International Journal of Engineering Science Invention (IJESI)
ISSN (Online): 2319 – 6734, ISSN (Print): 2319 – 6726
www.ijesi.org || PP. 45-49

Structural And Ftir Studies Of $Mg_{0.6}zn_{0.4}fe_2o_4$ Ferrite Nanoparticles Prepared By Sol–Gel Auto Combustion Method

M. Deepty[a,A#], S. A. V. Prasad[a], M. V. K. Mehar[b], B. V. Tirupanyam[c], Ch. Srinivas[a,]*, N. Krisha Mohan[d,*], K. Vijaya Babu[e,*]
a Department of Physics, Sasi Institute of Technology & Engineering, Tadepalligudem 534 101, India.
a# Department of Physics, Krishna University, Machilipatnam 521 001, India.
b Department of Physics, Government Degree College, Alamuru 533 233, India.
cDepartment of Physics, Sri Aravinda Satajayanthi Government Degree College, Narayanapuram 533 401, India.
d Department of Physics, Akkineni Nageswara Rao Degree college, Gudiwada, 521 301, India.
e Advanced Analytical Laboratory, Andhra University, Visakhapatnam 530 003, India.
Corresponding authors: M. Deepty

Abstract: *Nanoferrites with chemical equation $Mg_xZn_{1-x}Fe_2O_4$ (x = 0.5, 0.6, 0.7) have been prepared by sol-gel autocombustion method. In the present paper structural and morphological studies of $Mg_{0.6}Zn_{0.4}Fe_2O_4$ ferrite nanoparticles were reported. The X-ray diffractogram confirmed the spinel structure of ferrite phase. The traces of secondary phases are also evident. The vibrational frequencies observed in FTIR spectrum are consistent with the spinel structure as observed from XRD studies. The broadening of vibration bands is due to the presence of ultrafine particles in the ferrite sample. The SEM picture revealed the agglomeration of nanoparticles with strong magnetic interactions. The present ferrite particles may exhibit superparamagnetism and are supposed to be potential candidates for biomedical applications. The results are discussed presuming the cation redistribution and with the reported literature.*

Keywords – *XRD; FTIR; Ferrite nanoparticle; Secondary phases*

I. Introduction

Spinel ferrites having nanodimension crystallites have been intensively studied due to their versatile utility ranging from scientific and engineering to biomedical applications [1,2]. Nanoferrites exhibit unique properties like spin-glassy behaviour, single domain structure, superparamagentism, etc. [3]. The ferrite nanoparticles possessing critical domain structure with low magnetic anisotropy can show superparamagntism [3]. The preparation of ferrite nanoparticles with superparamagnetic behaviour is a challenging task. However, apart from the controlling the size of nanoparticles to critical domain size, but by proper choice of dopants in the spinel structure we can manifest the magnetocrystalline anisotropy to show superparamagnetism. In this scenario Mg-Zn ferrite is believed to be a potential candidate to possess low magnetocrystalline anisotropy due to diamagnetic character of magnesium (Mg) and zinc (Zn)[4]. These ferrite nanoparticles with superparamagentic behavoiur are supposed to be well suited for bio-medical applications like cancer treatment through hyperthermia [4].

Spinel ferrite with formula unit $(Fe_{1-\delta}M_{\delta})[Fe_{1+\delta}M_{1-\delta}]O_4$ is classifying into two spinel structures of normal spinel for δ=1 and inverse spinel for δ=0 [5]. It was well established that the zinc ferrite ($ZnFe_2O_4$) is a normal spinel and magnesium ferrite ($MgFe_2O_4$) is an inverse spinel. The magnetization of Zn-ferrite is zero due to diamagnetic nature of Zn^{2+}. Since Mg^{2+} is diamagnetic, we can expect the magnetization of Mg-ferrite is zero. But it was reported that the Mg-ferrite has a magnetic moment of 1.1 μ_B, showing that the Mg-ferrite is partly inverted with inversion parameter 0.1 [6]. Therefore, these interesting behaviours in Zn- and Mg- ferrittes enables us to study the some physical properties of mixed spinel of Mg-Zn ferrite.

