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# Hollow hematite microspheres obtained without hard templates

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### Introduction

The production of hollow microspheres is of current interest due to their promising applications in photonic crystals, encapsulation, drug delivery, catalysis, chemical storage, light fillers and low dielectric constant materials [1-14]. A variety of hollow spheres such as carbide [15], Ni [16], TiO<sub>2</sub> [17], NiS [18], Bi<sub>2</sub>Te<sub>3</sub> [19] and ZnO/SnO<sub>2</sub> [20] have been successfully fabricated. The most common techniques to produce hollow spheres are based on the use of core organic/inorganic hard templates such as monodispersed silica spheres [21-23], polymer latex colloids [11, 24], carbon spheres [25] and block copolymers [26, 27] or soft templates, such as emulsion droplets [28,29], surfactants vesicles [30] and liposome [31]. In general, the template technique involves four major steps (as represented in Fig. 5.1) [1]: (1) Preparation of the templates; (2) functionalization/modification of the templates surface to achieve favourable surface properties; (3) coating the templates with desired materials or their precursors; and (4) selective removal of the templates in appropriate solvents or calcination to obtain the hollow structures.



#### FIGURE 5.1

Schematic representation of the process of hollow spheres by using templates. A typical procedure consists of (1) Preparation of the templates (2) functionalization/modification of their surface, (3) coating them and (4) removal or dissolution of the templates to obtain the hollow structures. (Adapted from Reference [1])

The hard template technique is effective for controlling the morphology of the final product. Nevertheless, this technique requires tedious synthetic procedures such as a careful selection of an affine template and a lot of care to prevent the collapse to affecting the quality of the shell during template removal. Some other drawbacks include limited sphere size, quality, purity, cost of production, and low temperature capability of the produced hollow spheres.

Recently different free-template approaches have been developed to produce hollow spheres. Some of these methods are based on Oswald ripening [32, 33], simultaneous blowing and melting hidrogels [34-36], Kirkendall Effect [37-39], among others. However the average size of the hollow spheres produced by these methods are usually larger than 10  $\mu$ m. Furthermore, it is difficult to obtain small microspheres having a narrow particle size distribution, and high purity metal oxide composition. Another less explored method for the production of hollow spheres is 'the gas-bubble template method'. This method involves the production of gas microbubbles during the chemical preparation of nanoparticles by using selected ligands. It is believed that the nanoparticles cover the surface and form the shell of the hollow spheres after calcinations at high temperatures [40-47]. However the exact mechanism for the bubble nucleation and grow is unclear.

Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is the most stable iron oxide. It is *n*-type semiconductor ( $E_g$ =2.2 eV) under ambient conditions and it is easy to synthesize. Due to its magnetic properties, corrosionresistance, low cost and low toxicity it is widely used in catalysis [48-53], environmental protection [54-60], sensors [61-65], magnetic storage materials [66] and clinic diagnosis and treatment [67,68].  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystallizes in the rhombohedral primitive cell isomorphous to that of ilminite and corundum (hexagonal unit cell, space group  $R\overline{3}c$ ) [69]. The primitive cell contains ten atoms (six Fe and four O) in contrast to only two atoms in simple transition-metal oxides with the rock salt structure [70].

To date, the preparation of a variety of hematite morphologies such as rhombohedra [71], particles [72-75], nanocubes [76, 77], rings [78], wires [79, 80], rods [81, 82], fibbers [83], flakes [84], cages [85], airplane-like structures [86] and hierarchical structures [87-89] have been reported. Recently, some works have reported the production of crystalline hematite hollow spheres through various methods. Some of the approaches are listed in Table 5.1. Note that most of the existing methods for obtaining the hematite hollow spheres involve templates, surfactants, toxic organic solvents, or complex steps. Among them, the hydrothermal/solvothermal method has some advantage over the rest due to its fast reaction time, effective control of particle shape, and low incorporation of impurities into the products. However, this technique requires of steel pressure vessels or autoclaves during preparation to apply high pressure and thus to achieve the reactions [95-103]. In contrast, in this work we report the preparation of hematite hollow spheres by the gas-bubble template technique in which no high pressure or any special conditions of atmosphere are required. Here, the hollow hematite microspheres are formed by annealing a sol-gel iron oxide precursor in air. We propose a mechanism for the hollow formation based on the condensation, crystallization and oxidation of bubbles shells at high temperatures. This method is reproducible, simple, cheap, environmental friendly and it allows good control of the size, crystallization and oxidation of the product. We also analyze the magnetic properties of the samples obtained after annealing at different temperatures.

