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Dielectric behavior and AC conductivity of Tb^{3+} doped $Ni_{0.4}Zn_{0.6}Fe_2O_4$ nanoparticles

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ABSTRACT

Terbium doped Ni–Zn ferrite, $Ni_{0.4}Zn_{0.6}Tb_xFe_{2-x}O_4$ ($x = 0$, 0.05, 0.1, 0.15 and 0.2) have been prepared through sol–gel technique. Formation of single phase FCC spinel structure is identified in all the compositions using X-ray diffraction technique. The effect of Tb^{3+} doping on the crystalline phase, crystallite size, dielectric properties and AC conductivity has been investigated in detail. Lattice constant is observed to increase with terbium content; but beyond certain concentration of terbium ($x > 0.15$), it decreased. DC resistivity measurements were carried out in the temperature range 300–523 K. All the compositions exhibited usual semiconducting nature of ferrites and the resistivity of the samples found to increase with terbium content up to $x = 0.15$. The metallic behavior of the doped samples observed in the lower temperature region is explained in terms of elastic and inelastic scattering due to the rare earth ions. The investigations on dielectric constant, dielectric loss and AC conductivity was carried out in the frequency range 100 Hz–20 MHz from room temperature to 563 K. Frequency dependence of dielectric constant showed normal behavior and is in good agreement with Koop's phenomenological theory of dielectric dispersion. AC conductivity measurements suggested conduction due to small polaron hopping. AC conductivity as well as dielectric constant is found to increase with temperature and which is due to thermally enhanced drift mobility of charge carriers. The observed decrease in dielectric loss with terbium content up to $x = 0.15$ is explained in terms of increase in resistivity.

1. Introduction

Now-a-days material science research is focused on the invention of new materials with enhanced properties and novel synthesis techniques to cope with the increased technological demand. Nanocrystalline materials are the centre of attention due to their tremendous applications and interesting properties. The properties of nanomaterials are remarkably different from that of their bulk counterpart. The interest in ferrite nanoparticles is due to their important physical and chemical properties and potential for various technological applications such as high density magnetic storage, electronic and microwave devices, sensors, magnetically guided drug delivery etc. [1–3].

Ni–Zn ferrite is one of the best soft magnetic materials suitable for high frequency applications, owing to its low magnetic coercivity, high electrical resistivity, low loss, fairly high mechanical hardness and chemical stability. Ni–Zn mixed ferrite nanoparticles are widely investigated and it is well known that their properties can be tuned by varying nickel or zinc content [4–6]. Substitution of rare earth metal ions into the ferrite spinel structure has been reported to lead to structural distortions and to induce strain and thus significantly modify the electrical and magnetic properties [7,8]. The structural and physical properties of nickel ferrite, substituted by Tb^{3+} ions in the place of Ni^{2+} ions, have been reported [1]. But only limited literature is available on the effect of rare earth metal ion substitution on the properties of Ni–Zn ferrite nanoparticles. A.C.F.M Costa et al. have reported decrease in saturation magnetization and increase in coercive field in $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles by the doping of Sm^{3+} ions [9]. S.S. Rao and D. Ravinder have studied the changes in elastic moduli of Ni–Zn ferrite by Gd^{3+} substitution [10]. Thus a systematic study on the influence of rare-earth doping in Ni–Zn ferrite has significance. In this paper we report the effect of the substitution of Fe^{3+} ions by Tb^{3+} on the dielectric behavior and AC conductivity of $Ni_{0.4}Zn_{0.6}Fe_2O_4$ nanoparticles.

Properties of nanoferrites are very sensitive to the method of preparation and sintering conditions [11]. Hence the use of suitable preparation technique is the key to obtain ferrites with the required properties. Ferrite nanoparticles are usually prepared by various physical and chemical methods like mechanical alloying, high energy milling, plasma deposition method, inert gas condensation, hydrothermal reaction, citrate precursor technique, reverse micelle technique, sol–gel technique, chemical co-precipitation etc. [12]. Among the available chemical methods, sol–gel technique is an excellent method to prepare ferrite nanoparticles with maximum purity. This method is a combination of chemical gelation and combustion and has the advantage of good stoichiometric

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control and the production of ultra fine particles with a narrow size distribution. In the present work, terbium doped $Ni_{0.4}Zn_{0.6}Fe_2O_4$ nanoparicles were prepared using sol–gel technique. The influence of Tb^{3+} substitution on the dielectric properties and AC conductivity of Ni–Zn ferrite was thoroughly investigated.

2. Experimental

2.1. Synthesis

A series of five samples with general formula $Ni_{0.4}Zn_{0.6}Tb_xFe_{2-x}O_4$ (x = 0.0, 0.05, 0.1, 0.15 and 0.2) was prepared by the sol–gel technique. Stoichiometric ratios of AR grade ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$), zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$) and terbium nitrate ($Tb(NO_3)_2{\cdot}5H_2O$) (99.9% pure MERK) were used and the details of the method are given in our previous work [13]. The obtained powder was ground well and sintered for two hours in a muffle furnace at 673 K. For DC resistivity and dielectric measurements, cylindrical disc shaped pellets of the samples were made using a hydraulic press by applying uniform pressure of 5 ton. In order to avoid the effect of humidity, the pellets were dried and kept in a hot air oven before measurements.

