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Synthesis of $Mn_xGa_{1-x}Fe_2O_4$ magnetic nanoparticles by thermal decomposition method for medical diagnosis applications

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ABSTRACT

In this work, the synthesis of $Mn_xGa_{1-x}Fe_2O_4$ (x=0–1) nanosized particles by thermal decomposition method, using tetraethylene glycol (TEG) as a reaction medium, has been performed. The crystalline structure of the inverse spinel obtained in all the cases was identified by X-ray diffraction (XRD). Vibration sample magnetometry (VSM) was used to evaluate the magnetic properties of ferrites and to demonstrate their superparamagnetic behavior and the increase of magnetization values due to the Mn^{2+} ions incorporation into the $FeGa_2O_4$ structure. Transmission electron microscopy, energy dispersive spectroscopy (TEM-EDS) and X-ray photoelectron spectroscopy (XPS) were used to characterize the obtained magnetic nanoparticles (MNPs). These MNPs showed a near spherical morphology, an average particle size of 5.6 ± 1.5 nm and a TEG coating layer on their surface. In all the cases MNPs showed no response when submitted to an alternating magnetic field (AMF, 10.2 kA/m, 354 kHz) using magnetic induction tests. These results suggest that the synthesized nanoparticles can be potential candidates for their use in biomedical areas.

1. Introduction

Magnetic nanoparticles (MNPs) of iron oxide possessing a superparamagnetic behavior are ideal materials for their use in biomedical applications such as hyperthermia thermoseeds [1–4], contrast agents for MRI diagnosis [5–9], targeted drug delivery [10–13], cell separation, biosensors [14–16], etc. Thermal decomposition of metallic organic precursors at low temperatures (≤350 °C) is an efficient method used for MNPs synthesis with a nanometric size and a superparamagnetic behavior. In addition, the uncontrolled aggregation among them is decreased due to the deposition of a coating on MNPs during the synthesis process. This method has been used to synthesize several types of magnetic oxides such as Fe_3O_4 [17,18], $MnFe_2O_4$ [19,20], $CoFe_2O_4$ [21,22], $MnZnFe_2O_4$ [23], $ZnFe_2O_4$ [24] for their potential application in biomedical areas.

On the other hand, it has been reported that gallium can be used for the treatment of different kinds of diseases such as cancer and hypercalcemia [25], while manganese is required for many important ubiquitous enzymatic reactions [26], when these elements are present into the human body as ionic species. Based on the above mentioned properties of Ga and Mn elements and the known magnetic behavior of Mn and Fe ions, in this work the synthesis of $Mn_xGa_{1-x}Fe_2O_4$ (x=0–1) magnetic nanoparticles by thermal decomposition method is presented, evaluating the effect of Mn ions incorporation on the magnetic properties and heating ability of the synthesized samples.

2. Materials and methods

Iron III acetylacetonate ($C_{15}H_{21}FeO_6$), gallium III acetylacetonate ($C_{15}H_{21}GaO_6$), magnanese II acetylacetonate ($C_{15}H_{21}MnO_6$) and tetraethyleneglycol (TEG) were used for the synthesis of MNPs. Stoichiometric amounts of the organic precursors at a ratio 2:1 of Fe:Ga-Mn were placed into a three-necked flask that already contained 40 mL of TEG as reaction medium. The mixture was ultrasonically stirred during 15 min to obtain a homogenous precursor solution. The three-necked flask was then adapted to a reflux condenser system and heated at 250 °C for 60 min with the aim to promote the decomposition of organic precursor into CO_2 and water and the formation of the crystalline structure. The synthesized material was washed with ethanol and dried in a stove at 95 °C for their physicochemical characterization. Powders identification and the lattice parameter (a) calculation, taking into account the Miller indices (hkl) and the

