STRUCTURAL, OPTICAL AND MAGNETIC PROPERTIES OF MANGANESE ZINC FERRITE

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Abstract

The Manganese -Zinc Ferrite nanoparticles ($Mn_aZn_{(1-a)}Fe_2O_4$; 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), Photoluminescence (PL), Fourier Transform infrared spectrometer (FT-IR) and VSM techniques. 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. FTIR measurements show the presence of O-H stretching vibrations along with C=O, C-H, C-O in various regions.Vibrating sample results are presented and discussed the soft ferromagnetic nature of the material. The obtained results are presented and discussed. The study on optical absorption of a film is determined by photoluminescence spectroscopy.

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 $5S^25P^6$ 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 ($Mn(CH_3COO)_2.4H_2O$), Ferric chloride ($FeCl_3$) Sodium hydroxide (NaOH), Zinc Chloride($ZnCl_2$) 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.

Synthesis

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 ($Mn(CH_3COO)_2$. $4H_2O$) dehydrate and 8 gm of Sodium hydroxide (NaOH) were dissolved in 100 ml double distilled water separately under constant stirring of 400 rpm at room temperature (60 to 80°C) 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°C 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 NaOH was 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.)

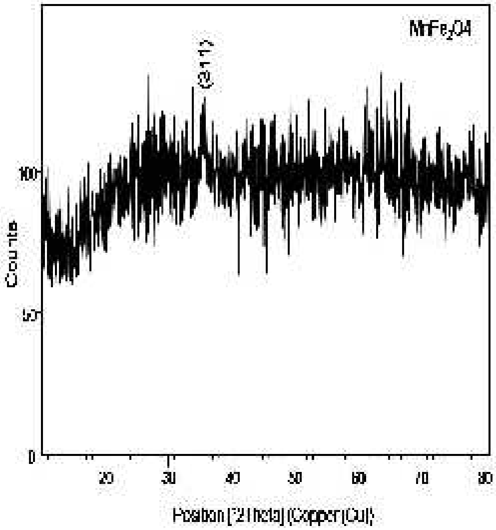


Fig 1. The peak corresponding to this cubic structure in XRD pattern of $MnFe_2O_4$

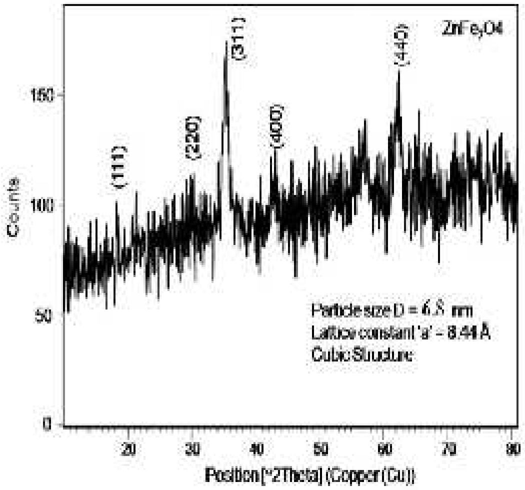


Fig 2. XRD pattern of $ZnFe_2O_4$

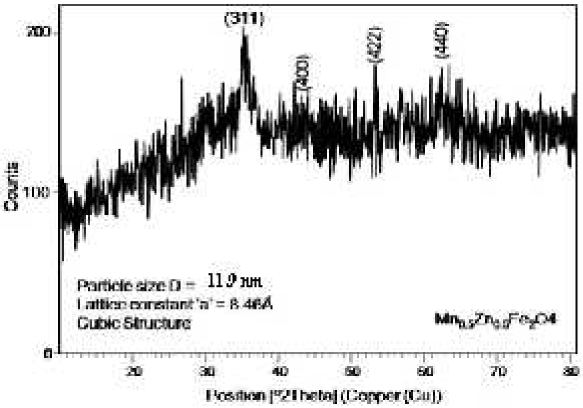


Fig 3. XRD pattern of $MnZnFe_2O_4$

Figure 2 shows that the positions of peaks were shifted to a higher value of 2θ with substitution of Zn^{2+} ions, indicating that the lattice parameter for the cubic $Mn_{1-x}Zn_xFe_2O_4$ 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, λ — is the wavelength of the radiation (0.154056 nm for CuKα radiation), and θ is the peak position. The most intense peak at (220), (311),(440), (442),(333) and (400) are used for calculation. 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 12 nm as shown in table 1. 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 Analysis

Figure 4 shows the FTIR spectrum of MZF nanoparticles. The band at 3200-3800 cm^{-1} corresponds 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 from Mn 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_2O_4 (585 cm^{-1}) impurities. This is the sign of high purity of the samples and the preparation of MZF from $Mn(CH_3COO).4H_2O$ 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)

