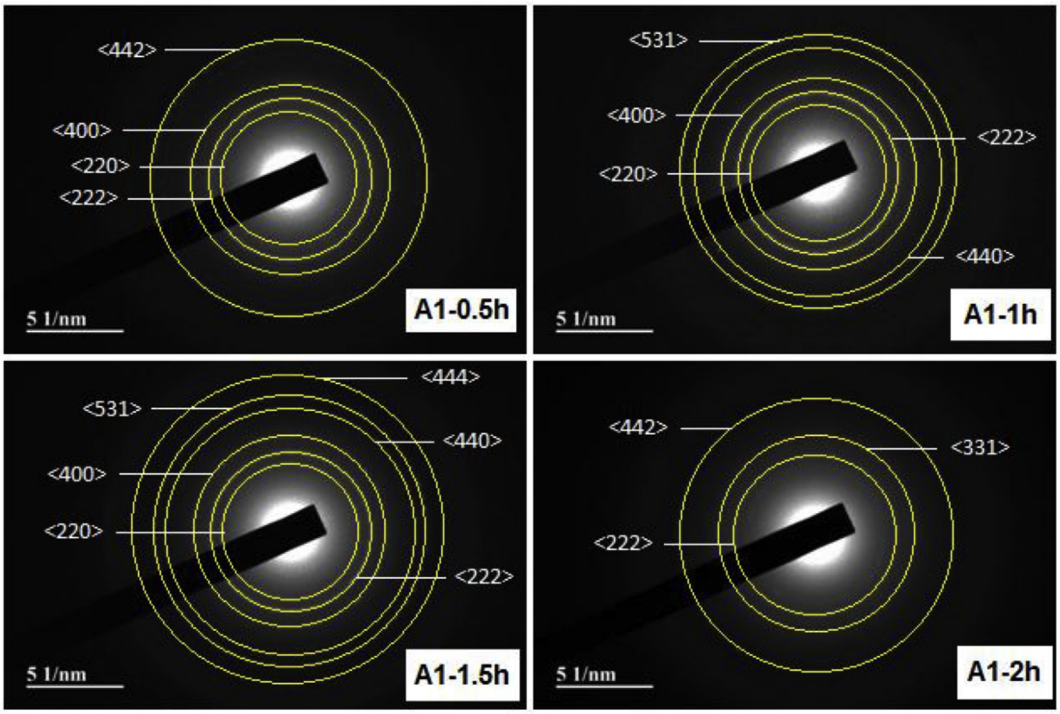

Fig. 3. Diffraction rings of series A samples (a) A1-0.5h; (b) A1-1h; (c) A1-1.5h; and (d) A1-2h.

(331) of $CoFe_2O_4$. Small area electron diffraction measurements are shown in Fig. 3, these images show characteristics rings ascribed to crystalline planes <440>, <442>, <531>, <222>, <220> and <331> due to the Co-ferrite crystalline structure. It is known that the critical size for the onset of a single magnetic domain is about 40 nm [25], therefore, all the samples in the present work are single domain.

The magnetization curves as a function of the magnetic field recorded at 300 K for series A1 and P1 are shown in Fig. 4. The M-H hysteresis for samples A1-0.5h and A1-2h are shown in Fig. 4a. These curves have very small coercivity field (Hc) and remanence magnetization (Mr). This indicates that these samples have some particles thermally blocked and some in the superparamagnetic regime, where their Fe and Co magnetic moments will experience a coherent fast relaxation between their magnetocrystalline easy axis directions. The saturation magnetization (Ms) value can be obtained by applying the law of approach to saturation equation to the high field magnetization data, *i.e.*, for $H \gg Hc$. The equation is given by

$$M(H) = Ms(1 - B/H^2) \quad (2)$$

where B is related to the magnetocrystalline anisotropy (K_1), *i.e.*, $B = 8K_1^2/(105Ms^2)$ [26]. Samples A1-0.5h and A1-2h have small Ms values, *i.e.*, 16 emu/g and 12 emu/g, respectively. This may indicate a disordered surface magnetic layer and noncollinearity of magnetic moments at the octahedral and tetrahedral sites, usually found in very fine particles. In fact, Pileni et al. studied Co-ferrite nanoparticles with sizes ranging from 2.3 nm to 5.4 nm, and at 200 K, the Ms decreased from 35 emu/g to 14 emu/g [27], suggesting that the lower Ms is related to surface disorder due to dangling bonds and to the increase of noncollinearity structure when the particle size decreases (Table 2).

