# Synthesis and magnetic studies of Ni-Zn ferrite nanoparticles

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Ni-Zn ferrite nanoparticles of the system, $Ni_{0.65} Zn_{0.35} Fe_2 O_4$, were synthesized by a soft chemical approach of co-precipitation method. These nanoparticles were separated into four batches and they were annealed at different temperatures from 200 to 800°C for improved crystallization. All the samples were then characterized by X-ray diffraction, vibrating sample magnetometer and ferromagnetic resonance spectrometer techniques. The XRD patterns confirm spinel structures while the particle sizes, ranging from 9.9 to 15.7 nm, increase with the increase in heat treating temperature. The magnetization values are extremely small even at 10 kOe fields with vanished hysteresis at lower heat treating temperatures; thus leading close to the superparamagnetic nature. The resonance parameters deduced from the FMR spectra are in support of the magnetisation data.

## 1. Introduction

Ferrite materials have been under intense research for so long due to their useful electromagnetic characteristics for a large number of applications [1]. The performance of these materials in their bulk form where the grain dimensions are in micrometer scales is limited to a few megahertz frequency due to their higher electrical conductivity and domain wall resonance [2,3]. However, the recent technological advances in electronics industry demand even more compact cores for work at higher frequencies [4]. One way to solve this problem is by synthesizing the ferrite particles in nanometric scales before compacting them for sintering. When the size of the magnetic particle is smaller than the critical size for multidomain formation, the particle is in a single domain state. Domain wall resonance is avoided, and the material can work at higher frequencies.

Ferrite particles in nano scales can be produced by soft chemical methods, such as co-precipitation, sol-gel and hydrothermal synthesis [5-7]. Among these methods, the co-precipitation has been chosen in the present study as the conditions of synthesis in this method are highly controllable and further it provides homogeneous powders of highest yield at temperatures close to 100 °C. In our former articles we have reported on pulsed laser deposition of NiFe2O4 thin films [8], on the properties of Nb doped [9] and $Ti^{4+}$ substituted [10] Ni-Zn ferrites. Moreover, the influence of Ni-Zn ferrite is reported recently, synthesis and characterization of Ni-Zn ferrites prepared by classical ceramic method and by mechano-synthesis [11, 12] were reported. Ni-Zn-Co ferrites were also prepared and investigated [13]. This paper reports and discusses the results of synthesis and characterization of Ni-Zn ferrite nanoparticles with respect to the heat treating temperature.

## 2. Experimental

Synthesis of the ferrite nanoparticles was done by coprecipitation [14] by taking high-purity Ni $Cl_2 \cdot 6H_2O$, Fe $Cl_3$ and $ZnCl_2$ as starting materials. According to the chemical formula of $Ni_{0.65} Zn_{0.35} Fe_2 O_4$, each starting material was weighted separately and added suitable quantity of de-ionized water to make them 0.5M solutions and then mixed all these cationic solutions while stirring to complete dissolution. The NaOH solution is prepared in sufficient quantity at 0.2M concentration and is heated to 60 °C. Then, the heated NaOH solution is poured into the cationic solution in a thin flow while maintaining the stirring and heating till the precipitation occurs. Heating of the precipitate in its alkaline condition is continued to a soaking temperature of 100 °C for 30 minutes in order to complete the reaction. Stirring was maintained further for 6 h for ageing and then the precipitated particles are washed and filtered six times before drying them at 60 °C for 48 hours. The co-precipitated ferrite agglomerates were then ground for few minutes using agate mortar and pestle to have very fine particles. These particles were subsequently heat treated at 200, 400, 600 and 800 °C for further crystallization.

X-ray powder diffraction patterns of the samples were taken on a Phillips X'pert diffractometer using Cu $K_\alpha$ radiation. Magnetization measurements were made on a

Vibrating Sample Magnetometer at room temperature using a field up to 10 kOe. Room temperature ferromagnetic resonance (FMR) spectra were taken using a microwave X-band reflection cavity spectrometer system operated at 9.8 GHz. The samples were settled in a small quartz tube and held in the cavity. DC field was applied parallel to the sample holder and the AC high frequency field was applied perpendicular to the sample.

