

## Effect of Cu substitution on the magnetic and magnetic induction heating response of CdFe<sub>2</sub>O<sub>4</sub> spinel ferrite

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**Abstract.-** In this work, a comparative study of the effect of Cu on the structural, magnetic and magnetic induction heating response in CdFe<sub>2</sub>O<sub>4</sub> spinel is presented. The ceramic nanoparticles (Cu<sub>1-x</sub>Cd<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub>; 0 ≤ x ≤ 1) were synthesized by co-precipitation from Cu(II), Cd(II) and Fe(III) salts. The samples, characterized by X-ray diffractometry, display the characteristic spinel cubic structure (space group *Fm3m*) where CdO is detected as main secondary phase (≈ 16% weight for x = 1). A high degree of nanoparticle agglomeration is inferred from the Transmission Electron Microscopy (TEM) images, as a consequence of the employed synthesis procedure. Regarding the magnetic properties, superparamagnetic behavior at room temperature can be disregarded according to the low field magnetization response (*ZFC-FC* curves). For 0.4 ≤ x ≤ 0.8 ratios, the samples display maximum values in the magnetic moment that should be correlated to the cation distribution between the octahedral and tetrahedral sites. Maximum magnetization values lead to an enhancement in the magnetic induction heating response characterized by highest heating temperatures under the action of an *ac* magnetic field. In particular, maximum *SAR* values are estimated for x = 0.8 as a combined effect of high magnetic moment, low *dc* coercive field (high

susceptibility). Although these Cu-Cd ferrite nanoparticles display moderate *SAR* values (around 0.7 W/g), the control of the maximum heating temperatures through the cation distribution (composition) provides promising properties to be used as nanosized heating elements (i.e. hyperthermia agents).

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## 1.- Introduction

Semiconductor ceramics represent an active current research topic in material science due to their applicability in different technological fields. In particular, a wide range of different applications has been proposed employing spinel ferrimagnetic ferrites ( $M\text{Fe}_2\text{O}_4$ ;  $M$ : Mn, Co, Ni, Cu): adsorbers and photocatalysts in the removal of contaminants in water [1, 2], gas sensors [3, 4], magnetic nanocarriers for biomedical applications as hyperthermia, drug delivery, MRI or MPI contrast agents [5, 6] and electromagnetic absorbers [7, 8]. In particular, Cu and Cd ferrites show excellent properties to be applied as efficient catalysts and chemical sensors [9-12], anode for lithium ion batteries [13, 14] or microwave electromagnetic absorbers [15, 16].

Spinel structure consists of a cubic compact package of oxygen anions in which cations occupy tetrahedral ( $A$ ) and octahedral sites ( $B$ ) [17]. The particular cation distribution depends on the composition and synthesis procedure and is usually characterized by the inversion parameter  $\delta$  (fraction of divalent ions on the octahedral sites) [18]. Bulk  $\text{CdFe}_2\text{O}_4$  is a normal spinel ( $\delta = 0$ ) where  $\text{Fe}^{3+}$  cations occupy  $B$  sites and  $\text{Cd}^{2+}$  ions on  $A$  sites [19]. However, mixed spinel structures ( $0 < \delta < 1$ ) are generally reported in nanostructured Cd ferrites, with  $\text{Cd}^{2+}$  cations distributed in both tetrahedral and octahedral sites [20]. The particular cation distribution plays a relevant role in physical parameters of these semiconductor ceramics. Particularly, the exchange coupling among ions in octahedral and tetrahedral sites ( $J_{BB}$  and  $J_{AA}$ ) and the antiferromagnetic superexchange  $J_{AB}$  interaction between sites of different symmetry mainly control the magnetic properties in these ferrite spinel structures. Bulk normal ( $\delta = 0$ )  $\text{CdFe}_2\text{O}_4$  displays antiferromagnetic behavior below

10 K as a consequence of the antiferromagnetic interaction between the  $\text{Fe}^{3+}$  cations ( $5 \mu_{\text{B}}$  per  $\text{Fe}^{3+}$  ion) within the octahedral  $B$ -sites. However, room temperature ferrimagnetic response is reported in Cd ferrite nanoparticles due to the partial occupation of  $\text{Fe}^{3+}$  ions in the tetrahedral  $A$ -sites [21, 22]. In this case, the exchange antiferromagnetic  $AB$  interaction between both sublattices dominates. Furthermore, the occurrence of complex magnetic phenomena are also reported and related to non-collinear (canted) spin structures [23].

Regarding  $\text{CuFe}_2\text{O}_4$  ferrite, partially inverted ( $\delta \rightarrow 1$ ) spinel structure is usually reported with  $\text{Cu}^{2+}$  cations tending to occupy octahedral ( $B$ ) sites and only a small amount of  $\text{Cu}^{2+}$  ions migrate from the octahedral ( $B$ ) to tetrahedral ( $A$ ) sites [24]. The ideal inverse configuration consists of  $\text{Cu}^{2+}$  on the octahedral sites and  $\text{Fe}^{3+}$  equally distributed between the tetrahedral and octahedral sites. Since the magnetization of  $A$  and  $B$  sublattices is antiparallel, being  $A$  and  $B$  sites ferromagnetically ordered, the total magnetic moment in this spinel comes from the uncompensated moments of the Cu cations ( $1 \mu_{\text{B}}$  per ion). Therefore, the migration of  $\text{Cu}^{2+}$  ions from  $B$  to  $A$  sites ( $\text{Fe}^{3+}$  from  $A$  to  $B$ -sites) would give rise to a net increase in the magnetic moment of the spinel unit cell as a consequence of the unbalanced  $\text{Fe}^{3+}$  cation distribution. Due to the strong preference of Cd cations to the tetrahedral  $A$ - sites, the inclusion of Cd in the Cu ferrite leads to an increase in the magnetic moment (i.e. saturation magnetization) associated to the migration of the  $\text{Fe}^{3+}$  from  $A$  to  $B$ -sites. Moreover, Cd rich ferrites display reduced magnetization values as a consequence of the trend to the normal spinel configuration ( $\delta = 0$ ) and the non-magnetic nature of the  $\text{Cd}^{2+}$  ions. Accordingly, maximum values of the saturation magnetization are experimentally observed in  $\text{Cu}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$  nanoparticles with  $0 < x < 1$  [25-27]. In fact, similar magnetic response is

