## Research Article

# STRUCTURAL , OPTICAL PROPERTIES OF MANGANESE –ZINC FERRITE

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**ABSTRACT**

The Manganese –Zinc Ferrite nanoparticles (Mna Zn (1-a) Fe2O4 ; a= 0,0.5,1.0) of controlled size were synthesized using chemical precipitation method and characterization for its structural and magnetic properties and compared the particle size in the range of nanometer. Manganese –Zinc Ferrite are of interest on account of their potential uses in many technological fields. The structural, optical and magnetic properties of the prepared samples are characterized  by X-ray diffraction (XRD) ,Scanning Electron Microscope (SEM), UV-Visible spectrometer, Fourier Transform infrared spectrometer(FT-IR). XRD pattern indicates the formation of polycrystals with cubic structure. The average crystalline size has been found to increasing with increase in Mn, Zn concentration. UV-Vis absorbance spectra of the synthesized nanoparticles show an increase in the band gap which indicates the decreases in the size of the Manganese- Zinc Ferrite nanocrystalline materials. FTIR measurements show  the presence of O-H stretching vibrations along with C=O, C-H, C-O in various regions. SEM micrograph shows the structure and morophology of Manganese –Zinc ferrite nanoparticles.

## INTRODUCTION

Magnetic materials which have combined electrical and magnetic properties are known as ferrites. Iron oxide and metal oxides are the main constituents of the ferrites. The importance of ferrite material has been known to mankind for many centuries. In early 12th centuries the Chinese were known to use lodestones ($Fe_3O_4$) in compasses for navigation [1]. Ferrite materials are insulating magnetic oxides and possess high electrical resistivity, low eddy current and dielectric losses, high saturation magnetization, high permeability and moderate permittivity. No material with such wide ranging properties exists and therefore ferrites are unique magnetic materials which find applications in almost all fields. Ferrites are highly sensitive to preparation method, sintering condition, amount of constituent metal oxides, various additives include in dopants and impurities [2-4].

The polycrystalline ferrites remain the best magnetic material which cannot be replaceable by any other magnetic materials because of their important contribution in technological applications. Therefore the processing of these materials is important in modifying the properties as per the desired applications [11].

The rare earth ions can be divided into two categories; one with the radius closes to Fe ions; while the other with ionic radius larger than Fe ions [19]. The rare earth ions have unpaired 4f electrons and the strong spin orbit coupling of the angular momentum. Moreover, 4f shell of rare earth ions is shielded by $5S^2 5P^6$ and almost not affected by the potential field of surrounding ions. Doping rare earth ions into spinel types ferrites, the occurrence of 4f-3d couplings which determine the magneto-crystalline anisotropy in spinel ferrite can also improve the electric and magnetic properties of spinel ferrites [20-23]. The rare-earth ions commonly reside at the octahedral sites by replacing $Fe^{3+}$ions and have limited solubility in the spinel ferrite lattice due to their large ionic radii [21, 23].

## MATERIAL AND METHODS

To synthesize Manganese-Zinc Ferrite nanoparticles, following materials were used. Manganese acetate (Mn (CH3COO)$_2$.4H$_2$O), Ferric chloride (FeCl$_3$) Sodium hydroxide (NaOH) and Polyethylene Glycol (PEG MW:400). All these analytical reagent chemicals were purchased from Merck. The chemical reagents were used without further purification. The glassware used in this work was acid washed. Double distilled water and ethanol were used as solvent and sample preparation. Manganese -Zinc Ferrite nanoparticles were successfully synthesized by simple precipitation method using the above mentioned chemicals. Three samples were synthesized for the present study. In a typical synthesis of MZF nanoparticle, 2 gm of Manganese acetate (Mn(CH3COO)$_2$. 4H$_2$O) dehydrate and 8 gm of Sodium  hydroxide (NaOH) were dissolved in 100 ml

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double distilled water separately under constant stirring of 400 rpm at room temperature (60 to 80℃) for 1 hr. pH of the solution was 12.93. Elico LI 120 digital pH meter was used to measure the pH of the solution. Manganese acetate reacted with sodium hydroxide, and then converted into $MnZnFe_2O_4$. The Ferrite dispersion in distilled water medium was clear and transparent and the solution was kept in an air tight container for 2 days towards the deposition of the powder, followed by the addition of 2 ml of Polyethylene Glycol (PEG) capping agent.

