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Structural and electrical properties of Zinc doped Nickel ferrites nanoparticles prepared via facile combustion technique

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ABSTRACT

Ni-Zn ferrite nanoparticles with a composition of $Ni_{(1-x)}Zn_xFe_2O_4$ ($0.0 \leq X \leq 1.0$) have been successfully prepared via facile combustion technique using urea as a fuel. The structural and electrical properties of the samples were studied using Powder X-ray diffraction *(PXRD)*, Scanning electron microscopy *(SEM)* and Fourier Infrared *(FITR)* Spectroscopy measurements. The PXRD analysis of all the samples shows the cubic phase without any impurity peaks. The average particle sizes were calculated by Scherrer's formula and W-H plots were found to be in the range of (20–36) nm. The SEM image shows the agglomeration and flakes type nanoparticles with many void spaces due to exhaust of gases. FTIR spectra of the samples show the nature of the chemical bonds. The dielectric parameters of the prepared nanoparticles were studied before and after γ-irradiation. The dielectric constant, loss tangent and AC conductivity were determined as a function of frequency at RT. These properties of the samples show that they are suitable material for absorption of energy at higher frequencies and good materials for electromagnetic interference suppression and microwave application. These dielectric properties form the basis for the technologies in space telecommunication and radar systems. The high D.C. resistivity and conductivity are the desired characteristics of $NiFe_2O_4$: Zn nanoparticles used to prepare Ferro fluids and magnetic coating.

1. Introduction

Ferrites are hard, brittle, iron containing, gray or black in colour and they are polycrystalline i.e. made up of large number of crystals. They are composed of iron oxide with one or more other metals in chemical combination. These are ferrimagnetic material which contains iron or iron alloys with body centered cubic crystal structure [1,2]. A ferrite is formed by the reaction of ferric oxide (iron oxide or rust) with any number of other metals including Mg, Ba, Mn, Ni, Cu or even iron itself. A ferrite is usually described by the formula $M(Fe_2o_4)$ where M represents any divalent metal that forms divalent bonds, such as elements Mg, Ba, Mn, Ni, Cu or even iron itself. Nickel ferrite for instance is $NiFe_2O_4$, Manganese ferrite is $MnFe_2O_4$, and both are spinel ferrites. The most familiar ferrite known since biblical times is Magnetite (lode stone or ferrous ferrite ($Fe(Fe_2O_4)$). Ferrite exhibit a form of magnetism called ferrimagnetism which is distinguished from the ferromagnetism of such materials as Fe, Co, and Ni [3–5].

In ferrites, the magnetic moment of constituent atoms aligns themselves in 2 or 3 different directions. A partial cancellation of the M-field results and the ferrite is left with an overall M-field that is stronger than that of a ferromagnetic material. This asymmetry in the part of the atomic orientations may be due the presence of two or more different types of magnetic ions to a peculiar crystalline structure. Ferrites can have different types of crystalline structure including spinel, garnet, perovskite and hexagonal. The most important properties of ferrites include high magnetic permeability and high electrical resistance. High permeability to M-field is particularly desirable in a device such as antennas [6–8]. High résistance to electricity is desirable in the core of transformers to reduce eddy currents. Ferrites of a type known as square loop ferrites can be magnetized in either of two directions by an E-current.

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This property makes them useful in the memory cores of digital computers. Since it enables a tiny ferrite rings to store binary bits of information. Another type of computer memory can be made of certain single crystal ferrites in which tiny M-domains called bubbles can be individually manipulated.

Zn ferrite are series of synthetic inorganic compounds which is paramagnetic in bulk form, which becomes ferrimagnetic in nano crystalline thin film format. The corrosion protection increases with increase in concentration of Zinc content. Spinel type ferrites are interesting materials due to their both magnetic and semiconductor properties. Spinel ferrite nano materials due to their transition metal semiconductor properties in the last decade are found to be used as gas sensors, photo catalytic materials and adsorbents for detoxication of biological fluids or removal of the heavy metals [9].

In the present work, $Ni_{(1-x)}Zn_xFe_2O_4$ nanoparticles with a compositional range $0.0 < x < 1.0$ have been successfully synthesized via facile combustion technique using Urea as a fuel. This method has an advantage in preparing multi-component materials easily without any contaminations with desired stoichiometry. With this technique, particle size, chemical homogeneity and degree of agglomeration can be easily controlled. The prepared samples were characterized using Powder X-ray Diffraction (*PXRD*), Scanning Electron Microscopy *(SEM)* and Fourier Transform Infrared Spectroscopy (*FTIR*). In addition to this electrical conductivity, dielectric constant and dielectric loss tangent as a function of frequency before and after γ - irradiated $Ni_{(1-x)}Zn_xFe_2O_4$ nanoparticles were studied in detail.

