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Structure, Morphology and Chemical Synthesis of $Mg_{1-x}Zn_xFe_2O_4$ Nano-Ferrites Prepared by Citrate-Gel Auto Combustion Method

D.Ravikumar[1,] B.Kiran Kumar[1], D.Ravinder[2*], Ch.Abraham Lincoln[1*].
1.Department of Chemistry, Osmania University, Hyderabad 500007,Andhrapradesh India
2.Department of Physics, Nizam college, Basheerbagh, Osmania University Hyderabad 500001,Andhra Pradesh,India.

ABSTRACT
Mg-Zn Nano ferrites having chemical formula $Mg_{1-x}Zn_xFe_2O_4$(where x=0.0, 0.2, 0.4, 0.6, 0.8, 1.0) were synthesized by the citrate-gel auto combustion method. Synthesized powders were sintered at 500^{o}C for four hours in air and characterized by XRD, SEM and EDS.XRD analysis shows that cubic spinal structure of the ferrites and the crystalline sizes (D) were found in the range 25-35 nm. The values of the lattice parameter (a) increases and X-ray density (d_x) increases with doping of Zn content. Scanning Electron Microscopy (SEM) studies revealed Nano nature of the samples. An elemental composition of the samples was studied by using Energy Dispersive Spectroscopy (EDS). The observed results can be explained on the basis of composition and crystallite size.
Keywords: Mg-Zn Nano- Ferrites; Citrate Gel Auto Combustion Method; X-Ray Diffraction; Scanning Electron Microscope; Energy Dispersive Spectroscopy.

I. Introduction:

Research on nanoparticles has opened as avenue for various potential applications due to their novel properties. More specifically materials with nano scale dimensions 1-100 nm show extraordinary physical and chemical properties. The reduction in the size of the particles leads to increase in relative surface area which results the increase in the surface to volume ratio. The quantum size effect and the large surface area of nanoparticles dramatically change some of the magnetic properties and exhibit super paramagnetic phenomena and quantum tunnelling of magnetization, because each particle behaves as single magnetic domain [1]. Nanomaterials therefore play a very prominent role in physical, chemical and biomedical applications due to their high surface energies. Among such materials Ferrites are useful magnetic materials because of their versatility, low cost and high electromagnetic performance over a wide frequency range [2]. Spinel type ferrites are commonly used in many electronic and magnetic devices due to their high magnetic permeability and low magnetic losses [3]. Usually ferrite materials have low conductivity i.e. high resistivity which greatly influences the dielectric and magnetic behaviour of ferrites [4]. Due to their high thermodynamic stability, low electrical conductivity magnetic properties of the nanosized ferrites are entirely different from those of their bulk counterparts, such as the super paramagnetic behaviour and the associated applications, magnetic data storage, etc [6].

Magnesium ferrite belongs to a class of compounds having the general formula $M^{+2}Fe^{+3}{}_2O_4$ (and also AB_2O_4) crystallizing with Spinel structure (where M represents tetrahedral site and Fe represents the octahedral site)[7]. The interesting properties of Spinel ferrites arise from their ability to distribute the cations among the Tetrahedral (A) and Octahedral (B) sites [8].For obtaining the specific properties ferrites can be fabricated by substituting various magnetic and non-magnetic ions which greatly affect the magnetic moments, lattice parameters and exchange interactions [9,10]. Magnesium nano ferrites are the potential materials for various applications due to their high electrical resistivity, low magnetic and dielectric losses. [11, 12]. Doping of $MgFe_2O_4$ with one or several metals is the best method to alter its properties. Several researchers have reported the synthesis of Mg-Cr ferrites using different techniques such as Double Sintering technique [13], Solid state ceramic sintering technique [14], Micro emulsion method [15], Co precipitation technique [16]. To my knowledge a little information is available about the nano sized Mg-Zn ferrites formed by Citrate-Gel Auto combustion method. The Citrate-Gel method is a simple process which speeds up the synthesis of complex materials. This method offers significant saving in time, energy consumption over the traditional methods. In this method the metal ions or

complexes are immobilized on atomic scale which allows obtaining oxides at temperature lower than that produced in solid state reaction. This method also produces homogeneous and stochiometricoxides[17].