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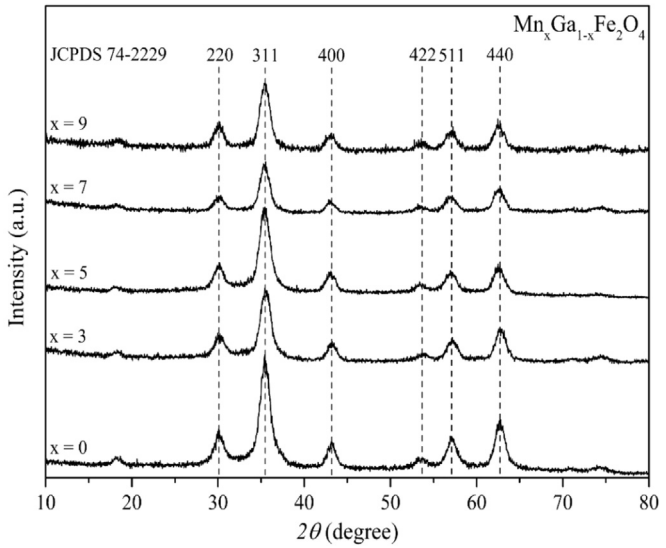

Fig. 1. XRD patterns of $Mn_xGa_{1-x}Fe_2O_4$ (x=0, 0.3, 0.5, 0.7 and 0.9 of Mn^{2+}) synthesized samples.

Table 1
Magnetic properties, cell parameter and crystallite size of $Mn_xGa_{1-x}Fe_2O_4$ (x=0–1).

Sample	*Ms* (emu/g)	*Mr* (emu/g)	*Hc* (Oe)	Crystallite size (nm)	Lattice parameter *(a)*, (Å)
$FeGa_2O_4$	22.8	0.045	2.610	6	8.3913
$Mn_{0.1}Ga_{0.9}Fe_2O_4$	48.2	0.007	0.186	7	8.3688
$Mn_{0.2}Ga_{0.8}Fe_2O_4$	33.4	0.013	0.562	6	8.3857
$Mn_{0.3}Ga_{0.7}Fe_2O_4$	36.3	0.378	12.06	6	8.3913
$Mn_{0.4}Ga_{0.6}Fe_2O_4$	36.5	0.002	0.097	6	8.3857
$Mn_{0.5}Ga_{0.5}Fe_2O_4$	28.4	0.209	10.38	6	8.3913
$Mn_{0.6}Ga_{0.4}Fe_2O_4$	33.1	0.008	0.344	7	8.4030
$Mn_{0.7}Ga_{0.3}Fe_2O_4$	44.9	0.065	1.830	6	8.3744
$Mn_{0.8}Ga_{0.2}Fe_2O_4$	50.5	0.004	0.142	7	8.3572
$Mn_{0.9}Ga_{0.1}Fe_2O_4$	32.6	0.006	0.278	6	8.3913
$MnFe_2O_4$	36.7	0.603	13.42	8	8.4374

