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Structural, electrical and magnetic properties of cadmium substituted nickel–copper ferrites

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ABSTRACT

Polycrystalline ferrites with the general formula $Ni_{0.95-x}Cd_xCu_{0.05}Fe_2O_4$ in which x varies from 0.1 to 0.3 were synthesized by standard double sintering ceramic technique. The existence of single phase cubic spinel structure of ferrites was confirmed from XRD measurement. Surface morphology and compositional features were studied by SEM and EDX measurements. Absorption bands observed in FTIR spectra at 600 cm^{-1} (υ_1) and 410 cm^{-1} (υ_2) corresponds to vibrations of tetrahedral and octahedral complexes respectively. In the dc conductivity measurements the decrease of dc resistivity with increase of temperature indicates the semiconducting nature of ferrites. The dielectric measurement of the samples at room temperature studied in the frequency range 20 Hz to 1 MHz shows dispersion in the low frequency region and remains constant at high frequency region. However, the small polaron hoping type of conduction mechanism was inferred from the linear increase of ac conductivity. The magnetic properties of ferrites such as saturation magnetization, magnetic moment and Y–K angles was estimated as a function of cadmium content by VSM technique. The smaller value of Mr/Ms reveals the existence of multidomain (MD) particles in the ferrite samples.

1. Introduction

Polycrystalline ferrites attracted special attention in the field of electronic technology due to their wide applications ranging from microwave to radio wave frequencies. The wide applications of ferrites in various fields created an interest to study the electric and magnetic properties such as high saturation magnetization, stability, resistivity and low loss energy over a wide range of frequency [1–3]. The substituted nickel ferrites are the subject of extensive investigation because of their microwave applications such as circulators, isolators, phase shifters, etc., due to its low electrical conductivity, squareness of hysteresis loop [4,5].

The nickel–copper ferrite has potential application in nanoscience and technology. Cadmium the nonmagnetic divalent metal ion doped with nickel–copper ferrite is of interest in fundamental and applied research. An understanding of their properties as well as variety of applications such as transformers cores, antennas rods and in high quality filters is of special interest [6]. Polycrystalline ferrites have very good dielectric properties; it depends on method of preparation, type of additives and sintering conditions. The electrical conductivity of spinel ferrites is of prime importance as it gives valuable information about the conduction mechanism [7]. The magnetic properties of spinel ferrites strongly depends on the choice of cations along with Fe^{2+} and Fe^{3+} ions and their distribution between tetrahedral (A-site) and octahedral (B-site) sites of the spinel lattice [8]. According to the earlier reports cadmium ions occupy tetrahedral A-site and the substitution of nonmagnetic Cd^{2+} ion in ferrite enhances the magnetic properties like saturation magnetization, magnetic moment [9–12]. The lattice parameter increases due to the increase of cadmium content in the ferrites because of its higher ionic radius compared to other ions in the ferrites. Several researchers have studied the structural, electrical and magnetic properties of substituted ferrites like Ni–Co–Cu [1], Ni–Cd–Zn [12], Ni–Cd [11,13–15], Ni–Cu [16], Mg–Cd [17] and Ni–Mn–Mg [18] mixed ferrites by different methods. However, the literature survey on Ni–Cd–Cu ferrites indicates that not much work has been done on these ferrites. In the present work standard double sintering ceramic technique was used to synthesize the polycrystalline ferrite having the composition $Ni_{0.95-x}Cd_xCu_{0.05}Fe_2O_4$. This method is easier and fabrication of the materials is cheaper as compared to other methods in addition, the grain size and sintering temperatures are easily controllable. The present work is focused on the study of structural, electric

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and magnetic properties of cadmium substituted nickel–copper ferrites.

2. Experimental details

2.1. Synthesis

Polycrystalline ferrite system $Ni_{0.95-x}Cd_xCu_{0.05}Fe_2O_4$ with composition $x = 0.1$, 0.2 and 0.3 were synthesized by standard double sintering ceramic technique. The samples were prepared by thoroughly mixing AR grade NiO, CdO, CuO and Fe_2O_3 oxides in stoichiometric ratio and later on well grounded in a planetary agate mortar for few hours. The powder samples were presintered at 800 °C for 8 h in a programmable furnace and slowly cooled to room temperature. The sintered powders were mixed with 2% of PVA as a binder and uniaxially pressed at a pressure of about 7 tons cm^{-2} to form pellets of 10 mm diameter and 2–3 mm thickness. These pellets were finally sintered at 1150 °C for 12 h in a programmable furnace to remove the organic binder.

