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journal homepage: www.elsevier.com/locate/jmmmStructural and magnetic properties of Gd³⁺ ion substituted magnesium ferrite nanopowdersAshraf S. Elkady^{a,b}, Shaban I. Hussein^b, Mohamed M. Rashad^{c,*}^a Department of Physics, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia^b Department of Reactor Physics, NRC, Atomic Energy Authority, Cairo, Egypt^c Central Metallurgical Research and Development Institute, Helwan, Cairo 11421, Egypt

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ABSTRACT

Nanocrystalline MgGd_xFe_{2-x}O₄ powders (where $x=0, 0.05, 0.1, 0.2, 0.25, 0.3$) have been synthesized by the ethylene diamine tetraacetic acid (EDTA)-based sol-gel combustion method. X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, high resolution transmission electron microscopy (HRTEM) and vibrating sample magnetometer (VSM) were applied in order to study the effect of variation of Gd³⁺ ion substitution and its impact on crystal structure, crystallite size, lattice parameters, nanostructure and magnetic properties of the formed powders. XRD indicated that, after doping and calcination at 400 °C for 2 h, all samples have two spinel ferrite structures namely cubic and tetragonal phases, which are dependent on Gd³⁺ ion concentration. The cubic phase is found to increase with increasing the Gd³⁺ ion molar ratio up to 0.1, compared to pure MgFe₂O₄ and higher Gd³⁺ content samples. Indeed, with increasing Gd³⁺ ion, the crystallite size was almost unchanged whereas the lattice parameter was found to increase. FT-IR spectrum showed broadening of the ν_2 band and the presence of another band in the range (465–470 cm⁻¹) upon adding Gd³⁺ ion, which confirm the presence of Gd³⁺ ion in addition to Fe³⁺ ion at octahedral site. Besides, these bands were assigned to the formation of (Gd³⁺-O²⁻) complexes at B-sites. HRTEM images showed that the studied samples consist of nanocrystallites having average particle sizes around 9 nm for pure MgFe₂O₄ up to 27 and 42 nm for the Gd³⁺ ion substituted MgFe₂O₄ of molar ratio 0.05 and 0.30, respectively. An examination of the magnetic properties revealed an increase in saturation magnetization with increasing Gd concentration incorporation up to $x=0.1$, as a result of the change of cubic and tetragonal spinel ratio and lattice parameters. Meanwhile, the formed powders exhibited superparamagnetic characteristics. Therefore, such newly synthesized superparamagnetic nanoparticles, containing Gd³⁺ ion can be considered as a promising candidate for use in several potential applications including neutron capture therapy (NCT), magnetic hyperthermia, ferrofluids and magnetic resonance imaging (MRI).

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1. Introduction

Magnetic nanostructured materials have gained much interest during recent years, due to their unique properties that allow for several potential technological and biomedical applications. Among them, magnesium ferrite (MgFe₂O₄) nanoparticles are considered one of such important materials, due to its wide range of applications in microwave devices, computer memory chips, high density recording media, high frequency transformers, heterogeneous catalysis, adsorption of arsenic and sensors [1–4]. Besides, if MgFe₂O₄ crystallite size is below a certain value, it will then possess unique superparamagnetic properties at room

temperature and has a potential for biotechnology applications such as magnetic separation, magnetic resonance imaging, and magnetic hyperthermia treatment. However, to use magnetic nanoparticles in biomedical applications they should meet the following requirements: (1) the dispersion of nanoparticles sizes is small and their hydrodynamic diameter should be less than 50 nm, (2) nanoparticles should have superparamagnetic properties, (3) they must be biocompatible, and (4) nanoparticles must be stable in aqueous solutions to ensure their transport in biological tissues [5].

It is worth mentioning in this context to the fact that the structural, electrical and magnetic properties of such nanomaterials are sensitive to the preparation conditions such as sintering temperature, time and type of additives. The origin of magnetic properties of magnesium ferrite is related to the variety of transition metal cations, which can be incorporated into the spinel

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lattice of the parent magnetic structure. The influence of metal ion substitution such as Dy [6], Sm [2], Co [7], Ni–Co [8], Li [9], Co–Cr [10], Cd [11], Cu [12], Pr [13], Tb [14], Cr [15] and Ca [16] on various structural, magnetic, electrical and dielectric properties of MgFe_2O_4 have been reported in the literature. Hence, the structural and magnetic properties depend on the nature of substituting ions, their charge and their distribution among tetrahedral and octahedral sites.

Gadolinium has the highest neutron cross-section among any stable nuclides, a fact that qualifies it for important applications like neutron capture therapy (NCT) for cancer treatment. In such type of therapy, the subsequently released electrons and γ -rays are utilized to induce local malignant cells death. Besides, gadolinium compounds have been actively explored for magnetic hyperthermia and magnetic resonance imaging applications.

In fact, there is no single modality proved to be 100% efficient in treating cancer, especially in its late stages to date. The combination of hyperthermia with neutron capture therapy and chemotherapy was reported to improve cancer treatments [17,18]. Thus, multimodal nanoparticles-based agents are highly demanding for achieving higher efficacy in cancer treatments. Besides, if the nanoparticles used in diagnosis can also be used in treatment, this would lower the applied doses and costs required for both diagnosis and therapy by using multimodal theranostic agents.