On the other hand, samples A1-1.0h and A1-1.5h, which depicted larger particle sizes, show a thermally blocked magnetic regime at 300 K. In these cases, the M-H curves show Ms of 65 emu/g (A1-1.0h) and 54 emu/g (A1-1.5h) and Mr/Ms ratio of 0.09 (A1-1.0h) and 0.16 (A1-1.5h). Additionally, their Hc of 172 Oe and 338 Oe are further evidence of their blocked regime.

The isothermal magnetization curves for samples P1 are shown in Fig. 4b. These samples show a thermally blocked magnetic regime with blocking temperatures above 300 K. The sample P1-0.5h has higher Ms of 77 emu/g, and samples P1-1.5h and P1-2.0h have similar Ms values of 69 emu/g. Their Hc are in the range from 617 Oe to 675 Oe, and their Mr/Ms are in the range from 0.29 to 0.31 emu/g, indicating uniaxial magnetocrystalline anisotropy. The calculated K_1 values at 300 K are 6.8×10^6, 5.8×10^6, and 5.8×10^6 erg/cm^3 for samples P1-0.5h, P1-1.5h and P1-2.0h, respectively. The obtained K_1 values are two orders of magnitude larger than the ones calculated by using the equation given by Shenker [28] to determine the K_1 for bulk samples. The results presented herein are apparently related to the surface contribution to magnetic anisotropy [29].

The M-H measurements recorded at 4 K for samples A1-0.5h, A1-1.5h and P1-0.5h are shown in Fig. 5. The Ms values were 23.5 emu/g (A1-0.5h), 68 emu/g (A1-1.5h), and 81.7 emu/g (P1-0.5h). Their high coercivity field of about 13 kOe and large Mr are typical of hard magnetic materials. Their Mr/Ms ratio of 0.49 (A1-0.5h), 0.65 (A1-1.5h), and 0.74 (P1-0.5h) show that the sample with smaller particle (A1-0.5h) seems to have axial magnetocrystalline anisotropy, for which the theoretical Mr/Ms value is 0.5 [30]. Meanwhile, samples (A1-1.5h and P1-0.5h) with larger crystallites have cubic magnetocrystalline anisotropy, where the expected Mr/Ms value is 0.83 [31]. Similar results were found by Ngo et al. [32] for particles with sizes ranging from 3.1 nm to 6.2 nm. The different values of Ms were ascribed to spin canting of surface spin moments. In the work of Ngo et al., at 3 K the spin canting effect strongly reduced the Ms values from 98 emu/g to 44 emu/g for Co-ferrites particles with sizes of 6.2 nm and 3.1 nm, respectively.

