

Synthesis and structural properties of Sm³⁺doped Mg Nano Particles

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Abstract

Mg-Sm nano ferrites having the chemical formula $Mg Sm_x Fe_{2-x} O_4$ (Where $x = 0, 0.025, 0.050, 0.075, 0.100$) have been citrate-gel auto-combustion technique were analyzed through various experimental techniques. XRD analysis confirmed single-phase cubic spinel structure while FTIR spectroscopic analysis displayed two absorption peaks that are characteristic of spinel nano ferrites. UV-visible spectral analysis was carried out to study the optical absorption behavior of the prepared ferrites.

Keywords: Citrate-gel Auto combustion , XRD, UV-visible spectra, FTIR

1.Introduction

Material science gained significance in research due to interesting applications and properties exhibited by materials in various fields. It deals with variety of applications in chemistry, physics biology, medical and engineering. The origin of material science is to observe the structure of materials and their properties. The main aspect of the material science is characterization of materials whose properties and performance are associated with microstructure of the materials. Magnetic nano-materials exhibit variety of applications such as storage of data, MRI, magnetic fluids and biotechnology etc. The preparation method of these materials is very significant due to its control over the size distribution, topography, shape, density of the particles on which its behaviors strongly depend. Mn nano spinel ferrite is a soft ferrite with low loss and high magnetic permeability having different kinds of applications that include magnetic recording media, transformer coils, microwave devices, computer memory chip etc. Magnetic nano-ferrite particles gained special attention over the last few years. These particles are widely used in high density magnetic recording [1]. Low cost, high curie temperature, high saturation magnetization and properties of hysteresis loop make them highly

suitable for microwave devices, high-density recording media and as absorbents [2]. They exhibit specific properties in comparison to bulk due to occupation of atoms in large volume at grain boundary area, which in turn leads to unusual properties like dislocation, spin canting, super paramagnetic (sp) and surface anisotropy etc. This property makes these materials to be tailored flexibly for specific applications [3]. Ferrites are widely used in various magnetic devices like inductors, transformers and magnetic heads in high frequency resonance circuits [4]. The interesting physical and chemical properties of the nano ferrites arise from the distribution of cations among tetrahedral (A) and octahedral (B) sites [5]. They are also used in MRI, Target drug delivery Hyperthermia for cancer treatment [6-7], high density storage devices and magnetic fluids [8-9]. The present work reports the synthesis, optical, and FTIR, of Mg-Sm Ferrites with the help of citrate gel auto combustion technique.

2. Materials and Experimental Method

Ferrite particles of chemical formula $\text{Mg Sm}_x \text{Fe}_{2-x} \text{O}_4$ ($x = 0.0$ to 0.1 with steps of 0.025) by using Magnesium, Samarium, Ferric Nitrates, Citric acid and ammonia of 99% purity as raw materials were synthesized by using the technique of citrate-gel auto combustion at low temperature. Required amount of metal nitrate and citric acid were dissolved in distilled water and was stirred to form homogenous clear solution and heated up to 80°C . Later the pH was set to 7 by adding ammonia. This liquid was evaporated at about 180°C resulting in to a burned powder which was grinded with Agate Mortar and calcinated at 500°C / 4 hours and cooled to normal temperature [10]. Structural characterization related prepared samples was taken up with X-ray diffractometer (Philips) using Cu K_α radiation ($\lambda=1.5405 \text{ \AA}$) within the Bragg's range 10° to 80° with step size of $4^\circ/\text{min}$.

3. Results and Discussion

3.1.XRD Analysis

XRD was used as an efficient tool for characterization of crystalline powders. Confirmation of phase formation and micro structural study was done through XRD analysis of $\text{Mg Sm}_x \text{Fe}_{2-x} \text{O}_4$ ($x = 0.0$ to 0.1) samples. The XRD patterns were depicted in **Fig. 1** and indexed as (111), (220), (311), (222), (422), (511), (440). It indicated cubic spinel structure of ferrites with single phase without any impurity pickup.