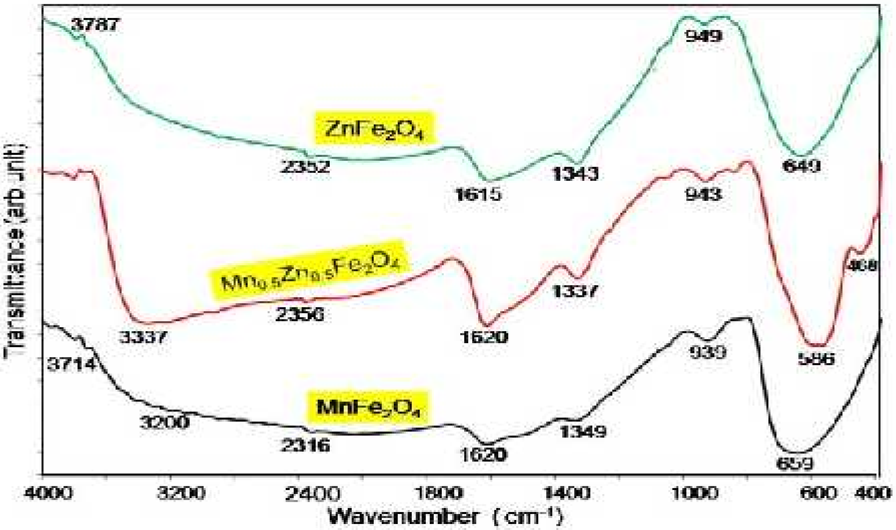


Fig 4. FTIR spectrum of MF,ZF and MZF Nanoparticles.

PL Analysis

The photoluminescence spectrum of the MZF ferrite nanoparticles have been observed at the excitation at 275 nm as shown in fig 5-7 respectively. The PL spectra consist of emission peaks at 420 nm, 460 nm, 491nm, 520 nm and 522 nm. It is also observed that the emission intensity of the peaks depends on the excitation wavelength. Regarding the mechanism of PL, it may be due to quantum confinement. This confinement can be explained in terms of shortening of the super exchange interaction bond length in the nano-crystallineferrite materials, which modifies the electronic structure of ferrite or in terms of the presence of the fast non-radiative relaxitation channels in nano-crystals which are talking part at the surface.

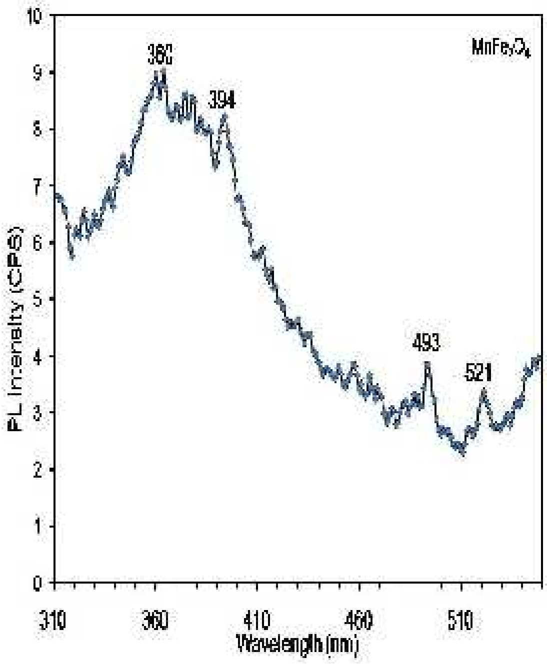


Fig 5. PL spectrum of MF nanoparticle

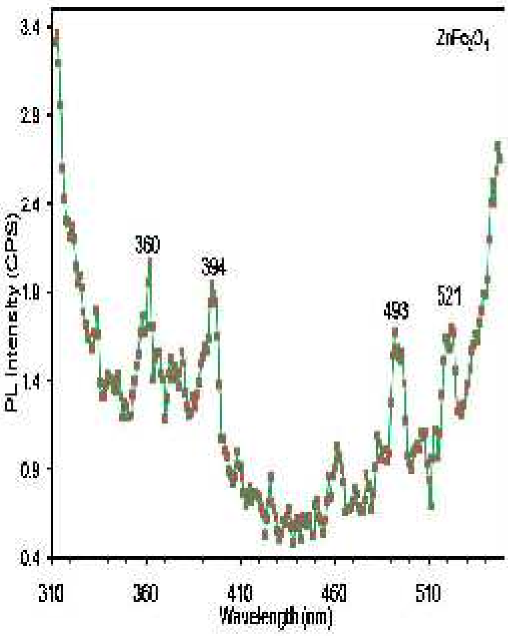


Fig 6. PL spectrum of ZF nanoparticle

The PL around 3 eV is needed mainly due to the quantum confinement because the peak valve approximately agrees with band gap of ferrite nanomaterials. The effect of the surfaceoxide and non-homogenous size is also important if there is a difference in the energies which is associated with the stokes shift between the absorption-surface defects or surface oxide.