## 3. Results and discussions

XRD patterns of all the samples of $Ni_{0.65}Zn_{0.35}Fe_2O_4$ annealed at different temperatures from 200 $^o$C to 800 $^o$C are shown in Fig. 1. The samples exhibit all the peaks indicative of single phase spinel crystal structure with increased crystallinity with the increase in annealing temperature. The increase in sharpness of XRD peaks with the increase in annealing temperature indicates the growth in crystallite size.
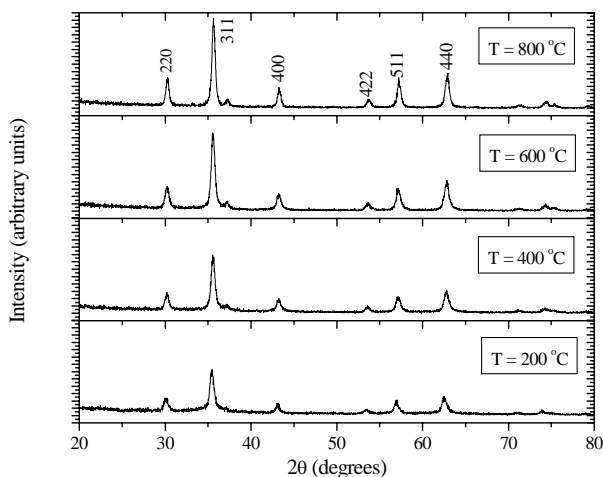
The particle sizes of the samples were estimated using the high intensity 311 peak and the Scherrer equation [14] while taking into account the instrumental broadening [15]. The values, ranging from 9.8-15.7 nm for different samples, are listed along with other magnetic parameters deduced from magnetization and FMR measurements in Table 1.

*Table 1. Various structural and magnetic parameters of $Ni_{0.65}Zn_{0.35}Fe_2O_4$ ferrite nanoparticles estimated by XRD, VSM and FMR characterization.*

| Sample | Particle size, nm ($\pm$ 3%) | Magnetisation emu/g ($\pm$ 2%) | Coercivity Oe ($\pm$ 2%) | Resonance field, Oe ($\pm$ 1%) | Linewidth Oe ($\pm$ 3%) | Relaxation time, ps ($\pm$ 5%) |
|---|---|---|---|---|---|---|
| NZ200 | 9.9 | 9.1 | 3.5 | 3328 | 836 | 65 |
| NZ400 | 10.8 | 10.5 | 5 | 3105 | 1071 | 48 |
| NZ600 | 12.7 | 19.5 | 17 | 3007 | 1666 | 29 |
| NZ800 | 15.7 | 23.0 | 55 | 2796 | 2242 | 20 |

Hysteresis loops of all the samples are shown in Fig.2. The samples exhibited vanished hysteresis as the annealing temperature is lower and smaller values of magnetization are observed (23 emu/g for the sample annealed at 800 $^o$C to 9.1 emu/g at 200 $^o$C) compared to the magnetization value of their bulk sample (73 emu/g) of similar composition [16, 17]. The observed coercivities, as listed in the table, are very small for all the samples and they have been found to decrease with the decrease in annealing temperature.