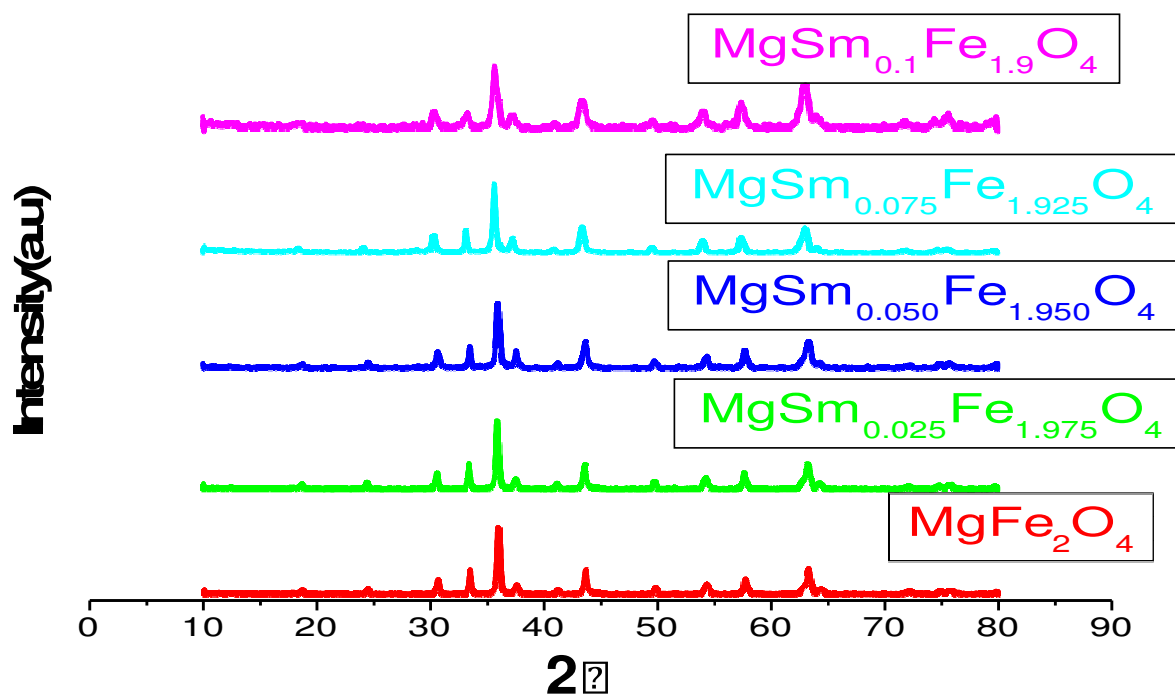


Fig. 1 X-ray diffraction patterns of $\text{Mg Sm}_x \text{Fe}_{2-x} \text{O}_4$

$$\text{Crystalline size of the sample } D = \frac{0.94\lambda}{\beta \cos \theta}$$

Where λ = wavelength of X-ray used

β = Full Width Half Maxima (FWHM) in radians.

θ = peak position

Fig. 2 indicate crystallite size of prepared samples ranging between 15nm to 20nm and lattice constant value increase with doping of samarium that confirm unit cell expansion with doping of rare earth [11].

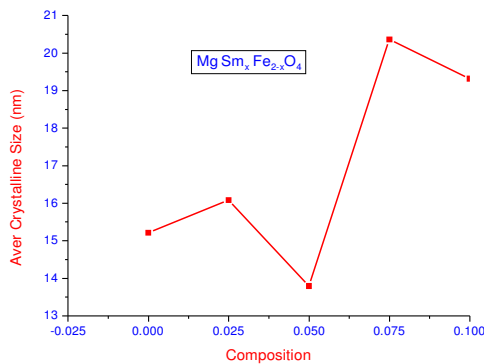


Fig.2 Average crystalline size variation for Sm doped Mg ferrites

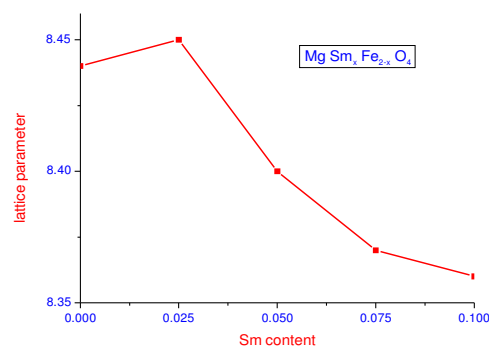


Fig.3 lattice parameter variation vs Sm doped Mg ferrites.