2.2. Characterization

The crystalline phases of the prepared samples were identified by X-ray diffraction (XRD) technique using BRUKER AXS D8 ADVANCE powder X-ray diffractometer with Cu–Kα radiation (λ = 1.5406 Å) at 40 kV and 35 mA. Scanning was performed from 20° to 70° at a step size of 0.02° per second for each sample. The crystal structure, lattice constant, crystallite size and X-ray density were determined. Dielectric properties of the samples were measured using impedance analyzer (WAYNE KERR 6500B) in the frequency range 100 Hz–20 MHZ and in the temperature range 300–563 K. Silver coating was done on the faces of sample pellets to make parallel plate capacitor geometry with the ferrite material as the dielectric medium. The capacitance of such a parallel plate capacitor is given by

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \tag{1}$$

where A,d respectively are the area and thickness of the pellet, ε_0 is the permittivity of free space and ε_r is the dielectric permittivity of the given ferrite sample. The dielectric permittivity of the samples has been calculated using the relation,

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \tag{2}$$

From the values of dielectric permittivity and loss tangent, AC conductivity of the samples was evaluated using the formula [14]

$$\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon_r \tan\delta \tag{3}$$

where f is the frequency of the applied electric field.

According to Mattiessen's rule, the total resistivity of a ferromagnetic material can be expressed as [15,16]

$$\rho(T) = \rho_r + \rho_{ph}(T) + \rho_e(T,\omega) \tag{4}$$

where ρ_r is the residual resistivity due to impurities and lattice defects, which is independent of temperature and frequency and $\rho_{ph}(T)$ is the contribution from the electron–phonon interaction which is related to the mobility of electric charge carriers and follows the Arrhenius relation given by,

$$\rho_{ph}(T) = \rho_0 exp\left(\frac{E_a}{K_b T}\right) \tag{5}$$

where, E_a is the activation energy for electric conduction and ρ_o is the pre-exponential factor. The term $\rho_e(T,\omega)$ is the contribution from electron-spin wave scattering, which is related to the dielectric relaxation caused by the localized electric charge carriers [15].

Temperature dependence of DC resistivity of the samples was recorded from room temperature to 523 K using an electrometer (KEITHLEY 6221 DC and AC Current source and 2182A nanovoltmeter) in two probe method. Current source applies constant current on sample pellets and the voltage developed is measured using the nanovoltmeter. Silver paste was employed for better electrical contact. The electrometer can be programmed to get the average resistance R of the pellet by repeating the measurement for different steady currents. The resistivity of the ferrite samples is evaluated, using the formula,

$$\rho = \frac{RA}{d} \tag{6}$$

where A,d respectively are the area and thickness of the pellet.

3. Results and discussion

3.1. XRD analysis

XRD patterns of $Ni_{0.4}Zn_{0.6}Tb_xFe_{2-x}O_4$ (x = 0.0, 0.05, 0.1, 0.15 and 0.2) nanoparticles sintered at 673 K are shown in Fig. 1. The well resolved broad diffraction peaks corresponding to (220), (311), (222), (400), (422) and (511) reflection planes show that all the samples have attained single phase and polycrystalline FCC structure. The experimental data of the samples is fitted through the Rietveld refinement procedure using BRASS (Bremen Rietveld Analysis and Structure Suite) program. A representative graph for the sample with x = 0.0 is shown in Fig. 2. The observed experimental data points (gray colored crosses) are shown along with the fitting result (black crosses). The fitted curve matches well with the experimental data. The lattice constants obtained from this refinement and the crystallite sizes calculated for the (311) peak using Scherrer formula [17] are given in Table 1. The actual (X-ray) density was calculated using the formula [1],

$$\rho_x = \frac{8M}{Na^3} \tag{7}$$

where, M is the molecular weight (kg) of the sample, N is the Avogadro's number (per mol) and 'a' is the lattice constant (Å). Bulk densities (ρ_b) of the samples were determined using the formula,

$$\rho_b = \frac{m}{\pi r^2 h} \tag{8}$$

where, m is the mass, r is the radius and h is the height of the pellet. Percentage porosity was calculated using the formula [3]

$$P = \left(1 - \frac{\rho_b}{\rho_x}\right)100 \tag{9}$$

Measurements were repeated on different pellets of the same sample and the average bulk density of each sample is determined. Mass of the pellet is measured with three decimal places of accuracy, but radius and height were obtained with an accuracy of two decimal places. Hence porosity values are accurate up to two decimal places. X-ray density, bulk density and percentage porosity of all the compositions are tabulated in Table 1.

The lattice constant of $Ni_{0.4}Zn_{0.6}Fe_2O_4$ is (8.4228 ± 0.0012 Å) observed to be close to that of Zn–ferrite (8.44 Å); but larger than that of Ni–ferrite (8.34 Å) [18]. The addition of Zn^{2+} ions in Ni–ferrite is reported to make expansion of the unit cell and there by increasing the lattice parameter [6,19,20]. The lattice constant exhibits a

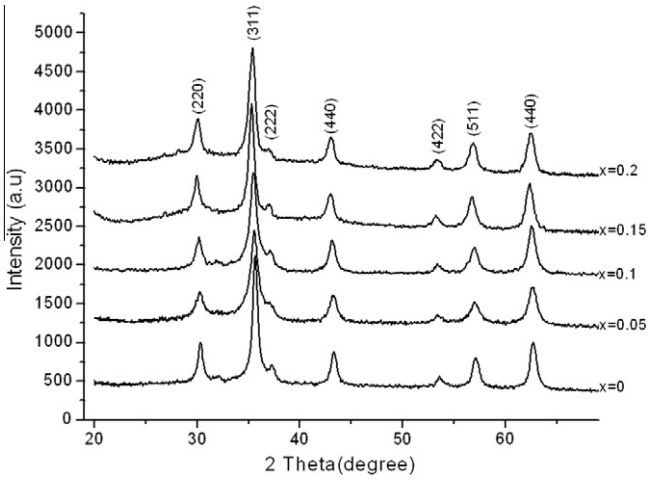

Fig. 1. XRD pattern of $Ni_{0.4}Zn_{0.6}Tb_xFe_{2-x}O_4$ system (x = 0, 0.05, 0.1, 0.15 and 0.2).