#### TABLE 5.1

Method	Diameter	Thickness of shells	Reference
Polystyrene template	Polystyrene template 2.3 μm		[90]
Carbonaceous template	From 100 nm to 1.2 μm	15 - 40 nm	[91-93]
Electrospinning	500 nm	60 nm	[94]
Hydrothermal	From 150 nm to 5 µm	10 - 500 nm	[95-100]
Polyoxometalate -assisted hydrothermal	From 600 to 700 nm	< 100 nm	[101]
Surfactant- assited solvothermal	From 0.5 to 2 μm	50 - 500 nm	[102-103]
Sonochemical	12 nm (inner)	NM	[104]

Some of the methods to produce hollow hematite micro- and nanospheres reported in the literature. N.M: Not mentioned

# Hollow microspheres as drug delivery vehicles

Nowadays, oral and tumoral drug delivery are based on liposome, micelles, polymeric nanoparticles, solid lipid particles, niosomes and other matrices [105-108]. Because direct delivery is prevented by a sort of biological barriers (cell membranes, metabolic enzymes, efflux transporters, binding proteins, etc.), an ideal drug carrier has to demonstrate many properties such as: (a) prolonged circulation in the blood; (b) ability to accumulate specifically in the required pathological zone, (c) responsiveness to local stimuli, such as pH and/or temperature changes (d) allow for an effective intracellular drug delivery and further to individual cell organelles, and (e)

bear a contrast/reporter moiety allowing for the real-time observation of its accumulation inside the target [109].

Hollow micro- and nano-spheres could be good candidates for drug delivery through oral, inhaling and intravenous dosification. In the latest case, hollow spheres can be used for delivering drugs to cancerous tumors since they fit very well the micro sized veins and vessels of the organs [110-112]. Commonly, the low solubility of anticancer drugs in the physiological conditions causes large aggregates and induces serious side effects [113-116]. It also causes insufficient drug accumulation around tumor sites and weakens chemotherapeutic efficiency [117]. Hollow micro- or nanospheres could be used to overcome this drawback. Fig. 5.1 shows a schematic illustration of the general strategy via injection. After loading the drug into the hollow spheres [118], it is injected to the patience. In this way the drug is protect by the shells from degradation during delivery. Magnetic field as represented in the figure. As suggested in this work, hematite can be used since it is highly magnetic and it is innocuous for humans [119, 120]. The speed of the delivery could be controlled by the intensity of the external magnetic field. Inside the tumour, the hematite shells can be dissolved and the drug is released.



#### FIGURE 5.2

Schematic illustration of how the hollow microspheres can be used in Drug Delivery for cancerous tumor treatment. Hollow micro/nano spheres containing the drug it is injected to the patience. The speed of the delivery could be controlled by the intensity of an applied magnetic field and to guide the spheres to the target

# **Methods and techniques**

Hollow hematite microspheres were produced by a modified gas-bubble template method following annealing in air an iron oxide precursor obtained by sol-gel [121, 122].

#### **Preparation:**

For the precursor, 200 ml of colloidal ferric nitrate nine-hydrate (Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O) particles and

mono hydrated citric acid ( $C_6H_8O_7$ . $H_2O$ , 0.2M) were dissolved in 800 ml of deionized water. The solution was vigorously agitated in a magnetic stirrer at 350 rpm (70 °C) for a period of 48 h to form Fe(OH)<sub>3</sub>. The citric acid was used as ligand, to promote hydrolisis and to balance any difference of ions in the solution. A gel is formed by the hydrolisis of the ferric nitrate to iron oxohydrate FeOOH polymer [123].

The gel was dried for two days at 40 °C to evaporate the acid, water residuals and other possible impurities formed during hydrolysis. This sample precursor was then introduced in a tubular furnace (LENTON LTF-PTF Model 16/610) for annealing in air at different temperatures, from 180 to 600 °C. The furnace was programmed to increase the temperature at  $2 \pm 1$  °C/min, to remain constant for 12 h, and finally to cool down at a rate of  $2 \pm 0.5$  °C/min. This step has two purposes. First, to thermally oxidize the gel to obtain pure hematite; and secondly, to form bubble structures via boiling in air from which the hollow spheres are formed after quenching. Remarkably, the solution precursor, is stable in air and has a shelf life longer than two years. After reacting with water and following the same annealing process, similar hollow spheres can be obtained.

#### Characterization:

The characterization of the samples was performed by X-ray diffraction (XRD). The data were collected from 20° to 65° (0.02° steps) using a powder universal diffractometer Bruker D8 Focus with Cu- $K_{\alpha}$  radiation (1.5406 Å). The diffractograms corresponding to the single hematite phase were refined using the Rietveld method and the peaks shape was modelled with a Pseudo-Voigt function (a combination of Gaussian and Lorentzian functions). The average crystallite size for the single-phase hematite samples was estimated with the Scherrer equation [124]. During Rietveld refinement,  $R_{WP}/R_{exp}$  (the rate of the parameters *R*-weighted and *R*-expected) was used to observe the convergence of the cell parameters and to obtain a good fitting [125]. The shape of the hematite crystallite was modeled by using the program Vesta v.3.2.1 [126] and their strain were calculated with the Williamson-Hall method [127]. The morphological analysis was performed using a scanning electron microscope (SEM–XL30 SFEG). With the help of the Image-J software, several SEM images have been used to count  $N \approx 1,000$  particles. Subsequently, particle size histograms have been mounted using the Sturges method [128, 129].