Lattice parameter (a) of the sample was calculated by the formula

$$a = d * (h^2 + k^2 + l^2)^{1/2}$$

Where a = Lattice Constant

(hkl) are the Miller Indices

d = inter planner spacing,

Fig. 3 shows the variation of lattice parameter with Sm^{+3} ion content. The lattice parameter of Sm doped Mg nano ferrite increases with Sm content initially and further decreases in small proportion. Such variation in the lattice parameter is due to F^{+3} ions having smaller ionic radius (0.067 nm) than that Sm^{+3} (0.0958) [12,13].

Table.1 crystallite size, lattice parameter, x-ray density and volume of the unit cell for various compositions of $\text{Mg Sm}_x \text{Fe}_{2-x} \text{O}_4$ ($x=0.000-0.1$).

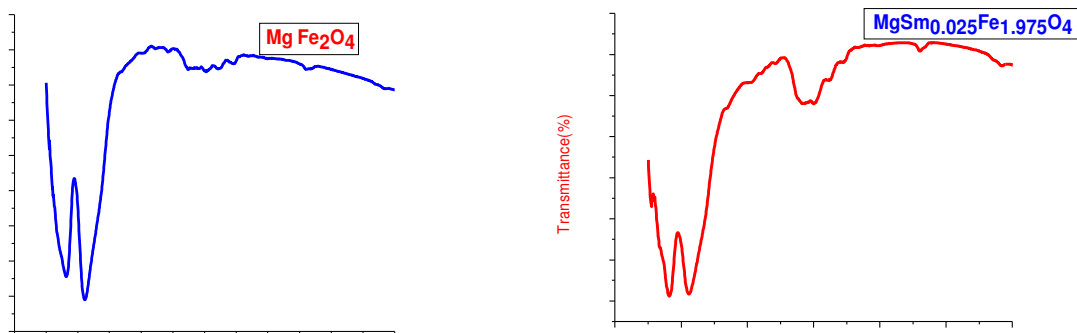
S. No	Name of the composition	Avr.cry. size (nm)	Lattice constant ($\text{\AA}$)
1	MgFe_2O_4	15.21	8.44
2	$\text{MgSm}_{0.025}\text{Fe}_{1.975}\text{O}_4$	16.08	8.45
3	$\text{MgSm}_{0.050}\text{Fe}_{1.95}\text{O}_4$	13.79	8.40
4	$\text{MgSm}_{0.075}\text{Fe}_{1.925}\text{O}_4$	20.36	8.37

