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# Tailoring the super-paramagnetic nature of $MgFe_2O_4$ nanoparticles by $In^{3+}$ incorporation

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ABSTRACT

$MgFe_{1-x}In_xO_4$ nanoparticles (where x = 0.00, 0.04, 0.08, 0.12 and 0.16) have been prepared by sol-gel method using citric acid. The appearance of two distinct bands corresponding to tetrahedral and octahedral occupied M—O bonds has been demonstrated in Fourier Transform Infra Red spectra (FT-IR). X-ray powder pattern confirmed the presence of a cubic spinel phase. X-ray Photoelectron Spectroscopy (XPS) has been employed to confirm the valence states of the metal ions present. Mössbauer spectroscopy shows the sextet for pristine sample and on $In^{3+}$ doping the super-paramagnetic doublet becomes prominent. AC susceptibility profiles shows transition from single domain structure to super-paramagnetic particles on doping. The magnetic properties have been studied using Vibrating Sample Magnetometer (VSM), here the *M-H* and *M-T* curves showed the formation of super-paramagnetic nanoparticles at room temperature, where the saturation magnetisation ($M_s$), remnant magnetisation ($M_r$) and coercivity ($H_c$) values decreased with $In^{3+}$ incorporation.



## 1. Introduction

Magnetic nano-ferrites have fascinated the science community over the years, owing to their unique properties which are contrary to those of bulk materials thereby entering into a vast applicative area of magnetic, optoelectronic, catalytic and biomedical sciences [1–3]. Super-paramagnetism is one such exceptional property of magnetic nanoparticles that is significant in modern technology including magnetic resonance imaging, ferro-fluids, magneto-caloric refrigeration, drug delivery etc [4–8]. Among the known spinel ferrites $MgFe_2O_4$ in nano-particle size below a certain value possess super-paramagnetic properties at room temperature hence shows a prospective in biomedical fields such as drug delivery, magnetic hyperthermia treatment and so on [9,10].

$MgFe_2O_4$ is a soft magnetic material which can be easily magnetised and (de)magnetised. The chemical and physical properties of the spinels depend on the distribution of the cations in tetrahedral (A) sites and octahedral (B) sites, which can be varied with size or the dopant impurity. In a bulk $MgFe_2O_4$ half of $Fe^{3+}$ ions occupy the tetrahedral sites and remaining half along with $Mg^{2+}$ ions occupy the octahedral sites. $MgFe_2O_4$ shows magnetism even though the $Mg^{2+}$ ions are diamagnetic, this might be due to the inverse spinel structure [11]. Here it will be even more interesting to study the change in properties of $MgFe_2O_4$ when doped with other metals. Earlier as per the literature Cr [3,12], Gd [13], Dy [14], Sm [15], Co [16], Ni—Co [17], Li [18], Co—Cr [19], Cd [20], Cu [21], Pr [22], Tb [23], Ca [24], etc. have been used as dopants in ferrites and their properties have been explored. The properties of the doped ferrites largely depend on the size, charge, concentration and nature of the dopant ion. Here the stoichiometry, cation distribution, as well as the final particle size plays a key role which is in turn highly influenced by the preparative method used. In the present study we have shown the indium ($In^{3+}$) induced variations in the magnetic properties of $MgFe_2O_4$ nanoparticles prepared by sol-gel method. To the best of knowledge there are hardly any reports on the properties of $In^{3+}$ doped $MgFe_2O_4$ nanoparticles in the literature which are prepared by sol-gel method, also $In^{3+}$ being a diamagnetic impurity, it was fascinating to study how interestingly it alters the properties of the $MgFe_2O_4$ particularly in nano-particulate size.