The magnetic measurements were carried out in a DC magnetic property measurement system (DC-MPMS-SQUID) from Quantum Design. The temperature dependence of the magnetization data, M(T), were taken in zero field cooling (ZFC) and field cooling (FC) modes from 8 K to near room temperature (RT), 290 K. The field dependence of the magnetization data, M(H), were taken under different applied magnetic fields (from -50 kOe to 50 kOe). The M(H) data were corrected by removing the diamagnetic contribution of the sample holder. Since hematite's ferromagnetism is so weak and its demagnetizing field is around 10 Oe, any field contribution from internal demagnetization was neglected.

# Crystallization

Figure 5.3 shows the X-ray diffraction patterns of the samples after annealing at different temperatures from 180 to 600 °C. Initially, after annealing at 180 °C, the sample consists of an amorphous solid with no preferred reflections in the XRD. After annealing at 250 °C, magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) coexisting with a small amount of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) were found. The first two phases were differentiated in the XRD by following the Kim's method [130], in which

the (511) peak around 57° is deconvoluted into two peaks corresponding to magnetite (PDF2-No. 85-1436) and maghemite (PDF2-No. 04-0755) respectively; whereas the hematite was identified from its main reflection (104) at 33.16°. The variation of the annealing temperature from 250 to 400 °C increases the presence of hematite (PDF2-No. 86-550) and its reflections (104), (110), (113), (024) and (300). Increasing the annealing temperature to higher values, such as 500, 550 or 600 °C, the total transformation of magnetite and maghemite into hematite is obtained. Similar results have been reported by other authors [131, 132]. Note that the sharpness of the hematite peaks improves with annealing temperature meaning that the crystallization improves and the grain size increase. Eventually, after annealing the sample at 600 °C, all Bragg reflections are consistent with the hematite phase, confirming the complete phase transition.

As mentioned above, hematite has a rhombohedrally centered hexagonal structure of corundum type (space group R-3C) with a close-packed oxygen lattice in which two-thirds of the octahedral sites are occupied by Fe(III) ions [133, 134]. The crystal parameters were obtained by Rietveld refinement method where  $R_{WP}/R_{EXP}$  (the R-weighted to R-expected ratio) was used to observe the convergence of the fitting parameters and to obtain a good fitting. The obtained values are listed in Table 5.2. Note that the crystallite size increases with annealing temperature while the residual strain decreases. In fact, these variations occur because the driving force increases with temperature making to overstep the equilibrium boundary to a more stable phase. The shape of the crystallite is described in more detail next.



#### FIGURE 5.3

X-ray diffraction patterns of the samples after annealing at different temperatures. After annealing at 180 °C, the sample consists of an amorphous solid with no preferred reflections. After annealing at 250 °C, magnetite and maghemite coexist with an small amount of hematite. Annealing at temperatures above 400 °C increases the presence of hematite. Annealing at 500, 550 or 600 °C results in the single-phase hematite

Crystallite size, lattice parameters and residual strains obtained by Rietveld refinements from XRD of the single-phase hematite samples

Annealing	< <i>D</i> >	Strain (%)	a=b (Å)	c (Å)	$R_{\rm WP}/R_{\rm Exp}$
Temperature ( <sup>o</sup> C)	(nm)				
600	73.50	0.121	5.0338	13.7472	1.11
550	57.30	0.128	5.0338	13.7378	1.15
500	46.60	0.195	5.0339	13.7487	1.13

Figure 5.4 shows the scanning electron micrographs of the raw sample and after annealing at 550 and 600 °C. Fig 5.4 (a) shows the morphology of the sample obtained after sol-gel processing. The sample consists mainly of an formless mass of  $Fe(OH)_{x}^{+(3-x)}$ , H<sub>2</sub>O and NO<sub>3</sub> [135]. Similar morphology was obtained for the samples annealed at temperatures below 500 °C (not shown here). This in contrast to the hydrothermal method, in which intermediate solid cores or urchain-like seeds were observed after increasing the temperature [95, 96, 100]. In the present work the morphology of the sample continued un-shaped even after annealing at 500 °C.

