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# Low Temperature Hydrothermal Synthesis and Characterisation of Nano Size Ni-Zn Ferrites

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**Abstract:** Ni-Zn ferrites of composition  $Ni_xZn_{1-x}Fe_2O_4$  [ $x = 0.0, 0.5, 1.0$ ] are synthesized at 140°C by hydrothermal method using EDTA as template. FTIR studies of NF1 before HT show the presence of moisture and after HT only two absorption bands are observed for all the ferrites, one around 420 cm<sup>-1</sup> for the vibrations of octahedral metal – oxygen bond and another around 610 cm<sup>-1</sup> for tetrahedral metal – oxygen bond vibrations. TGA-DSC analysis indicate formation of spinel phase at 250°C. However TGA-DSC analysis of NF1, NF2 and ZF1 after HT at 1400°C show no significant loss of mass which confirms presence of stable single spinel phase. XRD studies show the formation of pure and single spinel phase. The average crystalline size was determined from X-ray diffraction line broadening using Scherrer equation. FESEM studies revealed that all the synthesized ferrites are having nearly octahedron crystals with an average particle size of 20 to 40 nanometer

**Keywords:** hydrothermal synthesis, Ni-Zn ferrites, TGA-DSC analysis, spinel ferrites

## I. INTRODUCTION

Magnetic nano particles have received special attention over the last years due to their special properties such as high surface area, easy separation from reaction media. Nano material ferrites have applications in making cores of audio frequency and high frequency transformers, coils (inductors), chokes, permanent magnets, magneto optical displays, microwave absorbers, wave guides in the GHz region, chlorine gas sensors [1], high density information storage [2], color imaging [3], bioprocess [4], medical diagnosis [5], electromagnetic wave absorption [6] etc. Multi layer chip indicator (MLCI) has recently been developed as one of the key surface mounting devices [7,8]. Among the different mixed ferrites, Ni-Zn ferrites have a good utility as a conducted noise suppressor material in various electromagnetic interfaces compared to other ferrites [9,10] because of their high resistivity, relatively high permeability and low eddy current loss [11,12]. These soft magnetic materials, crystallize in the spinel structure of the type  $(Zn_{1-x}Fe_x)(Ni_xFe_{2-x})O_4$ , where the metallic cations  $Fe^{3+}/Zn^{2+}$  occupy the tetrahedral A sites, and the metallic cations  $Fe^{3+}/Ni^{2+}$  occupy the octahedral B sites [13,14]. In biomedical application, one can use nano magnetic materials as drug carriers inside body where the conventional drug may not work. For this purpose, the nanosize particles should be in the super paramagnetic form with a low blocking temperature. Ferrite nanomaterials are object of intense research because of their proper magnetic properties. It has been reported that when the size of particles reduced to small size or in range of nanomaterials, some of their fundamental properties are affected. It is known that magnetic properties of ferrites are sensitive to preparation technique and their microstructures [15]. The electrical and magnetic properties of such ferrites depend strongly on distribution of cations at the tetrahedral (A) and octahedral (B) sites in the lattice [16-18]. It is well known that zinc ions can be used to alter the saturation magnetization. It is believed that the addition of zinc ions also affects the lattice parameter and it would therefore be expected to change the Curie temperature of the material [19]. The substitution of divalent ions in pure ferrites leads to the modification of the structural, electrical and magnetic properties [20]. Several researchers have reported the synthesis of Ni-Zn ferrites using different techniques like, refluxing process [21], ceramic [22], hydrothermal [23], combustion [24], co-precipitation [25], reverse micelle process [26], spark plasma sintering [27], micro emulsion [28] and ball milling, etc. In this work, we present the results of substitution of non-magnetic Zn on the magnetic Nickel ferrite synthesized by low temperature hydrothermal method.