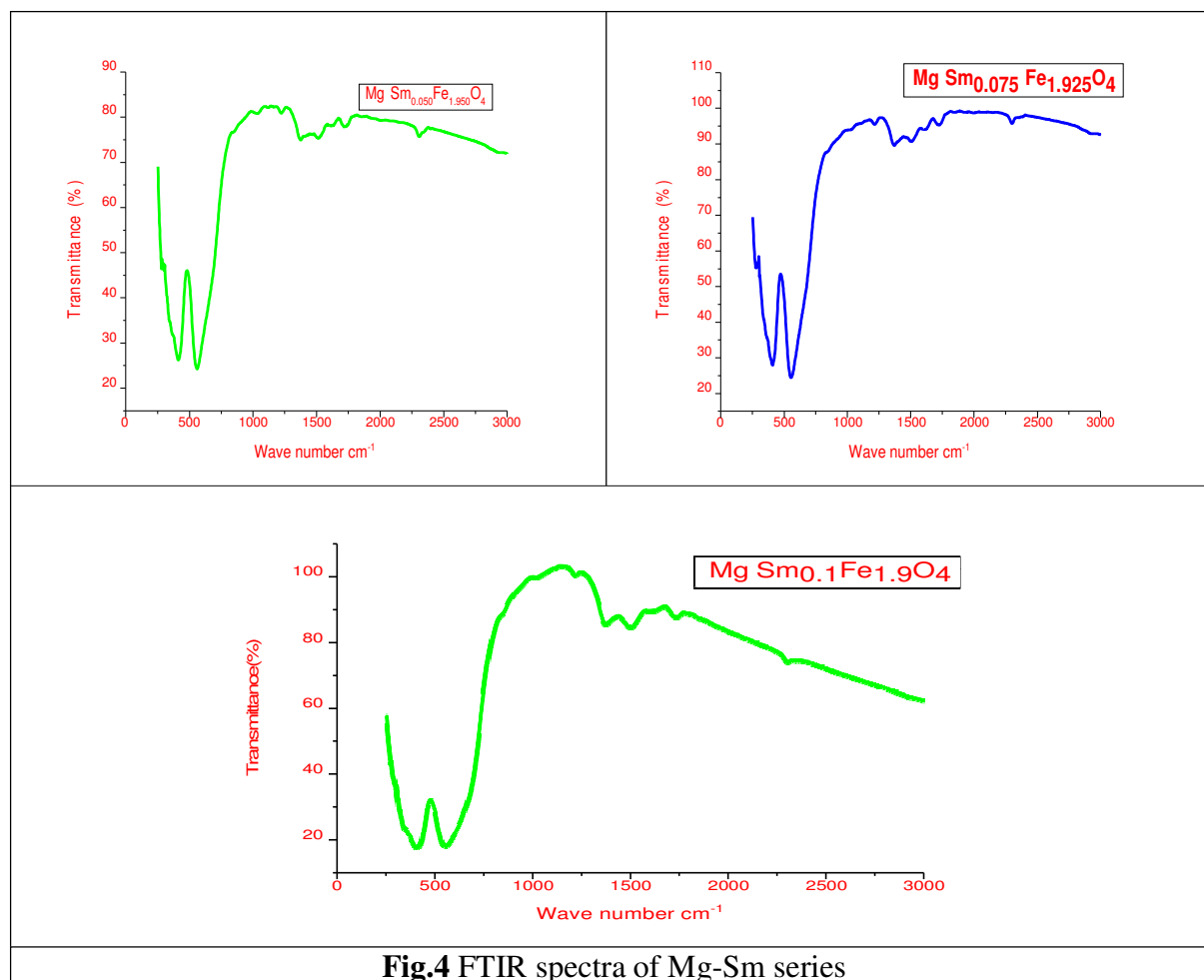
5	MgSm _{0.1} Fe _{1.9} O ₄	19.31	8.36
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3.2. FTIR Spectroscopic Analysis

FTIR spectra acts as a powerful technique for the structural characterization. FTIR spectral analysis witnesses the formation of spinel structure of synthesized Sm, doped Mg nano ferrites. FTIR spectra of the prepared ferrites was recorded between 200 to 3000cm⁻¹ at normal temperature and was used to locate the band positions. The spectra is recorded in KBr pellet that is mixed in 1:20 ratio. The FTIR spectra of all the compositions were shown in the **Fig.4** Where % Transmittance was plotted against wavenumber. From the figure, two clear absorption bands ν_1 and ν_2 were observed at about 600cm⁻¹ and 395cm⁻¹ which signify the intrinsic stretching vibrations of tetrahedral (A) and octahedral (B) sites respectively. The first Absorption band identified in the range of 626 – 570 cm⁻¹ indicate the stretching vibration of tetrahedral M-O bond and the second band detected in the range of 496 to 400cm⁻¹ results from stretching vibrations of metal-oxygen band at octahedral site [14-15].

Vibrational spectra of ferrites were studied by Waldron and Hafner and ascribed ν_1 at about 600cm⁻¹ (high frequency band) to A site and ν_2 at about 400cm⁻¹ (low frequency band) to B site. The observed absorption bands with in this range indicate single phased spinel structure formation with two sub-lattices namely tetrahedral and octahedral sites A & B. The variance between ν_1 and ν_2 is because of the differences in distances of positions of Fe³⁺ and O²⁻ at tetrahedral an octahedral site.