In this work we prepared Nano-ferrites of the composition

$Mg_{1-x}Zn_xFe_2O_4$ (where x=0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) by Citrate –Gel auto combustion method with a very low particles size with the assumption that the magnetic, electrical and dielectric properties would be improved by substitution of Zn with Mg ions. As per the authors knowledge it is the first observation of Mg-Zn nano ferrites obtained with low particles size by citrate-gel auto combustion method. In this paper, we present the Synthesis, XRD, SEM and EDS studies of zinc doped Magnesium ferrites using the Citrate-Gel auto combustion Method.

II. Experimental:

2.1 Materials:

Mg-Zn Nano ferrites having the chemical formula $Mg_{1-x}Zn_xFe_2O_4$ (where x=0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) were synthesized by Citrate-Gel auto combustion technique using magnesium nitrate ($Mg(NO_3)_26H_2O$, 99%, SD Fine Chem. Ltd. Mumbai, India), ferrite nitrate ($Fe(NO_3)_29H_2O$, GR grade, Otto Chemie Pvt. Ltd. Mumbai, India), Zinc nitrate ($Zn(NO_3)_26H_2O$, GR grade, Otto Chemie Pvt. Ltd. Mumbai, India) and Ammonia (NH_3, AR grade, SD Fine Chem. Ltd. Mumbai, India).

Chemical Reaction:

$$Mg(NO_3)_26H_2O + 2Fe(NO_3)_29H_2O + C_6H_8O_7H_2O \longrightarrow MgFe_2O_4 + 29H_2O + 4N_2 + 6CO_2 + 5.5O_2$$

2.2 Synthesis:

Calculated quantities of above nitrate salts were dissolved in double distilled water and required amount of aqueous citric acid solution was added as chelating agent. The mixture was thoroughly stirred to get a homogeneous solution. Ammonia solution was added to this nitrate-citrate mixture to adjust the pH to 7. The mixed solution was heated at about 100^oC with uniform stirring and evaporated to obtain a highly viscous gel denoted as precursor. The resultant gel was further heated on a hot plate maintained at a temperature of 180^oC to 200^oC. When finally all water molecules were removed from the mixture, the viscous gel began frothing. The gel gave a fast flameless auto combustion reaction with the evolution of large amounts of gaseous products (shown in the above chemical reaction). It started in the hottest zones of the beaker and propagated from the bottom to the top like eruption of a Volcano. The reaction was completed in a minute giving rise to dark grey voluminous product with a structure similar to Branched Tree. Finally the burnt powder was ground and was calcined in air at temperature 500^oC for four hours to obtain a spinal phase.

2.3 Characterisation:

The structural characterization of the synthesized samples was carried out by Rigaco X ray diffractometer using Cu Kα radiation (λ=1.5405A^0) at room temperature by continuous scanning in the range of 5^0 to 80^0at the scanning rate of 0.02^0 per sec to investigate the phase and crystallite size. The Morphology of the samples was studied by Scanning Electron Microscope (SEM). Elemental analysis was carried out by using Energy Dispersive Spectroscopy (EDS).

III. Results and Discussions:

3.1 XRD Analysis:

The structural characterization of all the nano-ferrites was carried out by X-Ray Diffraction. From the analysis of the 2theta and intensity data was used and graphs were plotted as shown in Fig1. The X-Ray Diffraction pattern, crystalline phases were identified by comparison with reference data from the ICDD card No. 71-1232 for Magnesium ferrites. All Bragg reflections have been indexed which confirms the formation of a well-defined single phase cubicSpinel structure without any impurity peak.