Fig. 5.4 (b) shows the morphology of the sample after annealing at 550 °C, in which most of the material consists of micropheres with soft surfaces, coexisting with a few unshaped grains. The corresponding histogram (top right inset figure) gives a mean diameter of  $889 \pm 20$  nm. The top left inset figure shows a broken sphere revealing its internal cavity. The broken sphere has an external diameter of around 1.45 µm and shell thickness of around 200 nm. Fig. 5.4 (c) shows the sample after annealing at 600 °C. The mean size of the spheres has increased to around 1.60 µm as noted from its respective histogram (top right inset figure). The top left inset figure shows a broken sphere of 2 µm and shell thickness of less than 100 nm. The difference in diameter and shell thickness than in the previous case suggests that, as the size of the spheres grows, the shells become thinner.

Fig. 5.4 (d) shows one sphere with diameter 1.85  $\mu$ m obtained after annealing at 600 °C. Note that the surface is not completely soft and it is rough suggesting that the shell is composed of different grains. A model of the crystallite shape of this sample is provided in the top right inset figure. Note that the shape of the grains conforming the shell are slightly similar to the modeled polyhedron crystallite orientated along the {104} and {110} family of planes. However, since the crystallite size of this sample is 73.5 nm (see Table 5.2), each grain in the shell should contain between 1 - 3 crystallites. Note that by increasing the annealing temperature from 550 to 600 °C the crystallite size increases and the shell thickness decreases. In this way, the calculated number of crystallites forming the shell of the sample annealed at 550 °C is around  $3.1 \times 10^3$ , whereas that for the sample annealed at 600 °C is around  $2.6 \times 10^3$ . This slightly difference number of crystallites indicates that the spheres growth is quasi-isotropic.



#### FIGURE 5.4

Scanning electron microscope micrograph of the raw sample and after annealing at 550 and 600 °C. a) Sample obtained after sol-gel processing (raw). b) Sample after annealed at 550 °C. Top right inset: histogram giving a mean diameter of 889  $\pm$  20 nm. Top left inset: A broken sphere revealing its internal cavity. c) Sample after annealing at 600 °C. Top right inset: Histogram giving a mean diameter of 1.60  $\mu$ m. Top left inset: A broken sphere revealing its internal cavity. d) An individual sphere obtained after annealing at 600 °C. Top right inset: A model of the polyhedron crystallite shape of the hematite orientated along the {104} and {110} family planes

# **Hollow formation**

In order to understand better the bubble formation we have exposed the raw precursor to an electron beam generated in a SEM. Figure 5.5 shows the SEM image of the raw sample obtained by secondary electrons accelerated at 5 kV at consecutive times. The inset figures show the topography profile on the areas pointed by the arrows. Fig. 5.5 (a) shows an image taken at an initial time set as 0 s when the electron beam starts heating the sample. Fig. 5.5 (b) shows the same area scan after 5 s of electron beam irradiation. Remarkably, bloating areas form in different parts over the surface. The arrow points a clear formed bubble caused by the heated sample due to electron beam incidence. The bubble should consist of diffusive gas tending to escape from the sample and remained trapped due to surface tension. Figure 5.5 (c) shows the morphology of the same area after 10 s of electron beam irradiation. The bubble pointed by the arrow has exploded. It is difficult to calculate the internal pressure of the gas before exposion because it depends not only on the diameter but also on surface tension of the bubble. However, since the internal pressure of a bubble increase on decreasing its diameter [136], the explosion observed in the figure should be

caused by increment on the outgass species promoted by heating due to the long beam exposure. Similar works about bubble formation in other annealed materials report that the internal pressure varies over a wide range (from 10 [137] to  $300 \times 10^6$  Pa [138]) and it also depends on the type of gas. Thus, this technique is suitable for the encapsulation of pure or preselected combination of gases.

The mechanism for the formation of the hollow spheres in this work might be as follow: 1st- Initially, dissolution of the reagents occurs via

$$Fe(NO_{3}).9H_{2}O_{(s)} \xrightarrow{H_{2}O} Fe^{3+}+NO_{3}^{-} (aq)$$
(1)  
$$H_{3}C_{6}H_{5}O_{7}.H_{2}O_{(s)} \xrightarrow{H_{2}O} H_{3}C_{6}H_{5}O_{7} (aq)$$
(2)

Reaction between the dissolved reagents occurs via hydrolyzation of iron and nitrate. The nitrate  $(NO_3)$  solubilize in water while the Fe<sup>3+</sup> ions react progressively with water and the decomposed products of the citric acid to form an hydrated iron-citrate gel which after drying (equation 6) an amorphous compound of Fe, C, H and O ions is formed, as observed in Fig. 5.4 (a) and Fig. 5.5.

$$\mathsf{Fe(OH)}_{3\,(gel)} + \mathsf{H}_3\mathsf{C}_6\mathsf{H}_5\mathsf{O}_{7\,(aq)} \xrightarrow{\mathsf{drying}} \mathsf{FeC}_6\mathsf{H}_5\mathsf{O}_{7\,(s)} + 3\mathsf{H}_2\mathsf{O}_{(g)} \quad (3)$$