found in other mixed spinels (i.e.  $Zn_{1-x}Co_xFe_2O_4$  [28-30]). In these ferromagnetic systems maximum saturation magnetization values are accompanied by a decrease in the effective Curie temperature as the Zn content increases as due to the weakening in *AB* superexchange interaction [31]. This behavior (increase in the effective magnetic moment accompanied by a decrease in the Curie point) enables the design of self-regulated magnetic hyperthermia systems [32]. Magnetic hyperthermia, associated to the temperature increase under the action of an *ac* magnetic field, has been widely analyzed in different magnetic nanoparticle systems [33]. Their main interest lies in the biomedical field, including different approaches as thermo ablation of tumors or drug delivery systems [34, 35]. While the increase in magnetization has generally associated an increase in the heating efficiency, the Curie point enables the control of the effective temperature of the hyperthermia therapy around therapeutic temperatures (45°C) [36]. However, these nanosized heating elements can be also employed in other technological fields: Magnetic Induction Swing Adsorption (MISA) systems (controlled gas capture and release) [37, 38]; new synthesis procedures of nanostructures [39, 40]; mechanical recovery or self-healing in polymers and glasses [41-45]; thermoplastic adhesives for bonded joints [46, 47]; heat assisted catalytic reactions [48, 49] and enhanced magnetic adsorbents in wastewater treatments [50].

Although previous studies reported the magnetic properties of Cu-Cd ferrite nanoparticles (i.e. occurrence of maximum values of saturation magnetization), a systematic analysis of the effect Cu substitution on characteristic magnetic parameters such as magnetic anisotropy is scarcely analyzed in the literature. Furthermore, the induction heating capacity (magnetic hyperthermia) of these ceramic nanosized systems has been barely reported.

Accordingly, in this work a comparative study of the effect of Cu on the structural, magnetic and magnetic induction heating response in  $\text{CdFe}_2\text{O}_4$  spinel is performed. The ceramic nanoparticles ( $\text{Cu}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ ;  $0 \leq x \leq 1$ ), obtained by co-precipitation method, show the typical spinel structure. X-ray diffraction and Transmission Electron Microcopy (TEM) was employed to structurally characterize the samples. The magnetic response, characterized by SQUID magnetometry, indicates the occurrence of maximum magnetic moments for intermediate compositions  $0.4 \leq x \leq 0.8$ . Regarding the magnetic heating response, the results indicate a moderate heating response, where maximum heating efficiencies are mainly linked to the maximum magnetic moments for particular Cu-Cd intermediate compositions.

## **2.- Experimental procedure**

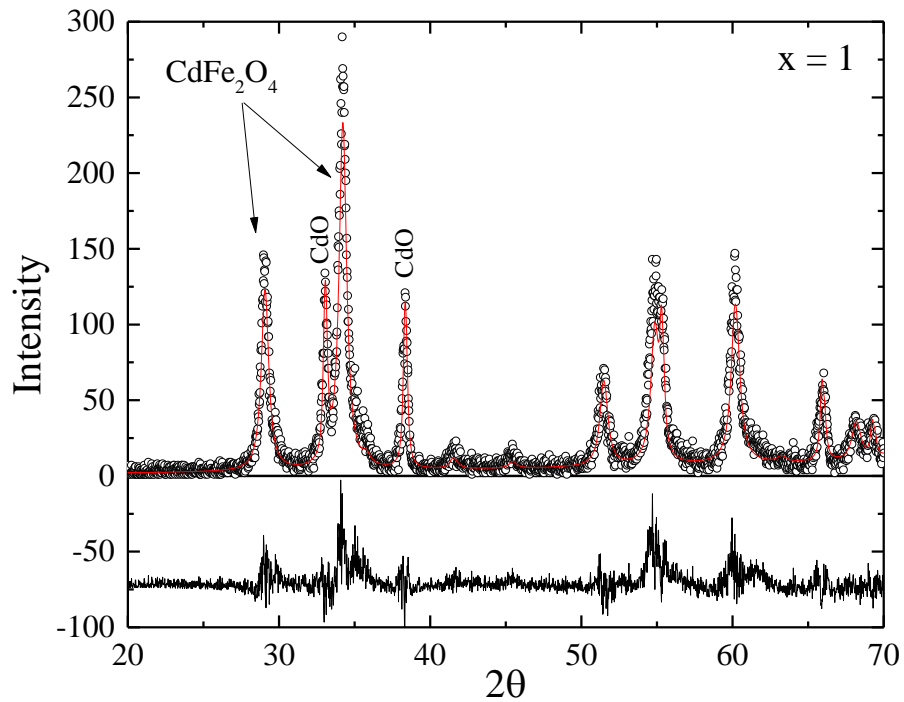
Poly Vinyl Pyrrolidone (PVP), Iron nitrate  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , Copper nitrate,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , Cadmium nitrate,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , were used in the experiments, all with analytical grade. Deionized water was used throughout the experiments.  $\text{Cu}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$  ( $x = 0, 0.2, 0.4, 0.6, 0.8$  and  $1$ ) nanoparticles were prepared in alkaline media from aqueous solutions [38]. Typically, 3.00 g of PVP were dissolved in 100 ml of deionized water at 353 K, and the obtained transparent solution was mixed with 0.20 mmol of iron nitrate and 0.10 mmol of a mixture of copper nitrate and cadmium nitrate (Fe:Cu, Cd = 2:1). After constant stirring for 2 h using a magnetic stirrer, the resultant homogeneous solution was added to a glass Petri dish where was heated at 363 K in an oven for 24 h in order to allow the evaporation of water. Afterwards, the obtained dried solid was ground for 20 min in a mortar to form powder. The powder was then annealed at 773 K for 9 h in order to obtain Cu-Cd ferrite nanoparticles.