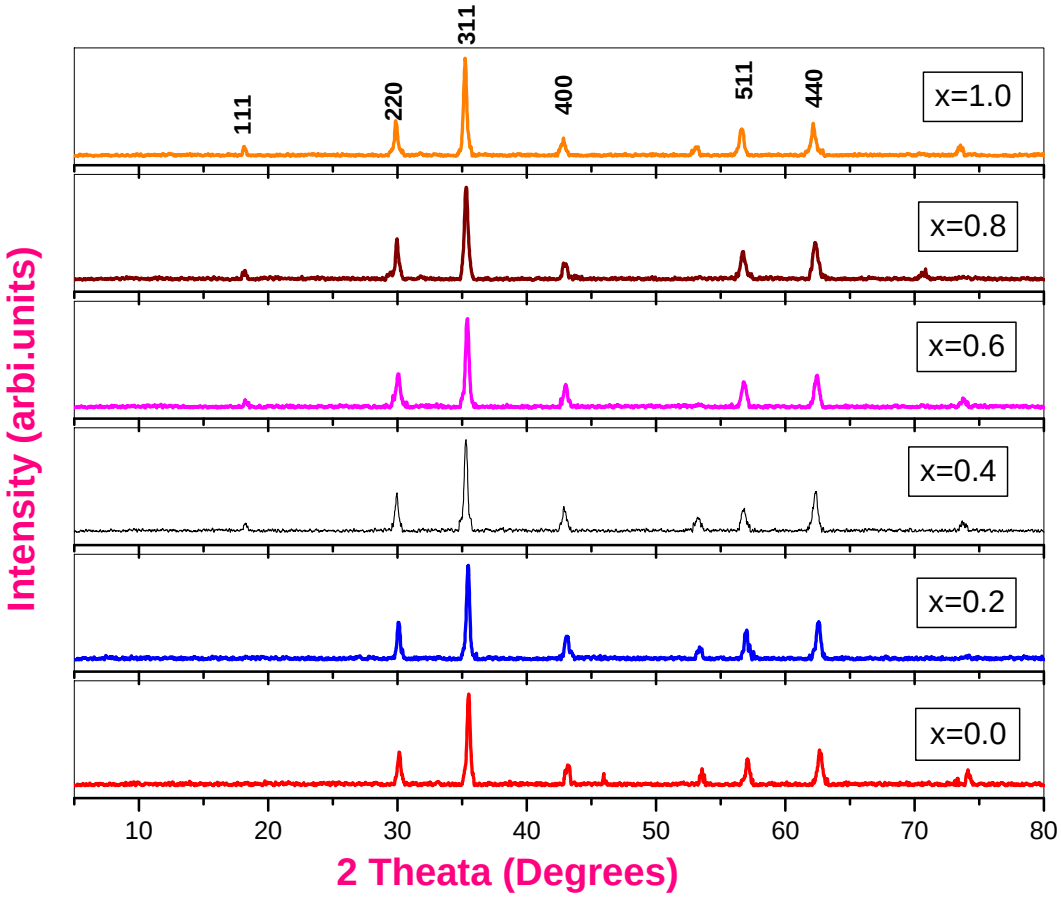

Figure 1.XRD patterns of $Mg_{1-x}ZnFe_2O_4$ nano ferrites

The crystallite size (D) was calculated for all the composition using maximum intensity peak fromScherrer's formula [18].

Crystallite size = D = 0.91λ/βCosθ

Where λ = wavelength of X-Ray; β = Full width half maximum (radians);

θ = Bragg's angle at the peak position

The crystallite size was in the range of 25 nm to 35 nm (shown in the **Table 1**) for different composition Conventional methods need a very high temperature and prolonged heating time [13, 14]. Advantages of Citrate gel method over the conventional methods are (i) simple and economic method (ii) use of relatively simple equipment (iii) formation of high purity products (iv) good stoichiometric control (v) production of ultra-fine particles with a narrow size distribution (vi) short processing time (vii) very low processing temperature (viii) low sintering temperature.