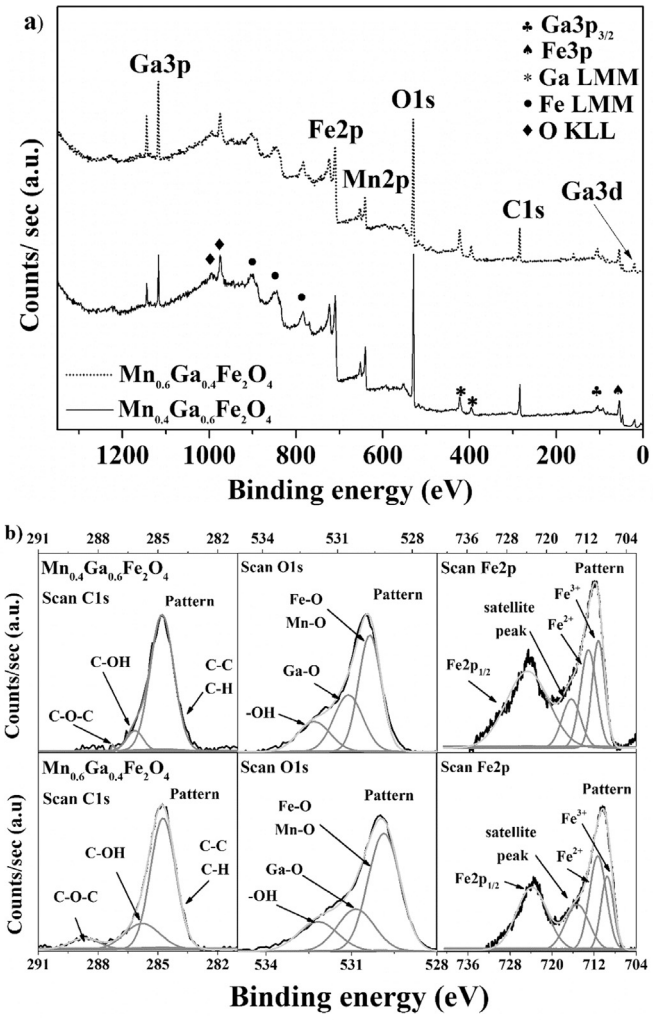

Fig. 2. XPS characterization (a) and C1s, O1s and Fe2p deconvolutions (b) of $Mn_xGa_{1-x}Fe_2O_4$ (x=0.4, 0.6) synthesized samples.

interplanar distance (*d*) [27], was performed by XRD. For all synthesized samples, the crystallite size was calculated by the Scherrer equation [28] and the evaluation of magnetic properties was carried out by VSM technique at a constant magnetic field intensity of 12 kOe at room temperature. Selected samples (x=0.4 and 0.6) were characterized by XPS and TEM-EDS, which allowed the determination of size, morphology and chemical composition of powders. By solid state magnetic induction, the heating capacity of aqueous suspensions of 3.0, 4.5, 6.0 and 10.0 mg of $Mn_{0.4}Ga_{0.6}Fe_2O_4$ and $Mn_{0.6}Ga_{0.4}Fe_2O_4$ nanoparticles per mL of deionized water was tested at a constant AC magnetic field (10.2 kA/m, 354 kHz).

3. Results and discussions

In Fig. 1 the XRD patterns of selected synthesized samples are presented. In these results a slight displacement of reflections was observed in some *hkl* planes at high quantities of proposed cationic substitution. The powders were identified as crystalline materials and the JCPDS 74–2229 card ($FeGa_2O_4$) was used for the identification of the sample with no Mn^{2+}(x=0) and that of the resulting crystalline structures. All samples possess an inverse spinel structure and the calculated lattice parameter (*a*, Table 1) has a slight variation with the successive substitution due to the lattice expansion that took place by the ionic exchange between ions with different radiuses. Lattice parameter (a) shows either an increase or a decrease in comparison to that of $FeGa_2O_4$ (8.363 Å) and $MnFe_2O_4$ (8.515 Å), when Ga ions are being replaced by Mn ions. As Mn and Ga ions are distributed into the spinel structure, the lattice parameter varies as a result of the different occupied tetrahedral (A) or octahedral (B) sites, mainly due the coordination number and the environment in which ions are found [29]. For this reason, the lattice parameter shows no tendency as Ga ions are substituted by Mn ions. The shape and intensity of the identified reflections suggest that particles with a reduced diameter size were successfully synthesized, as it can be observed in Table 1, where the magnetic properties, the calculated lattice parameter (*a*) and the crystallite size are listed. The values of *Mr* and *Hc* are close to zero in almost all cases indicating that the synthesized samples have a superparamagnetic behavior, in which the magnetic moments inside the particles can be rotated as a result of either thermic fluctuations or the magnetic field application. This rotation implies the movement of magnetic moments from axis of easy magnetization and then, each particle behaves as a paramagnetic atom but with a giant magnetic moment due to the existence of a defined magnetic order inside the particles. Zero hysteresis values and a single domain particles with a ferromagnetic behavior are the characteristic properties of nanoparticles in a superparamagnetic state, where the particle losses its ability to store information when their size is below the critical radius [30].

Variations in the saturation values (*Ms*) were observed as a result of magnetic interactions through oxygen anions between iron and manganese ions positioned into both tetrahedral (A) and octahedral (B) sites of the spinel structure, where the magnetic moments of A and B sublattices have a parallel alignment [31]. When the proposed ex-