2. Experimental

The Zn doped Nickel ferrites nanoparticles with nominal compositions $Ni_{(1-x)}Zn_xFe_2O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) were synthesized by a facile combustion technique. The precursors used in this typical synthesis were analytical grade Nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), Zinc nitrate [$Zn(NO_3)_2 \cdot 6H_2O$], ferric nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] and Urea (NH_2CONH_2). The stoichiometric ratios of these chemicals were taken and dissolved in about 50 ml of deionized water in a 500 ml borosil beaker and were stirred with magnetic stirrer for 30 min. The homogeneous mixture was rapidly heated in a preheated electric Muffle furnace (Technico lab product, Chennai) maintained at 500 ± 10 °C [10–12]. The reaction mixture boils and undergoes thermal dehydration, followed by smoldering with the liberation of gaseous (N_2 and CO_2) and produce foamy, voluminous fine brownish coloured $Ni_{(1-x)}Zn_xFe_2O_4$ nanoparticles. The chemical reaction of synthesis process is represented by

$$(1-x)Zn(NO_3)_2 + xNi(NO_3)_2 + 2Fe(NO_3)_3 + NH_2CONH_2 \rightarrow Zn_{(1-x)}Ni_xFe_2O_4 + 41N_2 + 26CO_2 + 52H_2O \quad (1)$$

2.1. Measurements

The structural characterization of all samples were carried out by PAN analytical X'pert PRO MPD Instrument with graphite-filtered CuK_α radiation (λ = 1.541 Å), Germany. The data was collected in the range of $20^\circ < 2\theta < 70^\circ$ with the scan rate of 0.033°/sec. The surface morphology of the prepared samples (pellets) was characterized by a SEM (JEOL JSM 6390LV). FTIR spectra were taken on Perkin Elmer Spectrometer (spectrum 1000) with KBr pellets was used for monitoring the structural changes of the synthesized samples from 4000 to 400 cm^{-1}. Highly polished pellets of dimensions (13 mm × 2 mm) with a thin layer of silver paste coated for electrical contact were used for measurements. The pellets were irradiated by γ - rays with dose of 5 Mega rad (50 kGy/h) at the effective dose rate of 4.97 kGy/h at room temperature (RT) for 10 h using Gamma source Co^{60} (1.25 Mev). The dielectric constant, dielectric loss and A.C. response measurements were made at RT using Hioki model 3532-50 programmable Computer (Japan) interfaced with a digital LCR meter before and after γ - rays irradiation. DC conductivity is measured by Keithley 2361 Trigger controller and Keithley 236 source meter unit before and after γ - rays irradiated pellets.

3. Results and discussion

3.1. Powder X-ray diffraction

The PXRD pattern of $Ni_{(1-x)}Zn_xFe_2O_4$ nanoparticles (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) synthesized samples are shown in Fig. 1 (a–f). From the PXRD pattern, it has been observed that all the reflection peaks of undoped as well as Zn doped compound matches well with Joint Committee for Powder Diffraction Set (JCPDS) Card Number 52-0278 for nickel ferrite. Furthermore, there is no impurity peaks for all the compositions, which indicate that all the samples crystallize in cubic phase with space group of $Fd\bar{3}$ m (227) [13]. The average crystallite size was obtained from the most prominent PXRD peaks using Debye-Scherrer's formula [14].

$$d = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

where, d is the average particle size, k is a constant lies between (0.88–0.92), the average value taken as 0.9 in the calculation, λ is wavelength of Cu-K_α irradiation (λ = 1.541 A°), β is the full width at half maximum intensity of the diffraction peak and θ is the diffraction angle. The particle size of the prepared samples is in the range of (20–28) nm.

Further, effective particle size and strain present in the $Ni_{(1-x)}Zn_xFe_2O_4$ nanoparticles was estimated using the W-H equation.

$$\beta \cos\theta = \frac{k\lambda}{D} + 4\varepsilon \sin\theta \quad (3)$$

where 'ε' is the strain associated with the nanoparticles. The above equation represents a straight line plotting the graph of 'β cosθ' verses '4sinθ'. The effective particle size for which the lattice strain has been taken into account can be estimated from the extrapolation of the plot as shown in Fig. 2 (a–f). From the W-H plots, the lattice strain is extracted from the slope and the crystalline size was extracted from the y-intercept of the linear fit [15]. The average crystallite size was in the range of (30–36) nm, well matched with the Scherrer's formula. Lattice strain of $Ni_{(1-x)}Zn_xFe_2O_4$ nanoparticles is in the range of $(3.88–4.71) \times 10^{-3}$ as shown in Table 1.

3.2. Morphological studies

The SEM photographs for $Ni_{(1-x)}Zn_xFe_2O_4$ nanoparticles (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) as shown in Fig. 3 (a–f). It is to be noted that, the grain size and the size of the samples prepared by the combustion method are much smaller than those for samples prepared by the conventional method. The micrograph of the samples shows that surface morphology is full of small grains and big pores complex, more like foam. The surface of the powder shows pores created by the escaping gases during the combustion reaction.