Table1. $Mg_{1-x}Zn_xFe_2O_4$ Nano Ferrites Particle size &Latice parameter

Name of the composition	Particle size(D) nm	Latice parameter(A) nm
$MgFe_2O_4$	34.55	8.356
$Mg_{0.8}Zn_{0.2}Fe_2O_4$	34.97	8.384
$Mg_{0.6}Zn_{0.4}Fe_2O_4$	30.42	8.394
$Mg_{0.4}Zn_{0.6}Fe_2O_4$	29.17	8.396
$Mg_{0.2}Zn_{0.8}Fe_2O_4$	26.58	8.400
$ZnFe_2O_4$	25.85	8.407

Lattice parameter (a) of the individual composition was calculated by using the following formula and were tabulated in **Table1**

$a = d * \sqrt{h^2 + k^2 + l^2}$

Where, a = lattice parameters; d = interplanar spacing and
h k l are the miller indices

A plot of the lattice parameters Vs compositions is shown in **Fig.2**, which indicates the variation of the lattice parameter with composition. The lattice parameters are found to decrease linearly with increase of ions in the Mg-Zn nano-ferrites system indicating that the system obeys Vegard'sLaw [19].

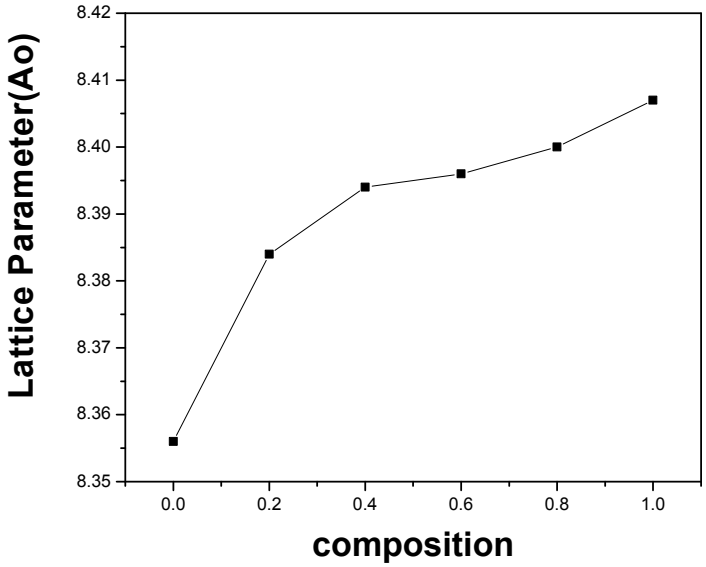

Figure2.Variation of latice parameter with composition for Mg-Zn nano-ferrites

The X-Ray density (d_x) is calculated using the following formula [20] and were tabulated in **Table2**

X-Ray density (d_x) = $8M / Na^3$ (gm/cc)

Where, M = molecular weight of the sample

N = Avogadro's number

a = lattice parameter

Table2. Density and unitcell volume of $Mg_{1-x}Zn_xFe_2O_4$ nano ferrites with composition

Name of the composition	Densitygm/cm^3	Unit cell Volume $(A^o)^3$
$MgFe_2O_4$	4.52	583.438
$Mg_{0.8}Zn_{0.2}Fe_2O_4$	4.692	589.323
$Mg_{0.6}Zn_{0.4}Fe_2O_4$	4.84	591.434
$Mg_{0.4}Zn_{0.6}Fe_2O_4$	5.064	591.857
$Mg_{0.2}Zn_{0.8}Fe_2O_4$	5.205	592.704
$ZnFe_2O_4$	5.4021	594.187

A plot of the x-ray density (d_x) Vs compositions is shown in **Fig3.** The X-Ray density depends on the lattice parameters.. From the plot it is observed that X-Ray density increase with increase in Zn content (x), this is because the decrease in mass overtakes the decrease in volume of unit cell. Hence X-Ray density is increased with increase in Zn content.

