

## Magnetic properties of cobalt substituted nanocrystalline Ni-Zn ferrites prepared by chemical route

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**ABSTRACT:** Spinel ferrites in the nano range having composition  $Ni_{0.7-x}Zn_{0.3}Co_xFe_2O_4$  where  $x$  varies as  $x=0.0-0.7$  were synthesized through chemical route using sucrose as fuel, PVA as chelating agent and metal nitrates. Structural analysis was done by XRD and TEM. They correspond to well defined crystalline FCC phase and confirm the formation of spinel structure. No additional peaks are found ensuring phase purity. The slow increase in the lattice constant is due to the replacement of  $Ni^{2+}$  ions ( $0.74\text{\AA}$ ) by slightly larger  $Co^{2+}$  ion ( $0.78\text{\AA}$ ). Characterization by TEM revealed a well defined nanocrystallite state with an average particle size of around 10nm. Magnetic properties measured from hysteresis patterns at room temperature reveal an increase in saturation magnetization with increase in cobalt content. Non linear increase is related to surface effects and method of preparation. Anisotropy constants obtained from coercive field measurements are found to increase linearly for low cobalt concentrations.

**Keywords:** XRD, TEM, saturation magnetization, dielectric parameters

### 1. INTRODUCTION

Nano structured materials are known to exhibit unique electrical, structural, and magnetic properties, with potential applications including: information storage, color imaging, bioprocessing, magnetic refrigeration, and ferrofluids. They exhibit a unique type of disorder, with very-low-energy regions (crystallites) existing at the expense of higher-energy boundary, interface, or surface regions. Studies of magnetic nanoparticles provide not only the information about the structural and magnetic properties of the materials but also improve understanding of the synthesis technique.

Among ferrites mixed Zn ferrites and especially Ni-Zn ferrites have been widely studied and reported [1]. While Ni-Zn ferrites possess high resistivity and saturation magnetization, cobalt ferrite possesses unique physical properties such as high Curie temperature, large magnetic anisotropy, moderate magnetization, excellent chemical stability and large Kerr and Faraday rotations [2, 3].

Synthesis and processing of metallic and ceramic nanostructure materials have been reviewed by several authors [4, 5]. Chemical techniques are widely used to produce nanostructure materials due to their straightforward nature and the potential for producing large quantities of the final product. Realizable particle sizes range from nanometer to micron scale, with particle size controlled during synthesis by the competition between nucleation and growth. Disadvantages include the possible incorporation of intermediate products in the final product, and lack of fine control over the composition of alloy materials. So in the present case synthesis was undertaken by using sucrose as fuel, PVA as chelating agent and required metal nitrates.

In the present paper we report the room temperature magnetic properties and temperature related dielectric studies of nanocrystallite ferrites of composition  $Ni_{0.7-x}Co_xZn_{0.3}Fe_2O_4$  where  $x$  varies from  $x=0$  to  $x=0.7$ . Hence, the study of magnetic properties can be thought of as an effective tool to investigate the finite size effects on the conduction mechanism in ferrites.

### 2. EXPERIMENTAL

#### 2.1 synthesis

The nanocrystallite ferrites with general formula  $Ni_{0.7-x}Co_xZn_{0.3}Fe_2O_4$  where  $x$  varies from  $x=0$  –  $x=0.7$  were synthesized by taking stoichiometric amounts of the desired metal nitrates, 10% (W/V) aqueous solution of PVA (the matrix) and aqueous solution of sucrose (2 mole per metal ion). The entire mixture was mixed thoroughly and evaporated to a viscous liquid. The evaporation is accompanied by the evolution of brown fumes of nitrogen dioxide from the decomposed nitrates. The fluffy voluminous carbonaceous pyrolysed mass produced during the complete evaporation of the precursor solution of metal – nitrate – PVA – sucrose was later thermolysed at around  $300^\circ\text{C}$  to get the nanosized powders of the desired ferrite. The carbonaceous evaporated

dry mass was ground and sintered finally at 400<sup>0</sup> C for 4h. The powder was pelletized into desired shape for further characterization.