In this study, the sodium hydrate (transparent solution) has been removed and the particles were washed with distilled water and ethanol several times, to remove the unreacted compounds. The powder thus obtained was dried at 80℃ for 8 hrs to remove the remaining water content in the sample. For the synthesis of $ZnFe_2O_4$ and $MnZnFe_2O_4$ samples, appropriate amount of zinc acetate, ferric chloride $FeCl_3$ were dissolved in 75 ml double distilled water separately under the same experimental procedure. However, 8 gm of NaOHwas used for all the three samples.

## RESULT AND DISCUSSION STRUCTURAL ANALYSIS

Figure 1. shows the XRD patteren of the prepared ferrite samples indicating that the sample shows a single phase polycrystals with cubic structure, which indicates the crystallographic planes of the characteristic peaks of cubic spinel structure that perfectly matched with the theoretical data of (ICCD card NO . 74-2402.)
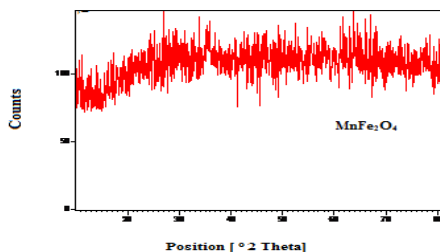


**Figure 1** The peak corresponding cubic patteran of $MnFe_2O_4$

Figure 1 shows that the positions of peaks were shifted to a higher value of $2\theta$ with substitution of $Zn^{2+}$ ions, indicating that the lattice parameter for the cubic $Mn_{1x}Zn_xFe_2O_4$ samples decreased with Zn-content. The crystalline (D) size of the prepared samples was calculated using Debye –Scherrer's Formula [15].

$$D = \frac{0.89\,\lambda}{\beta\,cos\theta}$$

Where $\lambda$, is the wavelength of the radiation (0.154056 nm for $CuK\alpha$ radiation), and $\theta$ is the peak position. The most intense peak at (220), (311),(440), (442),(333) and (400) are used for calculation.
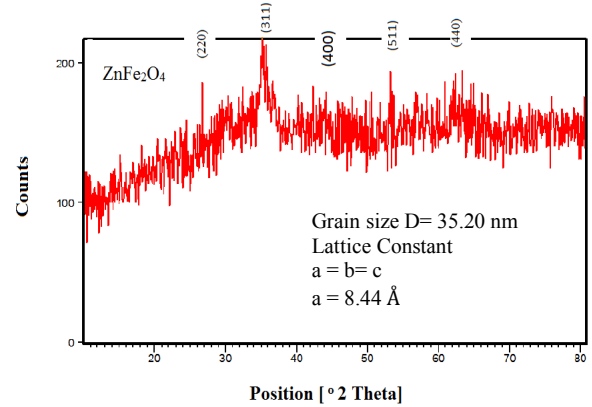


**Figure 2** XRD pattern of $ZnFe_2O$

The calculated crystalline size (D) as a function of Zn content shows that the substitution of the $Mn^{2+}$ ions is $Zn^{2+}$ ions results in decreases in crystallite size from 6.8 nm to 12nm as shown in table 1.
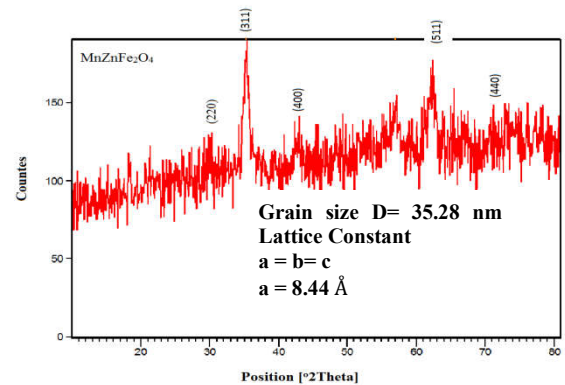


**Figure 3 – XRD pattern of $MnZnFe_2O_4$**

The lattice constant a,b and c of the samples have been determined to the following equation,

$$\frac{1}{dhkl^2} = \frac{h^2+k^2+l^2}{a^2}$$

The experimental lattice parameter ($a_{exp}$) of the prepared samples was calculated as a=b=c (i.e, a=8.44 Å).

