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Superparamagnetic response of zinc ferrite incrusted nanoparticles

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ABSTRACT

Zinc ferrite is synthesized via mechano-activation, followed by thermal treatment. Spinel $ZnFe_2O_4$ single phase is confirmed by X-ray diffraction. SEM micrographs show large particles with average particle size $\langle D_{part}\rangle$ = 1 μm, with particles in intimate contact. However, TEM micrographs show incrusted nanocrystallites at the particles surface, with average nanocrystallite size calculated as $\langle D_{inc}\rangle \approx 5$ nm. The blocking temperature at 118 K in the ZFC–FC curves indicates the presence of a superparamagnetic response which is attributable to the incrusted nanocrystallites. Moreover, the hysteresis loops show the coexistence of superpara- and paramagnetic responses. The former is observable at the low field region; meanwhile, the second one is responsible of the lack of saturation at high field region. This last behavior is related to a paramagnetic contribution coming from well-ordered crystalline microdomains.

The hysteresis loops are analyzed by means of two different models. The first one is the susceptibility model used to examine separately the para- and superparamagnetic contributions. The fittings with the theoretical model confirm the presence of the above mentioned magnetic contributions. Finally, using the Langevin-based model, the average superparamagnetic diameter $\langle D_{SPM}\rangle$ is calculated. The obtained value $\langle D_{SPM}\rangle$ = 4.7 nm (~5 nm) is consistent with the average nanocrystallite size observed by TEM.

1. Introduction

A continuous and growing interest has been focused on spinel ferrites due to their magnetic properties and unique structure, which makes them useful for technological application [1–4]. These ferrites have $MgAl_2O_4$ crystallographic structure and belong mainly to space group *Fd3m*. In this structure, oxygen conform a FCC structure, with 8 tetrahedral and 16 octahedral sites occupied by the divalent and trivalent transition metal ions. The general formula used to describe spinel ferrites is $(M^{2+}_{1-\delta}Fe^{3+}_{\delta})[M^{2+}_{\delta}Fe^{3+}_{2-\delta}]O_4$. Here M is a transition metal, δ is the inversion parameter (which can range from 0 to 1), round brackets represent the tetrahedral sites (A), and square brackets the octahedral sites [B] [5–7]. Depending on the inversion parameter the spinel can be named as normal ($\delta = 0$), inverse ($\delta = 1$) and, mixed ($0 < \delta < 1$). It is known that inversion degree of ferrites strongly affects their magnetic properties. Commonly, the exchange integrals J_{AB}, J_{BB}, J_{AA} are negative and the antiferromagnetic A–B interaction is stronger that the A–A and B–B interactions; therefore, ferrimagnetism arises from the decompensation of the magnetic moments in the A and B sublattices [2,5].

In the branch of studying the magnetic interactions in ferrites, zinc ferrite represents a very interesting material because Zn is a divalent nonmagnetic cation. In bulk material, the preferred Zn site is tetrahedral (A); and the ferrite orders in the normal spinel structure. As Zn does not have an associated magnetic moment, bulk zinc ferrite is an antiferromagnetic material below T_N = 10.5 K, where weak superexchange interactions between Fe^{3+} cations, located in B-sites, dominate [1,8–10].

However, it has been reported in several works that nanosized zinc ferrite particles produce a ferrimagnetic/superparamagnetic response, which differs markedly from the bulk. This change in the magnetic response is commonly attributed to a cation distribution where some Fe^{3+} ions are forced to move to tetrahedral sites, and consequently, Zn^{2+} migrates to octahedral sites, which alters the long- and short-range magnetic interactions of A and B sites.

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Therefore, the difference in the magnetic response could be attributed to a strong ferrimagnetic coupling due to superexchange interactions between iron ions occupying the A and B sites in the partially inverted spinel structure [2–4,11–14]. Moreover, some researchers report that magnetic properties of zinc ferrites are not only particle size dependent, but they are strongly affected by the synthesis method. For example, conventional ceramic method produces nanoparticles with high magnetization values; whereas, nanoparticles synthesized by co-precipitation method show smaller magnetization values for similar particle sizes [3,9,10,14,15]. Several interesting properties for technological applications may arise from these magnetic variations [16]. Commonly, chemical routes are used to synthesize ferrites; however, mechano-synthesis represents an interesting method because it could induce crystallographic defects that could reinforce the ferrimagnetic responses in zinc ferrites.

In the present work, the magnetic properties of zinc ferrites obtained via mechano-activation are investigated. Due to thermal treatment, nanocrystallites are produced at the surface of highly crystalline microparticles. The contributions of different magnetic responses are analyzed using ZFC/FC curves and hysteresis loops. Superpara- and paramagnetic contributions can be distinguished and analyzed separately by means of susceptibility analysis at the hysteresis loops. Finally, Langevin model is used to investigate the observed superparamagnetic response: nanocrystallite superparamagnetic diameter matches very well with the particle sizes determined by TEM.

