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Structural and Magnetization Behaviour in Magnetically Diluted Nickel Ferrite at Nanoscale

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Abstract

The present investigation deals with the sol-gel auto combustion synthesis of nanocrystalline Zn doped nickel ferrite with chemical formula $Ni_{1-X}Zn_XFe_2O_4$ (x = 0.0 and 0.4) using urea as a fuel and the effect of magnetic dilution by Zn on structural and magnetic properties. The single phase as well as nanocrystalline nature of the prepared $Ni_{1-X}Zn_XFe_2O_4$ sample has been confirmed through X-Ray diffraction (XRD) technique. The crystallite size obtained by using Scherrer's formula was found to be in the range of 12 nm to 19 nm. The doping of Zn^{2+} ion in place of Ni2+ ions causes the reduction in lattice parameter. The lattice parameter of the pure nickel ferrite calculated by XRD data is of the order of 8.334 Å which is in good agreement with the standard lattice parameter of nickel ferrite. The magnetic behaviour of pure and Zn doped nickel ferrite was studied through pulse field hysteresis loop technique. The hysteresis curve (M-H plot) was recorded at room temperature to know the magnetic behaviour. Using M-H plots, the magnetic parameters viz. saturation magnetization, remenance magnetization, coercivity and magneton number were deduced. It is observed that the doping of Zn dilutes the magnetic structure of Nickel ferrite. All the magnetic parameters were decreased after Zn doping. The magnetic behaviour of the present samples was discussed using Neel's theory. Using Neel's model the magneton number n_B was calculated. The observed and calculated magneton number nearly matches with each other indicating the magnetic structure is collinear.

Keywords: Nickel ferrite, Zn doping, XRD, M-H curve.

INTRODUCTION

The diverse and fascinating applications of nanosized spinel ferrites have opened new prospects in various field viz. electronics, information technology, storage media, biomedical, transport, ferrofluids, etc [1-3]. The ferrites at nanoscale exhibit the novel properties like superparamagnetism, quantum confinement, single domain structure, high permeability, and chemical stability [4]. The large scale applications of fine particles of spinel ferrites exhibiting novel properties have been promoted development of various preparation techniques such as sol-gel auto combustion [5], co-precipitation [6], hydrothermal [7], micro-emulsion [8] etc which offer the right condition to tune the fine size, structure and morphology resulting an acute control over their properties. The physical properties of these nanomaterials are largely depends on the synthesis method and the optimized parameters. Selecting the appropriate parameters is crucial for the diverse applications. The sol-gel auto combustion synthesis route comprised of nitrates and fuel is commonly used method for ferrite nanoparticles preparation, since it is easy, cost effective, provides homogeneous size distribution and fine particle size. The most commonly used fuel is a citric acid, but now the approach of using new inorganic as a fuel has gained much importance. Glycine, tartaric acid, L-ascorbic acid, sucrose, dextrose, acetic acid, ethylene glycol and urea have been reported as a fuel. The most important factor which drastically influences the magnetic properties of the nanoferrites is the size and shape. Moreover, the magnetic and electrical properties of spinel ferrites primly depend on the magnetic interactions between the cations, magnetic moments on tetrahedral (A) sites and octahedral [B] sites and hopping of electrons. In the family of spinel ferrite, Nickel ferrite is a unique and interesting ferrite exhibiting remarkable electrical and magnetic properties [9]. The crystal structure of nickel ferrite is an inverse in which Ni^{2+} ions occupy octahedral B site while Fe^{3+} ions occupy tetrahedral A and Octahedral B site. Many researchers have studied nickel ferrite in nanocrystalline form to study the structural, morphological and magnetic properties. These properties mostly depends on method of preparation, preparation condition and preparative parameters and therefore, nickel ferrite has been studied widely. In the preparation of nickel ferrite using wet chemical method fuels like citric acid and glycine were commonly used. To our knowledge, few reports are available on the preparation of nickel ferrite taking urea as a fuel [10, 11]. To understand the structural and magnetic properties of $Ni_{1-X}Zn_XFe_2O_4$ (x = 0.0 and 0.4) in detail, studies on synthesis, characterization and magnetic properties were carried out and the results obtained are presented in this work.