## II. EXPERIMENTAL

For the synthesis of  $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$  [ $x = 0.0, 0.5, 1.0$ ] appropriate mole ratios of Analargrade Cobalt chloride, Nickel chloride, ZincchlorideandFerricchloridewereweighedandeachofwhichwas dissolved in 50ml of a solution containing 0.5 gram of disodium salt of Ethylene Diamine Tetraacetic Acid (EDTA) with constant stirring by magnetic stirrer. 4.4 molar NaOH solution was added drop by drop into each mixture till the pH is increased to 12. The precipitate produced was stirred for another 3 hours at room temperature. Then the precipitate was transferred into an autoclave (23 ml capacity) and kept at a temperature of  $140^\circ\text{C}$  for 12 hours in an air oven. The precipitate obtained was centrifuged and washed with distilled water and ethanol. The synthesized materials were designated as follows:

NF1 -  $\text{NiZnFe}_2\text{O}_4$  [ $X = 0$ ]

NF2 -  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  [ $X = 0.5$ ]

ZF1 -  $\text{ZnFe}_2\text{O}_4$  [ $X = 1.0$ ]

## III. CHARACTERISATION

Powder X-ray diffraction (XRD) patterns were measured by using RICH-SIEFERT 3000-TT diffractometer employing  $\text{CuK}_\alpha$  radiation. The Fourier transform infrared (FTIR) was performed by the KBr tablet method in the range  $4000\text{--}250\text{ cm}^{-1}$ , in a BRUKER model IFS 66 V FTIR spectrometer. The morphologies of the samples were examined with field emission scanning electron microscope (FESEM, FEI Nova-Nano SEM-600, The Netherlands). TGA- DSC were carried out using Mettler Toledo TGA/DSC1 in the temperature range from  $25^\circ\text{C}$  to  $1100^\circ\text{C}$  at heating rate of  $10^\circ\text{C}$  per minute to investigate thermal properties of prepared samples.

## IV. RESULTS AND DISCUSSION

The FTIR spectra of the spinel ferrites after hydrothermal treatment are given in Fig.1. The vibrational spectra of absorption bands were observed only in the range between  $420$  to  $610\text{ cm}^{-1}$  which are characteristic to spinel structure of the synthesized ferrites. The absorption bands observed around  $420\text{ cm}^{-1}$  are due to the vibrations of octahedral metal – oxygen bond and around  $610\text{ cm}^{-1}$  are attributed to tetrahedral metal – oxygen bond vibrations. The difference in the frequency of the two vibrations might have resulted due to the longer bond length of oxygen – metal ions in the octahedral sites and shorter bond length of oxygen – metal ions in the tetrahedral sites. The absence of peaks at  $1300\text{--}1650\text{ cm}^{-1}$  and  $2000\text{--}3500\text{ cm}^{-1}$  shows nonexistence of the O–H mode, C–O mode, and C=H stretching-mode of vibrations. However the FTIR spectra of NF1 before hydrothermal treatment (Fig.2) shows additional peak around  $3305\text{ cm}^{-1}$  and  $1583\text{ cm}^{-1}$  which are attributed to O–H mode of vibrations. Very weak band at  $591\text{ cm}^{-1}$  and  $404\text{ cm}^{-1}$  are observed. These observations indicate the presence of moisture and no significant formation spinel phase before hydrothermal treatment.

