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Characterization of Rare earth material Samarium substituted Magnesium Nano Ferrites synthesized by Citrate-Gel Auto Combustion method

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Abstract: *A series of Samarium substituted Magnesium ferrites (Mg Sm_x $Fe_{2-x}O_4$ with x = 0.000, 0.025, 0.050, 0.075, 0.1) was synthesized by the Citrate–Gel auto combustion method at low temperature. Synthesized powders were sintered at 500^0C for 4 hours in an air and were characterized by XRD, SEM and EDS. XRD analysis reveals that the samples are single phase with crystallized sizes in the 51 nm to 62 nm region increases. In lattice parameter with doping concentration suggests the expansion in unit cell with Sm^{+3} doping. The values of lattice parameter (a) decreased and x-ray density (dx) was increased with the increasing of Sm substitution. Scanning Electron Microscopic (SEM) studies revealed nano crystal and nature of the samples. An elemental composition of the sample was studied by Energy Dispersive Spectroscopy (EDS). The observed results can be explained on the basis of composition and crystal size.*

Key words: *Sm–doped mg ferrite, citrate – Gel Auto Combustion, XRD, SEM, EDS.*

I. Introduction:

Nano materials have been produced and used by human for hundreds of years, however the understanding of possible by the advent of advanced tools, that are capable of resolving information at nano scale. The properties of ferrites are sensitive to synthesis method, synthesis conditions, synthesis parameters, nature and type of substitution and cation distribution. Ferrites are very important and widely used materials in technical designing and applications at high frequencies [1]. The interesting physical and chemical properties of the ferrites arise from their ability to distribute the cations among the tetrahedral (A) and Octahedral (B) sites [2]. In order to achieve a high degree of molecular mixing, chemical homoginity, control of stoichiometry, low calcination and sintering temperature/ time, various chemical methods have been used for the synthesis of spinel ferrites [3 – 6].

Magnesium ferrite is a partially inverse spinel with interesting ferromagnetic property, since Mg^{2+} is anti ferromagnetic. Due to diffusibility of Mg^{2+} ions, its distribution in the crystal lattice site greatly depends on the heat treatment [7, 8]. Magnesium ferrite is used as humidity sensor [9], Catalyst [10] and it also have Magnetic and gas sensing applications [11, 12]. Research on different rare earth substituted ferrites have revealed to improve its properties [13–15]. Several methods are used for synthesizing nano sized spinel ferrites, such as co-precipitation, sol-gel, micro-emulsion, hydrothermal and reverse micelle [16–18]. Refluxing process [19], Ceramic Method [20], Hydro Thermal Method [21], Combustion Method [22], Spark Plasma Sintering [23] and ball milling method etc. Substitution of large rare earth ions in place of small iron ions will result in strain which induce structural distortion and thereby modify the properties of samples in Nano-regine [24]. One of the major draw backs of $MgFe_2O_4$ material is the leakage current arising out of its non-stoichiometry. This is mostly because of the difficulty in obtaining stoichiometric single phase $MgFe_2O_4$ materials. Therefore it allows current to pass through when a high voltage is applied. Attempts to improve the electrical properties have been made by doping it with rare earth elements such as Lanthanum (La), Praseodymium (Pr), Samarium (Sm), Gadolinium (Gd), Terbium (Tb) and Cerium (Ce), Dysprosium (Dy), etc. The dopant can be at the A site or the B (site). A site being edges of the perovskite and the B site being the centre of the perovskite Cell [25] to the best of my knowledge, a little Information is available on nano sized Samarium substituted magnesium ferrites synthesized by Citrate-gel auto Combustion method, which is a simple process, speeds up the synthesis and offers a significant saving in time, energy consumption over traditional methods. Hence in the present study we preferred the citrate gel auto combustion method for the synthesis of Samarium substituted magnesium nano ferrites.

II. Experimental:

II.1 Synthesis:

A series of Samarium substituted nano ferrites having the chemical formulae Mg Sm_x Fe_{2-x} O_4 (where x = 0.000, 0.025, 0.050, 0.075 and 0.1) were prepared by Citrate Gel Auto combustion method. The starting materials were Magnesium Nitrate [Mg $(NO_3)_2.H_2O$], Ferric Nitrate [$(FeNO_3)_3.9H_2O$], Samarium Nitrate[Sm $(NO_3)_3$ $6H_2O$], Citric Acid [$C_6H_8O_7.H_2O$] and Ammonium [NH_3] all of 99% pure AR grade. SDF CLSD Fine Chemical Limited is the raw materials for the synthesis process.