2nd- During annealing, the latest product reacts with air to form magnetite, maghemite or hematite depending on the temperature (as detected by XRD in Fig. 5.3). In the case of hematite:

$$\operatorname{FeC}_{6}\operatorname{H}_{5}\operatorname{O}_{7(s)} + air \xrightarrow{\Delta} \operatorname{Fe}_{2}\operatorname{O}_{3(s)} + \operatorname{H}_{2}\operatorname{O}_{(v)} + \operatorname{CO}_{2(g)} \quad (4)$$

the reaction occurs with simultaneous melting, vaporization and degassing of the precursor components. In addition to  $H_2O$  and  $CO_2$ ,  $N_2$ , NO and  $O_2$  might also become volatile due to the decomposition of NO<sub>3</sub> [135].

3rd- At high annealing temperatures, such as 550 and 600 °C, the melt superheats and decompresses. Decompression exerts a major control on the physical state of the melt. This change in pressure influences the density and solubility of the gaseous components. A chaotic internal diffusion occurs forming a vesicular texture in which the superheated gases take place. These cavities act as heterogeneous nucleation centers for single crystal growth or polycrystalline aggregation [139].

4th.- The exact processes that control the nucleation and growth of the gas bubbles are complex and highly nonlinear [140]. It is assumed that a bubble nucleates when superheated liquid grows sufficiently to cause the vapour/gas trapped within the cavity to overcome the surface tension force and should grow following the theory of Hsu [141].

5th- Once a bubble nucleates, it grows through: (i) mechanical expansion due to compressibility of the gas phase and (ii) simultaneous diffusion from the superheated melt to adjacent bubbles and evaporation of the liquid in the surface bubble [142]. The transport of water to the bubbles' interface has not been much investigated, but the growth rate of a bubble was parameterized following the relation [143]:

$$\frac{R(t)}{R_i} = e^{\frac{\tau^2 t_{dec}}{2t_{vis}}}$$
(5)

where R(t) is the radius of the bubble at a particular time,  $R_i$  is the radius previous to decompression,  $t_{vis}$  is the timescale for viscous relaxation,  $t_{dec}$  is the timescale for decompression and  $\tau = \left| \frac{dp}{dt} \right| t$  in which p is the pressure.

6th- Whereas, the viscosity of the surrounding melt opposes a resistance to bubbles growth. The surface tension acts on the bubbles shrinking the surface and forces them back to the melt. Thus, there is a competition between the buoyancy and surface tension, which is mediated by the temperature. Approaching the surface, the external pressure decreases and the bubbles evolve in the liquid.

7th.- Thus, the microbubbles act as soft templates over which crystallites aggregate and grow. Eventually, the crystallization, condensation and oxidation of the shells is controlled by the heat treatments, thus forming the hollow spheres. A similar mechanism has been also proposed by other authors [144].



#### FIGURE 5.5

SEM micrographs of the raw sample obtained by secondary electrons accelerated at 5 kV at consecutive times: a) 0 s, b) 5 s and c) 10 s. The arrows point areas in which a clear bubble is formed. The inset figure shows the corresponding topography profile over the area pointed by the arrows

The parameters that can be adjusted for controlling the size, shell thickness, crystallization, oxidation and quality of the bubbles are: the annealing temperature, the increase/decrease ratio of temperature, the annealing time, the solvent and the concentration of the reactants (and hence viscosity of the melt). Among them, the annealing temperature has a high influence in the size, shell thickness and crystallization of the product. In this sense, it is expected that for higher annealing temperatures than 600 °C the percentage of broken bubbles in the final product increases. Moreover, the concentration of the reactants also plays an important role. We observed that citric acid with concentrations lower than 0.1 M (data not shown here) do not produce enough gas to form the microbubbles. The concentration of citric acid used in the present work was 0.2 M resulting in high quality hollow spheres. Whereas, it is expected that using higher molarities might result in thicker shells and smaller diameter for the bubbles [137]. In such a case, the diameter of the hollow spheres can be increased by raising the annealing temperature. Furthermore, the slow heating/quenching rate (2 °C/min) also assist in yielding intact, dense, and stronger spheres by allowing the nascent, individual bubbles to crystallize completely as separated particles.