2. Experimental procedure

2.1. Synthesis

ZnO and α-Fe_2O_3 powders are used to synthesize zinc ferrite via mechano-activation. First, the precursors are weighted according to stoichiometry to obtain the desired $ZnFe_2O_4$ phase. Then, they are ball-milled during 1 h to mechanically activate the powders, and also to diminish their particle size. The milled powders are pressed into cylindrical pellets of 6 mm of diameter using a pressure of 8 MPa. The pellets are thermally annealed in air at 1373 K during 9 h in order to get the $ZnFe_2O_4$ phase. The sample is cooled down by air quenching. Heat treatment is also used to sinter the sample, and thus ameliorate contacts between particles. Several samples are prepared under same experimental conditions.

2.2. Characterization

Powder samples are obtained by pulverizing the heat treated pellets in an agate mortar and used for some of the characterizations. First, in order to determine the microstructural properties of the samples, they are characterized by X-ray diffraction in a PANalitycal X'PertPro MPD diffractometer, by Scanning Electron Microscopy (SEM) in a field emission microscope JSM7000F, and by transmission electron microscopy (TEM) in a JEOL JEM-220FS microscope. In addition, high resolution TEM images (HRTEM) are obtained to observe nanostructure and crystallinity degree. For transmission electron microscopy characterization, powders of the pulverized sample are dispersed in alcohol and a drop of this is poured in the TEM sample holder. Zero field cooled and field cooled curves (ZFC–FC) are measured in a temperature range from 50 to 300 K with an applied magnetic field of $H = 8 \times 10^3$ A/m by using a Quatum Design VSM magnetometer. Finally, hysteresis loops are measured in the same temperature range, with temperature increments $\Delta T = 25$ K and maximum applied field $H_{max} = 1.6 \times 10^6$ A/m. As milled powders are used for VSM.

3. Theoretical basis

The analysis of magnetic response is carried out by two methods. The first one is the separation of the magnetic susceptibilities; this method is used as a base for the second analysis. The second method is a magnetization model using the Langevin function. This model helps to correlate the structural properties found by SEM/TEM and the magnetic responses observed at the hysteresis loops.

3.1. Hysteresis loops susceptibility analysis

The low field susceptibility, χ_{LF}, is usually calculated from 8×10^3 to 45×10^3 A/m and represents the contribution of all magnetic phases in sample. This can be expressed as follows:

$$\chi_{LF} = \chi_{PM} + \chi_{DM} + \chi_{AFM} + \chi_{FERRI} + \chi_{FERRO} + \chi_{SPM} \quad (1)$$

where PM stands for paramagnetic, DM for diamagnetic, AFM for antiferromagnetic, FERRI for ferrimagnetic, FERRO for ferromagnetic, and SPM for superparamagnetic.

On the other hand, because the ferro- and ferrimagnetic contributions saturate at high fields (HF), only paramagnetic, diamagnetic and antiferromagnetic ordering contribute [17,18]. Therefore, ferri- and ferromagnetic contributions can be discarded at HF, and high field susceptibility can be described as:

$$\chi_{HF} = \chi_{PM} + \chi_{DM} + \chi_{AFM} \quad (2)$$

Consequently, ferri/ferro magnetic contributions can be evaluated by calculating the susceptibility slopes at LF and HF, and subtracting the latter from the former such as:

$$\chi_{FM} = \chi_{LF} - \chi_{HF} \quad (3)$$

Using the previous equations, hysteresis loops that contain more than one magnetic response can be separately analyzed to study the different magnetic contributions [18].

3.2. Magnetization model

Once susceptibility analysis has been carried out, the hysteresis loops are analyzed by means of Langevin model to calculate the magnetization of a system with a particle volume distribution in the superparamagnetic regime [19,20].

The magnetization M of a system of superparamagnetic grains in a magnetic field H is given by

$$M(H,T) = \int_0^\infty \mu L\left(\frac{\mu H}{kT}\right) f(\mu) d\mu \quad (4)$$

where $L\left(\frac{\mu H}{kT}\right)$ is the Langevin function and $f(\mu)$ is the distribution of magnetic moments in a system of superparamagnetic grains. The number of grains per unit volume with magnetic moment between μ and $\mu + d\mu$ is given by $f(\mu)d\mu$.

Then, the saturation magnetization is given by

$$M_S = \int_0^\infty \mu f(\mu) d\mu = N\langle\mu\rangle \quad (5)$$

where $\langle\mu\rangle$ is the mean magnetic moment, and N is the number of grains per unit volume of the sample. On the basis of the M_S value provided by Eq. (5) in terms of the mean magnetic moment $\langle\mu\rangle$ per grain (in units of Bohr magnetons) and the saturation magnetization M_S^{bulk} for bulk $ZnFe_2O_4$ (in units of emu/cm^3) as reference, the average volume $\langle V\rangle$ of the superparamagnetic nanocrystallites can be calculated according to the following ratio

$$V = \frac{M_s}{M_s^{bulk}} \quad (6)$$

Assuming spheroid-like nanocrystallites, the average superparamagnetic diameter $\langle D_{SPM}\rangle$ follows from $\langle D_{SPM}\rangle = 2(3V/4\pi)^{1/3}$.

4. Results

4.1. Microstructural characterization

Fig. 1 shows the XRD pattern for the as sintered sample; all peaks can be easily identified with the $ZnFe_2O_4$ spinel crystalline