Study of Magnetic Properties of NanoStructured Mn-Zn Ferrite

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ABSTRACT

$Mn_{1-X} Zn_X Fe_2 O_4$ (x = 0 to 1) ferrite nanoparticles have been prepared by sol-gel technique and characterized by XRD, VSM, ESR and FTIR. From XRD we observed that particle size decreases with increasing Zn content. By varing the degree of Zn substitution it has been observed that the magnetic properties of fine particles can be varied due to influence of cationic stoichiometry and their occupancy in specific sites. From ESR calculation it has been observed that resonance linewidth is decreasing with temperature.

INTRODUCTION

During the last few decades, spinel ferrites plays important role in ferrimagnetic materials because of their remarkable magnetic properties particularly in radio frequency region, physical flexibility, high electrical resistivity, mechanical hardness and chemical stability. The unusual magnetic properties exhibited by nanoparticles and their promising technological applications have attracted much interest in recent years. Magnetic properties of the ferrites strongly depend on microstructure, particle size and surface to volume ratio [1].In nanoparticles of ferrites, a strong decrease in saturation magnetization Ms and increase of coercivity Hc as compared to the bulk material have been reported. This phenomenon have been explained by assuming the existence of random canting of surface spin [2]. In the present paper we report the dependence of cationic stoichiometry, effect of additive on ESR linewidth, change in molecular structure of ferrite by IR calculation and magnetic properties by VSM for the sample of composition $Mn_{1-x} Zn_x Fe_2 O_4$ (x=0 to 1) prepared at synthesis temp of 80^0c.

MATERIALS AND METHODS

Experimental:
Nanosized $Mn_{1-x} Zn_x Fe_2 O_4$ (x=0 to 1) were synthesized by chemical route i.e. sol-gel technique. The process has advantage of inexpensive precursors, simple equipment, low temperature and resulting homogenous nanosized particles [3]. Analytical grade precursor salts of $MnCl_2.4H_2O$,

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$FeCl_3.6H_2O$, $ZnCl_2.4H_2O$ were taken in stoichiometric amounts and dissolved in 75 ml of distilled water. P^H of solution was varied between 2-3 as it plays crucial role for producing sample in nanosize. At lower P^H precipitation of Mn is incomplete and for higher P^H there may be zinc loss therefore optimum P^H for gel formation of solution was found to lie between 2 to 3. The activation energy for formation of ferrites of different metals is not equal. Activation energy calculated from kinetics of the formation reactions for different ferrites in temperature range of $20-100^0c$ decreases in following sequence. E_A (Mn F)$>E_A$ (Z_n F). Thus it should be concluded that the heating at temperature closer to 100^0c is preferable for an easier and more rapid formation of Mn-Zn ferrite.During heating we add citric acid which removes the insoluble residue with formation of cation citric acid complex and holds the metal ions together. Ethylene glycol has also been added for homogeneity. The gel was then dried in oven at 250^0c for 12 hours and then calcined at 800^0c. According to density and grain growth, it was found that the sintering temperature of nanosized Mn- Zn ferrite powder was about 800^0c [4].The phase identification was carried out using XRD with Cu-Kά radiation. Magnetic measurements for synthesized nanoferrite was taken on VSM. FMR measurements have been made at 9.08 GHz using Varian E112 spectrometer [5].

RESULTS AND DISCUSSION

In the cubic system of ferrimagnetic spinals, the magnetic order in mainly due to a superexchange interaction mechanism occurring between the metal ions in A and B subtlattices. The substitution of non-magnetic Zn ion which is having a preferential A site occupancy results in reduction of the exchange interaction between A and B sites. Hence by varying the degree of Zn substitution the magnetic properties of fine particles can be varied [6].It has been observed that as Zn substitution degree increases the saturation magnetization (Ms), remenant magnetization (Mr) and coercivity (Hc) goes on decreasing.(Fig.1, Fig.2 and Fig.3) shown in Table 1,Table2 and Table3.