# **Magnetic properties**

In bulk  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> the spins are oriented along the [111] axis of the rhombohedral primitive cell [145]

(along the [001] direction of the hexagonal unit cell [146]). It presents a first-order magnetic transition, called the Morin transition with the corresponding Morin temperature ( $T_{\rm M}$ )= 263 K [147, 148]. Below  $T_{\rm M}$ , the two magnetic sublattices contain spins oriented antiparallel and the material is antiferromagnetic (AF). Between  $T_{\rm M}$  and the Néel temperature ( $T_{\rm N} \approx 960$  K [149]) the spins lie in the basal {111} planes of the rhombohedral cell ({001} planes of the hexagonal unit) and they are slightly canted away (approx 1°) from the antiferromagnetic orientation, resulting in a "weak ferromagnetism" or "canted antiferromagnetic state" [150-152]. In general,  $T_{\rm M}$  is dependent on a number of variables such as grain sizes [153], cation substitution [147, 154, 155], lattice defects (which generate internal strains) [156-159] and magnitude of the external magnetic field [160, 161].

In bulk hematite, the energy per unit volume due to exchange interaction is written by [150]:

$$E_{\rm M} = J_{\rm e} M_1 \cdot M_2 - {\rm C.} (M_1 \times M_2),$$
 (6)

where  $M_1$  and  $M_2$  are the sublattice magnetization with  $|M_1| = |M_2| = M$ ,  $J_e$  is the mean-field coefficient related to the isotropic exchange interactions, and C is a constant vector along the [111] direction. If a magnetic field  $\mu_0 H$  is applied, it gives rise to a Zeeman energy term:

$$E_Z = -\mu_0 H. (M_1 + M_2).$$
 (7)

The magnetocrystalline anisotropy energy of bulk hematite has the form [150]:

$$E_{\text{anisotropy}} = -\frac{\kappa_1}{2} (\cos^2 \theta_1 + \cos^2 \theta_2) - \frac{\kappa_2}{2} (\cos^4 \theta_1 + \cos^4 \theta_2), \quad (8)$$

where  $K_1$  and  $K_2$  are the first and second order anisotropy constants respectively and  $\theta_1$  and  $\theta_2$  are the polar angles between  $M_1$  and  $M_2$  and the [111] direction. Spin rotation is originated from the competition between  $K_1$  and  $K_2$ .  $K_1$  dominates at low temperatures, it is positive below  $T_M$  and it changes to negative above  $T_M$ . At room temperature  $K_1 >> K_2$  [150].

Regarding size, a small reduction in  $T_{\rm M}$  is observed when grain size decreases from 10,000  $\mu$ m to 100 nm (~10 K) [161]. However, in the case of hematite nanoparticles superparamagnetism is also expected together with an increase of magnetization in the weakly ferromagnetic state due to two contributions: the canted sublatices and the unpaired spins on the surface [150]. In fact,  $T_{\rm M}$  dramatically decreases for particle sizes below 100 nm following a 1/D dependence [162]. For example,  $T_{\rm M}$  is around 250 K for 100 nm-size-particles and 190 K for 30 nm-size-particles [161]. For particles with diameters 20 to 8 nm,  $T_{\rm M}$  is less than 4 K and it tends to disappear for smaller diameters [150, 151, 162-166]. The suppression of  $T_{\rm M}$  in hematite nanoparticles is believed to be caused by high internal strains [158, 167] and from small surface to volume ratio, which allows surface spins to dominate the magnetization [164].

All materials exhibit some type of magnetic behavior which can be sensed by using a magnetometer. As mentioned in the "*Methods and techniques*" section above, the magnetic properties of the hematite samples were obtained by using a DC-MPMS-SQUID (Quantum Design) magnetometer. There are two principal magnetic measurements which can be performed with this equipment [168]:

M(H)- magnetization as a function of the applied magnetic field, and M(T)- magnetization as a function of the temperature.

where, *H* is the *applied magnetic field* which is the magnetic field applied to the sample by a superconducting magnetic coil in the magnetometer. An M(H) measurement is made by fixing the temperature T and measuring *M* at a series of *H* values. An M(T) measurement is made by fixing the applied magnetic field *H* and measuring *M* at a series of *T* values. These measurements can be performed in two modes: i) ZFC (*zero field cooling*): by cooling dawn to low temperatures without any magnetic field present, once the desired low temperature is reached an external magnetic field is applied and the magnetization is measured by increasing the temperature, and ii) FC (*field cooling*): by cooling dawn to low temperatures in the presence of a magnetic field while measuring the magnetization. Therefore by studying how the magnetization changes with temperature and intensity of the applied magnetic field, we can determinate the magnetic properties of the hematite hollow spheres.