Therefore, it was intriguing, in this study, to synthesize gadolinium substituted magnesium ferrite ($\text{MgGd}_x\text{Fe}_{2-x}\text{O}_4$) nanoparticles, and further elucidates their structural and magnetic peculiarities that would qualify them for being multimodal theranostic agents. Such synthesized $\text{MgGd}_x\text{Fe}_{2-x}\text{O}_4$ nanomaterials would enable for significant enhancements in imaging and therapy by allowing for sustained higher local Gd payloads, and by providing a matrix to engineer selective targeting for malignant tissues. To this end, these vehicles would promise higher contrast images and improved therapy at lower Gd burden and can serve as multifunctional nanoparticles for potential theranostics applications [17,18]. Chand et al. [19] processed $\text{MgGd}_x\text{Fe}_{2-x}\text{O}_4$ by solid state reaction method and they found that saturation magnetization has been increased by two-fold and remnant magnetization has been increased by more than three times due to the doping of Gd^{3+} ions in Mg ferrite.

Herein, the aim of this article is to describe a versatile and cheap sol gel auto-combustion synthesis route to obtain nanosized $\text{MgGd}_x\text{Fe}_{2-x}\text{O}_4$ nanoparticles by decomposition of a (MgFe)–gel using EDTA as both a fuel and a complexation agent. Phase evolution and grain growth kinetics during the formation of $\text{MgGd}_x\text{Fe}_{2-x}\text{O}_4$ powders have been investigated by X-ray powder diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy. Our previous studies indicated the existence of pure superparamagnetic behavior of MgFe_2O_4 nanoparticles at room temperature for samples calcined at 400 °C, using EDTA based sol gel reaction method [20]. Therefore, the impact of the Gd^{3+} ion substitution on the crystal structure and magnetic properties of the newly synthesized $\text{MgGd}_x\text{Fe}_{2-x}\text{O}_4$ nanoparticles is comprehensively studied using different physical approaches in this work.

2. Experimental

2.1. Samples preparation

Certain amounts of iron nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, gadolinium nitrate $\text{Gd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and magnesium oxide MgO were dissolved in nitric acid. The resulting solution was stirred at room temperature for 1 h until a clear transparent solution was obtained using ethylene diamine tetraacetic acid (EDTA) as an organic

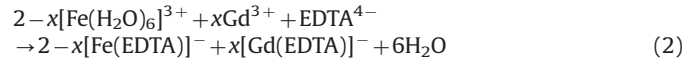
precursor agent. The molar ratio of EDTA to total metal cations concentration; $\text{EDTA}:\text{Fe}^{3+}:\text{Gd}^{3+}:\text{Mg}$ was fixed to 3:2- x : x :1 during preparation. The reactions can be expressed as the following.

When EDTA dissolved in an aqueous solution, the four carboxylic acid groups ionize to give a EDTA^{4-} ion. This can be represented by

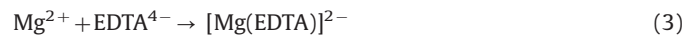


EDTA^{4-} is a hexadentate ligand. It forms complexes with many aqueous metal ions. Four oxygen atoms and two nitrogen atoms bond to the metal ion in an octahedral arrangement. These complexes are often called chelates.

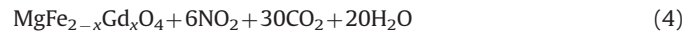
Soluble iron (III) salts dissolve in water to give a solution of hexaaquairon(III) ions, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$



Magnesium (II) salts react with EDTA^{4-} as the following:



heat
→



The obtained solution was stirred for another 1 h for complete homogeneity, followed by evaporation of water until a dried gel was formed. The obtained gel is dried at 200 °C for 24 h to remove the adsorbed and crystalline water; then it was calcined by further heating at 400 °C for 2 h in an open air oven to remove the organic compounds.

2.2. Samples characterization

To check the crystalline state of the prepared samples, powder X-ray diffraction (XRD) measurements were performed using a X'Pert PRO, Cu- K_α radiation ($\lambda = 1.5405 \text{ \AA}$) powered at 45 kV and 40 mA, a scattering angle 2θ range from 10.025° to 89.975° is applied with counting time 6.75 s and step size 0.05°.

In this work the Rietveld's structure refinement analysis of XRD data was adopted to obtain the structural parameters of the system under study [21–23]. These include the atomic coordinates, occupancies and lattice parameters. In addition, micro-structural parameters, such as particle size is determined. The Rietveld's software MAUD 2.33, a specially designed code for microstructure parameters refinement through the least-squares method was applied [23]. The peak shape was assumed to be an asymmetric pseudo-Voigt (pV) function during the refinement procedure. The cation distribution is calculated by refining the changes in intensities, while localizing the cation in a proper position, so that the sum of the fractional occupancies in octahedral or tetrahedral position for this cation equals to unity [21–24].

The background of each pattern was fitted by a polynomial function of order 5. To estimate the theoretical XRD pattern containing all the MgO (cubic, space group: Fm-3m, $a = 0.4217 \text{ nm}$ COD ID: 1000053), $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ (cubic, space group: Ia-3d, $a = 1.244 \text{ nm}$ COD ID: 1008147), Gd_2O_3 (cubic, space group: I 21 3, $a = 1.079 \text{ nm}$ COD ID: 1010338), $\alpha\text{-Fe}_2\text{O}_3$ (triangular, space group: R-3c: H, $a = 0.50355$ and $c = 1.37471 \text{ nm}$ COD ID: 2101167), and Mg-ferrite (cubic, mixed spinel, space group: Fd-3m: 2, $a = 0.83805 \text{ nm}$, COD ID: 9001446), and Mg-ferrite (tetragonal spinel space group: P 41 2 2, $a = 0.58309$, $c = 0.82218 \text{ nm}$ COD ID: 9010293) phases in a single pattern [25].

The Fourier Transform Infrared (FTIR) spectroscopy is a very useful tool for deducing structural information of chemical

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