The room temperature ^{57}Fe Mössbauer spectra are shown in

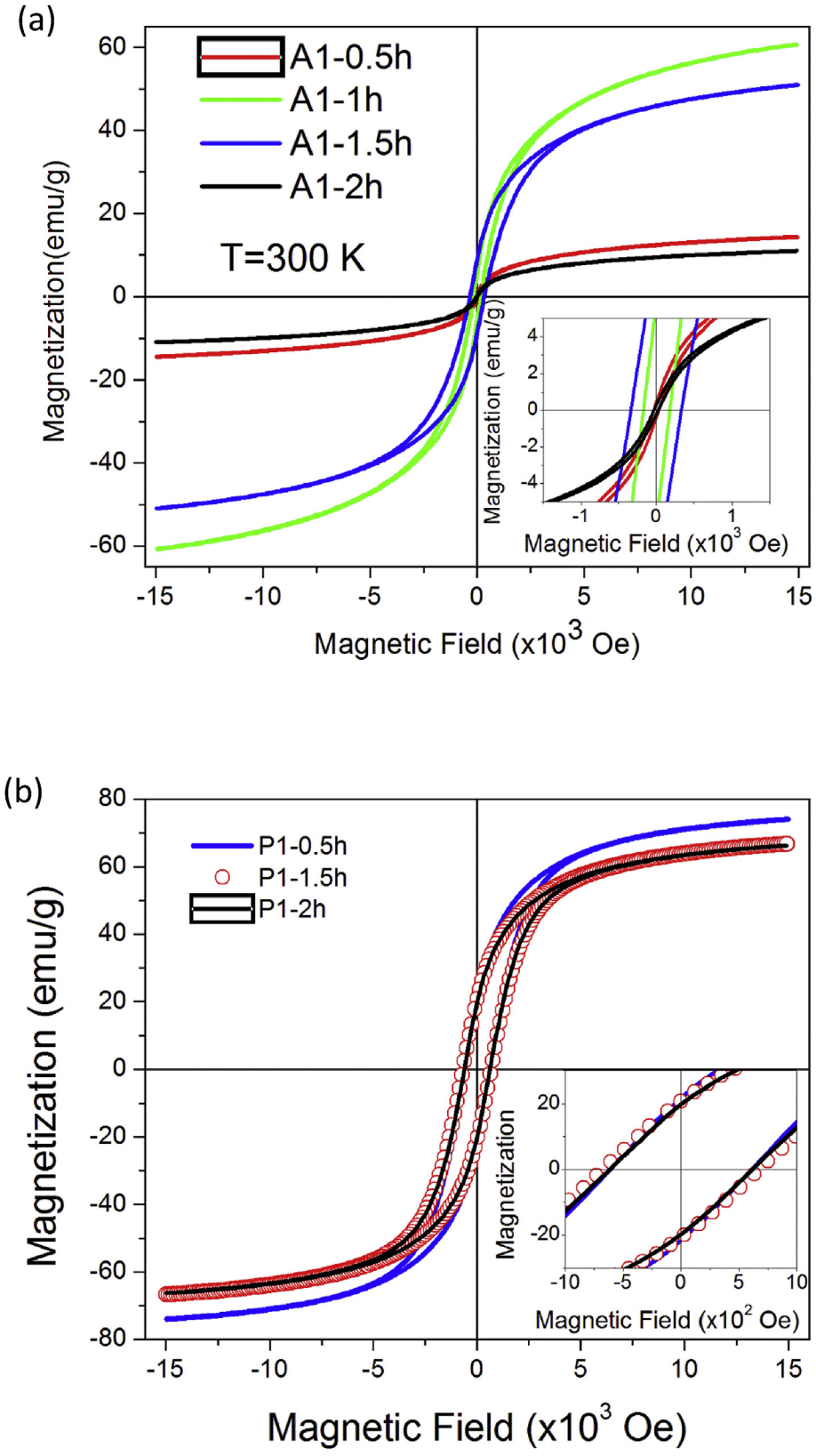

Fig. 4. Magnetization curves at room temperature for series (a) A; and (b) P.

Table 2
Magnetic and structural information for samples A and P. at 300 K.

Sample	Mr/Ms	Hc (Oe)	Size (nm)
A1-0.5 h	0.03	33.9	5.2
A1-1 h	0.09	171.8	11.3
A1-1.5 h	0.16	337.8	12.4
A1-2 h	0.02	26.1	5.7
P1-0.5 h	0.29	617.3	20.7
P1-1.5 h	0.31	675.3	21.3
P1-2 h	0.30	617.3	19.6