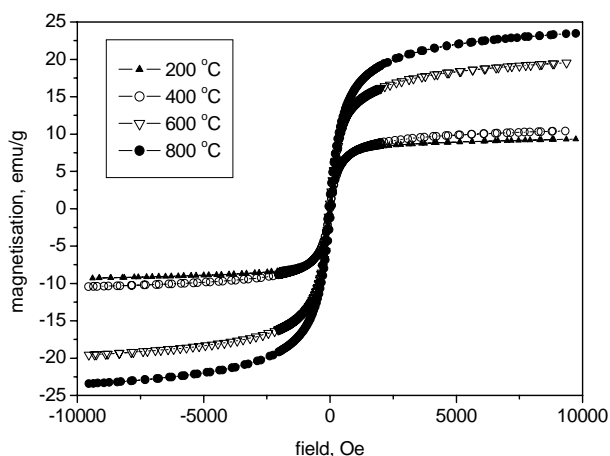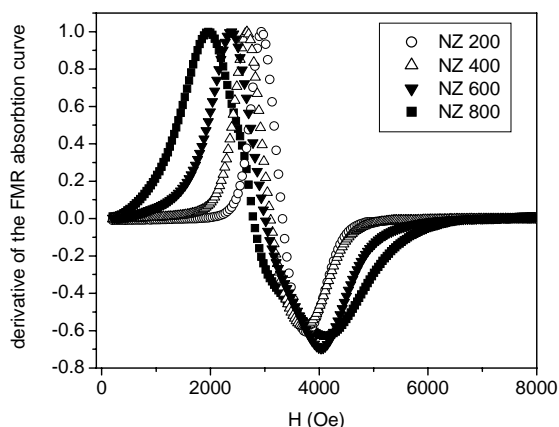*Fig. 1. X-ray diffraction patterns of $Ni_{0.65}Zn_{0.35}Fe_2O_4$ powder heat treated at different temperatures.*



*Fig 2. Room temperature hysteresis loops of $Ni_{0.65}Zn_{0.35}Fe_2O_4$ ferrite nanoparticles heat treated at different temperatures.*



*Fig. 3. Ferromagnetic resonance spectra of $Ni_{0.65}Zn_{0.35}Fe_2O_4$ ferrite nanoparticles heat treated at different temperatures from 200$^o$C to 800 $^o$C.*

It is known that the magnetic parameters, particularly magnetizations and coercivity, of nanoferrites prepared by coprecipitation are different from those prepared by ceramic methods due to the inversion degree of distribution of cationic ions between the tetrahedral (A-) and octahedral sites (B-) of the spinel lattice [17] and also due to the spin disorder in the shell around the core [18]. It implies that the cations in nanoscale materials occupy lattice sites by a certain degree against their preferences in

bulk materials and this degree (of inversion) is dependent on particle size. Since the magnetic parameters, within the same composition under investigation, are determined by microstructural features such as particle size and size distribution, there have been reports of changing the particle size and thereby the inversion degree and magnetic properties by an appropriate heat treatment [19]. In the present study, the increase in magnetization with the increase in annealing temperature could be understood as a result of the increase in particle size and thereby the change in degree of inversion parameter, i.e., there are more $Ni^{2+}$ ions occupying A-sites and also more $Zn^{2+}$ ions occupying B-sites in smaller Ni-Zn ferrites resulting in lower magnetizations for those samples. The observed lower values of coercivity with the decrease in annealing temperature and particle size can be explained as due to the localised randomizing effects of thermal energy of a disordered shell of a particle compensating the magnetic contributions made by its core. As the particle size further decreases, this may well lead to zero coercivities and a transition from ferrimagnetic to superparamagnetic state.

Ferromagnetic resonance (FMR) spectra for all the four samples are shown in Fig.3. All the samples showed single resonance peaks, but each of them is slightly asymmetric. This could be due to the contribution of non uniform resonance modes apart from the main mode of resonance. Since the composition under investigation is the same and only the heat treatment is different, the gyromagnetic ratio is supposed to be the same for all the samples, then the particle size and the resulting magnetizations obviously would be expected to influence the FMR parameters [20]. And, the observed values of resonance field, line width and relaxation time, as listed in the table, are also in accordance with the above.

## 3. Conclusions

In conclusion, the observed results of the materials under investigation are analysed to the following conclusions:

1. X-ray diffraction patterns confirm that the synthesis of fully crystalline Ni-Zn ferrite nanoparticles can be successfully done at lower temperatures.

2. The samples were resulting in smaller magnetizations and coercivities as the annealing temperature is lowered and this was attributed to particle size and inversion parameter.

3. The FMR spectra and the deduced parameters such as resonance field, line width and relaxation showed better correlation with the particle size and magnetisation data.

Further measurements are underway to complement the particle size as well as superparamagnetic nature, which could help to understand the system more clearly.

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