In the present study, the ferrite nanoparticles of $Mg_{0.6}Zn_{0.4}Fe_2O_4$ were prepared by using sol-gel auto combustion method. The sample powder was characterized by using X-ray diffractometer (XRD), Fourier Transform Infrared Spectrometer (FTIR) and scanning electron microscope (SEM). In the present paper the studies of structural and IR analysis are reported. The results are discussed in comparison with the supported documents.

II. Experimental Methods

2.1 Synthesis:

pinel ferrite with chemical formula $Mg_{0.6}Zn_{0.4}Fe_2O_4$ was prepared by sol–gel auto combustion method. Analytical grade magnesium sulfate ($MgSO_4H_2O$), zinc sulfate ($ZnSO_47H_2O$) and ferric nitrate ($Fe(NO_3)_39H_2O$) are taken as precursors and citric acid ($C_6H_8O_7H_2O$) is used fuel for auto combustion. The molar ratio of metal ions to citric acid is taken as 1:1 in this synthesis. The method of preparation has been described elsewhere [7]. The obtained sample was characterized by X-ray diffractometer (XRD), Fourier Transform Infrared spectrometer (FTIR) and scanning electron microscope (SEM).

2.2 Instrumentation:

- The XRD pattern was recorded at room temperature using PANalytical X'pert-PRO X-ray powder diffractometer with CuK_α ($\lambda = 1.5406$ Å) as a target.
- The morphology of the sample was examined from the SEM micrograph recorded by using JEOL JSM-6610L scanning electron microscope.
- Shimadzu IR-Prestige21 spectrometer has been used to record IR spectra for the ferrite samples in the range of 400 cm^{-1} to 4000 cm^{-1}.

III. Results and Discussion

3.1 XRD studies:

The X-ray diffractogram of $Mg_{0.6}Zn_{0.4}Fe_2O_4$ is shown in Fig.1. The diffractogram revealed the spinel structure of ferrite sample. The indexed planes (220), (311), (400), (511), (440) are on consistent with JCPDS no.71–1232 belonging to *Fd3m* space [8]. The traces of detectable antiferromagnetic phase of α-Fe_2O_3 are clearly evident from the diffractograms. It was also observed that the traces of secondary phases are intensive indicating the presence of higher amounts of secondary phases along with the ferrite phase. This is ascribed to the decomposition of ferrite phase into the secondary phases. The line broadening of the diffraction peaks is due to presence of different crystallite sizes, lattice defects, voids, etc. In the present study we can expect the major contribution for the line broadening is due to the presence of crystallites of different sizes with nanoscale dimensions.

Experimental lattice parameter (a) in the present study was calculated using the formula

$$a = d\sqrt{h^2 + k^2 + l^1} \qquad (1)$$

Where d is interplanar spacing and h, k, l is Miller indices.

The crystallite sizes are estimated using the Debye–Sherrer formula as given by

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad (2)$$

Where λ is wavelength of X-ray beam, β full width at half maximum (FWHM), θ is Bragg's scattering angle, K is shape factor (0.89).

The calculated values of experimental lattice parameter (a), crystallite size (D), interplanar spacing (d), full width at half maxima (β) are listed in Tab.1. It was well established that Zn-ferrite is a normal spinel ferrite and Mg-ferrite is a partly inverse spinel with inversion parameter $\delta = 0.1$ for Fe^{3+} ions [6]. Basing on these considerations the cation distribution in the present ferrite system can be expected as $(Mg_{0.06}Zn_{0.4}Fe_{0.54})[Mg_{0.54}Fe_{1.46}]O_4$. The theoretical lattice parameter (a_{th}) listed in Tab.1 was calculated according to the proposed cation distribution. In the materials possessing nanodimension particles, due to the frustration of spins with broken symmetry, the change in binding energy happens. This results in uneven distribution of ions in the lattice. It was observed that the experimental lattice parameter is less than the theoretical lattice parameter. Moreover, it was also observed that the lattice parameter in the present is less than