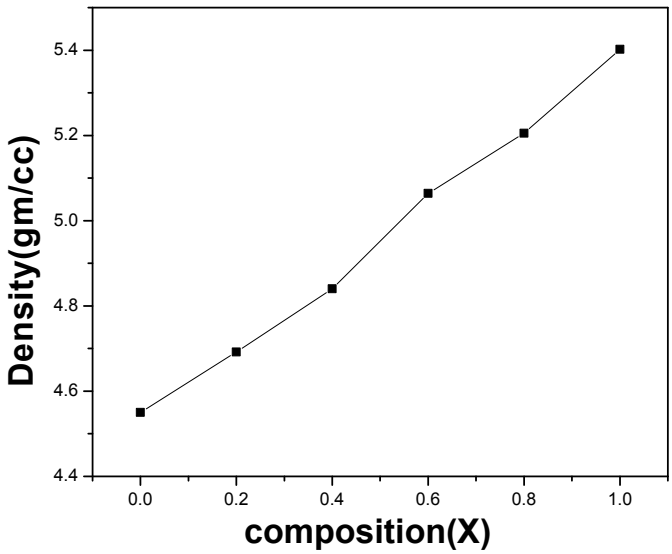

Figure 3.Variation of x-ray density with composition

Volume of the unit cell is calculated as $V=a^3$
The calculated values are tabulated in **Table 2.** It is observed that volume of this unit cell increases with increase in Zn content. It is because Volume of the unit cell depends on the lattice parameter which increases with increase in Zn content. The X-Ray density (d_x) and volume of the unit cell (V) of Magnesium Ferrite were in good agreement with the reported values 4.518 gm/cc and 588.06$(A^0)^3$ from ICDD data.

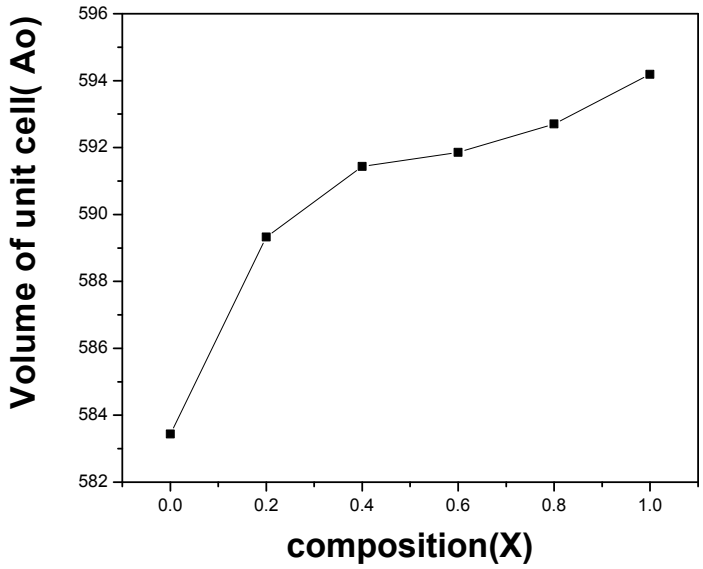

Figure4. Variation of Volume of the unit Cell with composition

The distance between magnetic ions (hopping length) in A site (Tetrahedral) and B site (Octahedral) were calculated by using the following relations [21].

$d_A = 0.25a\sqrt{3}$ *and* $d_B = 0.25a\sqrt{2}$

Where 'a' is lattice parameter

The values of the Hoping length for tetrahedral site (d_A) and octahedral (d_B) were tabulated in **Table 3.**

Table3. values of hopping length d_A and d_B of $Mg_{1-x}Zn_xFe_2O_4$ nano ferrites with composition