**Table 1** particle size and lattice parameter calculation from XRD profile.

| Sample | Position of (311) peak | Interplanar distance 'd' (nm) | Fwhm | Particle size 'd' nm |
|---|---|---|---|---|
| MF | - | - | - | - |
| ZF | 35.2047 | 2.54721 | 1.200 | 6.8 |
| MZF | 35.2874 | 2.54354 | 0.688 | 12.0 |
| From JCPDS data card No. 74-2402 | - | 2.54 | - | - |

### *Ftir Spectrum Analysis*

Figure 2 shows the FTIR spectrum of MZF nanoparticles. The band at 3200-3800 cm$^{-1}$ correspond to the O-H mode of vibration. Broad O-H peaks become wide with an increase in MF,ZF concentration. The additional amount of $CH_3COO$ fromMn acetate reduces the pH of the solution. A strong

symmetric stretching vibration of C=O has been observed between 1620-1512 cm$^{-1}$. The peaks between 1300-1209 cm$^{-1}$ corresponds to the symmetric stretching vibration of C-O. Because of diverging structural morphologies in acidic conditions, both of C=O, C-O peaks were shifted inconsistently. It is reported that C-O-C peak usually occurs at 1256cm$^{-1}$ , but we recorded this peak below 1000 cm$^{-1}$. No sign of FeO (857,713 cm$^{-1}$) or Fe$_2$O$_4$ (585 cm$^{-1}$) impurities. This is the sign of high purity of the samples and the preparation of MZF from Mn(CH$_3$COO).4 H$_2$O precursor. Result of FTIR analysis and the peak assignment are shown in table 2 . The Ferrite peak at 468 cm$^{-1}$ and MF,ZF and MZF peaks at 659 cm-1, 585 cm-1 and 649 cm-1 confirmed the intrinsic stretching vibration of metal ion of a octahedral and tetrahedral sites of ferrite compound respectively. The FTIR results support the SEM results.

**Table 2** function group identification of MF,ZF and MZF nanoparticles.

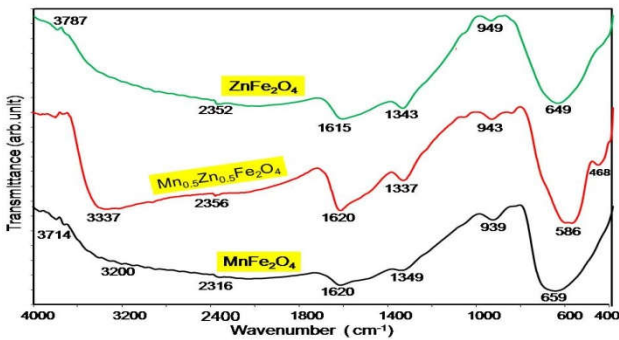| Functional group | wave number (cm$^{-1}$) | | |
|---|---|---|---|
| | **MF** | **ZF** | **MZF** |
| O-H mode of vibration | 3094 | 3728 | 3786 |
| CO$_2$ | 2069 | - | 1988 |
| C-H | 2316 | 2356 | 2352 |
| C=O stretching mode | 1620 | 1619 | 1614 |
| C-O symmetric stretching | 1349 | 1336 | 1343 |
| Bending vibration of ferrite | 659(Octahedral) | 585(octahedral) | 649(octahedral) |
| Stretching vibration of ferrite | 939(Tetrahedral) | 943(Tetrahedral) | 949(Tetrahedral) |



**Figure 4** FTIR spectrum of MF,ZF and MZF nanopowder.

### uv-vis Spectrum Analysis

Absorption spectroscopy is a powerful technique to explore the optical properties of nanoparticles. The UV-Visible absorption spectrum, of MF,ZFand MZF samples is shown in fig 5-7. UV always shows the quantum confinement size effect of the particles. When the size of the particle increases, band gap energy decreases and also absorption onset shift to longer wavelength. This enlargement of the band gap can be attributed to the quantum confinement size effect of MZF nanoparticles. The minimum energy required for the transition of electron from valence band to conduction band is known as band gap energy. The band gap can be calculated using the formula given below,

$$E = \frac{hc}{\lambda} eV$$

h is the plank's constant (6.626×10$^{-34}$ J)
C is the speed of light 3×10$^8$ m/s
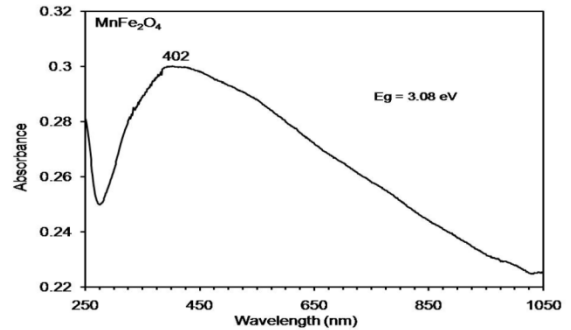$\lambda$ is the cut-off wavelength (nm)