X-ray measurements were carried out on a Siemens D-5000 powder diffractometer with monochromated Cu  $K_{\alpha_1}$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). Reflection X-ray powder diffraction data were collected from  $20^\circ$  to  $70^\circ$  in  $2\theta$ . The Rietveld Method and the Fullprof [51] program have been used to analyze the X-ray spectra. Transmission electron microscopy (HRTEM) and scanning transmission electron microscopy with a high angle annular dark field detector (STEM-HAADF) analysis were performed by using a FEI Tecnai Field Emission Gun operated at 300 kV. The magnetic response of the nanoparticles was analyzed through SQUID magnetometry (Quantum Design MPMS XL7). Finally, the magnetic induction heating (hyperthermia) curves under an *ac* field were measured with a home-made set up, composed of a *LC* resonant circuit connected to a 2 kW RF power amplifier (Electronic & Innovation, mod. 1240L). The time evolution of the temperature, *T*, of the nanoparticles in solid powder form (mass,  $m_{MNP} = 30 \text{ mg}$ ) was measured with a fibre optic thermometer (Neoptics, mod. T1) under an ac magnetic field (frequency 340 kHz and amplitude 384 Oe).

### **3.- Results and discussion**

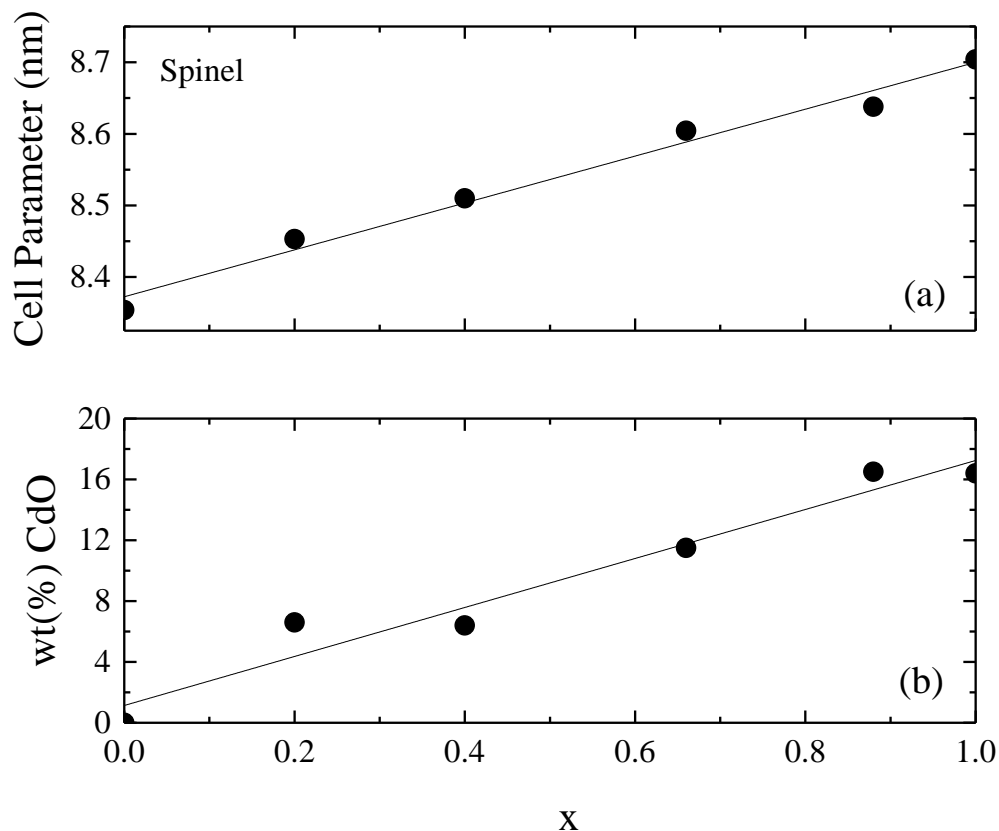
Firstly, the phase distribution was analysed through X-ray diffraction. The results indicate the coexistence in all the samples of the characteristic cubic spinel structure and a small fraction of CdO phase. As an example, Fig. 1 shows the X-ray diffraction pattern measured in the  $\text{CdFe}_2\text{O}_4$  sample (black Points) and the Rietveld refinement (full line) using the crystallographic structures of the Cd-spinel and the CdO both with the same space group *Fm3m*. The difference between experimental and theoretical values are shown at the bottom of the figure. Hematite with a rhombohedral corundum structure (Space group *R3c*) cannot

be detected. Furthermore, for  $\text{CuFe}_2\text{O}_4$  the low temperature tetragonal phase is not found, but the high temperature cubic phase characterizes the X-ray diffraction pattern. Actually, it is found that the formation of  $\text{CuFe}_2\text{O}_4$  with tetragonal or cubic structure depends on different factors such as preparation method, synthesis conditions and annealing temperatures [52].