#### The temperature dependence of the magnetization (M(T)):

Figure 5.6 shows the temperature dependence of the magnetization of the samples after annealing at different temperatures. The ZFC and FC loops corresponding to the samples annealed at 250 °C give an unidentified signal probably caused by a mixture of multidomain structures such as ferromagnetic and paramagnetic domains. Since no Morin transition is detected in the M(T) loop of this sample, then there is no formation of hematite. In contrast, for the samples annealed at higher temperatures, Morin transitions are clearly observed, thus revealing the formation of the hematite phase. Nevertheless, the ZFC and FC curves do not overlap, they form thermal hysteresis around the temperature interval 230-280 °C, meaning different  $T_M$  values. The  $T_M$  values were determined by the sharp peaks in the corresponding derivative curves as they are indicated in the inset plots. Note that for the case of the sample annealed at 450°C, the Verwey signal [169, 170] at  $T_V$ =118 K is also found. Verwey transition is the usual fingerprint to identify magnetite (Fe<sup>3+</sup>[Fe<sup>3+</sup>Fe<sup>2+</sup>]O<sub>4</sub>) [171, 172], in which an ordering of Fe<sup>3+</sup> and Fe<sup>2+</sup> ions within the octahedral sites is thought to occur below  $T_V$ . This effect reveals that this annealing temperature was not enough to achieve the complete oxidation of the gel to pure hematite and a remaining magnetite phase is also present.

The M(T) loop of the sample obtained at 500 °C does not show  $T_V$  indicating the complete oxidation of the magnetite to hematite. Note that irreversibility of the ZFC and FC branches below the Morin transition which indicates that a certain degree of canted spins remains even at low temperatures [91]. The M(T) loop of the samples obtained at 600 °C correspond to the hematite hollow spheres. Note that this annealing temperature produces bigger grain size and better crystallization than the other annealing temperatures, as it is discussed above, which might influence in a better defined and closed thermal hysteresis as it has also observed by other authors [173, 174]. However, the corresponding  $T_M$  values do not differ to much from the other cases indicating that the magnetization is not highly sensitive to the shape and configuration of the hematite domains. For the samples obtained after annealing at 450, 500 and 600 °C, the difference in  $T_M$  values obtained from the ZFC and FC loops ( $\Delta T_M$ ) are 10, 16 and 12 K respectively. We have not observed a clear dependence of  $\Delta T_M$  with annealing temperature.

Thermal hysteresis in hematite has been observed for many years mostly in thin films and submicron particles [158-162, 175-180] than in bulk. Nevertheless, up to now there is not a clear understanding about its origin because the exactly mechanisms by which the Morin transition takes place into the hematite crystals remain elusive. Recently, Özdemir and Dunlop proposed that lattice defects could cause internal stresses which could anchor extensive regions of surface spins preventing spin rotation and thus resulting in thermal hysteresis [161]. It has also been proposed that rotation of the surface spins can cause nucleation centres that generate the transition

throughout the entire crystal [179, 181]. Furthermore, according to Frandsen et al. exchange coupling between particles is larger than dipole coupling in interacting hematite particles [146]. Exchange interaction between hematite particles suppresses superparamagnetic relaxation and produce spin rotation in the sublattices up to 15°, depending on particle size [182]. The thermal hysteresis observed in this work reveal that there is a remnant magnetization upon thermal cycling. This must be caused by a difference between interacting spins oriented in-plane and out-plane. It includes zones of canted spins which resist to rotate with temperature. Since the hollow spheres presented here consist of multifaceted-polyhedron crystallites stuck together and forming the shells, we believe that remanence zones are mainly located in the grain boundaries were interactions between randomly distributed Fe<sup>3+</sup> moments do not lead to a magnetic ordering. They might be also susceptible to the magnetic interactions among the nanocrystals.



#### FIGURE 5.6

Temperature dependence, under 100 Oe applied field, of the magnetization (M(T)) of the samples after annealing at different temperatures (AT). The ZFC and FC loops corresponding to the samples annealed at 250 <sup>o</sup>C give an unidentified signal probably caused by a mixture of multidomain structures. Morin transitions are clearly observed in the case of the samples annealed at 450, 500 and 600 <sup>o</sup>C. The ZFC and FC curves do not overlap and form thermal hysteresis. Insets: Corresponding derivatives to determinate the Morin temperatures and the width of the thermal hysteresis ( $\Delta T_M$ )

