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Improvement in ferromagnetism of $NiFe_2O_4$ nanoparticles with Zn doping

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ABSTRACT

Structural, microstructural, infrared analysis and magnetic properties of $Ni_{1-x} Zn_xFe_2O_4$ (NZ) [x = 0.30 (NZ30), 0.35 (NZ35) and 0.40 (NZ40)] nanoferrites have been thoroughly studied. These NZ nanoferrites were synthesized by chemical combustion route and annealed at 500 ^oC for 5h. Fourier transform infrared (FTIR) spectra of these samples were used to identify formation of Ni-Zn spinel ferrites. These FTIR results show two characteristic absorption bands corresponding to M-O intrinsic stretching vibrations at the tetrahedral site and octahedral-metal stretching around 570-550 cm^{-1} and 450-435 cm^{-1}, respectively. The X-ray diffraction shows the polycrystalline with spinel phase of these ferrites. The value of lattice constant a(Å) = 8.370, 8.371 and 8.380 respectively, for NZ30, NZ35 and NZ40 which are consistent with that reported for pure $NiFe_2O_4$. The average particles size is measured using Debye-Scherer's relation which lies in the range of 25-65 nm. Transmission electron microscopy measured average grain size is 26, 41 and 66 nm, respectively for NZ30, NZ35 and NZ40 samples. The magnetic measurement shows saturation magnetization (Ms) of 67.63, 74.97, 80.63 emu/g, remanent magnetization (Mr) 20.01, 25.30, 25.30 emu/g and coercive field (Hc) 154.12, 154.13, 154.11 Oe, respectively for NZ30, NZ35 and NZ40. Highest saturation magnetization with Zn doping has been observed in the case of NZ40.

Keywords: Nanoparticles; ferromagnetism; TEM.

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Introduction

Spinel ferrites are technologically important due to their properties like high resistivity, memory storage capacity, mechanical hardness, chemical stability and reasonable cost **[1-2].** These properties are extensively depend upon the distribution of metal ions over tetrahedral and octahedral sites, nature and oxidation state [**3**]. $NiFe_2O_4$ have inverse spinel structure and $ZnFe_2O_4$ has normal spinel structure. So the doping of Zn in $NiFe_2O_4$ pushes inverse structure to acquire mixed spinel **[4].** In ferrites the distribution of the different ions in the tetrahedral and octahedral sites of the spinel lattice mainly depends on the method of preparation and processing conditions. Various physical and chemical methods of preparation have been developed to achieve nano-sized ferrite particles such as sol-gel, chemical co-precipitation, high-energy ball milling, hydrothermal, citrate precursor, mechanical alloying and Chemical combustion route **[5-8].** Highly pure and uniform particles of low fabrication temperature are essential to get the good performance of the materials with low preparation cost. Therefore, in the present work, simple Chemical combustion route is employed to synthesize zinc substituted nickel ferrite nanoparticles, which neither requires sophisticated instrument nor high annealing temperature. In the present paper we report the structural, microstructural and magnetization of $Ni_{1-x}Zn_xFe_2O_4$ (NZ) [x = 0.3 (NZ30), 0.35 (NZ35) and 0.40 (NZ40)] nanoferrite.

Experimental

NZ nanoferrites were prepared by a chemical combustion technique and detailed is given elsewhere **[1].** The precursors solutions of $Ni(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$, $Zn(NO_3)_2.6H_2O$, Urea and polyethylene glycol were used. The phase structure has been carried out by X-ray diffraction (XRD) using X-Pert PRO system and microstructures by transmission electron microscopy (TEM) using Hitachi H-7500. The magnetic measurements were carried out by using vibrating sample magnetometer (VSM-735). The effect of light on NZ nanoferrites has been studied in the infrared region by Fourier transform infrared (FTIR) spectroscopy using a Nicolet Avtar 5700 system.

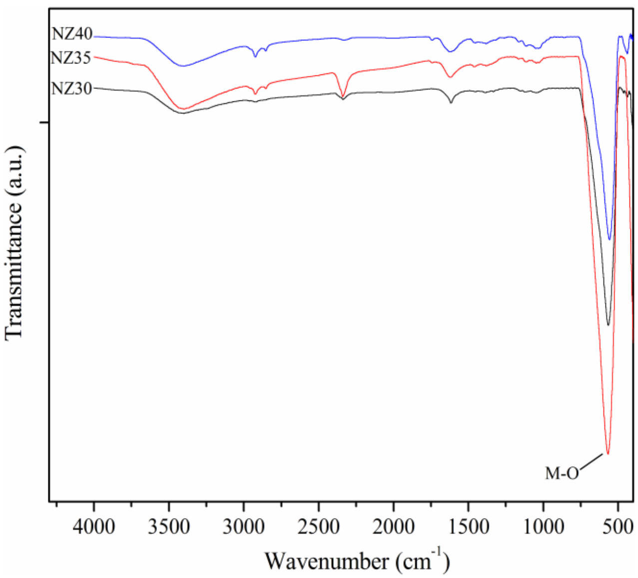

Fig. 1. FTIR spectra of NZ nanoferrites.