## 2.2 Characterization

### 2.2.1 XRD

X-ray diffraction patterns of the samples were taken by using CuK $\alpha$  radiation of wavelength 1.5418 Å, on Phillips PW 3710 diffractometer available at CFC (Shivaji University, Kolhapur). 2 $\theta$  was varied between 20<sup>0</sup> and 100<sup>0</sup>. Indexing was done by comparing the observed X-ray diffractogram with the standard JCPDS (Joint Code for Powder Diffraction Standards) data available for ferrite with cubic spinel structure. The spinel lattice gives rise to diffraction peaks with particular specific indices

### 2.2.2 TEM

TEM micrographs were recorded by using transmission electron microscope (Phillips model CM 200) to investigate powder morphology as well as grain size. Magnetic measurements were carried out using a high field magnetic hysteresis loop tracer interfaced with a computer. The magnetic properties such as saturation magnetization and coercivity were elucidated from the hysteresis curve. The magnetic moment  $n_B$  in Bohr magnetons was calculated using the relation

$$n_B = \frac{M \times M_s}{5585} \quad (1)$$

where M is molecular weight and  $M_s$  is magnetization per gram of the sample. The dielectric measurements were carried out as a function of temperature at three fixed frequencies viz. 1, 10 and 100 kHz using precision LCR meter (Model HP 4284A). For electrical measurements, all the samples were painted on either side with silver paste to ensure good ohmic contacts.

## 3. RESULTS AND DISCUSSION

### 3.1 XRD

The X-ray diffraction patterns of Ni<sub>0.7-x</sub>Zn<sub>0.3</sub>Co<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> for (x=0-0.7) are shown in the Fig 2.B.1. They correspond to well defined crystalline FCC phase and confirm the formation of spinel structure. No additional peaks are found ensuring phase purity. The peaks were indexed by comparing the interplanar distance with JCPDS data (JCPDS card no. 10-325, 22-1086), corresponding to Ni-Zn ferrite and cobalt ferrite respectively. In case of all ferrites (311) reflection appears as an intense peak. The other planes observed are (220), (400), (422), (511) and (440).

The lattice constants obtained for each composition by analyzing the XRD patterns are shown in Fig 2.B.1 along with the d values. The slow increase in the lattice constant is due to the replacement of Ni<sup>2+</sup> ions (0.74Å<sup>0</sup>) by slightly larger Co<sup>2+</sup> ion (0.78Å<sup>0</sup>). The lattice parameters obtained in the present case are in close agreement with the lattice parameters of Co<sub>0.7</sub>Zn<sub>0.3</sub>Fe<sub>2</sub>O<sub>4</sub> prepared by chemical method as reported by Gul et. al. [1]

### 3.2 TEM analysis

The TEM images of Ni<sub>0.7</sub>Zn<sub>0.3</sub>Fe<sub>2</sub>O<sub>4</sub> and Ni<sub>0.6</sub>Co<sub>0.1</sub>Zn<sub>0.3</sub>Fe<sub>2</sub>O<sub>4</sub> are shown in Fig 1a, 1b. It is clear that the particles are almost spherical in shape, and dispersed uniformly with a crystallite size of approximately 10 nm. Clear and bright rings in the electron diffraction patterns [Fig 2a.2b] suggest a very small particle size in the sample. The position and intensities of lines in the diffraction pattern confirm the spinel structure. The particle size determined from TEM micrographs are of smaller magnitude than that obtained from XRD measurements suggesting that each particle is a single nanocrystallite. Similar results have been reported for zinc- substituted cobalt ferrites prepared by forced hydrolysis method [6].