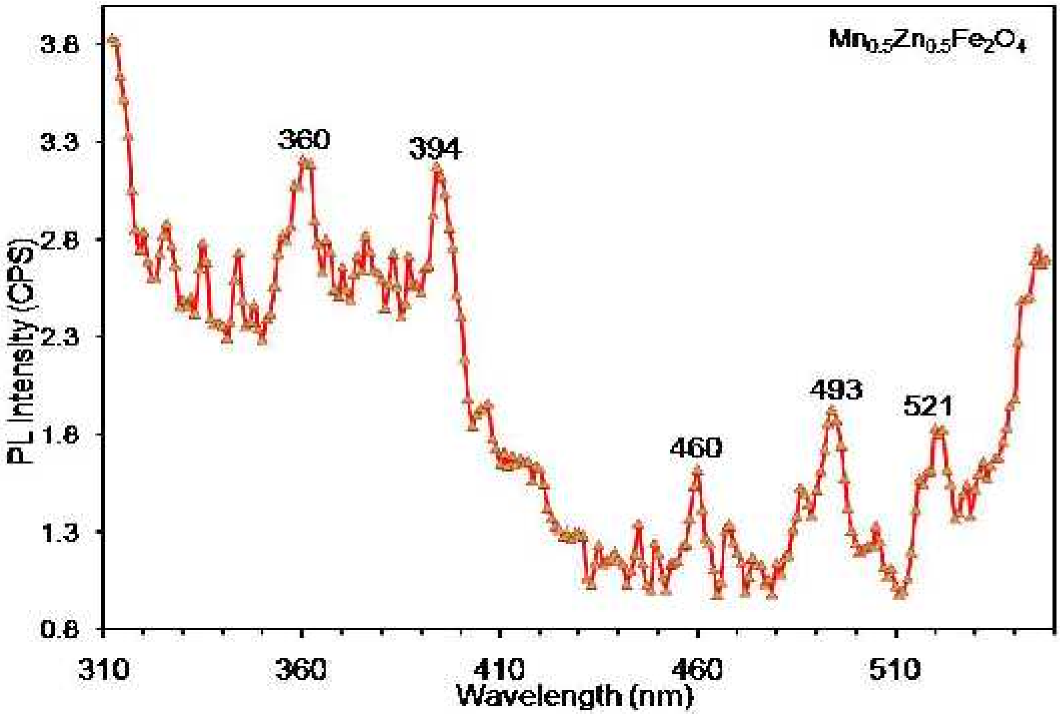


Fig 6. PL spectrum of MZF nanoparticle

The mechanism of charge transfer between the trivalent ions appears to be intervening oxide ions that support the ferromagnetic ordering. The PL has been found to be such that their intrinsic and extrinsic bands were within the visible range.

VSM Analysis

The magnetic properties of prepared MZF soft magnetic ferrite nanoparticles were studied using a Vibrating Sample Magnetometer at 60°c. Magnetic hysteresis curve for MZF nanoparticles are synthesized from precipitation method as shown in fig 7-9.

The magnetization of the nanoparticles at 275 Oe is 27.4 emu/g for MF, 4.9 emu/g for ZF and 6.84 emu/g for MZF. It is obvious that the increase in concentration leads to the increase of the magnetization value. The change in magnetization due to the compositional change may be explained simply by the different moment of ions.

Other factors such as the inversion parameters in the spinal structure may be considered for comprehensive sive elaboration of the mechanism. The magnetic coercively of the particles depends significantly on their magneto crysttine anisotropy, micro-strain, into-particle interaction, temperature, size and shape M^{2+} $(3d^5)$`

For this reason, the reduction in magnetic coercively at 6.5 G for MF, 175 G for ZF and 88.8 G for MZF contributed only to the increase. The saturation magnetization increases due to an increase in the particle size and an increase in the difference in the saturation magnetization. As the MF content increases, the magnetic coercively decreases, as a result of an increase in the saturation magnetization and the particle size.