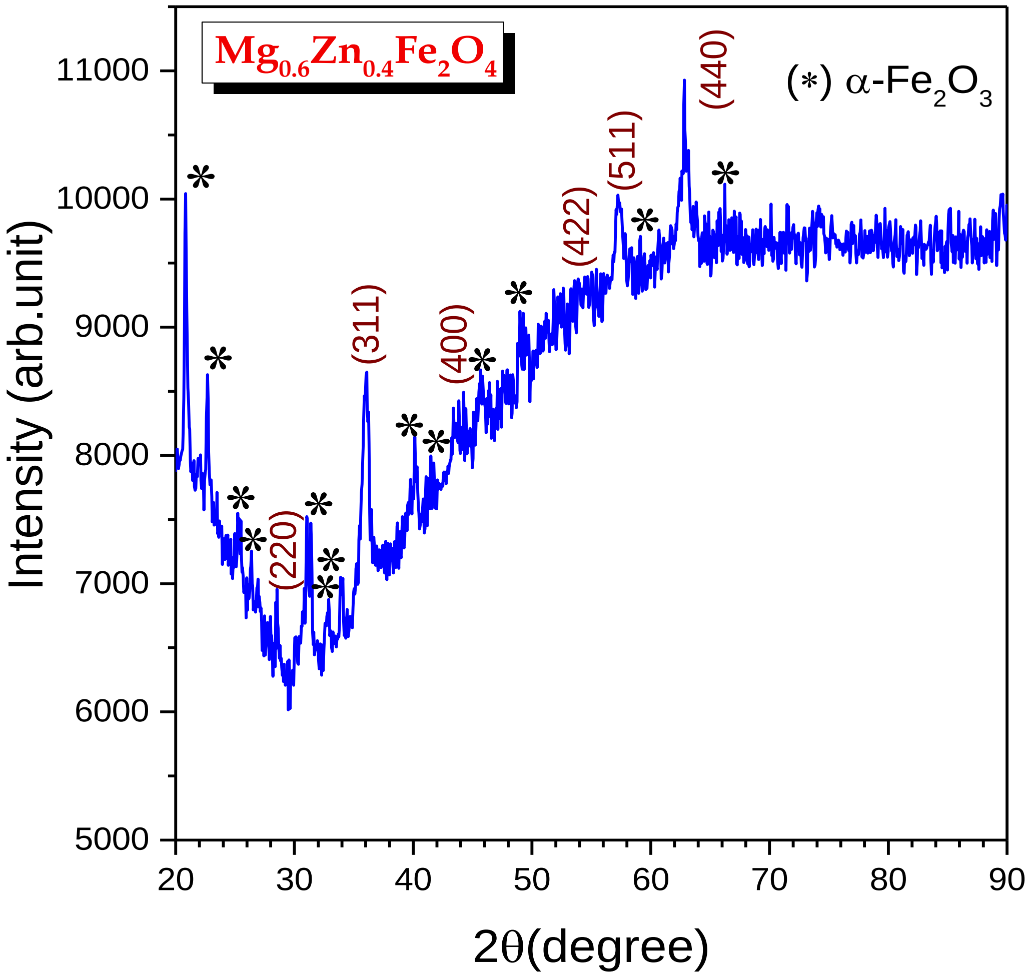

Fig.1 XRD **pattern of $Mg_{0.6}Zn_{0.4}Fe_2O_4$ and asterisk (*) represents secondary phase of □-Fe_2O_3**

our previous [9] reported value of lattice parameter (8.452Å) for the similar composition prepared by co-precipitation technique. In light of these, it was argued that cation distribution is predominating in the present ferrite system against to the stoichiometry of proposed cation distribution. The presence of the core-shell behaviour is affecting the structural properties of present ferrite system.

