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Abstract. ZnFe$_2$O$_4$ nanoparticles with a mean size ranging from 3 nm to 10 nm, have been prepared using the solvothermal method. The TEM images reveal a narrow particle size distribution for all samples. Bulk magnetic measurements indicate superparamagnetic behaviour with a blocking temperature ($T_B$) that increases from 10 K to 22 K upon increasing the particle size. At temperatures lower than $T_B$ the nanoparticles are in the “frozen” regime and the coercive field changes from 145 Oe to 220 Oe for nanoparticles with sizes from 3 nm to 10 nm. On heating, the Mössbauer spectroscopy data show a progressive crossover from a magnetic to a quadrupolar hyperfine interaction, with a blocking temperature coherent with that obtained from magnetization measurements. The spinel inversion parameter, which appears to be a function of the particle size, has been estimated from neutron diffraction experiments.

1. Introduction

Nanosized spinel-ferrites have attracted attention and efforts since the last two decades from both the technological and scientific research points of views. Despite of the great activity in this area, there are still many fundamental open problems in this field that need to be studied. In this sense, ZnFe$_2$O$_4$ is found to be one of the most interesting spinel system where its magnetic behaviour depends on the particle size [1]. It is also well known that bulk ZnFe$_2$O$_4$ is a normal spinel that behaves as an antiferromagnet with Neel temperature $T_N=10$ K [2]. By contrast, zinc ferrite with nanometric size shows a ferromagnetic mixed spinel state (Zn$_{1-x}$Fe$_x$)$_{Td}$[Fe$_{2-x}$Zn$_x$]$_{Oh}$ where the Zn$^{2+}$ and Fe$^{3+}$ cations are distributed in the tetrahedral (Td) and octahedral (Oh) sites, being $x$ the so-called inversion parameter. Depending on the particle size and the preparation method of nanosized spinel, different values of $T_B$, coercivity and saturation moment have been reported [3].

The purpose of the present work is to investigate the magnetic properties of nanosized ZnFe$_2$O$_4$ particles prepared by solvothermal method.

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2. Experimental

ZnFe$_2$O$_4$ spinel nanoparticles were prepared by using the solvothermal method in which stoichiometric amounts of zinc and iron nitrates were dissolved in ethylenglicol. After adding KOH until pH = 11, the mixture was transferred into a teflon stainless steel autoclave to be treated at different temperatures ranging from 160 °C to 200°C during different periods of time in order to control the particle size. The structure of the samples was characterized by means of X-ray powder diffraction using a Siemens D-5000 diffractometer. The morphology and particle size of the different ferrite samples were studied by TEM in a JEOL-2000FX microscope working at 200KV. Mössbauer spectra on the isotope $^{57}$Fe were carried out for the samples in the temperature range 1.4-50 K in a zero applied magnetic field, using a commercial $^{57}$Co:Rh $\gamma$-ray source. Magnetic susceptibility data were obtained in the FC and ZFC procedures with a magnetic field of 10 Oe and 500 Oe in a SQUID magnetometer.

3. Results and discussion

X-ray diffraction patterns for both the 3 nm and 10 nm particle size samples have been indexed in the space group Fd-3m showing sharper reflections for the 10 nm sample compared with the 3 nm one due to the higher crystalinity of the former. TEM images given in figures 1 a and b, reveal a narrow particle size distribution for both samples. Also, in the case of the bigger particles (10 nm), a regular polyhedral morphology is developed. The ZCF and FC magnetic susceptibility curves given in figure 2 are characteristic for superparamagnetic particles. Their estimated blocking temperatures, from the maximum of the ZFC curve are 10 K and 22 K for the 3 and 10 nm particle sizes respectively. It appears that dipolar interactions due to particle agglomeration have little effect on the blocking temperatures. There is no hysteresis in the magnetization curves for both samples measured at 300 K, i.e. both remanence and coercivity are zero which confirms the superparamagnetic behaviour. It has been also observed an increase in the coercivity with decreasing the particle size taking the value of 145 Oe for 3 nm and 220 Oe for 10 nm.

![Figure 1. TEM micrographs of ZnFe$_2$O$_4$ nanoparticles of a) 10 nm and b) 3nm](image1)

![Figure 2. ZFC and FC magnetic susceptibility curves as a function of temperature for 3 nm and 10 nm (inset) nanoparticles](image2)

The zero field Mössbauer spectra at different temperatures for the 3 nm and 10 nm samples are shown in figures 3 and 4. In both samples the spectra obtained at 1.4 K and 4.2 K show the presence of two
ill-resolved sextets which are attributed to the Fe$^{3+}$ ions in the Td and Oh sites of the spinel structure. In the case of the 3 nm particles, the majority component presents a hyperfine field of 46 T, while the minority component presents a field of 50 T. The intensities of these two subspectra are in the ratio 2.3:1 for the 3 nm sample, while in the case of the 10 nm this ratio is smaller. Our previous results concerning neutron diffraction experiments indicate a certain degree of inversion in these samples, according to the Mössbauer results.

Figure 3. Mössbauer spectra obtained at different temperatures for nanoparticles with mean size of a) 3 nm and b) 10 nm

Figure 4. Evolution of the superparamagnetic fraction as a function of temperature determined from the Mössbauer spectroscopy measurements
Above 4 K, the overall thermal evolution of these spectra is similar, and show a behaviour typical for superparamagnetic nanoparticles: as temperature increases, the magnetic hyperfine “sextet” (six line spectrum) is progressively replaced by a two lines “doublet”, reflecting the growing weight of particles whose magnetisation fluctuates faster than the hyperfine Larmor period associated to $^{57}$Fe $\tau_L \sim 5 \times 10^{-9}$ s. For the batch with the smallest particles, the total replacement of the sextet by the doublet occurs at lower temperature. A measure of this effect is the so-called Mössbauer blocking temperature $T_{BM}$, which is defined as the temperature for which the “frozen” fraction (sextet) and the “superparamagnetic” fraction (doublet) are equal to 50%. The Mössbauer blocking temperatures are 20 K and 38 K for 3 nm and 10 nm particle sizes respectively.

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References