Name of the composition	d_a	d_B
$MgFe_2O_4$	3.618	2.954
$Mg_{0.8}Zn_{0.2}Fe_2O_4$	3.63	2.964
$Mg_{0.6}Zn_{0.4}Fe_2O_4$	3.634	2.967
$Mg_{0.4}Zn_{0.6}Fe_2O_4$	3.635	2.968
$Mg_{0.2}Zn_{0.8}Fe_2O_4$	3.637	2.969
$ZnFe_2O_4$	3.64	2.972

The relation between hopping length for Octahedral and Tetrahedral sites as a function ofZn content (x) was shown in **Fig.4**. It is observed that the distance between the magnetic ions increases as the Zn content increases. It may be explained due to the fact that Mg ion has smaller radius ($0.714A^0$) than Zn ion i.e. ($0.828A^0$) which makes the magnetic ions become closer to each other and hopping length decreases.

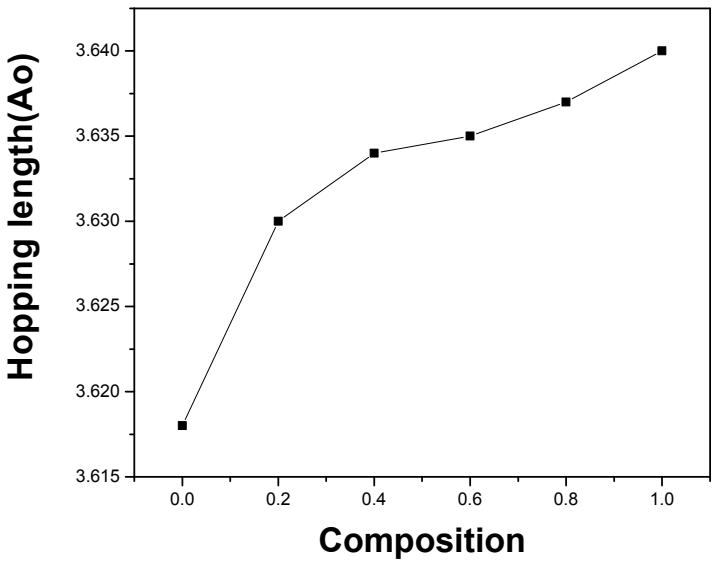

Figure4. Variation of hoping length d_A with composition

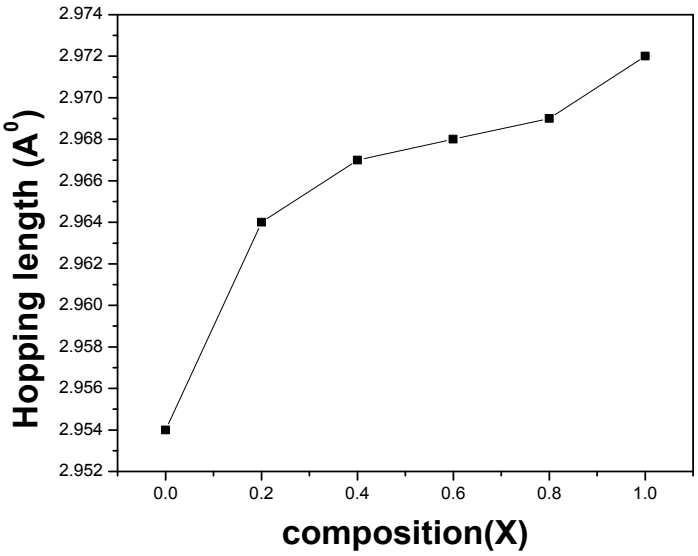

Figure5. Variation of hoping length d_B with composition

3.2Morphology by SEM:

The morphological analysis was performed using SEM (Scanning Electron Microscope). The secondary electron images were taken at different magnifications to study the morphology by SEM.Fig.6 shows SEM representative micrographs of the sample with different amounts of substitution.

It can be seen from SEM micrographs of various compositions that the morphology of the particles is similar. They reveal largely agglomerated, well defined nano particles of the sample powder with inhomogeneous broader grain size distribution. Such broader size distribution is characterized of mechanically activated nano sized particles. The agglomeration of particles is also because they experience a permanent magnetic moment proportional to their volume [22].