Calculated quantities of metal nitrates and citric acid were dissolved in minimum amount of distilled water to get clear solution. Here citric acid acts as a chelating agent and helps in the homogenous distribution of metal ions. The above mixture was stirred to get homogenous clear solution which is heated to 80^0C using a hot plate magnetic stirrer. Then the pH of the solution is adjusted at 7 by addition of ammonia. A sol is formed. The resulting solution was evaporated to dryness heating at about 180^0C on a hot plate with continuous stirring. The gel gave a fast flameless auto combustion reaction with the evolution of large amount of gases which results a burned powder. The burned powder was grinding using Agate Mortar and pestle to get a fine ferrite powder. Finally the grinded powder was calcinated in air at 500^0C for 4 hours and cooled to room temperature to obtain spinel phase.

II.2 Characterisation:

BrukerD8 advanced X-ray diffractometer with Cu Kα (λ=1.5405A^0) was used to study the single phase nature and nano phase formation of the Mg-Sm ferrite system at room temperature by continuous scanning in the range of 10^0-80^0C. Micro structural analysis of the prepared samples was carried out by Scanning Electron Microscopy (SEM) and elemental compositional analysis for all samples was done by Energy Dispersive Spectroscopy (EDS).

III. Results And Discussions

III.1 XRD Analysis: The X-ray Diffraction pattern of all the samples were shown in fig(1) which confirms the single phase cubic spinal structure formation without any impurity peak. The strongest reflection has come from (311) peak for every sample. The crystalline size of all samples was calculated from the Half Width at Full Maximum (HWFM) of the (311) reflection peak in the XRD pattern using Debye-Scherrers formula[26].

Scherrer Formula:

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

Where λ =wavelength of X-ray used

$\boldsymbol{\beta}$ = Full Width Half Maxima(FWHM) in radians.

θ = peak position.

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,

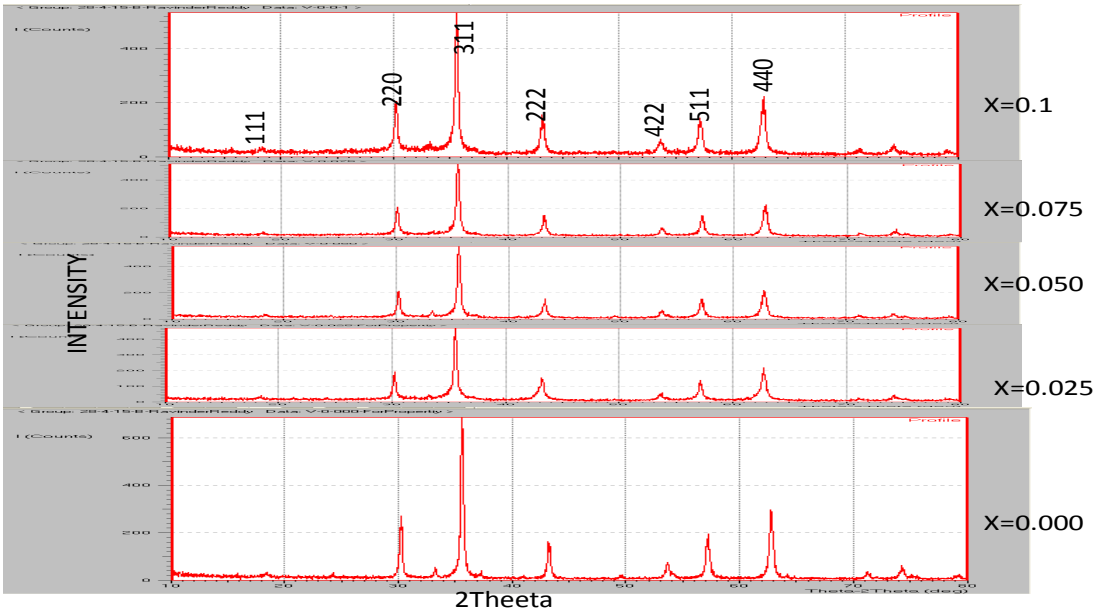
The X-ray density $dx = \frac{nM}{a^3 N}$ [g/cm^3] [27]

Where M = molecular weight of the sample

n = number of molecules in a unit cell of spinel lattice.

a = lattice parameter and N is the Avogadro number.