3.2 FTIR studies:

Fourier Transform Infrared spectroscopy (FTIR) is a power tool to probe the different functional groups present in the material. The FTIR spectrum of $Mg_{0.6}Zn_{0.4}Fe_2O_4$ is depicted in Fig.2. In general, the cubic spinel ferrites are characterized by four vibrational frequencies υ_1 , υ_2 , υ_3 and υ_4 . The first three vibrational frequencies are due to the M–O complexes at tetrahedral (*A*) and octahedral (*B*) sites whereas fourth one is due to lattices vibrations [10]. According to Waldron, the vibrational frequency υ_1 is attached to the tetrahedral site (*A*) with higher vibrational frequency in the range (450–600 cm^{-1}) and the vibrational frequency υ_2 is attached to the octahedral site (*A*) with lower vibrational frequency in the range (350–450 cm^{-1}) [11]. The vibrational frequencies listed in the Tab.1 are reliable to confirm cubic spinel phase of the ferrite system. The reported values of vibrational frequencies [9] in our previous study for the similar composition are less than the present values supporting the variation of lattice parameter. The broadening of octahedral site is obviously evident from the IR spectrum. This is attributed to the presence of ultrafine particles in the sample supporting the observation is given in the XRD studies. The other vibrational frequencies in the IR spectrum are in the line of absorbed water in the sample during the synthesis and evaluation of CO_2, CO, SO_2, C–H.

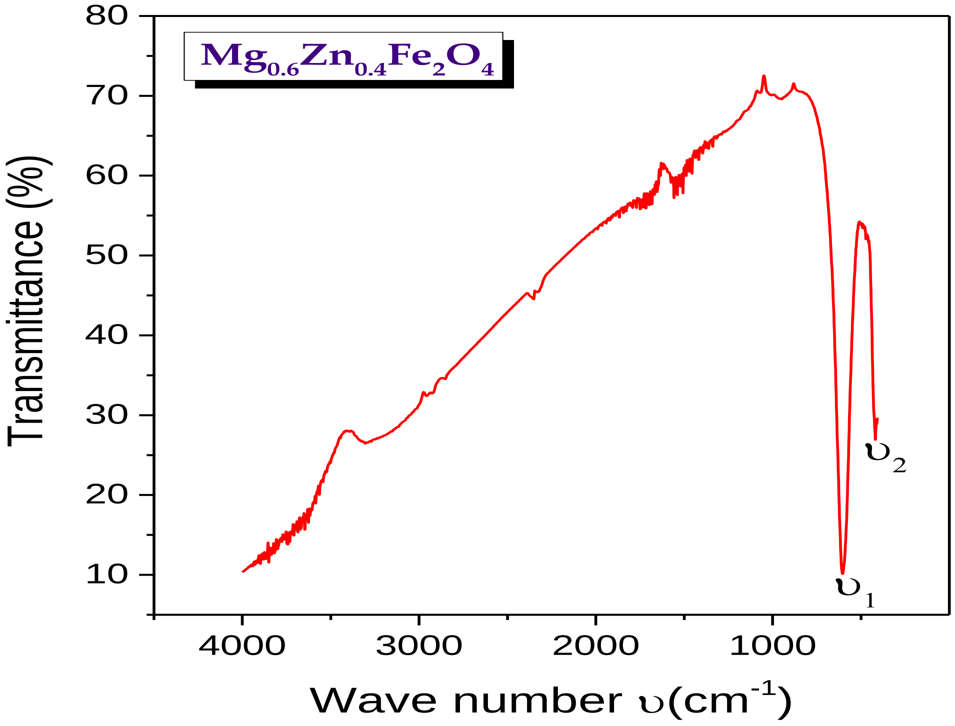

Fig.2 FTIR spectrum of $Mg_{0.6}Zn_{0.4}Fe_2O_4$

3.2 SEM studies:

The SEM micropicture of $Mg_{0.6}Zn_{0.4}Fe_2O_4$ is shown in Fig.3. From the SEM picture the size of ferrite nanoparticles have not been estimated due to the strong agglomeration of the nanoparticles into big clusters. But the microscopic examination revealed the diffusion of the clusters, indicating the presence of distribution of ferrite particles in different sizes. This supports the broadening of the octahedral vibrational frequency due to presence of ultrafine particles distribution of different sizes.

