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Structural and Magnetic Properties of MFe_2O_4 Prepared by Solution Combustion Method

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Abstract- **— Nan particles of spinel ferrite MFe_2O_4 where M= Co, Ni and Zn, were prepared using self-combustion technique. Using a combination of x ray diffraction and DC magnetization, the structural and magnetic properties of the nano particles have been studied. Although the preparation conditions were kept same, the particle size of $NiFe_2O_4$ (39.2nm) were smaller than that of $CoFe_2O_4$ (43.6nm) and $ZnFe_2O_4$ (42.1nm) hence the formation of $NiFe_2O_4$ is more exothermic in nature than the formation of $CoFe_2O_4$ and $ZnFe_2O_4$. The dependence of DC magnetization doping have been studied.**

Index Terms**—nanoparticles, saturation magnetization, spinel ferrites, X-ray diffraction .**

I. INTRODUCTION

In the last few decades, ferrite nanoparticles have been studied extensively as they have remarkable magnetic and electrical properties such as high electrical resistivity, low eddy current and dielectric losses, high saturation magnetization, high Curie temperature and permeability [1]. Due to these remarkable properties these materials are used in a numerous technological applications such as high density magnetic storage devices, electronic communication devices, targeted drug delivery, sensors, magnetic printing inks, applications in ferrofluid technology, magnetic refrigeration, catalysts and in magnetic resonance imaging enhancement [2]. These exceptional properties of spinel ferrites depend on several factors including the method of preparation, chemical composition, different doped cations and grain size. The spinel structure, belongs to Fd3m space group, consists of a closed packed fcc arrangement of 32 oxygen ions and two interstitial sites with 8 tetrahedral (A site) and 16 octahedral (B site) symmetries. The magnetic properties in spinel ferrites are decided by the type of metal ions (cations) on the A and B sites and relative strengths of the inter-sub lattice interactions J_{AB}, and intra-sub lattice interactions J_{AA} and J_{BB}. All the above stated exchange interactions are generally negative with J_{AB} being the strongest and J_{AA} the weakest [3].

In the present study the dependence of magnetic and structural properties on doping of Co, Ni, and Zn cation is reported

II. EXPERIMENTAL

Nanoparticles of MFe_2O_4 where M= Co, Ni and Zn were prepared by self-combustion method using analytical grade $Fe(NO_3)_3.9H_2O$, $Co(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, $Zn(NO_3)_2.6H_2O$ and citric acid $C_6H_8O_7$. The ratio of metal nitrate to citric acid was taken as 1:1. The fuel to oxidation ratio is kept constant throughout the process and is taken as 1.35.The mixture was stirred for 30 minutes at RT and then stirred at a higher temperature of 90^0C till self-combustion takes place (as prepared samples). Then the prepared samples were annealed at 900^0C. Structural characterization and determination of the average sizes of nano sized samples were done using X-ray diffract meter (XRD) with Cu-Kα radiation. .Magnetic measurements were done using a Lake Shore 7304 vibrating sample magnetometer (VSM).

III. RESULT AND DISCUSSION

A. *Structural Analysis:*

X-ray diffraction pattern of as prepared MFe_2O_4 where M = Co, Ni, and Zn are shown in Fig. 1(a). From the X-ray spectra it is evident that all the samples have single phased spinel structure with the space group of Fd3m. The increase in the sharpness of X-ray diffraction peaks when annealed at 900^oC indicates increased crystallinity of the prepared samples (Fig. 1(b)). Average particle sizes of the samples estimated using the Scherrer formula [4]

$$Particle\ Size = \frac{0.9\lambda}{B\cos\theta}$$

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[1] Where λ is wavelength of X rays, and *B* corresponds to the width of most intense peak in the XRD spectrum. The calculated particle size shows that the crystallite size increases due to annealing at 900°C. The crystallite size and the lattice parameter, are listed in Table 1 for the prepared samples. When annealed, two or more particles of the sample fuse together due to melting of surfaces. The particles' surfaces are melted well below the melting point of their bulk form as in nano sized materials, a large fraction of atoms are present at the boundaries. These weakly bound atoms with enhanced diffusivity leads to a sharp decrease of the surface melting point of the particles [5]. Lattice constant of $NiFe_2O_4$ is less compared to the same for $CoFe_2O_4$ and $ZnFe_2O_4$ as the ionic radius of Ni^{+2} (0.69 Å) is less than that of $Co^{+2}$and Zn^{+2}. The lattice constant ofprepared samples decreases when annealed at 900°C. This decrease in the lattice constant is associated with the increase in the particle size. With the decrease in the particle size thenumber of atoms in an isolated particle is reduced. The excess free energy associated with the large surface increases the Table 1: Structural parameters of As prepared MFe_2O_4 where M = Co, Ni and Zn and sample annealed at 900°C

Sample	As prepared		900°C Annealed	
	Lattice Constant (Å)	Particle Size (nm)	Lattice Constant (Å)	Particle Size (nm)
$CoFe_2O_4$	8.380	9.49	8.367	43.6
$NiFe_2O_4$	8.353	17.9	8.328	39.2
$ZnFe_2O_4$	8.447	10.2	8.431	42.1