**Figure 5** UV-Vis absorption spectrum of MF samples.
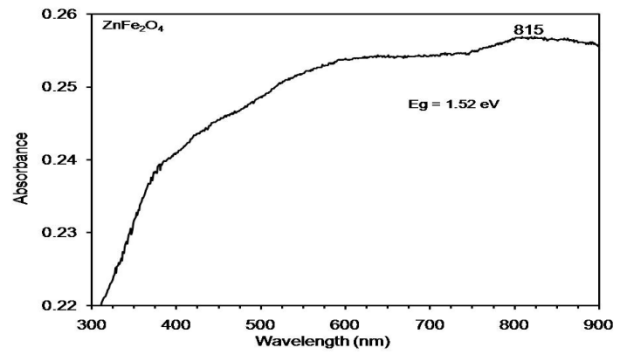


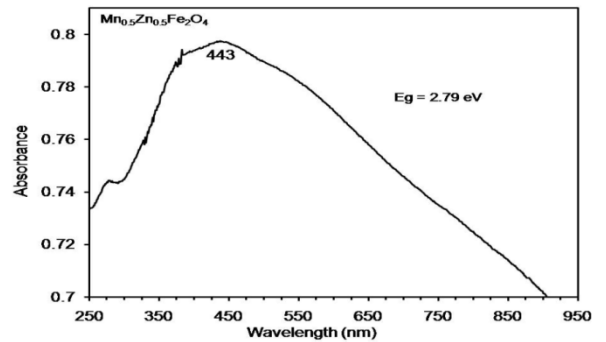**Figure 6** Optical absorption spectrum of ZF sample.



**Figure 7** Optical absorption spectrum of MZF sample.

The samples show sharp peaks around at 402 nm (3.08 eV) , 443 (1.52 eV) and 815 (2.79 eV). The band gap increases with decreasing particle size and the absorption spectra of both the samples were strongly red shifted because of the quantum confinement effect of the particles.

**Table 3** band gap and cut off wavelength from UV profile.

| S.NO | Samples | Planck's constant(h) in joules | Speed of light C m/s | $\lambda$ Wavelength (nm) | Band gap E (eV) |
|---|---|---|---|---|---|
| 1. | MF | 6.626×10$^{-34}$ | 3×10$^8$ | 402 | 3.08 |
| 2. | ZF | 6.626×10$^{-34}$ | 3×10$^8$ | 815 | 1.52 |
| 3. | MZF | 6.626×10$^{-34}$ | 3×10$^8$ | 442 | 2.79 |

Optical transmittance spectra of the prepared samples are displayed in figure 3. The recorded transmittance of the MF sample is nearly 60.67% , ZF sample is 19.65 % and MZF sample is nearly 60.25% in the red region. The decrease in transmittance from UV to IR region suggest that MZF nanoparticles produced by chemical precipitation method.
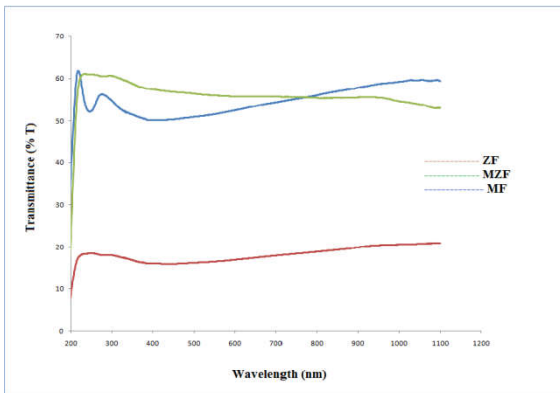