**Fig 1.** X-ray diffraction patter of  $\text{CdFe}_2\text{O}_4$  nanoparticles



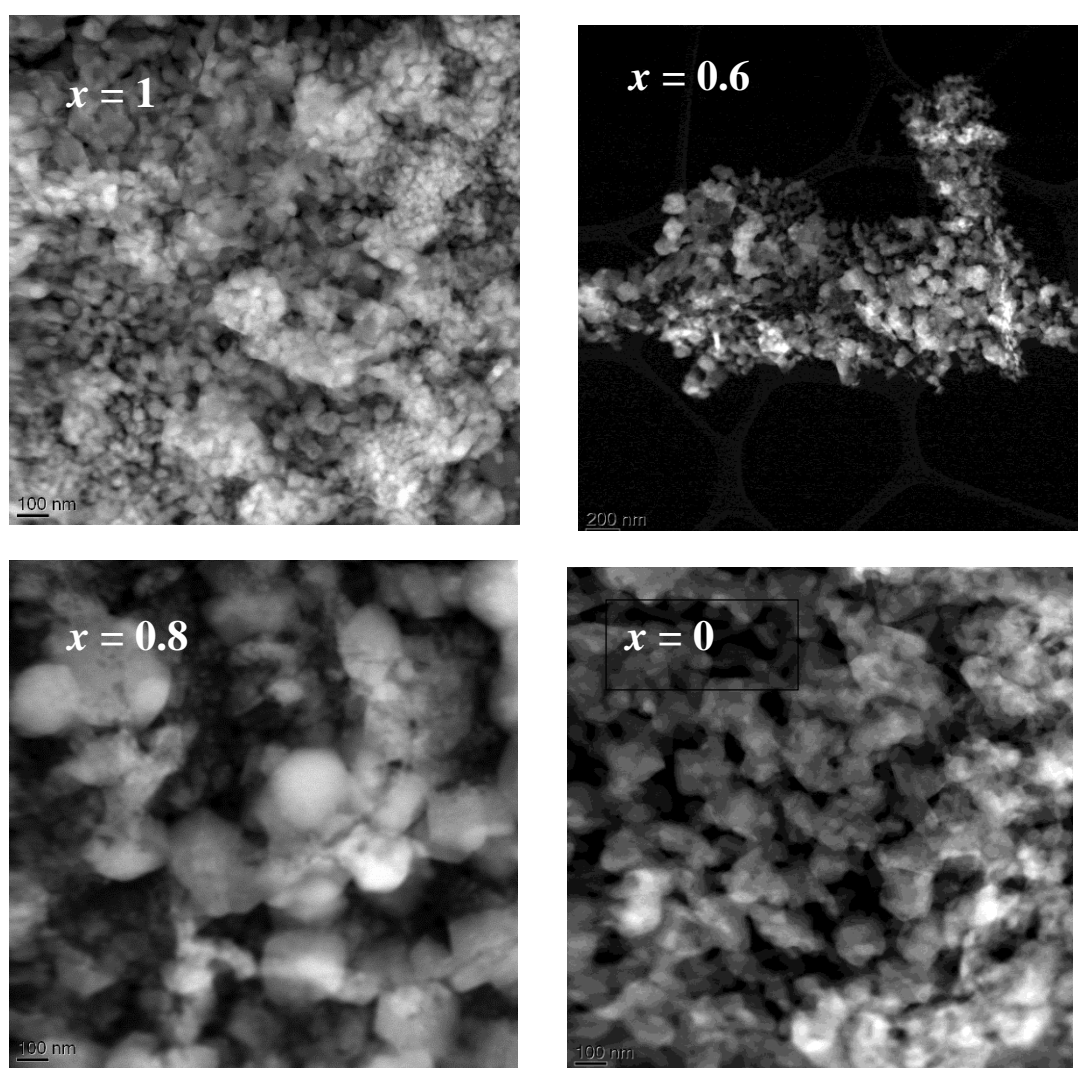


**Fig 2.** (a) Lattice cell parameter and (b) weight % of CdO phase as a function of Cd percentage  $x$  ( $\text{Cu}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ ).

The evolution of the cell parameter,  $a$ , as a function of Cd content ( $x$ ) is shown in Fig. 2a. The changes of the cell parameter with  $x$  should be ascribed to the substitution of  $\text{Cd}^{2+}$  with larger ionic radius ( $0.78\text{\AA}$ ) by  $\text{Cu}^{2+}$  ions ( $0.57\text{\AA}$ ). Similar results have been previously reported in the literature [25-27]. Regarding the occurrence of the CdO secondary phase, an almost linear increase in the weight percentage with  $x$  is detected, (see Fig. 2b) reaching a maximum value around 16% for the  $\text{CdFe}_2\text{O}_4$  sample.

Furthermore, TEM analysis shows a uniform particle size distribution with a high degree of agglomeration. Fig. 3 displays the obtained micrographs for  $x = 1, 0.8, 0.6$  and 0.

The high degree of nanoparticle agglomeration is a direct consequence of the employed synthesis procedure [53]. In this case, it is not possible to detect a clear decrease in the mean nanoparticle size with the Cd content as reported in other studies [25, 26]. In fact, the average crystallite size,  $d$ , calculated by considering the strongest peak (311) and using Debye-Scherrer equation, leads to the following estimated values: 31 nm ( $x = 1$ ), 13 nm ( $x = 0.8$ ), 18 nm ( $x = 0.6$ ), 21 nm ( $x = 0.4$ ), 18 nm ( $x = 0.2$ ), 27 nm ( $x = 0$ ).

