

## Synthesis, characterization and magnetic properties of $\text{ZnFe}_2\text{O}_4$ spinel nanoparticles encased in porous matrices

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$\text{ZnFe}_2\text{O}_4$  in bulk ceramic form is known to crystallize with a normal spinel structure where the tetrahedral sites are occupied by the  $\text{Zn}^{2+}$  ions. The  $\text{Fe}^{3+}$  cations are located in the octahedral holes given rise to a very weak Fe-O-Fe superexchange interactions showing a Néel temperature as low as 10K. However, many studies have been reported concerning nanosized ferrite nanoparticles exhibiting a very different magnetic behaviour, i.e. superparamagnetism. The onset of these magnetic properties has been accounted for the partially inverted spinel, where a small amount of  $\text{Fe}^{3+}$  are located in tetrahedral coordination causing the appearance of a new Fe(Td)-O-Fe(Oh) superexchange interactions which yields a net magnetization component and a remarkable increasing of the Néel temperature. To avoid the particle aggregation and to control the particle growth many attempts have been done to synthesise these  $\text{ZnFe}_2\text{O}_4$  nanoparticles encased in different non-magnetic porous matrices (1,2). Under these conditions the magnetic properties can be modulated by controlling the particle size diminishing the interparticle interactions and the interactions with the matrices.

The aim of this work is minimize the interparticle interactions in order to evaluate the particle size effect on the magnetic properties of these nanoparticles. For this purpose different matrices have been used to encapsulate  $\text{ZnFe}_2\text{O}_4$  nanoparticles. Moreover, different synthetic methods have been also used to study the influence of the synthesis conditions on size distribution and inversion degree on the resulting nanoparticles.

$\text{ZnFe}_2\text{O}_4$  nanoparticles were prepared by two different methods: i) solvothermal conditions at temperatures from 160 °C to 200°C for different times and using  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  solution as precursor and ii) thermal decomposition of ferrite precursors in a high boiling point solvent. In this last case,  $\text{Zn}(\text{acac})_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{acac})_3 \cdot 9\text{H}_2\text{O}$  were used as precursors and phenylether as solvent. Oleylamine, 1,2-hexadecanediol and oleic acid were used as stabilizing agents in order to protect the surface of the particles (Figure 1a, sample MZn3.5) and to control the growth.

The nanoparticles were also prepared encased in porous matrices: MCM-41 and TUD-1 types and amorphous silica. Aqueous solutions containing stoichiometric amount of Zn nitrate and Fe nitrate were infiltrated in MCM-41 and TUD-1 and the infiltrated materials were kept at room temperature for 24 hours and then, the solids were heated at 600 °C during 2 hours. After this treatment, ferrite nanoparticles inside the porous networks of the matrices were obtained (Figure 1b-d, samples MC-FZ, MH-FZ and T-FZ).  $\text{ZnFe}_2\text{O}_4$  nanoparticles embedded in amorphous silica were prepared by dissolving stoichiometric amount of Zn and Fe nitrates in ethanol and adding distilled water and tetraethylorthosilicate (TEOS) in a molar ratio TEOS/EtOH/ $\text{H}_2\text{O}$  of 1:4:11.7. After a gelling period of 4 days, the silica precursor was polymerized and the metal nitrates are distributed in the silica network. The embedded nanoparticles were obtained after thermal treatment of the gel at temperatures from 500 °C to 1000 °C.

Representative TEM images corresponding to monodisperse  $\text{ZnFe}_2\text{O}_4$  nanoparticles and nanoparticles embedded in different matrices are collected in Figure 1. From images corresponding to the nanoparticles free of matrix (Figure 1a) statistical analysis has been done by measuring about 100 particles and 3.5 nm has been obtained as mean particle size. In images 1b and 1c we can see nanoparticles with size of 1.2 nm-1.7 nm (1b) and 1.2 nm-2.5 nm (1c) inside the tubular channel of the MCM-41 matrix. Image 1d corresponds to ferrite nanoparticles (3-5 nm) inside the disordered mesopores of TUD-1 matrix.