The Volume of the Unit Cell $\mathbf{V = a^3}$



Fig(1). XRD pattern of Sm substituted Mg Nano Ferrite

Values of Crystallite size, lattice parameter, X-ray density and volume of all the samples were given in the table(1).

Table (1): Crystalline size, Lattice Parameter, X-ray density & volume.

S. No	Sample	Mol. wt (gm/mol)	Crystallite size(nm)	Lattice constant (A^o)	X-ray density (gm/cc)	Volume $(A^o)^3$
1	$MgFe_2O_4$	199.991	62.87	8.360	0.454	584.277
2	$MgSm_{0.025}Fe_{1.975}O_4$	202.353	57.79	8.368	0.458	585.956
3	$MgSm_{0.050}Fe_{1.95}O_4$	204.716	49.76	8.366	0.464	585.535
4	$MgSm_{0.075}Fe_{1.925}O_4$	207.079	51.57	8.364	0.469	585.116
5	$MgSm_{0.1}Fe_{1.9}O_4$	209.442	56.30	8.365	0.475	585.326

From the table we can observe that the crystallite size of the prepared samples were in the range of 51 nm to 62 nm. Lattice parameters of the prepared samples were decreased by increasing the Sm concentration which obeys the Vigurd's law [28]. The observed decrease in the crystallite size can be explained by on the basis of relative ionic radii of Sm and Fe ions. Compared with and without doping value of lattice constant is increasing with samarium doping shows the expansion of unit cell with rare earth doping this is excepted due to substitution of large ionic radius of Sm^{3+} ions ($0.964A^0$) with small ionic radius Fe^{3+} ions ($0.645A^0$)[29].

III.2 SEM Analysis:

Morphology of the prepared samples by Citrate-gel method was studied using Scanning Electron Microscope (SEM) where the secondary electron images were taken at different magnifications to study the morphology. The scanning electron microscopic images of all the synthesized samples were shown in Figure-2.The SEM micro graphs shows that the grains have almost homogenous distribution and clusters between the particles. The grain sizes of the samples lies in the nano meter region have a spherical shape and narrow size distribution. SEM image revealed that with increasing in the Sm concentration, then the grain size has increased which is an evidence for the XRD analysis.

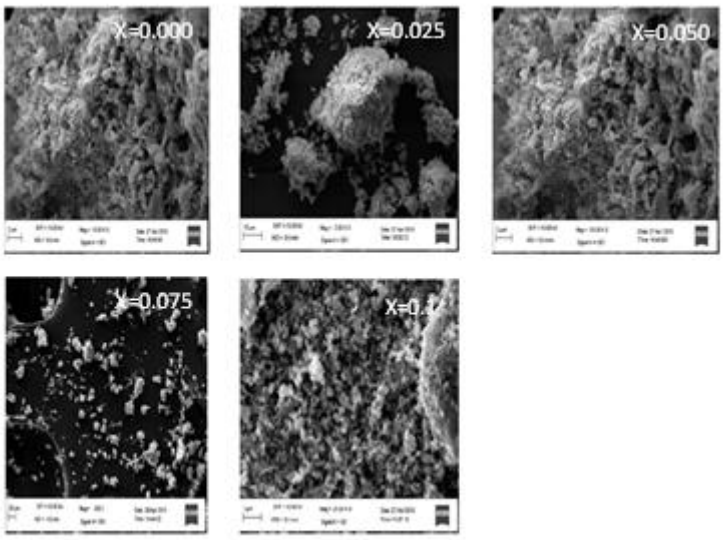


Fig . (2). SEM Micrographs mg-sm nano ferrites.

III3 Elemental Analysis by EDS :

The elemental analysis of all the Mg-Sm nano ferrite samples with different compositions was analyzed by Energy Dispersive Spectrometer (EDS) and the elemental % and atomic % of different elements in the were shown in the Table 3. The EDS pattern of samples with x = 0.000, 0.025, 0.050, 0.075 and 0.1 were shown in Figure 3, which indicates the elemental and atomic composition in the sample. The compounds show the presence of Mg, Sm, Fe and O without precipitating cations.