2.2. Characterization

The powder samples of ferrites were characterized by using X-ray diffractometer (Philips model PW-1710) with Cu-Kα radiation (λ = 1.5405 Å) and the lattice parameter of the synthesized samples were estimated using the relation [13]

$$a = d_{hkl}\sqrt{(h^2 + k^2 + l^2)} \tag{1}$$

The X-ray densities of the samples were estimated using the relation [15]

$$dx = \frac{ZM}{Na^3} \tag{2}$$

where Z is the number of molecules per unit cell of spinel lattice, M is the molecular weight of the samples, N is the Avogadro's number and a is the lattice parameter of the samples.

The porosity of the sample was estimated using the formula

$$p = 1 - \frac{da}{dx} \times 100\% \tag{3}$$

where da is actual density and dx is X-ray density of the sample.

The average crystallite size and strain induced inside the samples has been estimated using the Williamson-Hall plot relation [19].

$$\beta \cos\,\theta = \frac{k\lambda}{D} + 4\varepsilon \sin\theta \tag{4}$$

where D is the average crystallite size, k is a constant, λ is the wavelength, β is the full width half maximum of diffraction peaks, ε is the strain induced inside the samples and θ the Bragg's angle.

The surface morphology and compositional features were studied using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) techniques (ESEM Quanta 200, FEI). IR studies were carried out by FTIR spectrometer (Nicolet, model-*Impact*, 410, USA) from 400 cm^{-1} to 800 cm^{-1} to assign the vibrations of ferrites (tetrahedral/octahedral).

Electrical conductivity (dc) of the samples was studied after silver pasting the two polished surfaces of each pellet. The temperature dependent dc resistivity were carried out by using two probe method and was estimated by using the following relation

$$\rho = \frac{R\pi r^2}{t} \tag{5}$$

where R is the resistance, r is the radius; t is the thickness of the samples.

The drift mobility of the samples were estimated using the relation

$$\mu_d = \frac{1}{ne\rho} \tag{6}$$

where e is the charge of electron, ρ is the resistivity, n is the charge carrier concentration and which is calculated using the following relation [14]

$$n = \frac{N\rho_m P_{Fe}}{M} \tag{7}$$

where ρ_m is the measured density, P_{Fe} is the number of iron atoms in the ferrites.

The dielectric measurements were carried out in the frequency range 20 Hz to 1 MHz at room temperature using an impedance analyzer (Model 6540A Wayne Kerr, UK).

The ac conductivity of the ferrites was calculated using the relation

$$\sigma_{ac} = \varepsilon'\varepsilon_o\omega \tan\delta \tag{8}$$

where ε' is the dielectric constant, ε_o is the permittivity of free space, ω is the angular frequency, $\tan\delta$ is the loss tangent.

Vibrating sample magnetometer (VSM model 735 LakeShore) was used to measure the saturation magnetization and magnetic moment (in Bohr magneton) and can be estimated by using the following relation [6]

$$\mu_B = \frac{M\sigma'_s}{5585} \tag{9}$$

where M is the molecular weight of the samples, σ'_s is the magnetization per gram of the samples.

The Y–K angles of ferrite samples were estimated using the following relation [13]

$$\cos\,\alpha_{yk} = \frac{n_B + 5(1-x)}{7(1+x)} \tag{10}$$

where n_B is the Bohr magneton, x is the concentration of substituted ion.

3. Results and discussion

3.1. X-ray diffraction

The X-ray diffraction pattern of ferrite samples is shown in Fig. 1. And all the peaks appeared in the diffraction patterns are identified with the help of JCPD'S data and confirmed the formation of cubic spinel structure of single phase ferrite without impurities. The lattice parameters of the ferrite samples were estimated using the relation (1) for the prominent peak (3 1 1) and listed in Table 1. The lattice parameter, X-ray density and porosity increases with increase of Cd^{2+} content in the ferrite systems. This is because the Cd^{2+} ion have larger ionic radii (0.097 nm) than that of Cu^{2+} (0.073 nm), Ni^{2+} (0.069 nm) and Fe^{3+} (0.0645 nm) ions [20]. The average crystallite size and strain induced inside the ferrite sample was estimated from the intercept and slope of the Williamson-Hall plot shown in Fig. 2 (for $x = 0.1$) and it is to be noted that as the cadmium content increases strain induced inside the sample increases (Table 1).

3.2. Scanning electron microscopy

The SEM micrographs of ferrite samples are shown in Fig. 3(a–c). These figures show fine particles in all the samples without segregation of impurity. The average grain size estimated by Cottrell's method [21] lies in the range of 1.256–1.759 μm. The average grain size increases with decreasing the grain boundary area, as this grain