

Effect of Zinc doping on Structural and Magnetic Properties of NiFe₂O₄ Nanoparticles

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Abstract: The present work deals with the synthesis, structural and magnetic characterizations of pure and zinc doped nickel ferrite (NiFe₂O₄ and Ni_{0.65}Zn_{0.35}Fe₂O₄) nanoparticles. The Ni_{0.65}Zn_{0.35}Fe₂O₄ nanoparticles were synthesized by sol-gel auto combustion method. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) techniques were used for the characterization of the prepared samples. The structural properties were estimated from X-ray diffraction (XRD) studies. The principle absorption bands correspond to octahedral lattice site was observed from FTIR spectra. The average particle size was calculated by using Debye Scherer's formula and the obtained values are of few nanometer. The M-H curves recorded at room temperature exhibits a typical hysteresis loop indicating that the sample exhibits ferrimagnetic behaviour. The large coercivity (H_c) values indicate nanocrystalline nature of the present samples. The coercivity, saturation magnetization, remanence magnetization and magneton number found to be influenced by zinc doping.

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I. INTRODUCTION

Ferrites are magnetic ceramics of great importance in many technological applications on account of their various electrical, dielectric and magnetic properties. Ferrites with cubic spinel structure forms an important class of magnetic materials and exhibit interesting electrical and magnetic properties. Owing to their numerous applications ferrites are being studied from last six to seven decades with a view to understand and improve their properties for suitable applications. On account of their combined electric and magnetic properties they show wide applications in technology, particularly at high frequency [1, 2]. Ferrite materials find high frequency applications due to their high permeability and permittivity [3-7]. These materials are being used in transformer cores, antennas, radio frequency coil and radar absorbing materials (RAM) [8].

The literature report mainly focuses on nanosize magnetic materials having significant potential for many applications. Research in this area for better and improved materials still continues as they find some new applications. During the last decades there has been an interest in developing and understanding the basic magnetic and electrical properties of spinel ferrite at nanometric scale. The progress made in the area of nanotechnology in the recent years has motivated the scientist and technologist to synthesize spinel ferrites in nanometric size and characterize them for their structural, electrical and magnetic properties. It is well known that the properties of spinel ferrites are changed when the size of the particle reduces from bulk to nano.

In the recent years, the design and synthesis of magnetic nanoparticles of spinel ferrites in nanosize has been the focus of intense fundamental and applied research due to their enhanced properties that are different from those of their bulk counterparts [9]. Technological demand of high performance devices has triggered the synthesis and research in nanoscale spinel ferrite. Nanosize spinel ferrites find applications in high density magnetic data storage [10], microwave absorbing material [11], magnetic resonance imaging [12], targeted drug delivery [13], magnetic fluids [14], biotechnology [15] etc.

Nickel ferrite is a well-known hard magnetic material with inverse spinel structure. The saturation magnetization and coercivity of nickel ferrite is higher than the other nickel, manganese spinel ferrites [16]. Nickel ferrite is the most important and abundant magnetic materials that have large magnetic anisotropy, moderate saturation magnetization, remarkable chemical stability and mechanical hardness, which make it good candidate for the recording media [17, 18]. The chemical composition method of synthesis, nature of dopant, site preference of dopants etc parameters strongly influences the structural, electrical and magnetic properties of spinel ferrites [19, 20]. In the present study, the effect of Zinc doping on the magnetic properties of nanocrystalline nickel ferrite prepared by sol-gel auto combustion method is reported.

II. MATERIAL AND METHODS

Preparation

NiFe₂O₄ and Ni_{0.65}Zn_{0.35}Fe₂O₄ nanoparticles were synthesized by sol-gel auto combustion method using citric acid as a fuel. The stoichiometric proportions of metal nitrates to fuel (citric acid) ratio as 1:3 were taken into separate glass beakers. The mixed solution was stirred for 15-20 minutes to dissolve completely into distilled water. After complete dissolution they were mixed together. Ammonia was added drop-wise into the solution to adjust pH value to about 7 and stabilize the nitrate-citric acid solution. Then the neutralized solution was constantly magnetically stirred and heated at 80-90 °C for 6 h on a hot plate. On the formation of sol-gel, very viscous gel the temperature was further raised up to 120 °C so that the ignition of the dried gel started and finally powder was obtained. The as prepared loose Nickel ferrite powder was grinded for 30 minutes and annealed at 700°C for 4 h in muffle furnace.