METHODOLOGY

The sol-gel auto combustion method which is most versatile, easy, low temperature, low cost and very much convenient to optimize the synthesis parameters was chosen to synthesize the pure nickel ferrite and zinc substituted nickel ferrite nanoparticles. The nitrates of nickel, zinc and ferric metal elements as oxidants and urea as a fuel were used as raw materials. The ratio of metal nitrates to fuel was selected as 1:2.5 (metal nitrates: urea) by balancing the metal nitrate to fuel valences adopting the propellant chemistry [22]. The calculated proportion of the urea was 1:4 but we have adopted the fuel deficient approach in the present synthesis. The weighed metal nitrates of respective elements were dissolved separately in 100ml distilled water and mixed together. The urea was also dissolved in 100ml distilled water and then added to mixed solution of metal nitrates. Then the solution was stirred at temperature of 90°C with 400 rpm for nearly 5h. Upon formation of very viscous gel the temperature was further raised to 120°C. The auto combustion of the gel carried out and the powder was formed which was ground using pestle and mortar. The as prepared fine powder was sintered at temperature 600°C for 6h to get better crystallization of the prepared spinel ferrite nanoparticles. The sample was coded as NF ($NiFe_2O_4$) and NZF ($Ni_{0.6}Zn_{0.4}Fe_2O_4$). The sintered powder of sample was used to characterize it by using Panalytical Xpert Pro X-ray powder diffractometer in the 2θ range of 15° - 80° degrees with Cu-kα radiation at room temperature. The magnetic measurements as M-H curve of all samples was studied with help of pulse field hysteresis loop tracer technique at room temperature with applied magnetic field of 5000 Oe.

RESULTS AND DISCUSSION

X-Ray diffraction studies

The phase identification and structural analysis of the $NiFe_2O_4$ and $Ni_{0.6}Zn_{0.4}O_4$ nanoparticles was done by XRD studies and the XRD patterns are shown in figure 1 which has the sharp and intense peaks. All the peaks were indexed by comparing them with the JCPD Card no. 019-0629 [12]. The presence of planes (220), (311), (222), (400), (422), (511), (440) and (533) in the XRD pattern reveals the cubic spinel structure of all the samples. The obtained XRD pattern exhibits the single phase cubic spinel structure since there is no other impurity peak and the only allowed peaks of cubic structure were observed. The structural parameters such as lattice parameter, crystallite size, unit cell volume and X-ray density were obtained using XRD data and their values are tabulated in table 1. It is observed from table 1 that, the lattice constant, X-ray density etc. are in the reported range. The crystallite size obtained through Scherrer's formula is found to be 20.87 nm which confirmed the nanocrystalline nature of the sample. The structural parameters and crystallite size obtained in the present case are better than the reported values. The doping of nonmagnetic zinc ion in place of Ni ions in nickel ferrite leads to increase in lattice constant and hence increase in unit cell volume and X-ray density. The increase in lattice constant is attributed to lower ionic radii of Ni ions (0.78Å) as compared to Zn ions (0.82Å).

Magnetic studies

The M-H curve recorded at room temperature of $NiFe_2O_4$ and $Ni_{0.6}Zn_{0.4}O_4$ nanoparticles is depicted in figure 2 which represents the dependence of the magnetization (M) over the applied magnetic field (H) of nickel ferrite nanoparticles. These nanoparticles exhibit the ferrimagnetic nature which can be characterized by hysteresis loop with the magnetic parameters as saturation magnetization (M_S), remanence magnetization (M_r) and coercivity (H_C). The values of these magnetic parameters are tabulated in table 2.