**Figure 8** Transmittance spectrum of MZF samples.

### Morphological Study

Microstructure of MZF nanopowders are shown in figure 9-11. SEM image of MF (Fig 9) clearly shows that the particles are uniformly distributed over the entire surface. Most of them are flags. The average particle size has been measured from the SEM micrographs and it varies in between 6-12 nm. There is no void between the crystalline. For flattened particles, mean value of length in long and short axes were used. Nanoparticles are well known for its agglomeration. The effect of MF,ZF addition on microstructure of MZF is clearly shown in the SEM micrographs [9-11].
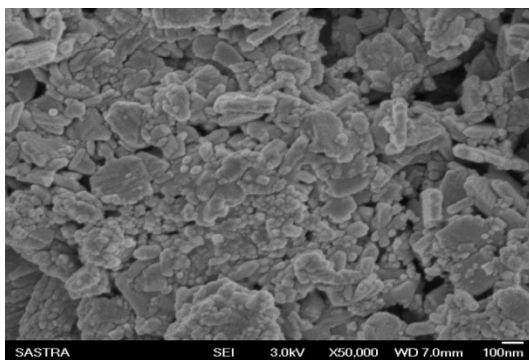


**Figure 9** Scanning Electron <icroscope image of MF nanopowders at room Temperature.

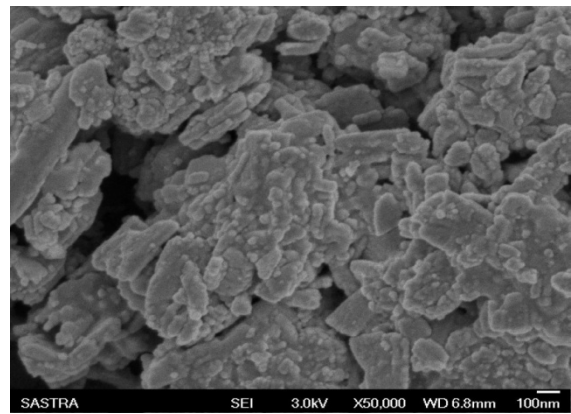It is noticed that MZF sample consists of smaller particles comparatively less than the size of ZF.



**Figure 10** Scanning Electron Microscope image of ZF nanopowder.
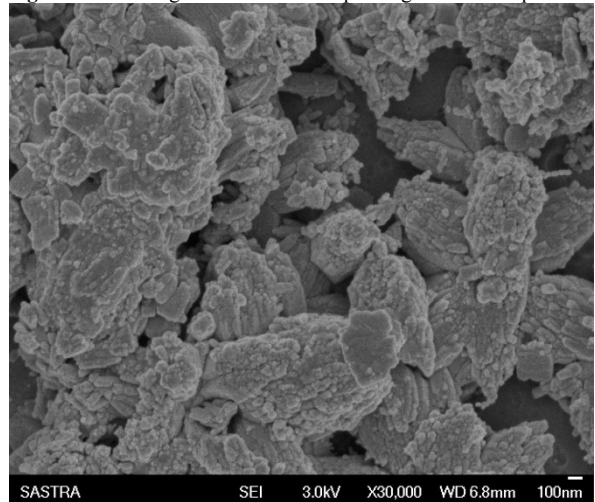


**Figure 11** scanning electron microscope image of MZF nanopowder.

All the crystals are seem to be well defined particles of nanometer size. Hence the SEM image confirms that the particle size increases on ZF and then further decreases. SEM result reported here reveals the XRD analysis.

## CONCLUSION

In this work an effort was made to synthesize Manganese –Zinc ferrite nanoparticles. The $Mn_aZn_{(1-a)}Fe_2O_4$ for a= 0,0.5,1.0 were prepared using the chemical co-precipitation technique. The method is relatively simple, low cost and particle size can be easily controlled. From XRD pattern, the particles exhibit polycrystal with cubic structure, with the average size ranging from 6-12 nm. The average crystalline size has been found to increase with the increasing in Mn,Zn concentration. The SEM image shows the nanoflags structure of the particles. The FTIR shows the absorption bands near 900 and 600 cm$^{-1}$ respectively. The high frequency band around 900cm$^{-1}$ is attributed to the tetrahedral complexes and the band near 600cm$^{-1}$ corresponds to the octahedral complexes. From UV-Visible spectrum it is found that the band gap increases in the absorption spectrum and the transmittance decreases.

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