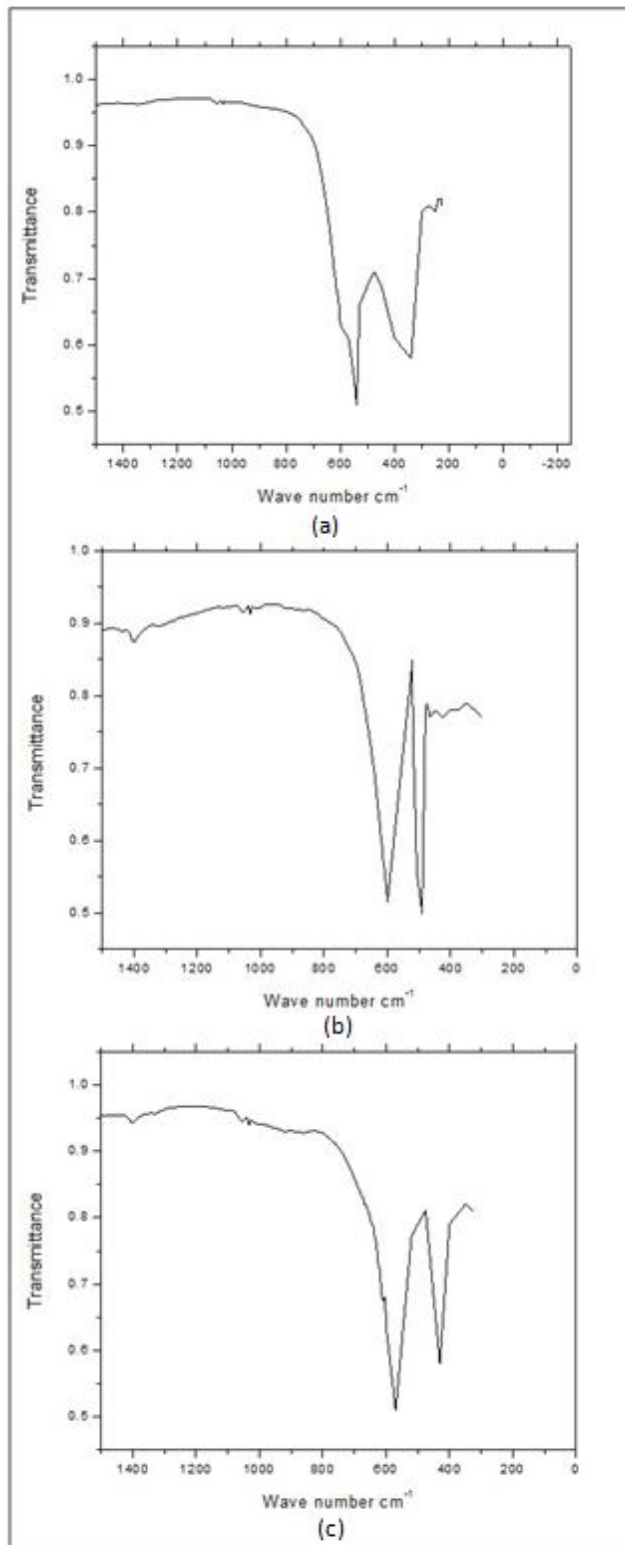


Fig 1: FTIR Spectra of (a)NF1, (b)NF2 and (c) ZF1 after HT

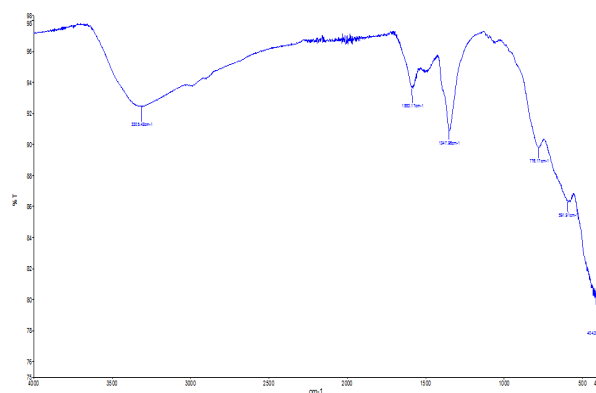
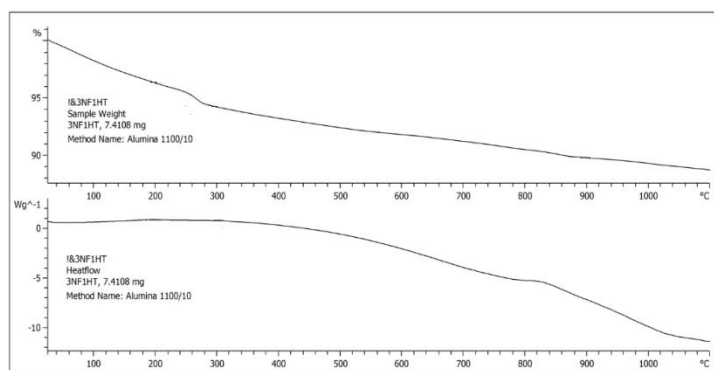