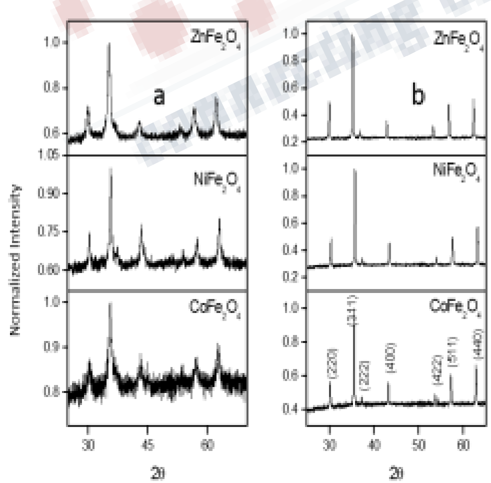

Fig. 1: X-ray diffractograms of MFe_2O_4 where M = Co, Ni, and Zn (a) as prepared and (b) annealed at 900°C.

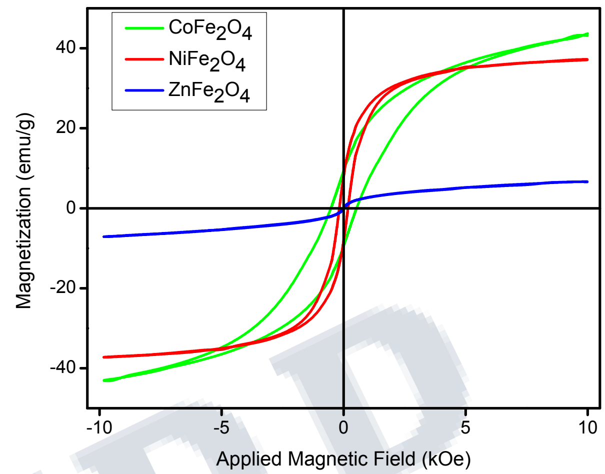

Fig. 2: Room Temperature M-H loops of MFe_2O_4, where M = Co, Ni, and Zn, annealed at 900°C.

Particle's total free energy.This excess free energy can be reduced by changing its lattice structure in an appropriate manner. This reduction in the excess free energy is responsible for conversion of the lattice to an energetically less favorable crystallographic structure; however, the overall energetics increases the stability [6].

IV. DC MAGNETIZATION:

The field dependent magnetization (M-H curve) of MFe_2O_4, annealed at 900°C are shown in Fig. 2. M-H curves for all the samples annealed clearly display hysteresis and indicate the ferrimagnetic nature of the particles. Saturation magnetization M_S of the samples annealed at 900°C is estimated by plotting *M* Vs 1/*H* for 1/*H* tends to zero (Table 2).

The observed variation in Saturation Magnetization (Table 2) can be described on the basis of difference in the contributions from the magnetic moment of the substituted ion on A – and B site of the spinel ferrite (i.e. total magnetization $M_S = M_B - M_A$)[7]. A decrease in the saturation magnetization is expected when Ni^{+2} is substituted instead of Co^{+2}in $CoFe_2O_4$, since Ni^{+2} has lower magnetic moment of $2\mu_B$ as compared with $3\mu_B$ for Co^{+2} [8].Ideally ferrimagnetic hysteresis loop should not be obtained for $ZnFe_2O_4$ as Zn^{+2}has zero magnetic moment. But in the present study the presence of hysteresis loop indicates the presence of Zn cation on both A and B site [9].

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The anisotropy constant K is calculate using anisotropy field by [10]

$$K = \frac{H_K M_S}{2} \quad \text{............ [2]}$$

Where H_K is anisotropy field and M_S is saturation magnetization. The effective anisotropy is given by

$$K = K_1 + K_S + K_{sh} + K_{in} \quad \text{................. [3]}$$

Where K_1 is the magneto crystalline anisotropy, K_S is a constant of surface anisotropy, K_{sh} is shape anisotropy constant, and $K_{in}$is the constant of supplementary anisotropy that reflects nanocrystalline interactions [11]. The contribution of K_{sh} and K_{in} has negligible influence on the effective anisotropy. Furthermore in the present study as the particle size of all the prepared ferrite samples (MFe_2O_4 where M= Co, Ni and Zn) are approximately same, the variation in anisotropy constant is result of change in magneto crystalline anisotropy K_1. The large anisotropy constant in $CoFe_2O_4$ is a result of unquenched spin orbit coupling.

Table 2: DC Magnetization parameters for MFe_2O_4 where M = Co, Ni, and Zn, annealed at 900°C

Sample	Coercivity (G)	Saturation Magnetization (emu/g)	Anisotropy Field (G)	Anisotropy constant (erg/g)
$CoFe_2O_4$	525	43.7	8500	185725
$NiFe_2O_4$	175	37.35	4500	84037.5
$ZnFe_2O_4$	9	6.7	400	1340

V. CONCLUSION

In summary, nanoparticles of MFe_2O_4 where M= Co, Ni, and Zn, were synthesized by self combustion technique. The magnetic properties of nano ferrite particle are highly dependent on doping.

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