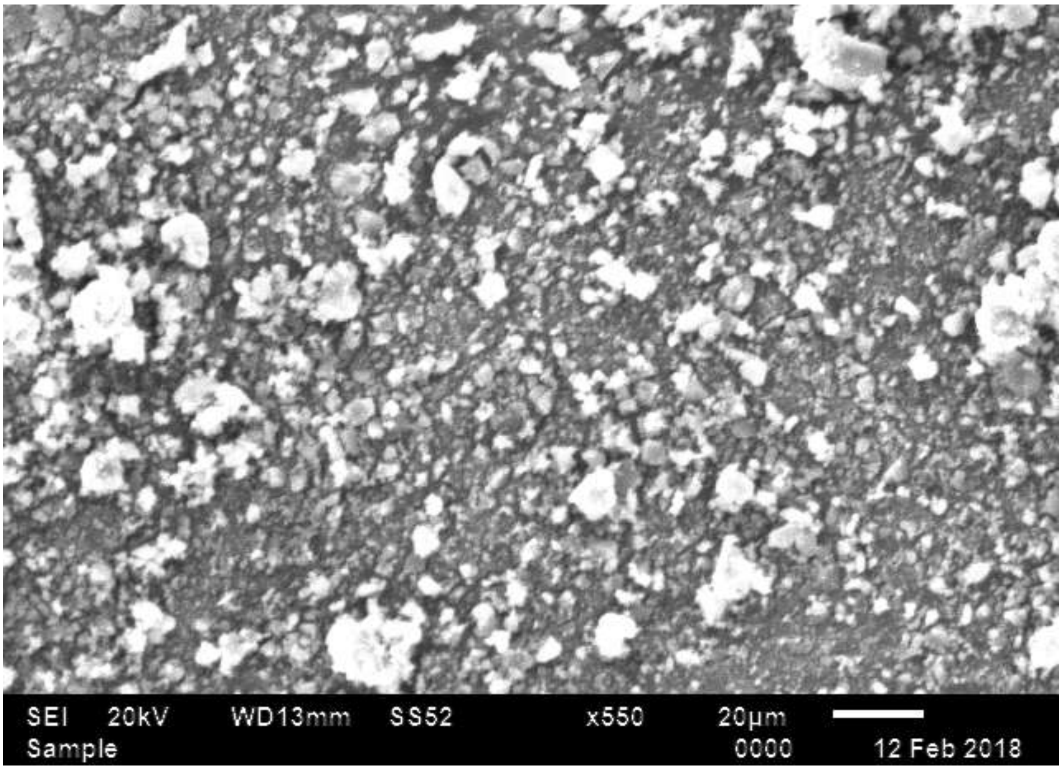

Fig.3 SEM picture of $Mg_{0.6}Zn_{0.4}Fe_2O_4$

Tab.1 FWHM, Bragg's angle, interplanar spacing, crystallite size, experimental and theoretical lattice parameter, higher and lower vibrational frequencies

Composition	β (radian)	2θ	(hkl)	d (Å)	D (nm)	D_{ave} (nm)	a (Å)	a_{th} (Å)	υ_1 (cm^{-1})	υ_2 (cm^{-1})
$Mg_{0.6}Zn_{0.4}Fe_2O_4$	0.0123	31.08	(220)	2.875	11.6	12.3	8.345	8.393	598.93	418.55
	0.0109	36.03	(311)	2.491	13.2					
	0.0115	43.38	(400)	2.084	12.8					
	0.0144	57.23	(511)	1.608	10.8					
	0.0121	62.83	(440)	1.478	13.3					