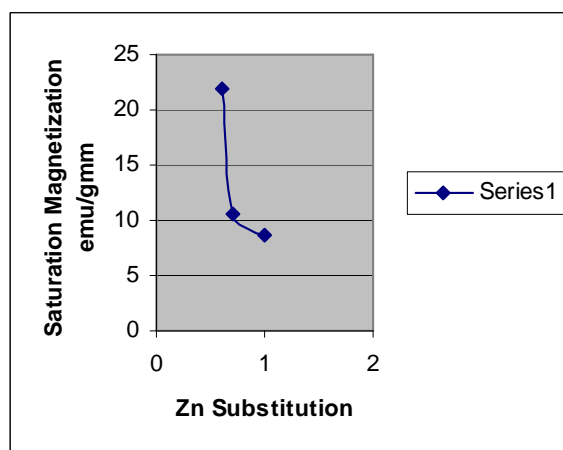**FIG.1 Zn substitution verses Saturation magnetization**

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Table1

Zn Substitution x.	Saturation Magnetization emu/gm
0.6	21.92
0.7	10.59
1	8.58

Table2

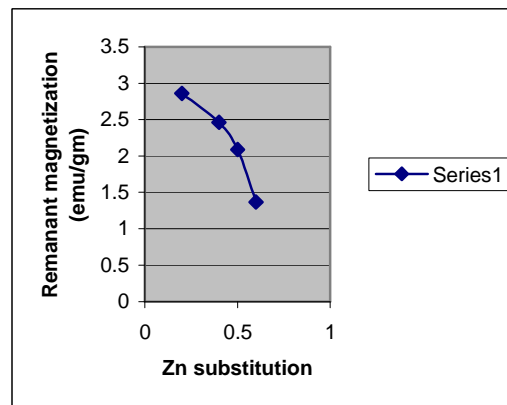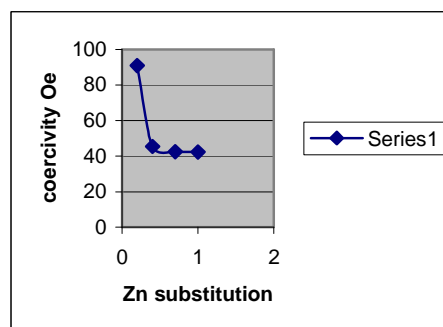| Zn Substitution x.	Remenant Magnetization emu/gm
0.2	2.86
0.4	2.46
0.5	2.09
0.6	1.37

FIG.2   Zn substitution verses Remenant magnetization

FIG.3 Zn substitution verses Coercivity

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Table3

Zn Substitution x.	Coercivity Oe
0.2	90.98
0.4	45.44
0.7	42.40
1	42.26

The room temperature hysteresis loop of the prepared powder samples for various Zn substitution are shown in Fig.4, Fig.5 and Fig.6
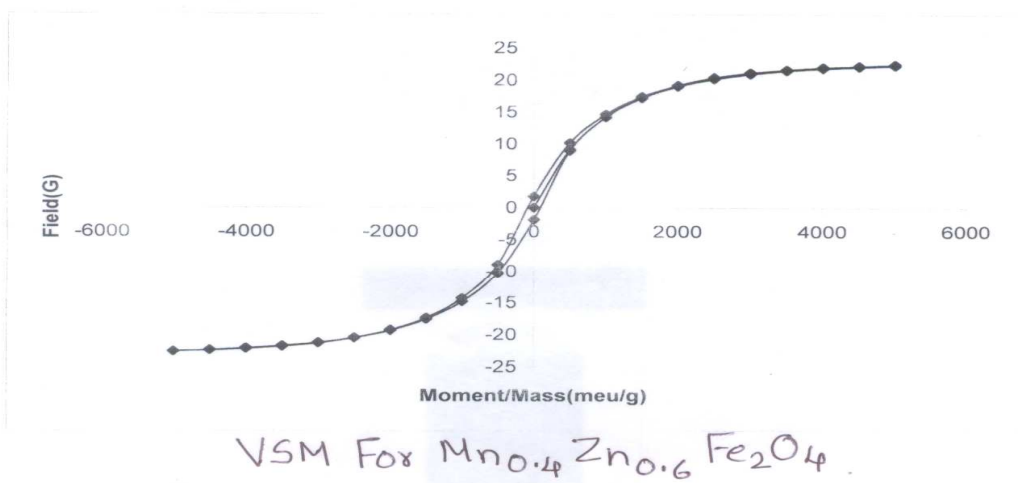

VSM For $Mn_{0.4}Zn_{0.6}Fe_2O_4$.