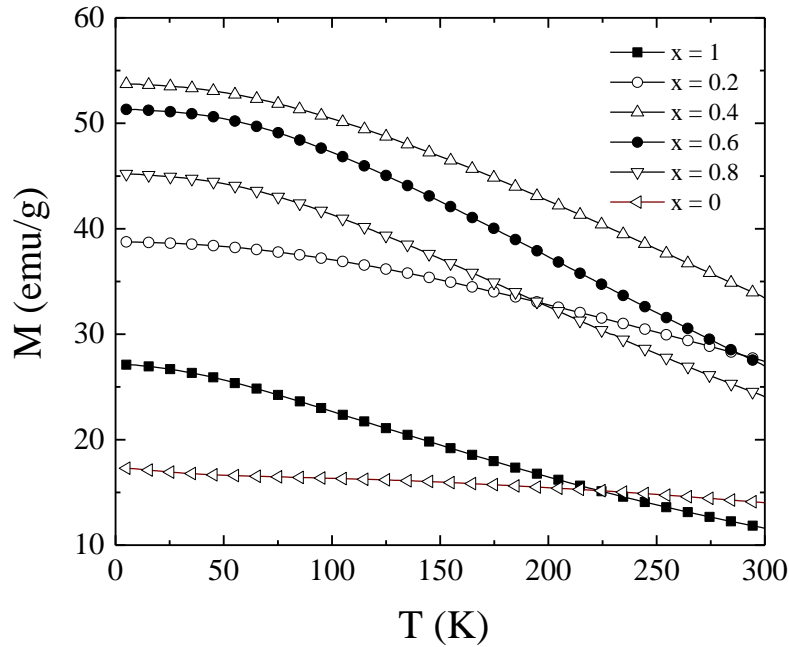


**Fig 3.** TEM images of  $\text{Cu}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$  nanoparticles.

With respect to the magnetic properties, Fig. 4 displays the temperature dependence of the high field magnetization,  $M$  (applied magnetic field  $\mu_0H = 6$  T). A maximum value in  $M$  is found for  $x = 0.4$ . In order to evaluate the evolution of  $M$  with the temperature,  $M(T)$  was fitted at low temperature ( $T < 100$  K) to the Bloch's law:

$$M(T) = M_S(0)[1 - BT^\alpha] \quad (1)$$

with  $M_S(0)$  the magnetization at 0 K,  $B$  the Bloch constant and  $\alpha$  a parameter which value depends on the size of the particles. Table I summarized the obtained results. Firstly, the Bloch constant decreases as the Cd is partially substituted by Cu, displaying similar values than those reported in other ferrite nanoparticles [54, 55]. Regarding  $\alpha$  parameter, it ranges between the reported values in bulk systems ( $\alpha = 3/2$ ) and those obtained in the nanoscale (coming closer to 3 for small clusters) [56].

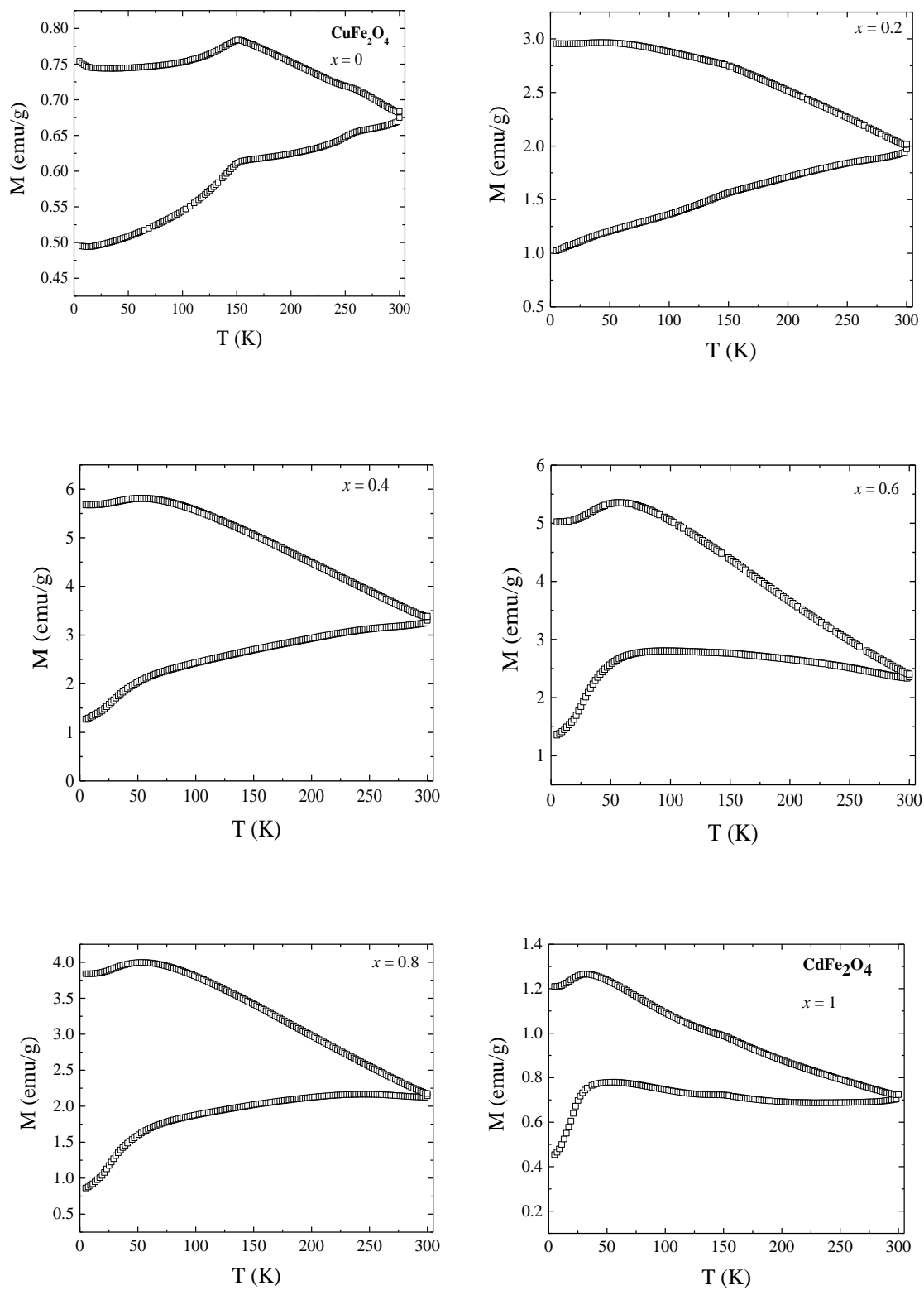


**Fig. 4.** High field magnetization curves (applied field  $\mu_0H = 6$  T) for  $\text{Cu}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$  nanoparticles.

**Table I:** Magnetic parameters obtained from the fitting of  $M(T)$  to the Bloch's law (eq. 1) and the estimated magnetic moment, number of Bohr magnetons,  $n_B$ , per formula unit ( $\text{Cu}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ ).