#### The magnetic field dependence of the magnetization (M(H))

The magnetic field dependence of the magnetization (M(H)) of the hollow spheres obtained after annealing at 600 °C is presented in Fig. 5.7. The measurements were taken at three different temperatures around the Morin transition: 200, 230 and 290 K. The M(H) hysteresis loop formed near RT (290 K) confirms the weak ferromagnetic state above  $T_M$ . At this temperature, magnetic saturation is reached at around  $H_{S} \approx 20$  kOe. The ratio between the remanence magnetization ( $M_r$ ) and the saturation magnetization ( $M_s$ ) is  $M_r/M_s \approx 0.81$ . According to Özdemir and Dunlop, values between 0.5-0.9 are typical from multidomain hematite particles [183]. Note that in our case, the shells are composed by multiple hematite grains and they might be forming interacting domains. Remarkably a large coercive field ( $H_c$ ) of around 2.7 kOe is found and it becomes zero as the temperature scales down. It is commonly accepted that the enhancement of the coercivity in bulk magnetic materials can be obtained by increasing either: (i) the resistance of domain rotation via increment of the magnetic anisotropy and (ii) the resistance of domain wall displacement via enhancing the distribution of internal stress and the volume concentration of impurity. However, up to date, there is not agreement of the exactly causes for the coercivity increase in the case of hematite nanoparticles. Large H<sub>c</sub> values have been recently reported near RT for particle diameters in the interval 120-450 nm (1.5-3.5 kOe) while for bigger sizes  $H_c$  tends to decreases exponentially [166]. The possibility of enhanced stress is discarded in this work since annealing at high temperatures reduces the number of strains centres. In contrast, similar to other works which relate the high coercivity values with the shape of the hematite particles and the amount of crystallites contained into them [184-186], we believe that the relative large coercivity obtained in this work might be associated to the shape and amount of the crystallites conforming the hollow spheres. Since the brick crystallites are mulfaceted-polyhedron (see Fig. 5.4 (d) above), they should have large shape anisotropy in addition to crystallyne anisotropy. This effect might be also affected by the number of crystallites composing each sphere  $(2.6 \times 10^3, \text{ see above})$ , which follows very well the correlation of coercivity values vs. number of composing crystallites reported by Rath et al. [186]. In other words, similar to the thermal hysteresis reported above, the high coercivity obtained in this work should be caused by the large difference between domains alignment occurred into the crystallites and grain boundaries. As more polyhedron crystallites conform the shells, more grain boundaries and different spin alignments there are, thus resulting in a large coercivity.

At 230 K, a coexistence of antiferromagnetic and canted antiferromagnetic domains is detected. Note that the antiferromagnetic state is dominant at the lowest applied fields since the magnetization tends to negative values and there is a lack of remanence and coercivity. Positive magnetization signals are obtained at higher magnetic fields than 30 kOe, enhancing the canted amount of spins (weekly ferromagnetism state). At 200 K, no remanence magnetization, nor coercivity, are obtained and the inverse sigmoidal curve in the M(H) loop reveals the complete antiferromagnetic state of the hematite hollow spheres.



#### FIGURE 5.7

Magnetic field dependence of the magnetization (M(H)) of the hollow spheres obtained after annealing at 600 °C. The measurements were taken at three different temperatures (200, 230 and 290 K) as indicated. At 290 K, the hysteresis confirms the weak ferromagnetic and  $H_c \approx 2.7$  kOe. At 230 K, a coexistence of antiferromagnetic and canted antiferromagnetic domains is detected with a lack of remanence and coercivity. At 200 K, the inverse sigmoidal curve reveals the complete antiferromagnetic state

# Conclusions

Hollow hematite microspheres were prepared without using hard templates by following the gasbubble template method. Boiling at high temperatures promotes bubble formation on which crystallites agglomerate, crystallize and oxidize to the hematite phase leading in the formation of hollow microspheres. The size and crystallization of the hematite hollow spheres increases with annealing temperature. After annealing at 550 °C, hollow spheres with mean diameter of 0.889 µm are obtained, whereas after annealing at 600 °C, hollow spheres of 1.6 µm are obtained. The increase in diameter is accompanied with a slight decrease of the thickness of the shells suggesting that the growth of the hollow spheres depends on the bubble growth. For the samples obtained after annealing at 450, 500 and 600 °C, thermal hysteresis in the M(T) loops taken in ZFC and FC modes with different  $T_M$  values were obtained. The thermal hysteresis observed in this work might be caused by remanence zones located in the grain boundaries. Exchange interactions in these zones might also be the responsible in generating the large coercivity observed in this work (~2.7 kOe) since as more crystallites conform the shells, more grain boundaries and different spin alignments there are.

Due to the simplicity of the technique presented here for the preparation of hematite hollow spheres, we feel that the results of this work could have important application in the emerging fields of targeted treatment, such as targeted cancer treatment. Our group has pioneered studies of the influence of specially synthesized magnetic nanocomplexes, formed by synthesizing magnetic nanoparticles together with anticancer drugs [187-192], and we have been collected clinical data from animal studies that show a remarkable influence in the survival rates of animals (rats) infected with cancer. The hollow spheres presented here could be used as drug delivery vehicles and potentially this approach could result in replacing chemotherapy with the well known very adverse and serious side effects, with a targeted delivery of the anticancer drug only to the areas of the tumours, for example by directing injection to the solid tumours. Moreover, hyperthermia in which the temperature around solid tumours is raised is also very promising approach in cancer treatment in which we have been working. Since the ferromagnetic behaviour of the hollow hematite spheres is sensed better to higher temperatures than RT, then they can be very suitable candidates as agents of targeted hyperthermia.

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