Heating results in the well-faced grains to form solid bodies. It is a porous network of sintered bodies' exhibiting foam like structure.

An enlarged mass of compound formation was observed due to the influence of magnesium ions.

The SEM micrographs also indicate that the particle size of the sample lies in the nanometer region. They indicate that with increase in Zn composition the grain size decreased (from x = 0 to x = 1).

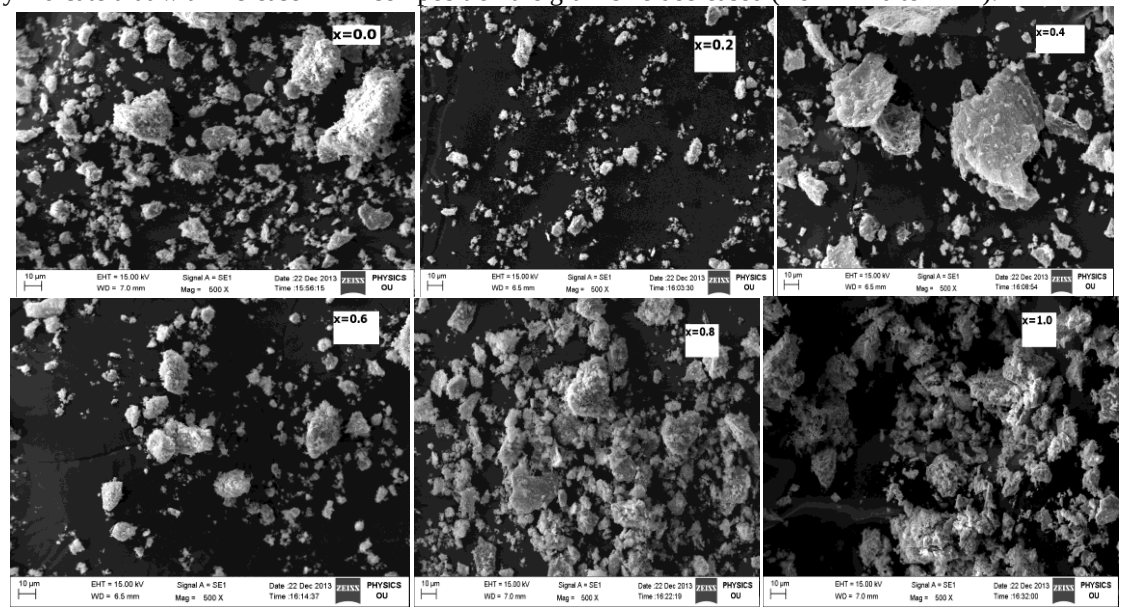

Figure5SEM Diagrams of Mg-ZnNano Ferrites

3.3 Elemental Analysis by EDS:

The elemental analysis of all the Mg-Zn nano ferrite samples with different composition was analyzed by an Energy Distribution Spectrometer (EDS) and the weight % and atomic % of various elements in the samples were shown in **Table4**.