Characterizations

In the present work, pure and zinc substituted nickel ferrite samples were synthesized by sol-gel auto combustion method and characterized by X-ray diffraction technique. X-ray diffraction patterns of all the samples were recorded at room temperature by using a Regaku Miniflex-II X-ray powder diffractometer operated at 40 kV and 30 mA. The diffraction patterns were recorded in the 2θ range 20° to 80° with scanning rate of 2° per minute using Cu-K_α radiation of wavelength 1.5406 Å. The vibrational band position was estimated from the FTIR spectroscopy. The magnetic properties were measured using pulse field hysteresis loop technique at room temperature (Magnata Mumbai).

III. RESULTS AND DISCUSSION

Fig. 1 depicts the XRD pattern of zinc doped nickel ferrite nanoparticles recorded at room temperature. The analysis of XRD patterns reveals the formation of single phase cubic spinel structure for doped and undoped nickel ferrite. All the peaks in the XRD pattern were indexed by using Bragg's law. The presence of planes (220), (311), (222), (400), (422), (511) and (440) in the XRD pattern reveals the cubic spinel structure of all the samples. It is also evident that all the peaks are intense and sharp. No impurity peaks were observed, thus the samples are single phase in nature. It is also evident from XRD pattern that the intensity of Bragg's peak is higher and the peaks are broader. Similar XRD patterns have been observed for spinel ferrites in literature [14].

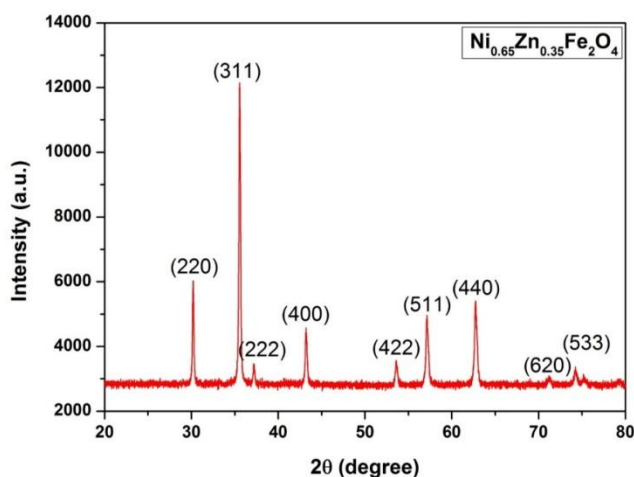


Fig.1: XRD pattern of Ni_{0.65}Zn_{0.35}Fe₂O₄

The intensity of (311) plane is more as compared to other planes. The lattice constant (a) values were calculated using standard relation,

$$a = d\sqrt{(h^2+k^2+l^2)} \quad \text{Å} \quad \dots(1)$$

Where, (d) is interplanar spacing; (h k l) is Miller Indices.

The obtained values of the lattice constant (a) are listed in table 1. The increase in lattice constant with zinc as compared to the pure nickel ferrite and variation in lattice constant can be interpreted on the basis of the ionic radii of the constituent ions Ni²⁺, Zn²⁺, Fe³⁺. The substitution of Zn²⁺ ions in place of Ni²⁺ leads to increase in lattice

constant. Similar behaviour of lattice constant was reported in the literature [15]. The values of structural parameter like X-ray density and unit cell volume also calculated and listed in table 1.

The particle size was calculated by using the most intense peak (311) and using the Debye-Scherrer relation for small and uniform sized cubic crystals mentioned below [16] and is found to be in nanometer size (Table 1).

$$t = \frac{0.9\lambda}{\beta \cos \theta} \quad \text{nm} \quad \dots(2)$$

Fourier transform infrared spectroscopy

Fig. 2 shows the FTIR spectra of zinc doped nickel ferrite (Ni_{0.65}Zn_{0.35}Fe₂O₄) nano particles. These spectra were recorded in the frequency range 500-4000 cm⁻¹. Two main broad metal-oxygen bands are seen in the IR spectra of all samples. These two bands, according to Waldron attributed, band around at 500 cm⁻¹ and 600 cm⁻¹ confirms the spinel ferrite structure.

The high frequency band ν₁ is caused by stretching vibrations of tetrahedral metal-oxygen band and low frequency absorption band ν₂ is due to the metal-oxygen vibrations in octahedral sites. The difference in frequencies of bands ν₁ and ν₂ may be due to changes in the bond length Fe³⁺- O²⁻ at tetrahedral and octahedral sites.