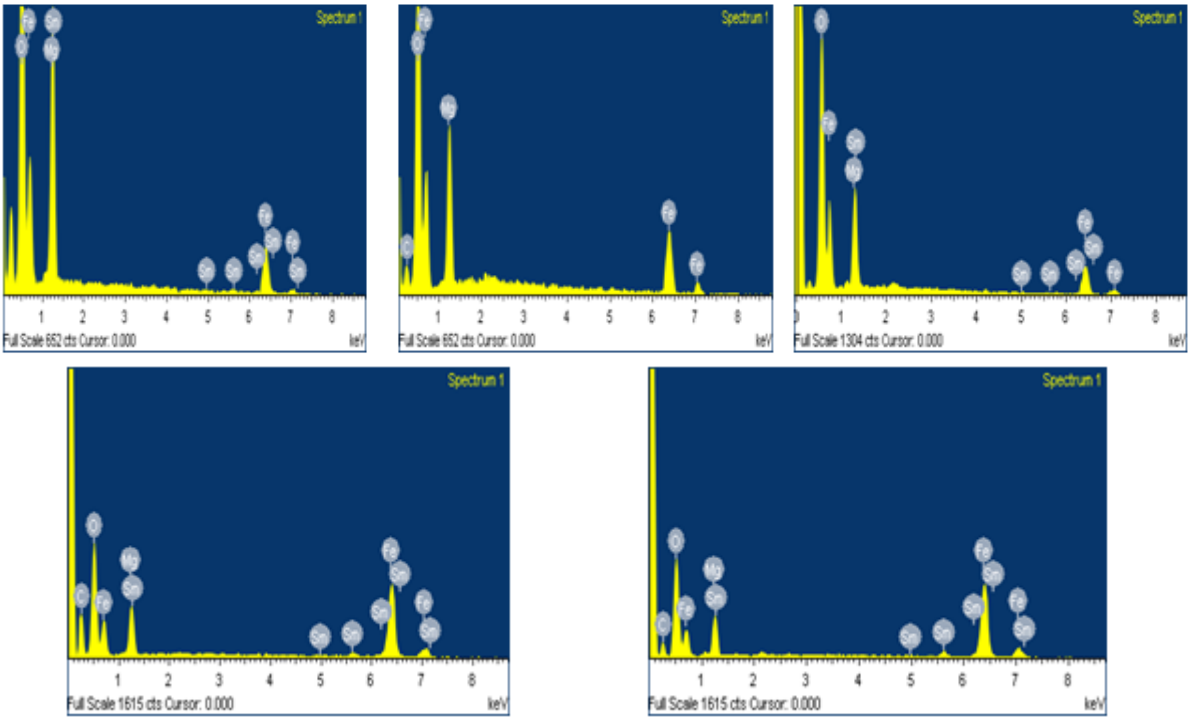


Fig (3). EDS Pattern of Mg Sm_x $Fe_{2-x}O_4$ with x = 0.000, 0.025, 0.050, 0.75, 0.1.

Table-2. Elements of each sample composition analyzed by (%weight) obtained by EDS

S.No	Element	O		Fe		Mg		sm	
	Ferrite Composition	Element%	Atomic%	Element %	Atomic %	Element %	Atomic%	Element %	Atomic%
1	$MgFe_2O_4$	37.48	62.75	51.76	25.92	10.76	11.33	0.00	0.00
2	$MgSm_{0.025}Fe_{1.975}O_4$	34.15	59.19	45.21	22.44	15.26	17.20	5.38	0.99
3	$MgSm_{0.050}Fe_{1.95}O_4$	31.79	58.38	56.98	29.09	9.98	12.29	1.25	0.24
4	$MgSm_{0.075}Fe_{1.925}O_4$	32.30	55.67	50.79	34.77	12.09	7.95	4.82	1.61
5	$MgSm_{0.1}Fe_{1.9}O_4$	30.71	55.98	54.49	31.51	7.51	9.99	7.29	2.52

IV. Conclusion:

i) X-ray diffraction pattern of the prepared samples confirms the formation of single phase cubic spinal structure
ii) By the substitution of Sm in the Mg ferrite system, the lattice parameter is decreases and the crystallite size of the sample was in the range 51-62 nm.
iii) X-ray density of the samples increases with Sm Substitution.
iv) SEM micrographs of the various compositions indicate the morphology of the particles was similar. They are largely agglomerated.

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