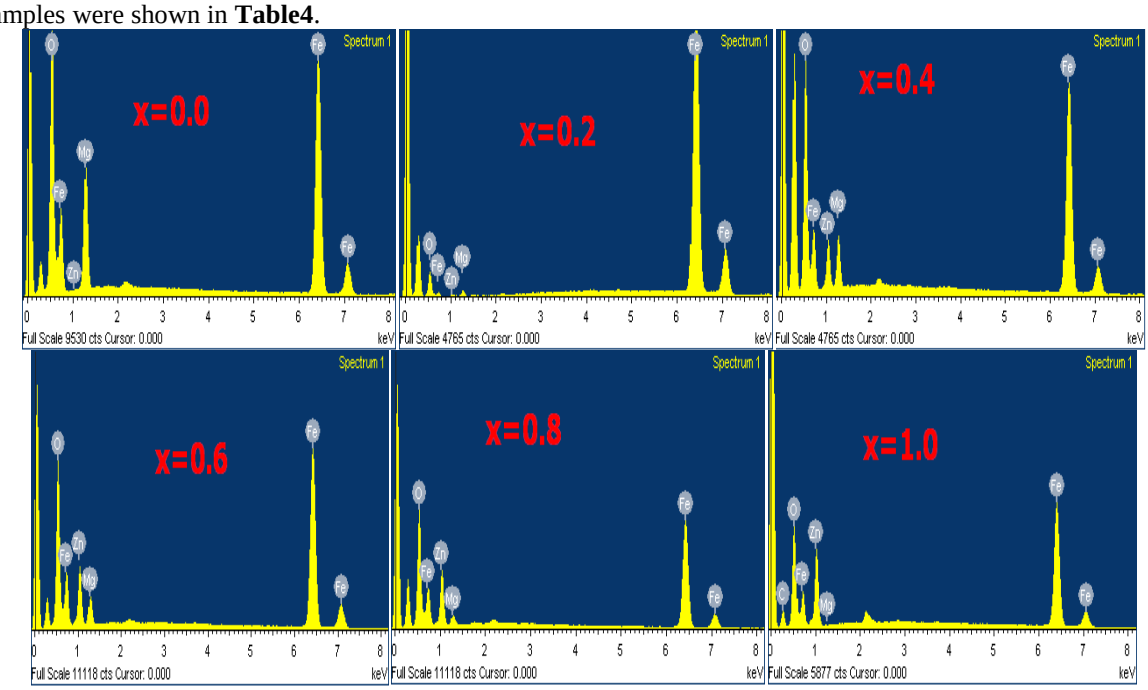

Figure6. $Mg_{1-x}Zn_xFe_2O_4$ EDS with composition

Table 4.Elements of each sample composition analysed by % of weight and atomic % obtained by EDS

Element → / FerriteComposition ↓	O		Fe		Mg		Zn	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
$MgFe_2O_4$	36.37	61.56	51.56	25.00	2.06	3.44	0.00	0.00
$Mg_{0.8}Zn_{0.2}Fe_2O_4$	5.47	16.81	84.78	74.61	0.98	1.98	8.77	6.59
$Mg_{0.6}Zn_{0.4}Fe_2O_4$	34.85	62.99	47.00	24.34	6.21	7.38	11.94	5.28
$Mg_{0.4}Zn_{0.6}Fe_2O_4$	30.49	59.46	47.30	26.42	4.36	5.60	17.85	8.52
$Mg_{0.2}Zn_{0.8}Fe_2O_4$	32.98	63.26	43.13	23.70	2.31	2.91	21.58	10.13
$ZnFe_2O_4$	16.08	41.05	60.55	44.29	0.00	0.00	23.32	14.57

Conclusions

- Citrate-Gel Auto Combustion Technique is a convenient way for obtaining a homogeneous nano sized mixed Mg-Zn ferrites.
- The process involves no impurity pickup and material loss. It is a very simple and economical method where no specific heating or cooling rate is required. It is a low temperature processing technique and shorter sintering time duration.

- X-Ray Diffraction pattern confirms the formation of cubic Spinel structure in single phase without any impurity peak. It is in good agreement with the standard data from ICD.
- The size of various Mg-Zn Nano- ferrites was in the range of 20-35nm.
- The lattice parameters are increases with the increase of Zn substitution in Mg-Znferrites which indicates that the mixed Mg-Zn nano-ferrite system obeys Vegard's Law.
- SEM micrographs of various compositions indicate the morphology of the particles is similar. They reveal largely agglomerated, well defined nano particles of the sample powder with inhomogeneous broader grain size distribution.
- EDS data gives the elemental % and atomic % in the mixed Mg-Zn ferrites and it shows the presence of Mg, Zn, Fe and O without sprecipitating cations.

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