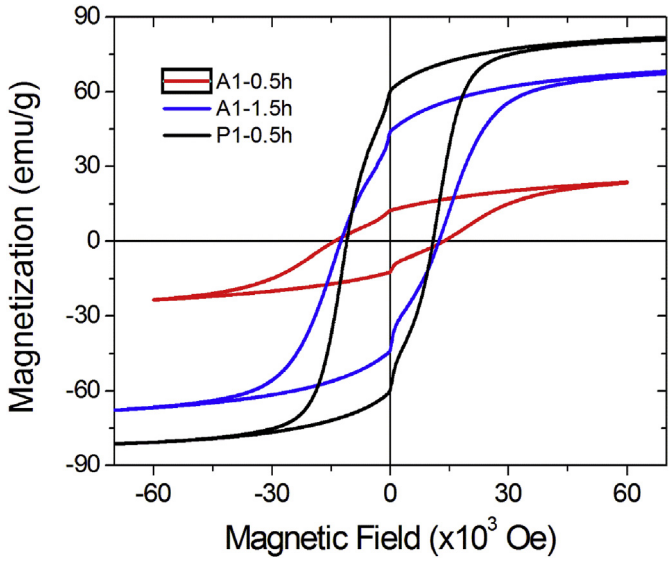

Fig. 5. Low-temperature (4 K) hysteresis loops.

Fig. 6. The spectrum for sample A1-0.5h (Fig. 6a) is fitted with a doublet and a sextet. The paramagnetic component (doublet) has a relative absorption area (RAA) of 70%. Therefore, this sample has their Co and Fe magnetic moments fast relaxing between the magnetocrystalline easy axis of the particle. The sample is mostly in the superparamagnetic regime, which is thermally activated and occurs above the blocking temperature, below 300 K for this sample. The sample A1-1.5h was fitted to a sextet and a doublet. The former is related to thermally blocked magnetic moments and the latter is ascribed to fast relaxing moments. Since the RAA of the sextet is larger than that of the doublet, it is concluded that the sample is thermally blocked. This result is in agreement with the M-H measurement at 300 K. Each of the Mössbauer spectrum for samples P1-0.5h and P1-2h were fitted to two sextets, *i.e.*, sextet-1 and sextet-2 related to Fe^{3+} in octahedral and tetrahedral sites, respectively. The large hyperfine magnetic field (Hhf) and isomer shift (IS) are indicative of Fe^{3+} in octahedral sites [33]. These samples are thermally blocked at 300 K, thus confirming the conclusions from the analysis of M-H measurements (Table 3).

Table 3
Hyperfine parameters obtained from Mössbauer analysis.

Sample	Component	IS(mm/s)	QS (mm/s)	Hhf (T)	RAA (%)
A1-0.5h	Sextet	0.2032	−0.2167	44	30
	Doublet	0.3485	0.6703	–	70
A1-1.5h	Sextet	0.2871	0.0231	46	84
	Doublet	0.3401	0.8251	–	16
P1-0.5h	Sextet 1	0.3956	0.0153	47	58
	Sextet 2	0.1563	−0.0023	44	42
P1-2h	Sextet 1	0.4120	0.0011	48	68
	Sextet 2	0.1869	−0.0408	46	32