FIG.4 Applied Field verses Magnetization

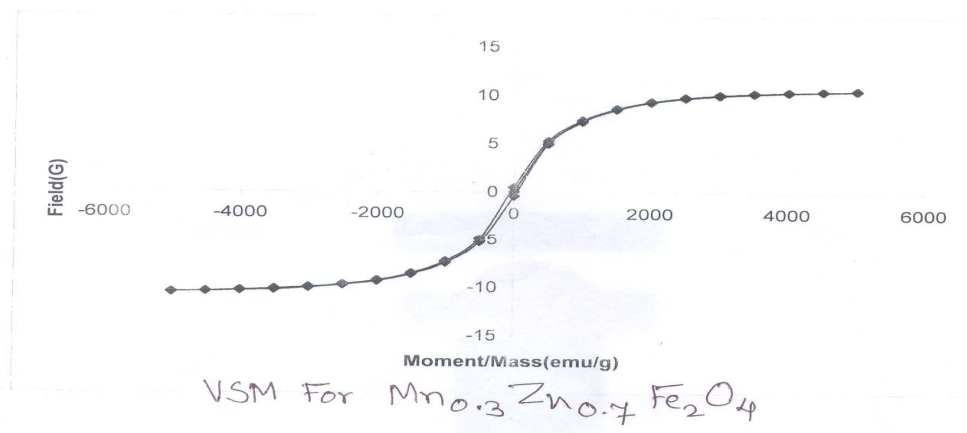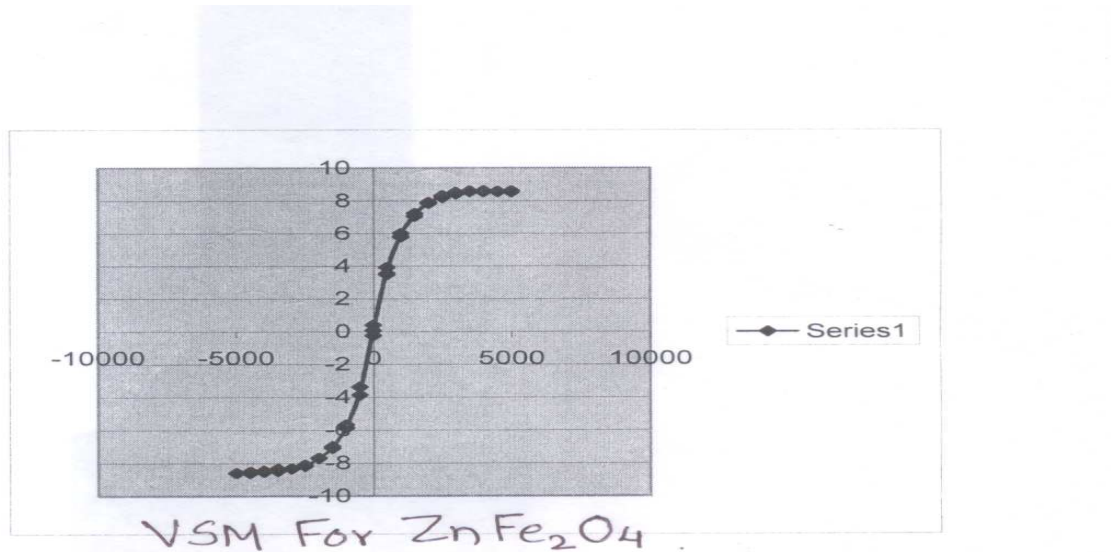VSM For $Mn_{0.3}Zn_{0.7}Fe_2O_4$

FIG.5 Applied Field verses Magnetization

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FIG.6 Applied Field verses Magnetization

