1. Introduction

One of the most active areas of materials research is the behavior of nanostructured media. Nanocrystalline spinel ferrites find important applications in many engineering areas. They are used, for example, in miniaturization of electronic devices. Moreover, nanoparticle ferrites are considered outstanding materials for high-density magnetic recording, since their magnetic properties differ markedly from single ferrites [1]. Other practical areas of importance are medical diagnosis and biomedical applications [2, 3]. Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ belongs to the group of cubic spinel structures with magnetic ions Fe$^{3+}$ and Fe$^{2+}$ distributed in octahedral and tetrahedral sites, depending on the x-value (see Table 1) [4].

<table>
<thead>
<tr>
<th>Ionic Formula [4]</th>
<th>Mn$<em>{0.84}$Fe$</em>{0.16}$O$_4$</th>
<th>Mn$<em>{0.60}$Zn$</em>{0.20}$Fe$_{0.12}$O$_4$</th>
<th>Mn$<em>{0.40}$Mn$</em>{0.50}$Fe$_{0.07}$O$_4$</th>
<th>Mn$<em>{0.60}$Mn$</em>{0.20}$Fe$_{0.20}$O$_4$</th>
<th>Mn$<em>{0.70}$Mn$</em>{0.20}$Fe$_{0.30}$O$_4$</th>
<th>Mn$<em>{0.90}$Mn$</em>{0.10}$Fe$_{0.50}$O$_4$</th>
<th>Mn$<em>{0.95}$Mn$</em>{0.05}$Fe$_{0.50}$O$_4$</th>
</tr>
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<tbody>
<tr>
<td>Cation distribution for Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$.</td>
<td>Square and round brackets for octahedral sites (3+) and tetrahedral sites (2+) respectively. Fe$^2+$ represents the iron ions with reversed spins.</td>
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</table>

The magnetic properties of the ferrite nanoparticles are found to undergo changes because of superparamagnetism, surface spin effects, and cation distribution, which depends mainly on the stoichiometry and synthesis method [5, 6]. Among the many experimental research methods to study the magnetic properties of the ferrite nanoparticles, electron paramagnetic resonance (EPR) proves to be a useful and sensitive technique to provide information about local magnetic properties, correlation between the particle moments, and the internal field distribution [7–10]. The magnetic resonance study of assemblies of nanoparticles is interesting because the magnetic properties of the surface atoms differ radically from the corresponding bulk atoms. It is also known that surface spins resist from being aligned with even a large external magnetic field [11], which gave rise to the conception of spin canting [12]. As it is well known, the magnetic response of the nanoparticle system to the external field depends on the cation distribution [13], temperature, and size [14]. On Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$, Rath et al. [14] found a change in the crystallite size between 4.5 nm and 10.5 nm in the 0 < x < 1 range for nanoparticles prepared via hydrothermal precipitation method. Arulmurugan et al. [15] found similar values for nanoparticles prepared by chemical precipitation method. In this paper, the EPR and VSM techniques are used to study the magnetic properties of magnetic nanoparticles synthesized by normal micelle micro-emulsion method at room temperature.

2. Experiment

Magnetic nanoparticles were synthesized by normal micelle micro-emulsion method at room temperature [16, 17]. Sodium dodecylsulphate was used as the surfactant, added to an aqueous solution containing soluble...
FeSO₄, ZnSO₄, and MnSO₄; hence, the normal micelles are formed. A 6 M NaOH solution is added to the previous solution, which shows a dark appearance. It is, then, stirred for 2 h. The spinel structure is formed when H₂O₂ (30%) is added by the complete oxidation of Fe²⁺ to Fe³⁺. The ratio between Mn/Zn and Fe cations is adjusted to 1:2 for every sample, the value of x varied in the 0 < x < 0.75 range (see Table II).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nanocrystallite size D [nm] from the Scherrer formula D [nm] from AFM images</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = 0</td>
<td>30</td>
</tr>
<tr>
<td>X = 0.25</td>
<td>31</td>
</tr>
<tr>
<td>X = 0.5</td>
<td>26</td>
</tr>
<tr>
<td>X = 0.75</td>
<td>15</td>
</tr>
</tbody>
</table>

The size measurements were performed on an Asylum Research MFP-3D AFM. The height channel was corrected using the sensor in the Z-direction that this instrument features (closed loop in the three axis) by performing line-by-line (of scanning) fits between the two signals (Z-sensor and height). Repeated measurements were carried to ensure that the particles were mono-dispersed and well attached on the mica surface. Measured diameters were calculated from height histograms on masked images (considering only the apex of the particles). The magnetic behavior was studied by EPR technique by using a Bruker EPR-300 spectrometer in the X-band frequency range, at 170–350 K. The magnetization curves were measured by using vibrating magnetometer (VSM) from Quantum Design physical property measuring system (PPMS).