Fig 2: FTIR Spectra of NF1 before HT

In order to find temperature range for the growth of system, TGA/DSC in temperature range 25°C to 1100°C at a heating rate 10°C per minute were performed for NF1 before and after

hydrothermal treatment (HT). TGA curveanalysis of NF1 before HT(Fig.3) shows that there is mass loss with temperature.Around temperature 120°C , loss of mass is due tovaporization of surface water molecules and more loss ofmass up to 160°C , due to vaporization of trapped watermolecules.For temperature range 200°C to 260°C , mass loss of samplemay be due to loss of organic material. Ranges oftemperature corresponding to no significant loss suggestrecrystallization process. DSC Endothermic peak ( Fig.3)at 250°Cshows that at this temperature , ferrite formation getscompleted and Enthalpy change is found to be 325 Jg<sup>-1</sup>of synthesized samples as-prepared. Hence addition of EDTA as template significantly reduces the spinel phase formation compared to conventional co-precipitation methods without addition of any template. However in the present study zinc substituted ferrites are synthesized by hydrothermal methodwith EDTA as template at a temperature of 140°C. The TGA-DSC analysis of NF1 (Fig.4) after Hydrothermal treatment shows no significant weight loss indicating the presence of stable single phase spinel structured ferrites. The role of EDTA in controlling size and shape of ferrites with rapid the spinel phase formation is under investigation.



(a)

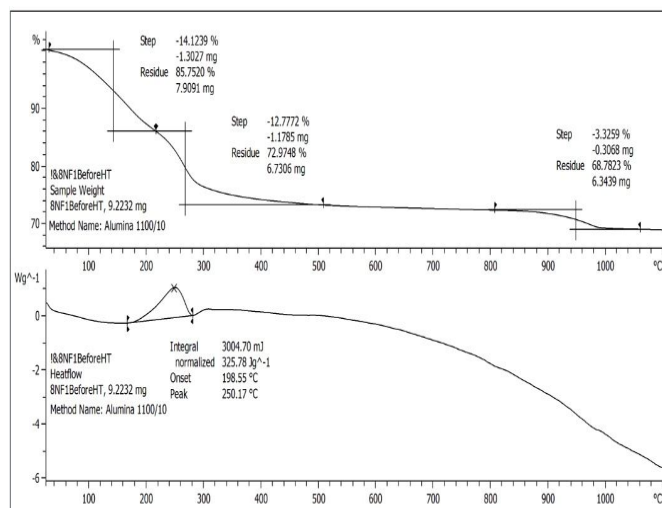
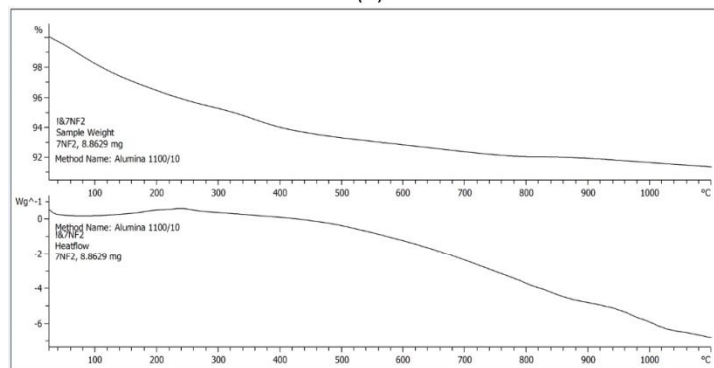
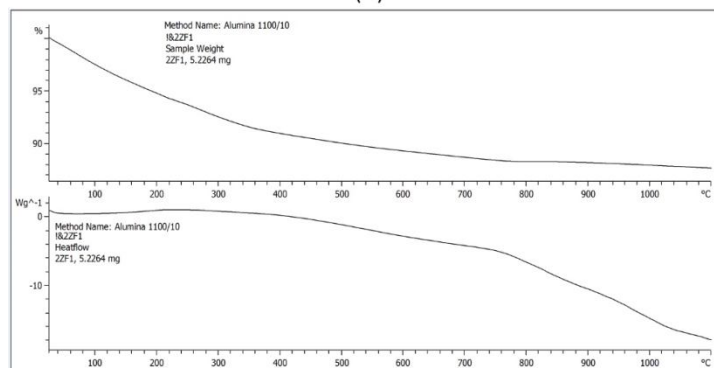


Fig 4: TGA-DSC curve of NF1 before HT



(b)



(c)