The change in magnetic properties such as Ms, Mr, Hc are due to influence of cationic stoichiometry and their occupancy in specific sites. In addition, formation of dead layer on the surface [7], existance of spin canting, non-saturation effects were due to reduction of magnetic properties of nanosized particles[6,8]. The XRD measurement showed that the formation of Fe_2O_3 particles along with Mn-Zn ferrite. Formation of Fe_2O_3 may be due to preferential loss of one or more of divalent cations, during precipitation stage because of unfavorable P^H range. [6,8] as shown in Fig.7 and Fig.8
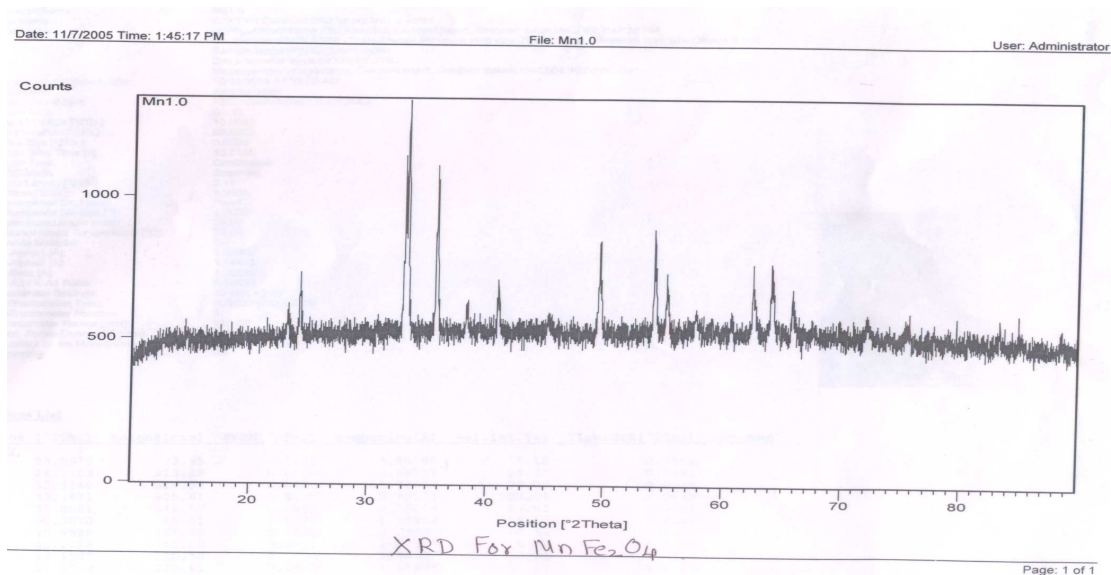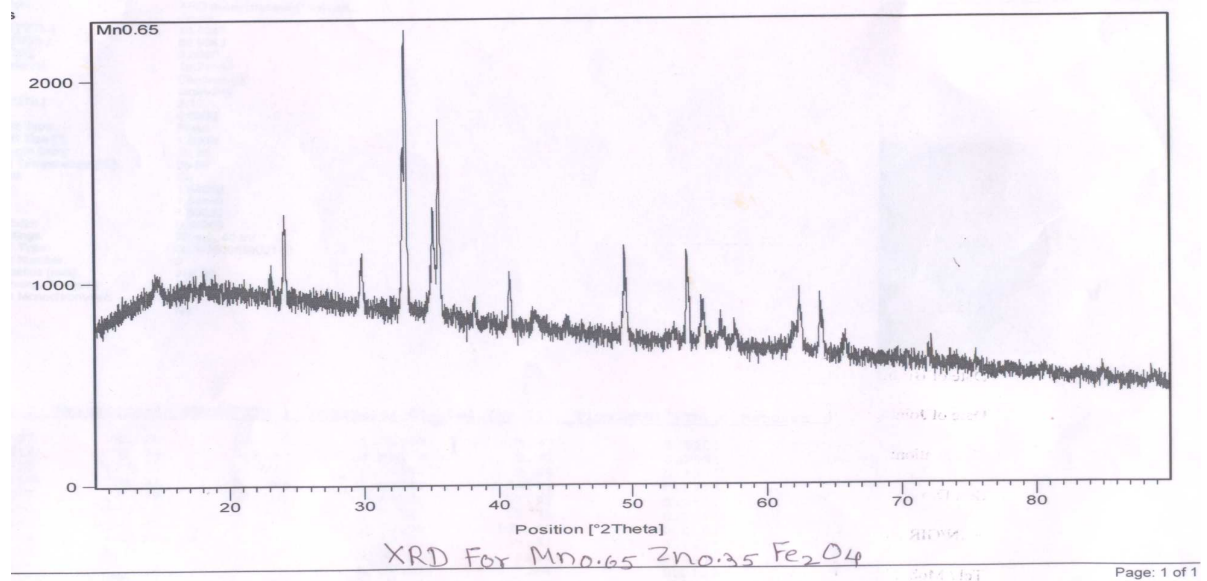

FIG.7 XRD Pattern of $MnFe_2O_4$

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FIG.8 XRD Pattern of   Mn$_{.65}$Zn$_{.35}$ Fe$_2$O$_4$

It has been observed that as zinc decreases the lattice constant 'a' increases as shown in Fig.9.Values of lattice parameter, crystal density, and crystallite size with Zn Substitution are shown in **Table 4.**