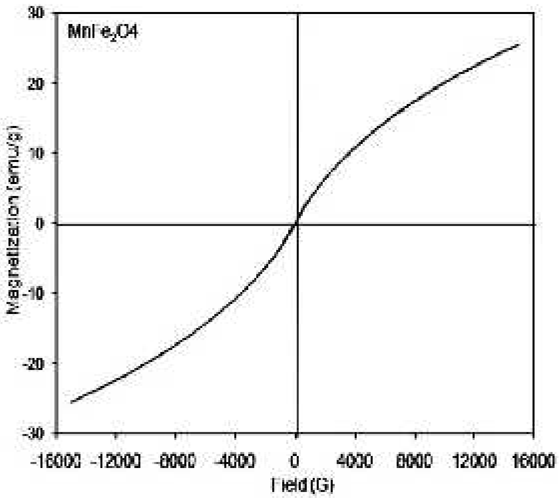


Fig 7.VSM spectrum MF paramagnetism

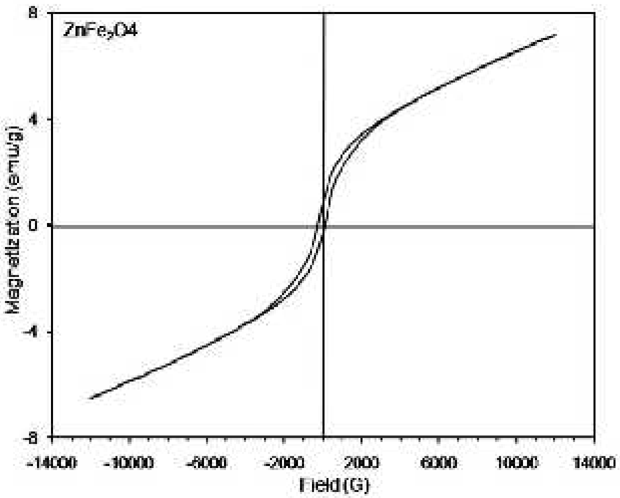


Fig 8. VSM spectrum ZF paramagnestism

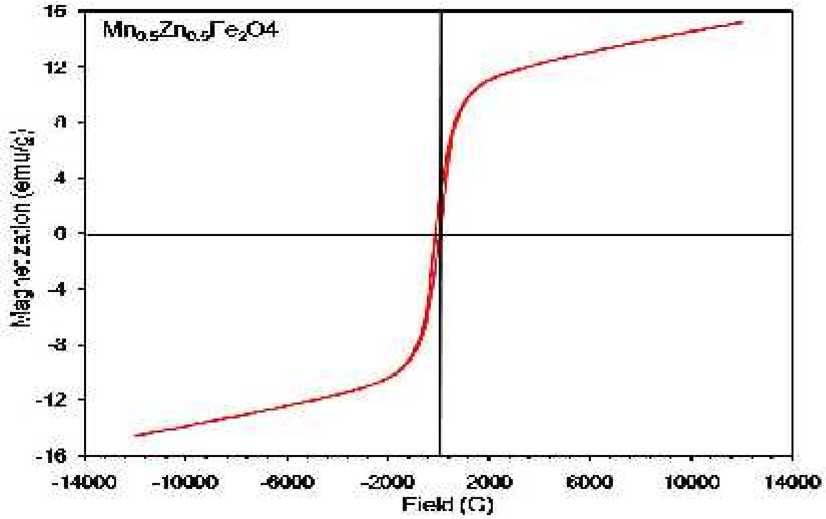
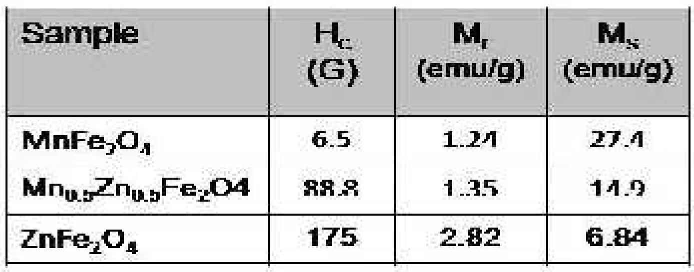


Fig 9. Magnetic field vs Magnetization of MZF ferromagnetism.

Table 3. magnetic parameters of the MZF nanoparticles



Sample	H_c (G)	M_r (emu/g)	M_s (emu/g)
$MnFe_2O_4$	6.5	1.24	27.4
$Mn_{0.5}Zn_{0.5}Fe_2O4$	88.8	1.35	14.9
$ZnFe_2O_4$	175	2.82	6.84

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 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 VSM the soft ferromagnetic nature of the nanoparticles is conformed For this reason, the reduction in magnetic coercivity at 6.5 G for MF, 175 G for ZF and 88.8 G for MZF contributed only to the increase and The saturation magnetization increases due to an increase in the particle size and an increase in the difference in the saturation magnetization. As the MF content increases, the magnetic coercively decreases, as a result of an increase in the saturation magnetization and the particle size. The PL around 3 eV is needed mainly due to the quantum confinement because the peak valve approximately agrees with band gap of ferrite nanomaterials. The spectra of Manganese zinc ferrite nanoparticle show a broad emission spectrum from 300 to 550 nm.

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