Fig 3: TGA-DSC curve of (a) NF1, (b) NF2 and (c) ZF1 after HT

TABLE 1  
CRYSTAL PARAMETERS

Sample	Lattice constant(a) Å	Volume of Unit Cell (a <sup>3</sup> ) Å <sup>3</sup>	Average size from XRD (nm)	Average size from FESEM (nm)
NiFe <sub>2</sub> O <sub>4</sub>	8.33	578	33.28	26.38
Zn <sub>0.5</sub> Ni <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub>	8.36	584.27	33.42	28.44
ZnFe <sub>2</sub> O <sub>4</sub>	8.44	601.24	16.69	22.78

The XRD patterns of the synthesized ferrites are shown in Figure

5. Which exhibit typical reflections of (220), (311), (222), (400), (422), (511) and (440) planes that are indications of the presence of the cubic spinel structure. All of the diffraction peaks match well with the reported values (JCPDS file No: 10-0325 for Nickel Ferrite, and File No. 22-1012 for Zinc Ferrite).

The average crystallite size is determined by the Scherrer equation using the peak broadening (FWHM) of the most intense peak (311):  $t = 0.9\lambda / \beta \cos\theta$  where  $\lambda$  is the wavelength of  $\text{CuK}\alpha$  (1.54059 Å),  $\theta$  is the angle of Bragg diffraction at full width half maximum (FWHM). The average crystallite size obtained for all the spinel ferrites are given in table 1.