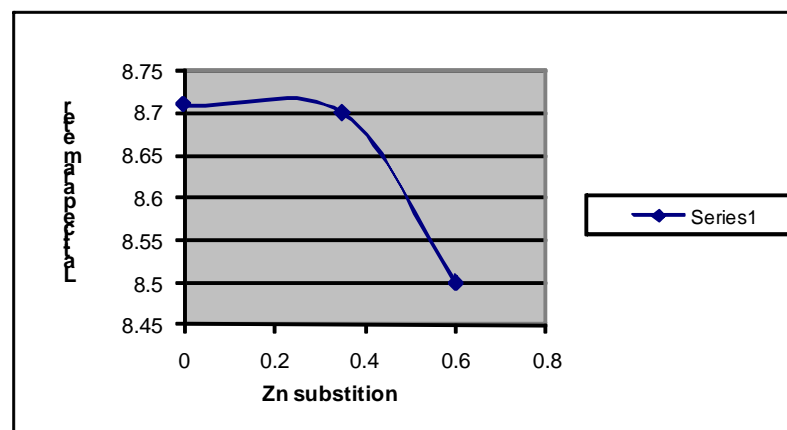| Zn Substitution x.	Lattice Parameter. 'a' A^0	Crystal Density Dx gm/cm^3	Crystallite Size. nm
0	8.71	4.64	156
0.35	8.70	4.72	67
0.6	8.50	5.13	41

FIG.9   Zn substitution verses Lattice Parameter

This increase of lattice parameter 'a' can be attributed to the ionic radii of the ions.It has also been observed that as Zn decreases the crystal density also decreases as shown in Fig.10
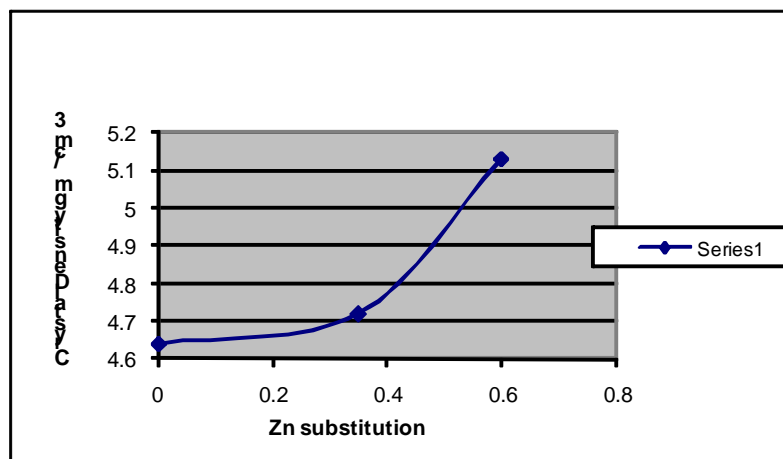
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FIG.10 Zn substitution verses CrystalDensity

The value of Dx for Mn Fe$_2$ O$_4$ was 4.640 gml cm^3. The decrease of crystal density with decreasing Zn could be attributed to atomic weight and radii of constituent ions.[9] Also we have calculated the crystallite size by using Debye sherrer formula. It has been observed that crystallite size decreases as zinc addition increasing as shown in Fig 11.
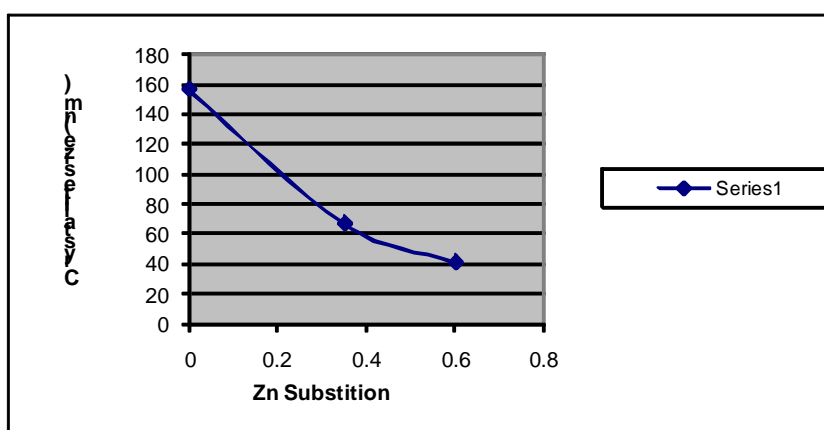

FIG. 11 Zn substitution verses Crystallite size

From the ESR observation it has been observed that the resonance linewidth is decreasing with temperature and resonance field is increasing with temperature as shown in Fig.12 and Fig.13.