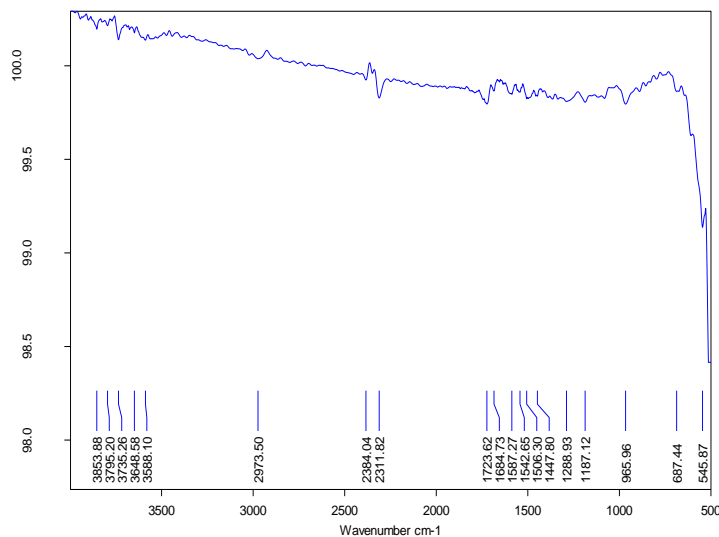


Fig. 2 FTIR for Ni_{0.65}Zn_{0.35}Fe₂O₄ nano crystalline material

Magnetic properties

The magnetic hysteresis curves for zinc doped nickel ferrite (Ni_{0.65}Zn_{0.35}Fe₂O₄) are shown in Fig. 3. These hysteresis curves are used to determine saturation magnetization (M_s), remanence magnetization (M_r), remanence ratio (M_r/M_s) and coercivity (H_c). All the values of magnetic parameter are listed in table 2. It is evident from table 2 that the saturation magnetization, coercivity and remenent magnetization get decrease on doping of zinc ions. This may be due to the fact that zinc is a nonmagnetic ion and have a tendency to occupy tetrahedral site. This leads to decrease in A-B interaction and therefore all these magnetic parameters are decreased on doping of zinc ions in nickel ferrite. Similar results are reported in the literature for spinel ferrite [14].

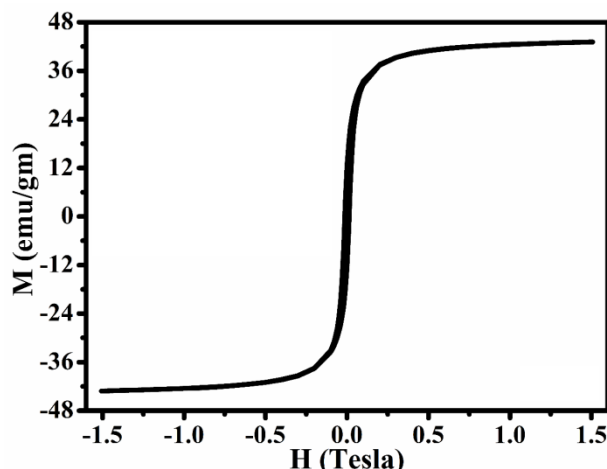


Fig.3: M-H plots recorded at room temperature for Ni_{0.65}Zn_{0.35}Fe₂O₄ nanoparticles

Table 2: Saturation magnetization (Ms), Remanence magnetization (Mr), Coercivity (H_c) and Remanence ratio (Mr/Ms) for doped and un-doped nickel ferrite

Sample	Ms (emu/g)	Mr. (emu/g)	H _c (Oe)	Mr/Ms
NiFe ₂ O ₄	45.40	12.16	175.88	0.301
Ni _{0.65} Zn _{0.35} Fe ₂ O ₄	42.83	8.873	151.71	0.241

IV. CONCLUSION

The nanocrystalline pure and zinc doped nickel ferrite were successfully synthesized by sol-gel auto combustion technique. The X-ray diffraction results showed the formation of single phase cubic spinel structure. The value of crystallite size confirms the nanocrystalline nature of the prepared sample. The structural parameters are found in the reported range. The substitution on Zn ions in nickel ferrite increases lattice constant. The absorption bands in FTIR spectra show formation of spinel cubic structure. The substitution of zinc ions in nickel ferrite results in decrease of magnetic properties of pure nickel ferrite nanoparticles.

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