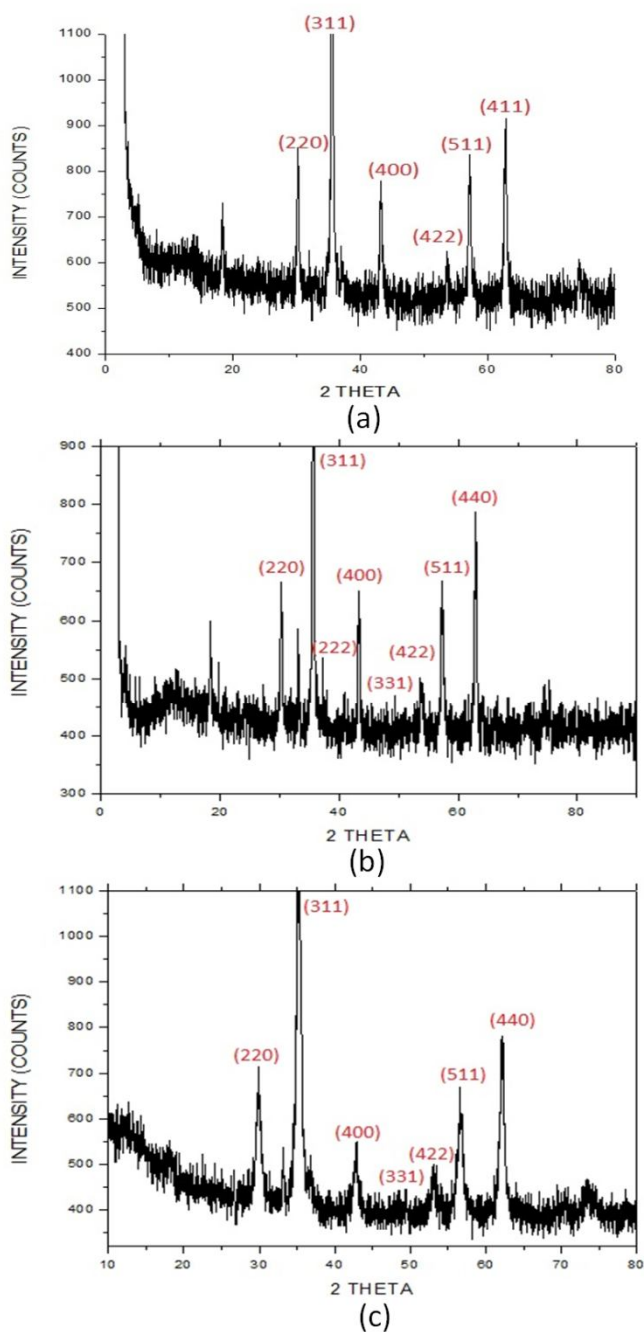


Fig 5: XRD Spectra of (a)NF1, (b)NF2 and (c) ZF1

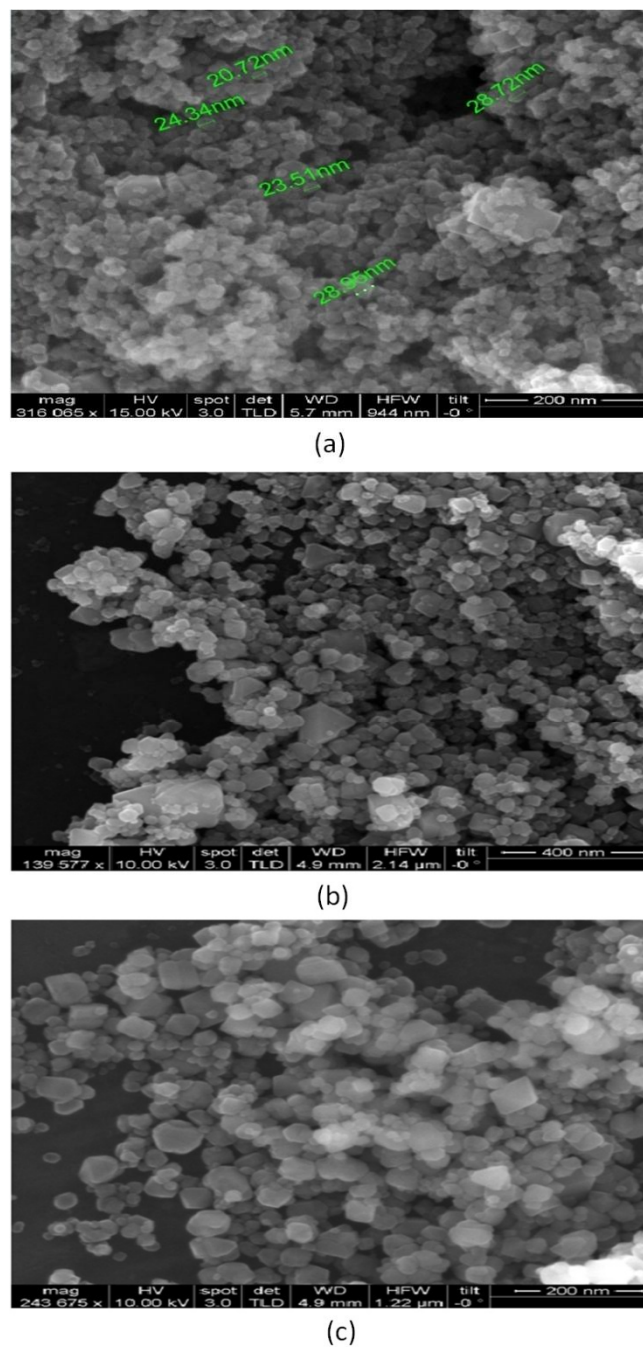


Fig 6: FESEM images of (a)NF1, (b)NF2 and (c) ZF1

The morphology obtained by FESEM analysis (Fig 6) shows incomplete octahedron structures for all the synthesized ferrites. The addition of EDTA, the complexing agent, controls the size as well as the shape of nanoparticles and prevents their agglomeration. The average crystal size observed from FESEM images are in good agreement with the calculated values by XRD. Lattice constant ( $a$ ) and Volume of unit cell ( $a^3$ ) are also calculated for NF1, NF2 and ZF1 which are given in table 1.

## V. CONCLUSIONS

Hydrothermal treatment carried out at a lower temperature of 140°C using EDTA as template found to yield Ni-Zn ferrites of nano size and incomplete octahedron shape with spinel structure. FTIR investigation confirmed the presence of metal ions in the tetrahedral and octahedral holes. TGA - DSC analysis indicated spinel phase formation at 250°C. However hydrothermal treatment facilitated the spinel phase formation at much lower temperature of 140°C. XRD study showed presence of pure and single spinel phase in all HT treated samples. FESEM analysis clearly indicated the existence of isolated nanoparticle with nanosize and incomplete octahedron shape of ferrites. The average crystallite size obtained by XRD and FESEM analysis indicate significant size reduction in ferrite particles.

## VI. ACKNOWLEDGEMENT

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