3. Results

The ferrite structure was identified by XRD, where peaks can be indexed to planes (220), (311), (400), (422), (511), and (440) of single-phase MnZn ferrite (see Fig. 1). From the Scherrer equation:

\[ B = \frac{k\lambda}{D \cos \theta} \]

we obtained experimental nanocrystallite size values from 30 nm to 15 nm for x = 0 and x = 0.75 respectively, as presented in Table II. In Eq. (1) B is the width of the diffraction peak after subtracting the instrumental effect, λ the wavelength of the x-ray used, k ≈ 1 for cubic crystals and θ is the Bragg angle. As is expected [15], the particle size decreases with the increase in the Zn concentration. These values correspond to the magnitude expected by Rondinone's approach [17]. This last method correlates nanoparticle size to synthesis conditions: metal salt concentration, sodium hydroxide concentration, and temperature. Using Rondinone’s approach, the mean value for nanoparticle size was estimated roughly as D = 33.1 ± 0.1 nm.

4. Magnetic properties

For x > 0.5, the EPR spectra consist of a single resonance signal, strongly symmetrical, with g ≈ 3.25 (see Fig. 3a) and a resonant field approximately constant \( H_r \approx 2073 \) G. This signal is attributed to the ions Fe³⁺ distributed in octahedral coordinates sites. While the x concentration decreases, the symmetry of the signal reduces (see Fig. 3b and 3c), indicating a random distribution of the anisotropy in the system, with perpendicular and parallel modes, giving information about the effective anisotropy of the system.

For each concentrations x, the central field remains approximately constant as a function of the temperature (see Fig. 4).

The peak to peak line width \( \Delta H_{PP} \) at 180 K presents a maximal value for x = 0.25 (see Table III). Above x > 0.25, \( \Delta H_{PP} \) decreases when x increases (shown in Fig. 4).
TABLE III

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature [K]</th>
<th>Peak to peak line width $\Delta H_{PP}$ [G]</th>
<th>$\pm 3%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0$</td>
<td>180</td>
<td>940</td>
<td></td>
</tr>
<tr>
<td>$x = 0.25$</td>
<td>180</td>
<td>1038</td>
<td></td>
</tr>
<tr>
<td>$x = 0.50$</td>
<td>180</td>
<td>717</td>
<td></td>
</tr>
<tr>
<td>$x = 0.75$</td>
<td>180</td>
<td>650</td>
<td></td>
</tr>
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</table>

Fig. 3. EPR signal at $T = 180$ K, (a) $x = 0.0$, (b) $x = 0.25$ and (c) $x = 0.50$.

It is interpreted as a reduction of the effect of magnetic interaction (local fields), due to a reduction of magnetic ions (i.e. Mn ions) per unit cell. This behavior is similar to the behavior predicted by the model for solid solutions with magnetic dilution (1-$x$): $\Delta H_{PP} \propto (1 - x)^{1/2}$. The behavior $0 < x < 0.25$ indicates the existence of a critical grain size for the transition from single to multi-domain regime for nanoparticles which size increases from 32 nm to 49 nm with the subsequent reduction in $\Delta H_{PP}$.

The effect of the temperature can be observed on the sample $x = 0.5$ (indicates in Fig. 5), where $\Delta H_{PP}$ shows a marked increase with decreasing temperature, e.g. the growth up of magnetic domains with strong ferromagnetic correlated spins.

Fig. 5. EPR normalized signals for $x = 0.50$.

Fig. 6. Temperature-dependence of the magnetization under zero field-cooling (ZFC) and field-cooling (FC) for $x = 0.75$.

Fig. 4. EPR signal for different concentrations of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ at 180K.

Fig. 4. EPR signal for different concentrations of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ at 180K.

5. Conclusions

EPR and magnetization measurements of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanoparticles synthesized by a normal micellar technique are reported. The concentration was varied in the $0 < x < 0.75$ range. For $x > 0.5$, a single resonance signal, strongly symmetrical is observed. This line is attributed to the ions Fe$^{3+}$ distributed in octahedral coordinates sites. For low $x$ concentration the symmetry of the signal EPR reduces indicating a random distribution of the anisotropy in the system, with perpendicular and parallel modes, giving information about the effective anisotropy of the system.
From the $\Delta H_{PP}$ behavior we suggest the existence of a critical monodomain size between 32 nm to 49 nm. The flattening of the MFC evidences the presence of strong interparticle interactions at low temperatures.

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References