The FMR data tend to yield g value slightly larger than the free electron value.It has been observed that g value increase by Zn addition from 2.04 to 2.24 This can be explained by spin-spin and spin lattice relaxation models. The spin lattice relaxation process is characterized by a time constant, which is function of static magnetic field and depends on the rate at which microwave energy can be absorbed and dissipated. The relaxation time is correlated with the linewidth of ESR. The spin spin relaxation time (which arise from the influence of one magnetic ion on another) limits the broadening of linewidth.[10] Values of Resonance linewidth , Resonance field and g$_{eff}$with Zn substitution are as ahown in Table5.
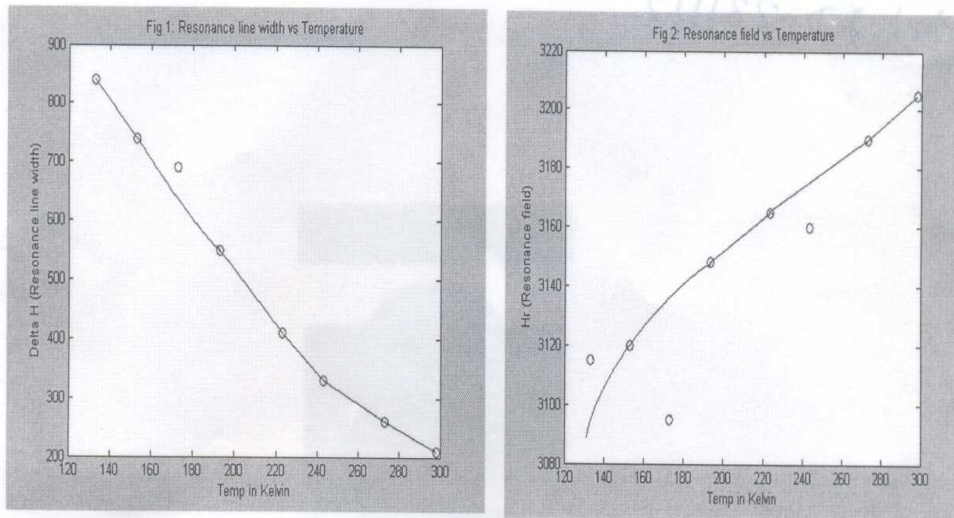
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For $Mn_{0.5}Zn_{0.5}Fe_2O_4$

FIG.12 Variation of ΔH and H_{res} with temperature for $Mn_{0.5}Zn_{0.5}Fe_2O_4$
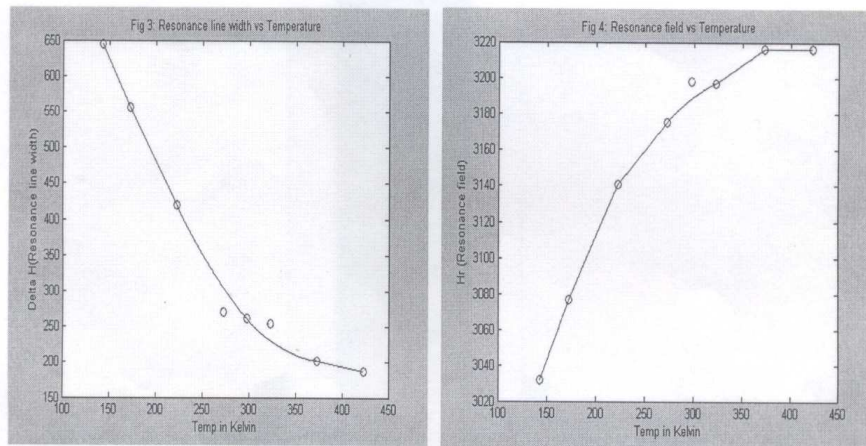
For $Mn_{0.65}Zn_{0.35}Fe_2O_4$

FIG. 13 Variation of ΔH and H_{res} with temperature for $Mn_{0.65}Zn_{0.35}Fe_2O_4$

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Table 5

Zn Substitution x.	Resonance Linewidth. ΔH Oe	Resonance Field. Hr Oe	g_{eff}
0	1060	2970	2.19
0.2	1100	2525	2.57
0.35	262	3197	2.04
0.4	2400	2100	3.00
0.5	210	3205	2.03
0.6	1000	2900	2.24

CONCLUSION

The Mn-Zn nanoferrites has been prepared successfully using sol-gel technique. With increasing Zn substitution crystallite size and lattice parameter decreases and crystal density increases. With increasing non metallic Zn, saturation magnetization decreases.

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