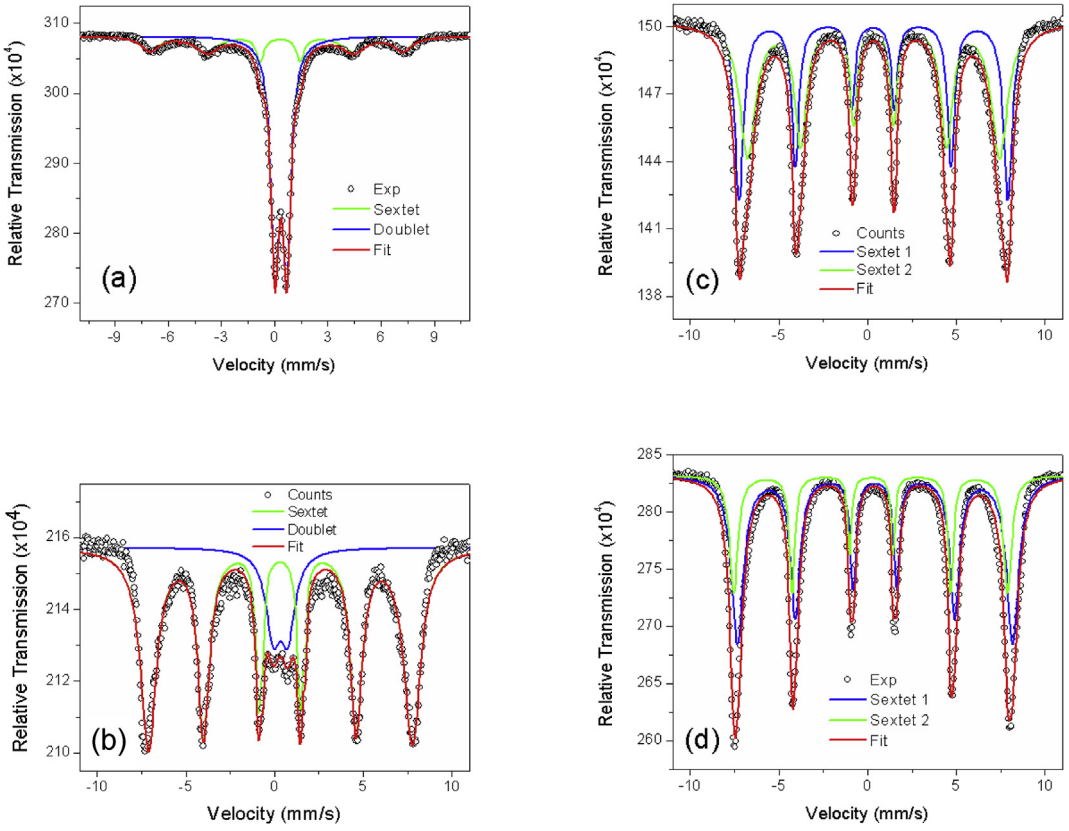

Fig. 6. Mössbauer spectra of samples (a) A1-0.5h; (b) A1-1.5h; (C) P2-0.5h; and (d) P2-2h.

4. Conclusions

Single phase $CoFe_2O_4$ nanoparticles were produced by microwave-assisted hydrothermal synthesis using NH_4OH or KOH. The $CoFe_2O_4$ samples were prepared using a fast procedure, with a maximum total time of about 3 h, thus confirming the advantage of microwave-assisted hydrothermal synthesis over other methods. Rietveld refinements of the XRD patterns demonstrated the high purity of the samples, and their crystallite sizes ranged from 5.2 to 21.3 nm. The preheating temperature, prior to microwave treatment, played a major role in determining the crystallite size of samples prepared with NH_4OH. The Synthesis with KOH resulted in larger crystallite sizes. The crystallite sizes tuned the magnetic properties of $CoFe_2O_4$ nanoparticles. Samples with crystallite size ~5 nm depicted superparamagnetic behavior at room temperature, whereas $CoFe_2O_4$ particles with crystallites between 11.3 and 21.3 nm were in the thermally blocked magnetic state. Therefore, the crystallographic phase, average crystallite size and magnetic behavior of the $CoFe_2O_4$ powders were mainly determined by the preheating temperature and the mineralizing agent used in the synthesis. The TEM images of preheated samples synthesized using NH_4OH revealed spherical particles, whereas samples prepared with KOH have cubic and sphere-like morphology. Magnetometry measurements showed smaller Ms values for smaller crystallites, and this result may be related to the increase of noncollinearity structure when the particle size decreases. The magnetocrystalline anisotropy K_1 for all samples have enhanced values due to surface contribution to the effective magnetic anisotropy. The Mössbauer data revealed superparamagentic behavior for samples preheated at high temperature and in the presence of NH_4OH. The spectra for the bigger particles exhibited Fe^{3+} occupying tetrahedral and octahedral sites in the $CoFe_2O_4$ structure. The present work demonstrated that the microwave-assisted hydrothermal method with a preheating step is a timesaving process that results in nanoparticles with high purity and tunable magnetic properties.

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