## 2. Experimental

### 2.1. Preparation

$MgFe_{1-x}In_xO_4$ nanoparticles (where x = 0.00, 0.04, 0.08, 0.12, 0.16) were prepared by sol-gel method using citric acid as complexing agent. All the chemicals used were of analytical grade. Indium oxide ($In_2O_3$, Sigma Aldrich 99.9%) was first brought into solution by dissolving it in dilute nitric acid (Sigma Aldrich). To this

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magnesium nitrate $Mg(NO_3)_2 \cdot 6H_2O$ (Thomas Baker 99.8%) and iron nitrate $Fe(NO_3)_3.9H_2O$ (Thomas Baker 99.0%) were added as per the calculated stoichiometries with continuous stirring which was followed by the addition of citric acid. The metal nitrates to citric acid (Thomas Baker 99.0%) molar ratio was 1:3. These were further heated with constant stirring until a thick gel was obtained. The gel was characterised by Thermogravimetry. It was then decomposed at 400 °C and the obtained powder (as prepared sample) was ground in mortar and pestle. This was later sintered at 600 °C for 10 h in a furnace wherein the desired nanoparticles were obtained. These nanoparticles were then characterised using different techniques and explored for their magnetic properties.

### 2.2. Characterisation techniques

Thermo gravimetric – Differential Thermal Analysis (TG/DTA) (NETZSCH TG-DTA STA 409PC) was employed to study the thermal decomposition of the gel. The measurements were carried out in air at the heating rate of 10 °C /min in the range of 30 °C to 700 °C. X-ray diffraction (XRD) analysis using a RIGAKU MINIFLEX Difractometer with Cu K$\alpha$ radiation, filtered through Ni absorber in steps of 0.02° were carried out to confirm the phase formation of all the samples. Fourier Transform Infra Red spectroscopy (FTIR) measurements of the metal oxides were carried out on SHIMADZU IR-PRESTIGE-21 to characterize specific M-O vibration bands for spinels. The morphology was investigated on a JEOL JSM-6360 LV Scanning Electron Microscope (SEM) where elemental analysis was done using Energy Dispersive X-ray Spectroscopy (EDX). Particle size of the calcined samples was determined using PHILIPS CM 200 Transmission Electron Microscope (TEM), operating at an accelerating voltage of 200 kV and providing a resolution of 2.4 Å. Shimadzu UV 2450 UV–Visible spectrophotometer in the wavelength range of 200–800 nm was employed to record the Diffused Reflectance Spectra (DRS) of the prepared nanoparticles. The valence states and the binding energies of the elements were determined by the X-ray Photoelectron Spectroscopy (XPS) employing a VSW SCIENTIFIC INSTRUMENT with Al K$\alpha$ as the incident source and excitation energy of 1486.6 eV. The vacuum maintained in the sample analyzer chamber was about $10^{-8}$ Torr. The room temperature $^{57}$Fe Mössbauer measurements were carried out in transmission mode with a $^{57}$Co radioactive source in constant acceleration mode using a standard PC based Mössbauer spectrometer, equipped with a Weissel velocity drive. Velocity calibration of the spectrometer was performed with a natural iron absorber at room temperature. The AC susceptibility measurements were carried on DOSE AC susceptibility instrument by ADEC Pvt. Ltd., in a magnetic field of 5000 Oe at an operating frequency of 315 Hz. The instrument was calibrated with Ni standard. The magnetic measurements were performed using QUANTUM DESIGN PPMS Vibrating Sample Magnetometer (VSM). The magnetisation with varying magnetic field of up to 30 KOe was measured at 50 K and 300 K. The Magnetisation with varying temperature at a specific fixed magnetic field was also studied.