3.3 Optical Studies

The optical studies of synthesized nano ferrites studied by UV-DRS (diffuse reflectance spectroscopy). The UV-DRS spectroscopy absorption and reflection in the UV region and, it was performed using reference which is barium sulphate (BaSO_4) with absorbance verses wavelength. In the absorption molecules of Electron or non –bonding (n-electron) can absorb the energy in the form of ultraviolet or visible light to excite this electron to higher or anti-bonding molecular orbit. Sm doped Mg ferrites wave length is 520 nm regions shown in **Fig.5** and it is a visible region.

Table.2 band gap energy of Sm-Mg nano ferrite series

Name of the composition	Cut off wavelength (nm)	Band gap energy (Ev)
MgFe ₂ O ₄	495	2.50
MgSm _{0.025} Fe _{1.975} O ₄	493	2.51
MgSm _{0.050} Fe _{1.95} O ₄	490	2.53
MgSm _{0.075} Fe _{1.925} O ₄	485	2.55
MgSm _{0.1} Fe _{1.9} O ₄	475	2.61

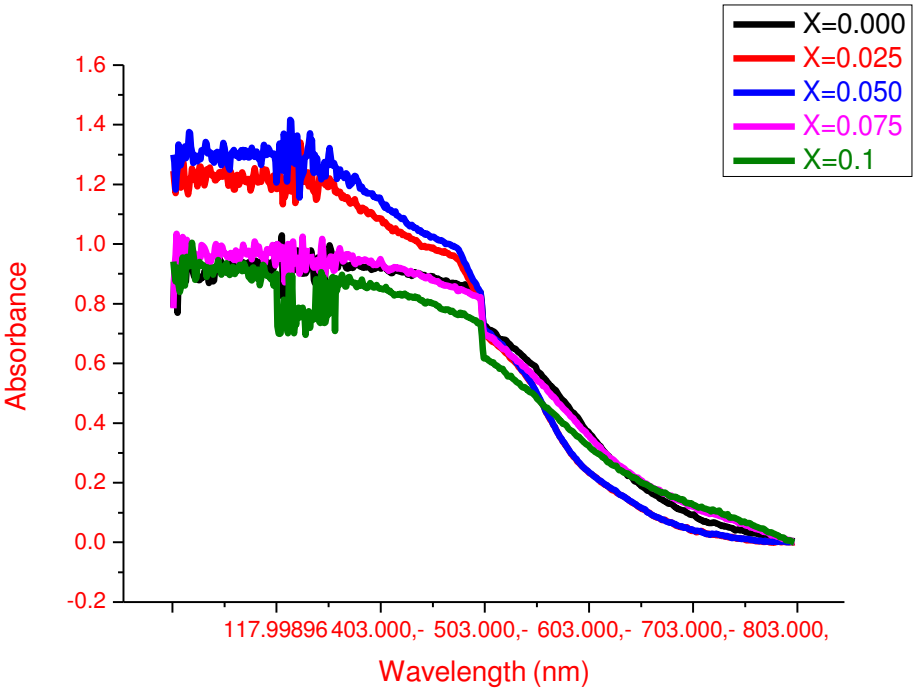


Fig.5 UV-Vis spectra of Sm doped Mg nano ferrites

From the spectra it can be seen that absorption bands wavelength is low region with dopant concentration it is due to the variation of ionic radii of Sm^{3+} and Fe^{3+} ions. The band gap energy is increases with increasing in Sm^{3+} content which is 2.50 to 2.61 eV [16-17].

Conclusions:

A series of samarium doped Mg nano ferrites $\text{MgSm}_x\text{Fe}_{2-x}\text{O}_4$ with ($x=0.000, 0.025, 0.050, 0.075, 0.1$) were synthesized by citrate- gel auto combustion method. XRD analysis confirmed that the formation of single-phase spinal structure without any impurity in all the compositions. The substitution of samarium in Mg ferrite has resulted in an increase in lattice parameter and average crystalline size. The decrease in lattice parameter for the composition $x=0.050, 0.075$ indicates a possible cationic distribution. The absorption bands in FTIR spectra of all the prepared samples are found in expected range that is $400\text{--}600\text{ cm}^{-1}$. The UV-Vis spectroscopy gives the optical absorption range that is 450 nm -500 nm range and also observed that by samarium concentration increases the absorbance decreases.

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