Table 1. Values of lattice parameters a, average particles size (x) from TEM, saturation magnetization (Ms), remanent magnetization (Mr) and magnetic moment (μB).

Sample	*a*(Å)	*x* (nm)	M_s (emu/g)	M_r (emu/g)	μ_B
NZ30	8.370	26	67.63	20.01	2.862
NZ35	8.371	41	74.97	25.30	3.178
NZ40	8.380	66	80.63	25.30	3.422

Results and discussion

Fig. 1 shows the FTIR spectra of NZ nanoferrites carried out to understand the mechanism of self-combustion reaction as they form Ni-Zn spinel ferrites with evolution of large amount of gases and heat. The analysis was carried out in the range of 400 ~ 4000 cm^{-1} for samples annealed at 500 °C for 5 hrs. These FTIR results confirm that Ni^{2+} is stabilized in the octahedral crystal field whereas Zn^{2+} prefers tetrahedral sites because of its ability to form covalent bonds. These spectra shows two characteristic absorption bands of spinels corresponding to M-O intrinsic stretching vibrations at the tetrahedral site (V1) and octahedral - metal stretching (V2) around 620-550 cm^{-1} and 450-435 cm^{-1} for Zn^{2+} and Ni^{2+}, respectively and remaining were filled by 16 Fe^{3+} ions. The spectrum also shows evidence of presence of very light bands of CO_3^{2-} and NO^{3-} and moisture. The band at 3433.31 cm^{-1} and ~1626.12 are due to moisture (OH- groups) and 2300.00 and 1000.00 cm^{-1} correspond to atmospheric or adsorbed CO_3^{2-} and nitrate ions respectively.

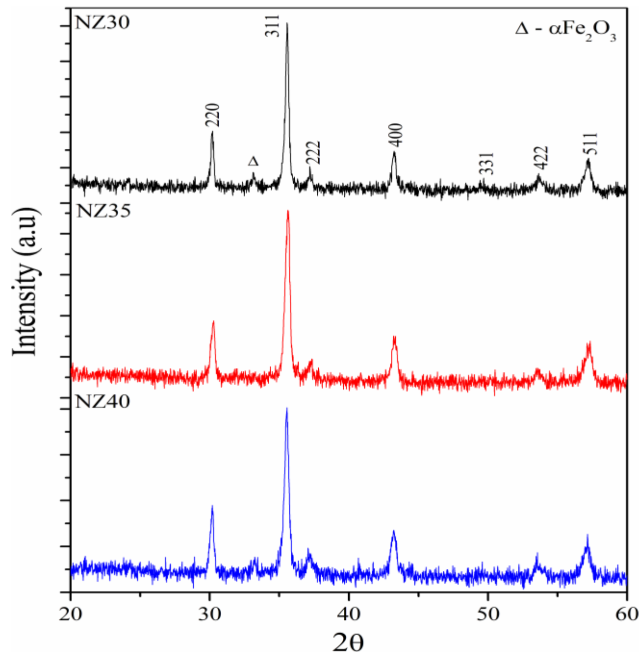

Fig. 2. XRD pattern of NZ.

Fig. 2 show the XRD pattern of NZ nanoferrites annealed at 500 °C/5h. The peaks at 2θ = 30.48°, 34.99°, 37.48°, 42.58°, 48.02°, 51.23° and 55.85° attributed to (220), (311), (222), (400), (331), (422) and (511) reflections of the cubic spinel are observed. The average crystallite sizes using Scherer formula is 27, 43 and 67 nm, respectively, for NZ30, NZ35 and NZ40 ferrite. The values of lattice parameter, a(Å) 8.370, 8.371 and 8.380, respectively, for NZ30, NZ35 and NZ40 ferrite and are also given in **Table 1**.