Figure 2 show the ZFC and FC magnetic susceptibility versus temperature curves of different samples. The high values of susceptibility suggests that, in all cases, the nanoparticles behave as superparamagnetic above the blocking temperature ( $T_B$ , see inset in Figure 2). The shape of the FC curve in the  $T_B$ -5K temperature range and the high difference between the ZFC and FC susceptibility values at low temperature suggests that the interparticle interactions for all of the samples are not significant (3). Nanoparticles free of matrix, sample MZn3.5, presents susceptibility values higher those

obtained for nanoparticles with similar size prepared by the solvothermal method (4). This fact together with the intensity ratio (220)/ (400) X-ray reflections, suggest that the inversion parameter is higher for sample MZn3.5. Moreover, the high values of coercive field at 5K ( $H_{c,5k}$ ) for nanoparticles embedded in amorphous silica and in TUD-1 seems to be due to the mechanical stress imposed by the matrix (4). This matrix effect is less important for nanoparticles embedded in MCM-41 matrices.

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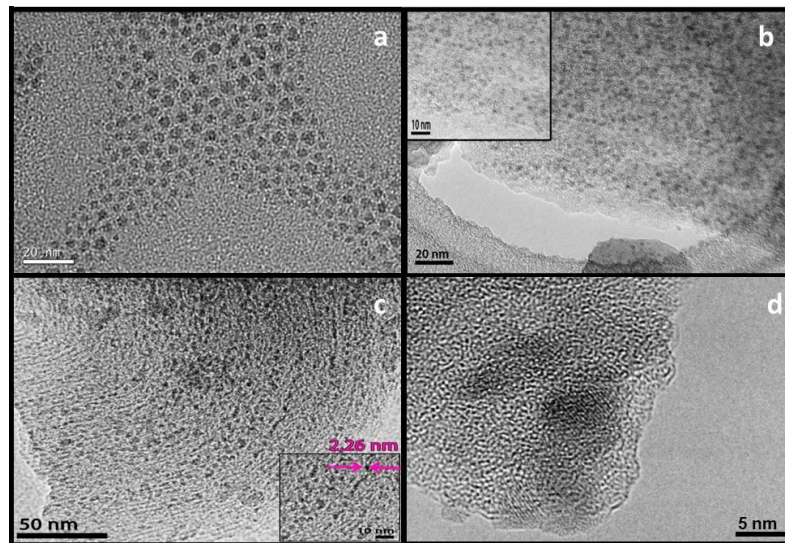


Figure 1. TEM micrographs of: (a) monodisperse  $ZnFe_2O_4$  nanoparticles (sample MZn3.5) and embedded in (b, c) MCM-41 (samples MC-FZ, MH-FZ) and (d) TUD-1 (sample T-FZ) matrices.

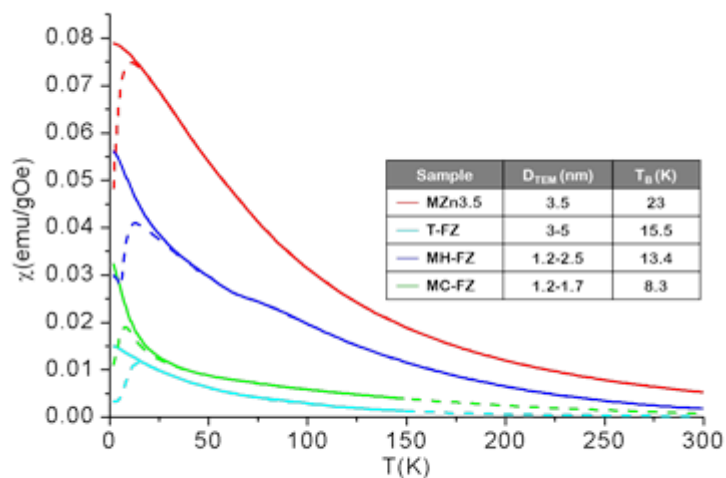


Figure 2. ZFC and FC magnetic susceptibility curves measured at 5000 e.