Table 1 Lattice parameter (a), Unit cell volume (V), Crystallite size (t), X-ray density (dx), Bulk density (dB), and Porosity (P) of nickel ferrite nanoparticles

Sample	a (Å)	V (cm³)	t (nm)	d_x (gm/cm³)	d_B (gm/cm³)	P (%)
NF	8.334	578.9	20.875	5.379	3.638	32
NZF	8.376	587.6	18.028	5.359	3.587	33

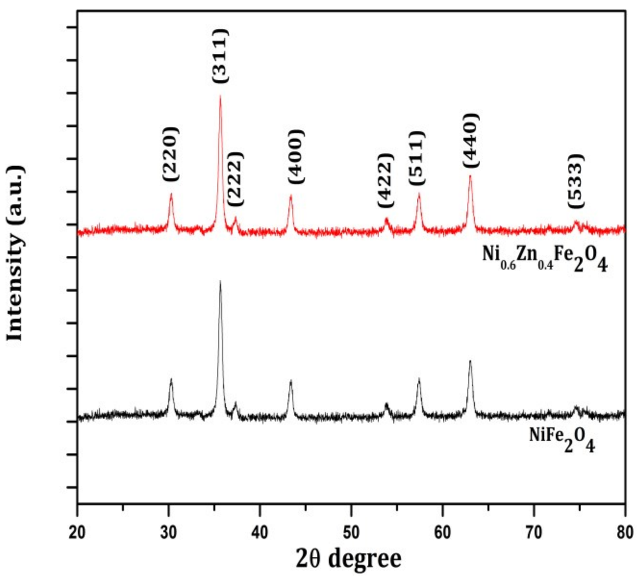

Figure 1: XRD patterns of $NiFe_2O_4$ and $Ni_{0.6}Zn_{0.4}O_4$ nanoparticles

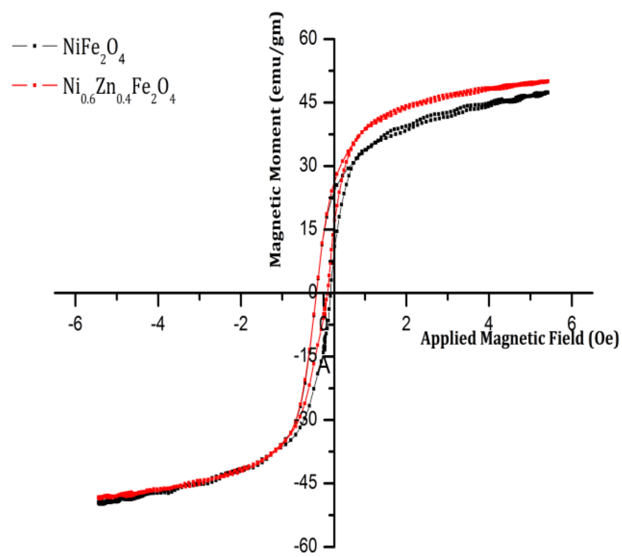

Figure 2: M-H curve of $NiFe_2O_4$ and $Ni_{0.6}Zn_{0.4}O_4$ nanoparticles

Table 2 Saturation magnetization (Ms), remenance magnetization (Mr), coercivity (Hc), remenance ratio (R) and magneton number (n_B) of nickel ferrite nanoparticle

Sample	M_S (emu/gm)	M_r (emu/gm)	H_C (Oe)	M_r/M_s	n_B (μ_B)
NF	47.44	13.64	170.07	0.287	1.9909
NZF	83.44	12.51	104.54	0.149	3.5417

It is observed from the table 2 that the values of saturation magnetization and other magnetic parameters are in close agreement with that reports in literature. However, we observed enhanced values of magnetic parameters. The doping of Zn ions leads to decrease in saturation magnetization and other magnetic parameters. This is because of the facts that, zinc ion are nonmagnetic in nature with zero magnetic moment which replaces magnetic Ni ions with two magnetic moment. Thus, the magnetic structure dilutes due to the doping of zinc ions. Further, the decrease in magnetization also may be due to the decrease in A-B interaction as zinc ions have a strong preference towards tetrahedral A site.

CONCLUSION

Urea assisted sol-gel synthesis of nickel ferrite produces high quality nanocrystalline particles with better structural and enhanced magnetic properties. The doping of Zn ions increases lattice constant and other structural parameters but decreases magnetic properties very significantly.

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