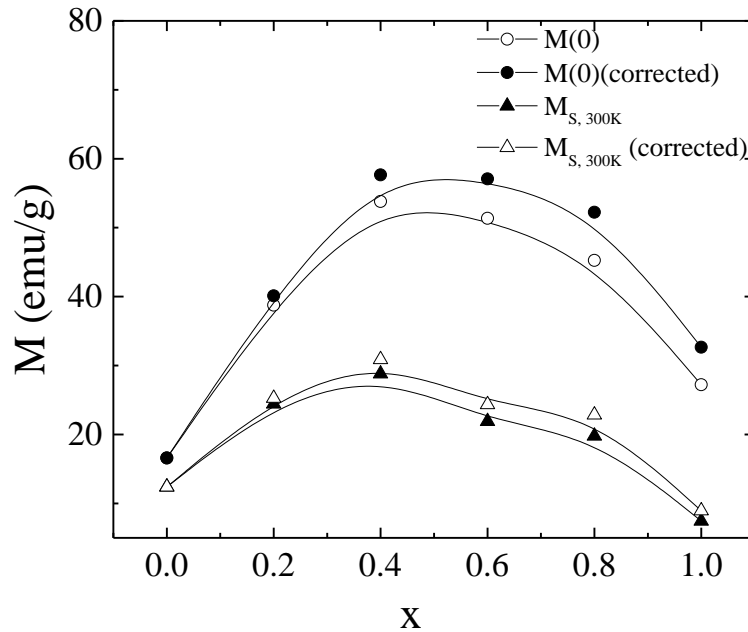
$x$	$M(0)$ (emu/g)	$B$ ( $10^{-6} \text{ K}^{-\alpha}$ )	$\alpha$	$n_B$
1	27.21	138.0	1.54	1.7
0.8	45.25	13.3	1.90	2.6
0.6	51.36	6.0	2.05	2.7
0.4	53.8	13.5	1.83	2.7
0.2	38.77	7.8	1.87	1.8
0	16.6	0.6	2.2	0.7

With respect to the low field magnetization (i.e. *dc* magnetic susceptibility), Fig. 5 shows the *ZFC-FC* curves under an applied magnetic field of 50 Oe for the set of analyzed nanoparticles. The occurrence of superparamagnetic behavior at room temperature can be disregarded since a clear irreversible behavior between both magnetization curves is found for  $T < 300$  K in all the samples. For  $x > 0.4$  the samples display at low temperatures ( $T < 50$  K) a decrease in both *ZFC-FC* magnetization curves. This behavior could indicate a certain degree of magnetic frustration at low temperatures (i.e. spin-glass state) as previously reported in other ferrite nanoparticle ferrites [30, 57]. The occurrence of Fe secondary phases in the  $\text{CuFe}_2\text{O}_4$  cannot be excluded looking at the kink in both *ZFC-FC* magnetization curves around 150 K (i.e. Verwey transition of  $\text{Fe}_3\text{O}_4$ ) [58].



**Fig. 5.** ZFC-FC curves of  $\text{Cu}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$  nanoparticles (applied magnetic field  $H = 50$  Oe).

As previously described, a maximum value in magnetization can be detected for  $x = 0.4$ . This result should be interpreted as a consequence of the cation (Cu, Cd) distribution between the spinel octahedral and tetrahedral sites. To confirm the contribution in the magnetization of the non-magnetic (diamagnetic) CdO,  $M(0)$  values were corrected taking into account the estimated wt(%) CdO from Fig. 2b ( $M(0)$  (corrected) =  $M(0)/(1 - \text{wt}(\% \text{ CdO}))$ ). As can be deduced from Fig. 6, such corrections do not introduce significant changes in  $M$  values. With respect to the magnetic moment, Table I summarizes the number of Bohr magnetons,  $n_B$ , per formula unit employing the corrected values of  $M(0)$  ( $n_B = \frac{M_w M(0)(\text{corrected})}{5585}$ ;  $M_w$ : molecular weight). Equivalently, maximum  $n_B$  values are found for  $0.4 \leq x \leq 0.8$ .

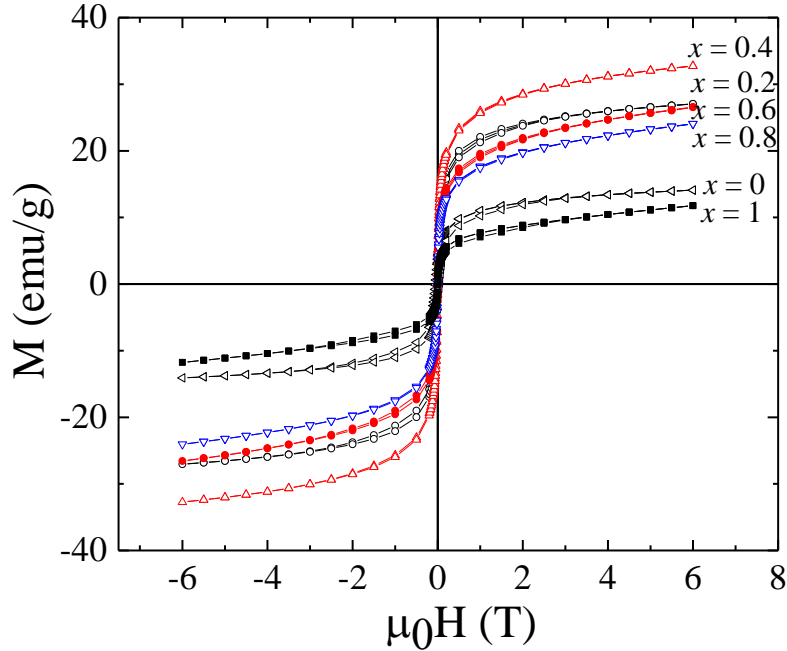


**Fig 6.** Saturation magnetization  $M(0)$  obtained from the Bloch's law (eq. 1) and from the law of approach to saturation  $M_S$  at 300 K (eq. 2) as a function of Cd percentage  $x$  ( $\text{Cu}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ ). the corrected values taking into account wt(%) CdO are also displayed.