## 3. Results and discussion

### 3.1. Thermal analysis

The TG/DTA curve for the metal-citrate gel is shown in Fig. 1. The first weight loss was observed in the region 60 °C to 140 °C with a prominent endothermic peak which is owing to the water loss as the gel was highly hydrated. This was followed with the decomposition of the metal citrate complex between the 140 °C and 350 °C accompanied by two exothermic peaks at 206 °C and 322 °C respectively, suggesting that the complete decomposition

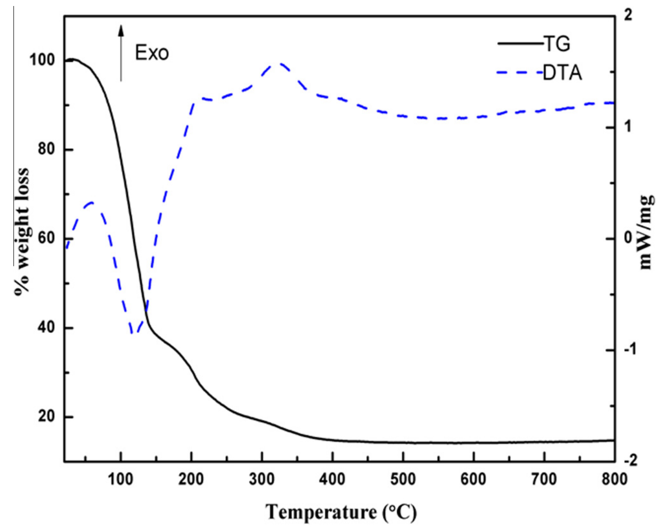


**Fig. 1.** TG/DTA curve of metal – citrate gel for $MgFe_{1.92}In_{0.08}O_4$ composition.

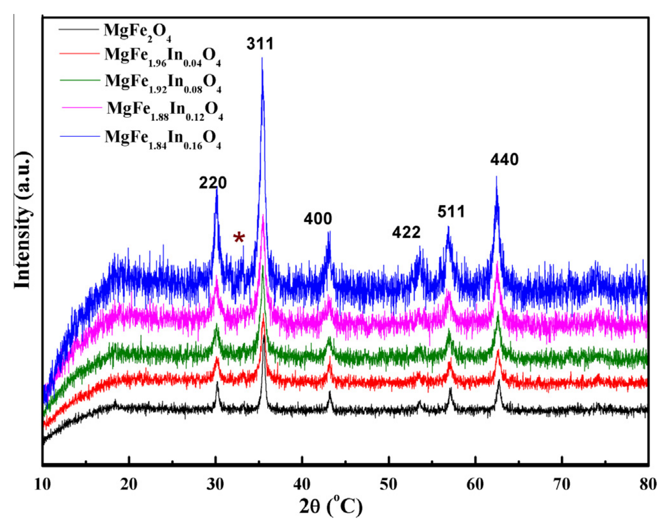


**Fig. 2.** X-ray powder pattern for $In^{3+}$ doped $MgFe_2O_4$ nanoparticles.

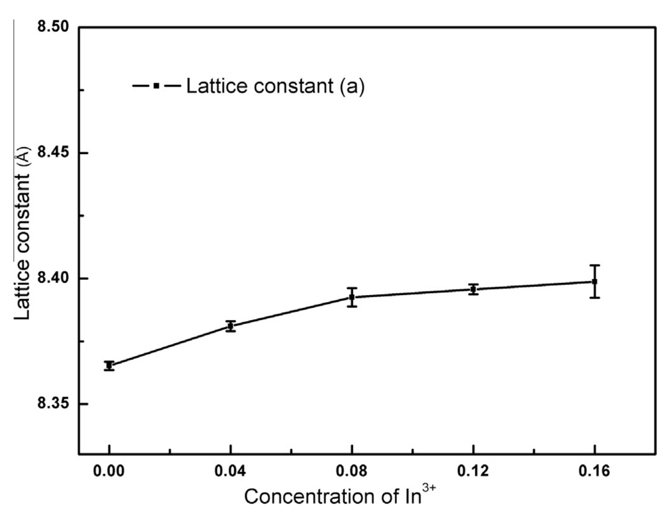


**Fig. 3.** Variation in lattice constant (a) with respect to $In^{3+}$ concentration with error bars.