IV. Conclusion

The spinel ferrite with chemical composition $Mg_{0.6}Zn_{0.4}Fe_2O_4$ has been successfully prepared by sol-gel auto combustion method. On comparison with our earlier reported values of similar composition, core-shell morphology of fine particle effects was clearly evident. This core-shell morphology of ferrite nanoparticles is affecting the structural parameters in the present ferrite system, leading to cation redistribution. This cation redistribution drastically affects the magnetic anisotropy of the ferrite nanoparticles. The present ferrite nanoparticles are supposed possessing low magnetic anisotropy showing superparamagnetism are suitable for bio-medical applications and high density storage materials.

References

[1] A. E. Saba, E. M. Elsayed, M. M. Moharam, M. M. Rashad, R. M. Abou-Shahba, Structure and magnetic properties of $Ni_xZn_{1-x}Fe_2O_4$ thin films prepared through electrodeposition method, J. Mater. Sci 46 (2011) 3574–3582.

[2] Jitendra Pal Singh, Gagan Dixit, R. C. Srivastava, Hemant Kumar, H. M. Agrawal, Prem Chand, Magnetic resonance in superparamagnetic zinc ferrite, Bull. Mater. Sci. 36 (4) 2013 751–754.

[3] I. Nedkov, R.E.Vandenberghe, A.Zaleski, Surface magnetic disorder in nanostructured $Ni_{0.5}Zn_{0.5}Fe_2O_4$ particles, J. Magn. Magn. Mater. 322 (2010) 2732–2736.

[4] [4] S. B. Singh, Ch. Srinivas, B. V. Tirupanyam, C. L. Prajapat, M. R. Singh, S. S. Meena, Pramod Bhatt, S. M. Yusuf, D. L. Sastry, Structural, thermal and magnetic studies of $Mg_xZn_{1-x}Fe_2O_4$ nanoferrites: Study of exchange interactions on magnetic anisotropy, Ceram. Int. 42 (2016) 19188 –19195.

[5] J. Smit, and H. P. J. Wijn, Ferrites (Philips Technical Laboratory, Netherlands, 1959)

[6] A. Franco. Jr, M. S. Silva, High temperature magnetic properties of magnesium ferrite nanoparticles, J. Appl. Phys. 109(2011)07B505-3.

[7] Ahmad Gholizadeh, Elahe Jafari, Effects of sintering atmosphere and temperature on structural and magnetic properties of Ni-Cu-Zn ferrite nano-particles: Magnetic enhancement by a reducing atmosphere, J. Magn. Magn. Mater. 422(2017)328–336.

[8] M. Raghasudha, D. Ravider, P. Veerasomaiah, Investigation of superparamagnetism in MgCr0.9Fe1.1O4 nano-ferrites synthesized by the citrate – gel method, J. Magn. Magn. Mater. 355(2014) 210–214.

[9] S. B. Singh, Ch. Srinivas, B. V. Tirupanyam, C. L. Prajapat, M. R. Singh, S. S. Meena, Pramod Bhatt, S. M. Yusuf, D. L. Sastry, Structural, thermal and magnetic studies of $Mg_xZn_{1-x}Fe_2O_4$ nanoferrites: Study of exchange interactions on magnetic anisotropy, Ceram. Int .42(2016)19188 –19195.

[10] Ch. Srinivas, B. V. Tirupanyam, S. S. Meena, S. M. Yusuf, Ch. Seshu Babu, K.S. Ramakrishna, D. M. Potukuchi, D. L. Sastry, Structural and magnetic characterization of co-precipitated $Ni_xZn_{1-x}Fe_2O_4$ferrite nanoparticles, J. Magn. Magn. Mater. 407 (2016) 135 – 141.

[11] R.D. Waldron, Infrared spectra of ferrites, Phys. Rev. 99(1955)1727–1735.