With the aim to characterize the magnetic properties of the nanoparticles at room temperature, *dc* hysteresis loops were measured for the set of analysed samples (see Fig. 7). Maximum magnetic moments correspond with low values (close to the limit of the SQUID resolution) of coercive field,  $H_C$  (see Table II). However, as Fig. 7 shows, the samples do not reach the magnetic saturation at room temperature under the maximum applied field ( $\mu_0 H = 6$  T). Accordingly, the approach to saturation law was applied to fit the reversible magnetization response ( $M$ - $H$ ) curves in the range of applied fields from 3 to 6 T [59]:

$$M(T) = M_S(T) \left( 1 - \frac{a}{H} - \frac{b}{H^2} \right) + \chi_{hf} H \quad (2)$$

where  $M_S$  is the saturation magnetization and  $\chi_{hf}$  the high field susceptibility resulting from the linear increase in magnetization by the application of  $H$ .



**Fig. 7.**  $M$ - $H$  hysteresis loops at 300 K.

For the case of independent grains with cubic symmetry, the anisotropy term  $b/H^2$  is

correlated to the magnetocrystalline anisotropy,  $K$ , by  $b = \frac{8K^2}{105M_S^2}$ . The term  $a/H$ , associated to the contribution of local inhomogeneities (i.e. structural defects, non-magnetic inclusions or microstresses), should be fixed equal to 0 to properly fit the experimental curves. The obtained fitted parameters as a function of the Cd content ( $x$ ) of the nanoparticles are summarized in Table II. As expected from the previous analysis (Figs. 4 and 7), the saturation magnetization,  $M_S$ , displays a maximum value for Cd concentration  $x = 0.4$ . A proper correction taking into account the weight percentage of CdO does not significantly modify the trend of  $M_S$  vs  $x$  (see Fig. 6).

**Table II:** Magnetic parameters obtained from the room temperature hysteresis loops at 300 K and initial slope in the magnetic induction heating experiments.

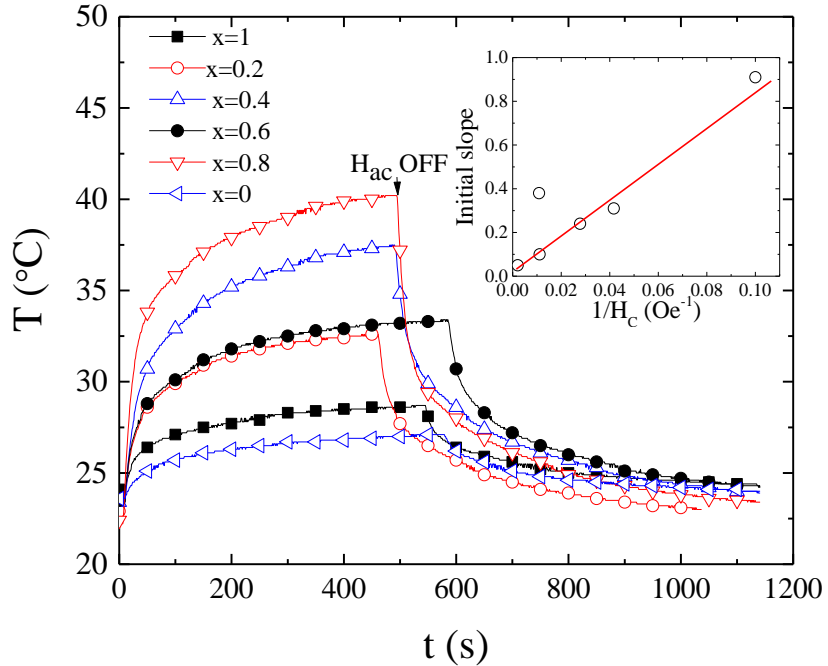
$x$	$H_C$	$M_S$	$b$	$K$	$\chi_{hf}$	$\left. \frac{dT(t)}{dt} \right _{t \rightarrow 0}$
	(Oe)	(emu/g)	( $10^7$ Oe <sup>2</sup> )	( $10^5$ erg/cm <sup>3</sup> )	( $10^{-5}$ Oe <sup>-1</sup> )	(Ks <sup>-1</sup> )
1	90	7.44	2.37	1.6	3.0	0.10
0.8	10	19.79	3.80	5.1	4.7	0.91
0.6	36	21.90	3.58	5.3	7.0	0.24
0.4	24	28.81	2.41	5.5	8.2	0.31
0.2	92	24.42	2.43	4.5	7.4	0.38
0	481	12.4	2.55	2.7	6.4	0.05

Regarding the magnetic anisotropy, the estimated values are of the same order of magnitude of bulk magnetite ( $K = 1.35 \times 10^5$  erg/cm<sup>3</sup>). However, ferrite nanoparticles usually display higher effective anisotropy values attributed to surface spin disorder effects. In fact, higher anisotropy values (close to one order of magnitude higher,  $K \approx 10^6$  erg/cm<sup>3</sup>) are estimated in Co-Zn ferrites employing similar approach to saturation analysis [30]. The occurrence of the high field susceptibility term  $\chi_{hf}$  also represents a common feature in



nanoparticle systems [60], and can be correlated to the occurrence of canted spin arrangement (Yafet-Kittel angle) in the spinel lattice [30].

Finally, the samples in powder form were submitted to the action of  $ac$  magnetic field,  $H_{ac}$ , to explore their characteristics for induction heating elements. Fig. 8 shows the time ( $t$ ) evolution of the temperature,  $T$ , under the action of the alternating magnetic field. The temperature increases reaching a nearly constant value due to the non-adiabatic experimental conditions. Under these conditions, there is a heat balance between the heat generated by the magnetic nanoparticles and heat losses. Switching off  $H_{ac}$  magnetic field (see Fig. 8) gives rise to a sharp temperature decay associated to the quick heat dissipation due to the non-adiabatic conditions and the thermal interaction with the environment.