### 3.3 Magnetic characterization

Hysteresis patterns of the samples are shown in Fig 3. Values of saturation magnetization and magnetic moment are given in Table-1. Saturation magnetization is found to increase with cobalt content. Inclusion of Co<sup>2+</sup> ions ( magnetic moment 3 $\mu_B$  ) in Ni-Zn ferrite system has a tendency to replace Ni<sup>2+</sup> ions ( magnetic moment 2  $\mu_B$  ) on the octahedral site causing an increase in its magnetic moment , resulting in an overall increase of the total magnetic moment. The increase in  $M_s$  is found to be non linear. This non linear increase may be related to the method of preparation and change in magnetic structure on the surface of the particles. In case of nanoparticles surface effects become significant due to large surface/volume ratio [7]. Nanoparticles with large surface/volume ratio show enhanced spin disorder as compared to large particles. The surface spin disorder in case of nanocrystalline ferrites may be due to broken exchange bonds high anisotropy layer on the surface or a loss of the long -range order in the surface layer. These effects are particularly strong in case of ferrites because

of the super exchange interactions through the oxygen ions. The magnetic ions tend to have magnetic interaction mediated by the electrons in their common nonmagnetic neighbors (oxygen in this case) which is more important than their direct exchange interaction. The presence of another atom (ion) in the form of impurity or an absence of the oxygen ions at the surface leads to the breakage of the superexchange bonds between the magnetic cations introducing a large surface spin disorder [8].

The lower values of saturation magnetization can also be explained considering the type to which the nanomaterial belongs to [9]. As per the study of physical properties majority of nanocrystalline ferrites fall in the type-B category. In type-B particles, the presence of a shell can prevent particle-particle interactions, but often at the cost of interactions between the core and the shell. In many cases, the shells are formed via oxidation and may themselves be magnetic. Klabunde, Sorensen, and Hadjipanayis have investigated the core-shell morphology in both elemental and alloy particles [10-12]. A reduction in saturation magnetization is often reported in type-B core-shell particles, usually due to the loss of net moment in the ferromagnetic oxide shell.

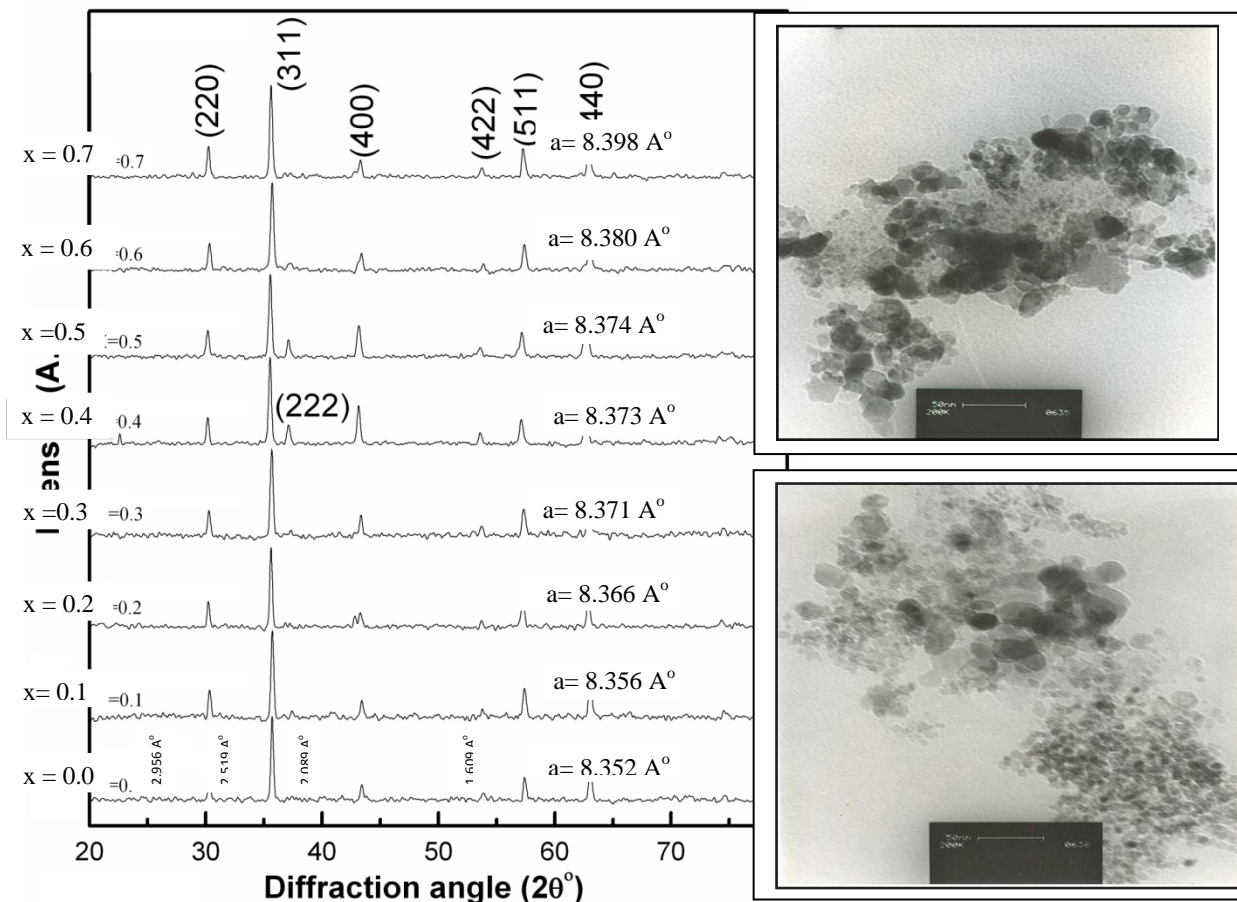
Cobalt is known for its high anisotropy constant so an attempt is made in the present case to calculate the anisotropy constant using the Brown's relation [13]:

$$H_c \geq \left( \frac{2K}{\mu_0 M_s} \right)$$

(2)

where, K is the anisotropy constant. One can see that the coercivity has a direct relation with the anisotropy constants K. Therefore, an increase of  $H_c$  suggests the increase of the magnetic anisotropy. The values of anisotropy constant are given in Table 1. It is observed that for low concentrations of cobalt ( $x < 0.3$ ) the increase is linear which may be due to the isolated behavior of  $Co^{2+}$  ions. But for higher concentrations ( $x > 0.4$ )  $Co^{2+}$  ions cannot be considered as isolated and contributions from local configurations become important.

#### 4. FIGURES AND TABLES



**Fig.1 XRD patterns of  $Ni_{0.7-x}Zn_{0.3}Co_xFe_2O_4$  ferrite**

**Fig. 2 Typical TEM images for (a)  $x=0.0$  and (b)  $x=0.1$  of  $Ni_{0.7-x}Zn_{0.3}Co_xFe_2O_4$  ferrite.**

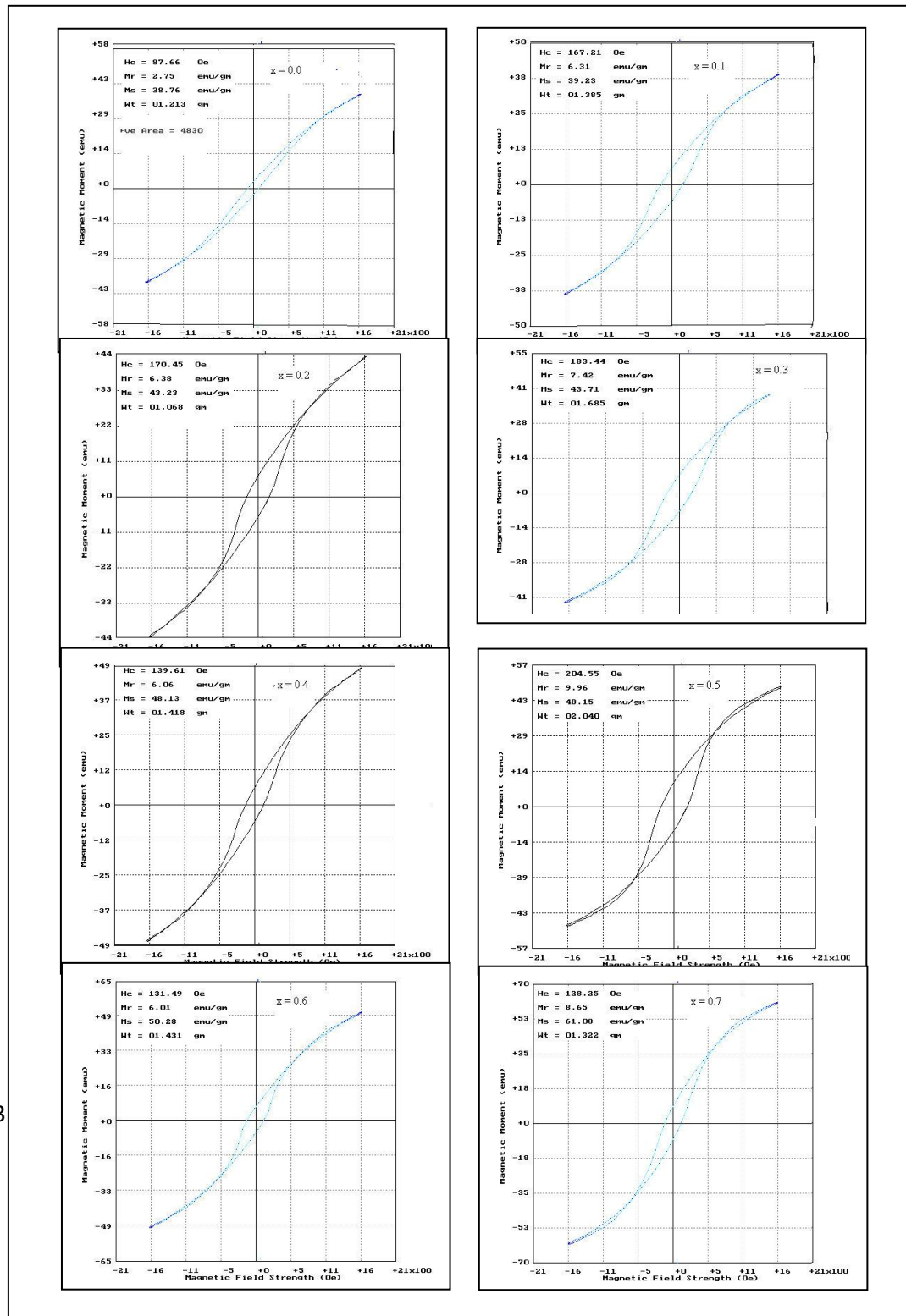


Fig. 3 Hysteresis plots for  $Ni_{0.7-x}Co_xZn_{0.3}Fe_2O_4$  ferrite system.

**Table -1** Data on saturation magnetization (Ms), magnetic moment per formula unit in Bohr magneton ( $\eta_B$ ), Coercivity (Hc) and Anisotropy constant (K) for  $Ni_{0.7-x}Co_xZn_{0.3}Fe_2O_4$  system

Cobalt content (x)	Saturation magnetization Ms(emu/gm)	Magnetic moment (Bohr magneton)	Coercivity Hc (Oe)	Anisotropy constant K (erg/gm)
0.0	38.76	1.64	87.66	3,539
0.1	39.23	1.66	167.21	6,833
0.2	43.23	1.83	170.45	7,676
0.3	43.71	1.85	183.44	8,352
0.4	48.13	2.04	139.61	7,000
0.5	48.15	2.05	204.55	10,260
0.6	50.28	2.13	131.49	6,887
0.7	61.08	2.59	128.25	8,160

## 5. CONCLUSIONS

Chemical synthesis of nanocrystalline ferrites using sucrose, PVA and metal nitrates was found to be successful in yielding a particle size of around 10 nm, the same was confirmed by TEM micrographs. XRD studies correspond to well defined crystalline FCC phase and confirm the formation of spinel structure. No additional peaks are found ensuring phase purity. The slow increase in the lattice constant is due to the replacement of  $Ni^{2+}$  ions ( $0.74A^\circ$ ) by slightly larger  $Co^{2+}$  ion ( $0.78A^\circ$ ). Saturation magnetization was found to increase with cobalt content but the magnitude of increase was not appreciable. This is attributed to surface spin effects, method of preparation and core shell morphology.

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