Fig. 3 shows the TEM image of NZ ferrites. The particles size determined from TEM was found to be in close agreement with that obtained from XRD studies. It shows homogeneous microstructures with nano grain size. The values of average particles size from TEM images is 26, 41 and 66 nm, respectively, for NZ30, NZ35 and NZ40 ferrite.

The magnetization hysteresis loops recorded at room temperature for the NZ ferrites are shown in **Fig. 4**. The magnetic measurement shows enhancement in the value of saturation magnetization (Ms) with increasing Zn^{2+} substitution. The measured values of the saturation magnetization (Ms), 67.63, 74.97 and 80.63 emu/g, remanent magnetization (Mr) 20.008, 25.30 and

25.30emu/g, and coercive field (Hc) 154.12, 154.13, 154.11 Oe, respectively, for NZ30, NZ35 and NZ40 ferrite.

Magnetic moment per unit formula in Bohr magnetron (μB) was calculated from saturation magnetization of hysteresis loops by using relation [**9**]:

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

where M is the molecular weight, Ms is saturation magnetization (emu/g) and 5585 is magnetic factor. The values of μB for NZ are 2.862, 3.178 and 3.422, respectively, for NZ30, NZ35 and NZ40.

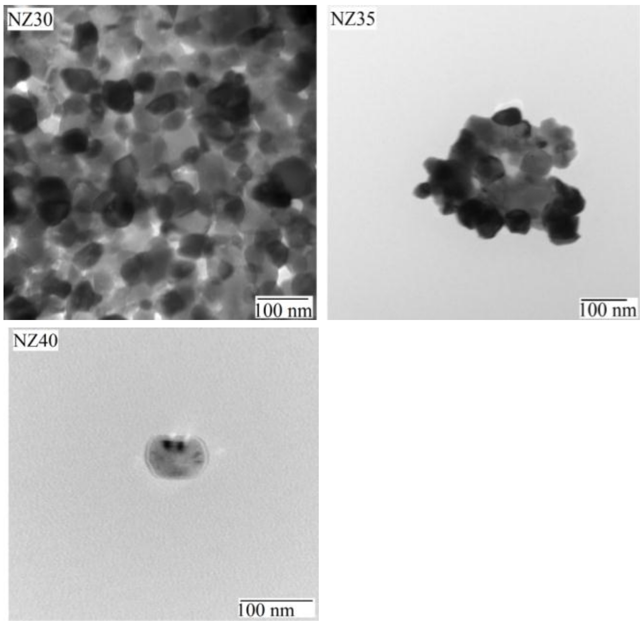

Fig. 3. TEM images.

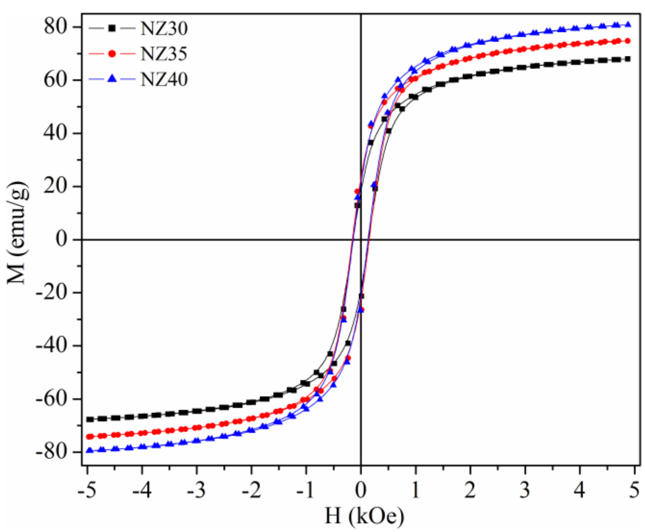

Fig. 4. *M-H* hysteresis.

Conclusion

NZ nanoferrites were prepared by a chemical combustion route and annealed at 500 °C for 5h. The FTIR spectra show the existence of M-O bond in the samples and the absence of organic groups leads to an enhancement in crystallization. XRD spectra show the cubic spinel phase of each NZ sample and the value of lattice constant is matched well with the parent $NiFe_2O_4$. The values of average particles size lie in nano range which measured by Scherer relation from FWHM. The average particles size from TEM is 26, 41 and 66 nm, respectively, for NZ30, NZ35 and NZ40 ferrite. The values Ms 67.63, 74.97 and 80.63 emu/g, Mr 20.008, 25.30 and 25.30 emu/g, and Hc 154.12, 154.13, 154.11 Oe, respectively, for NZ30, NZ35 and NZ40 ferrite.

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