**Fig. 8.** Temperature,  $T$ , versus induction time,  $t$ , for the  $(\text{Cu}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4)$  nanoparticles. Inset: Initial

slope  $\left(\frac{dT(t)}{dt}\right)_{t \rightarrow 0}$  versus the inverse of the dc coercive field,  $H_C$ .

Under isoperibol conditions where the temperature of the sample varies but the temperature of its environment remains constant, the specific absorption rate,  $SAR$ , can be estimated through initial slope method [61]:

$$SAR = \frac{C}{m_{MNP}} \left. \frac{dT(t)}{dt} \right|_{t \rightarrow 0} \quad (3)$$

where  $C$  is the heat capacity of the system (measured in  $\text{J K}^{-1}$ ),  $m_{MNP}$  the nanoparticles mass and  $\left. \frac{dT(t)}{dt} \right|_{t \rightarrow 0}$  the initial  $T$ - $t$  slope. Assuming a linear temperature dependence of the heat

power losses,  $T$  vs  $t$  can be expressed for heating and cooling as  $T(t) = T_0 + \Delta T_{max}(1 - e^{-t/\tau})$  (Box-Lucas law) and  $T(t) = T_0 + \Delta T_{max}(e^{-t/\tau})$ , respectively, with  $\Delta T_{max} = T_{max} - T_0$  ( $T_{max}$ : maximum temperatures). In both cases,  $\tau$  represents a time constant related to the thermal characteristics of the system [61] and thus  $\left. \frac{dT(t)}{dt} \right|_{t \rightarrow 0} = \frac{\Delta T_{max}}{\tau}$ . Table

II includes the estimated initial slope obtained from the fitting of the exponential temperature increase to the Box-Lucas law. As deduced from the experimental curves, maximum  $T_{max}$  corresponds with a maximum value in the initial slope. Surprisingly, the sample with  $x = 0.8$  displays maximum heating power capacity. A careful inspection of the room temperature coercive field (see table II) shows that this sample displays the smallest  $dc$  coercivity. In fact, as the inset of Fig. 8 indicates a linear relationship between the initial slope and the inverse of  $H_C$  ( $H_C^{-1} \propto \chi$ , magnetic susceptibility) can be deduced. Although the magnetic heating induction is determined by the  $ac$  hysteresis losses of the sample, the analysis of the quasistatic magnetic response gives some hints about the main parameters controlling the heating capacity of the samples: high magnetic moment (magnetization) and low  $dc$  coercive field. The low  $H_C$  values would favor the  $ac$  magnetization process under the  $ac$  magnetic field. However, the lowest coercivity is not reflected in the estimated high field anisotropy,

$K$ , as no clear relationship between both magnitudes is found (see table II). Moreover, it should be noted that the heating behavior is a temperature dynamic effect and that, in turn, the increase in the temperature may modify the magnetic parameters. Particularly, the proximity of the Curie point,  $T_C$ , has associated a sharp increase in the magnetic susceptibility (Hopkinson effect) [62]. A large reduction of  $T_C$  with the Cd content ( $x$ ) is found in these spinels [63] as a consequence of weakening of the  $AB$  interaction as the non-magnetic  $\text{Cd}^{2+}$  ions occupy the tetrahedral positions. In particular, values around  $T_C \approx 400$  K are reported in bulk  $\text{Cu}_{0.2}\text{Cd}_{0.8}\text{Fe}_2\text{O}_4$  ( $x = 8$ ), close to the measuring temperature in the performed experiments. Thus, the proximity of the Curie temperature to room temperature for  $x = 0.8$  would also contribute to the maximum values in  $T_{max}$  and in the initial heating slope. Nevertheless, these nanoparticles displays a moderate heating capacity in comparison with other nanoparticle systems employed for hyperthermia applications. In fact, assuming specific heat  $c \approx 0.6\text{-}0.8 \text{ Jg}^{-1}\text{K}^{-1}$ , maximum SAR values around  $0.7 \text{ W/g}$  are achieved for  $x = 0.8$ , less than one order of magnitude than the typical SAR values reported in other Fe based ferrites. However, the possibility to optimize the magnetization values together with the reduction of the Curie point with the Cd content around therapeutic temperatures, provides to these spinel ferrites interesting properties to be applied as self-regulated heating agents, in the biomedical field (therapeutics agents and drug delivery systems) or environmental applications (catalysts and chemical and gases adsorbers) or self-healing of polymers and thermoplastic adhesives.

#### **4. Conclusions**

$\text{Cu}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$  ( $0 \leq x \leq 1$ ) nanoparticles were synthesized by co-precipitation from Cu(II), Cd(II) and Fe(III) salts. The structural characterization, performed by X-ray diffractometry and TEM microscopy, show that the nanoparticles display the characteristic cubic spinel structure with lattice parameter increasing with the Cd content. A high degree of nanoparticle agglomeration is found associated to the employed synthesis procedure. The magnetic characterization, both at low and high applied magnetic field, indicates the occurrence of maximum values in the magnetic moment for intermediate Cd concentrations ( $0.4 \leq x \leq 0.8$ ). The samples display the characteristic features of nanoparticle ferrites (i.e. large temperature exponent in Bloch's law and high field susceptibility). Nevertheless, the occurrence of superparamagnetic behaviour should be disregarded as the *ZFC-FC* magnetization curves show. Regarding the magnetic heating induction response, maximum heating efficiency (i.e. *SAR* value) is found for  $x = 0.8$  that should ascribed to the combined effect of the high magnetic moment and high magnetic susceptibility (low coercive field). The control of the maximum heating temperature through the magnetic moment and the Curie temperature through the spinel composition (cation distribution), makes these ceramic nanoparticles interesting systems to be applied in a wide range of applications including, among others, hyperthermia treatments in the biomedical field and heat assisted catalytic and adsorption elements in environmental areas.

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