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Low temperature synthesis and enhanced electrical properties by substitution of Al³⁺ and Cr³⁺ in Co–Ni nanoferrites



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ABSTRACT

Aluminum and chromium substituted Co–Ni spinel nanoferrites were prepared by sol–gel auto combustion method. Structural parameters along with electrical and magnetic properties have been investigated in the present work. Crystallite sizes of nano ferrite estimated from the peak (311) lies in the range of 13–21 nm \pm 2 nm and compared with crystallite sizes calculated from Williamsons–Hall plots. DC electrical resistivity variations due to the concentration of aluminum and chromium in the host ferrite have been measured from 368 K to 573 K. Increase in the room temperature DC electrical resistivity was observed up to a concentration $x=0.2$ and then decreases for $x > 0.2$. Dielectric parameters (real and imaginary part of complex permittivity, dielectric loss tangent) were studied as a function of frequency (20 Hz–5 MHz) and a decrease in the dielectric parameters was observed due to substitution of nickel, aluminum and chromium ions in cobalt nanoferrites. AC conductivity, complex impedance and complex electrical modulus were studied as a function of frequency for the conduction and relaxation mechanisms in the present ferrite system. Saturation magnetization, coercivity, canting angles and magneto crystalline anisotropy variations with composition were observed and presented for the present ferrites under an applied magnetic field of 10 kOe at room temperature. It was found that both magnetization and coercivity decreases with increase in the concentration of aluminum and chromium along with a decrease in the anisotropy parameters. High DC resistivity with low dielectric parameters of the present nanoferrites make them suitable for high frequency and electromagnetic wave absorbing devices.

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1. Introduction

Spinel ferrites of Fd_3m space group having the general formula of MFe_2O_4 ($M=Co^{2+}$, Ni^{2+} , Mn^{2+} , Mg^{2+} , Zn^{2+}) is a class of hybrid functional materials which are very important for many recent technical designing of electrical, magnetic and microwave devices [1,2]. They are considered hybrid as they exhibit good electrical and magnetic characteristics at one time in high frequency applications. An important advantage of ferrites is the huge compositional variability by the substitution of different cations in the parent crystal structure (cubic closed packing of tetrahedral and octahedral sublattices) and this variation in cation distribution impacts many physical properties of these ferrites such as increase in DC resistivity, low dielectric losses and required magnetization characteristics [3]. Cobalt ferrite is partially inverse spinel material having semiconducting nature and exhibits high resistivity, along with moderate magnetization and magnetoresistance [4] and very high magnetocrystalline

anisotropy [5]. These properties can be tailored by proper choice and composition of trivalent cations (Al^{3+} , Cr^{3+} , Gd^{3+} , Ho^{3+} , and Nd^{3+}) to replace Fe^{3+} in the parent lattice of cobalt ferrite caused by a structural variation in the host lattice. Not only a single cation but a combination can be incorporated into the parent ferrite structure to make a mixed ferrite system. Some of the works are available where a divalent cation substitution in cobalt ferrites enhances the electrical behavior of cobalt ferrites. Gul et al. [6,7] has reported the work related to DC electrical resistivity and dielectric behavior of Co–Ni and Co–Zn–Zr ferrites. Singhal et al. [8] has focused the structural and magnetic behaviors of Co–Ni ferrites and describe the cation distribution of Ni^{2+} doping in cobalt ferrites. Structural and electrical properties of Co–Cd ferrites were studied by Farea et al. [9], Urvi has studied the Al^{3+} and Cr^{3+} co-substituted ferrites and provided the information of metal–insulator transition [10]. Tawfik [11] has done detailed study of electromechanical properties of cobalt ferrites transducers. It is the distribution of cations among A-sites and B-sites that is responsible for mobility of the charge carriers which in turn imparts different electrical and dielectric behaviors (dielectric constant and losses). Magnetic parameters also depend upon the A–B exchange interactions due to different cations

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substitution [12,13]. The way of synthesizing the cobalt ferrite and sintering temperatures influence mainly the above mentioned behaviors. Several methods have been employed to synthesize the nanocobalt ferrite with controlled microstructure and particle size including co-precipitation [14], sol-gel [15], reverse micelles [16], hydrothermal [17], and solvothermal [18]. Impedance spectroscopy is an important way to study the electrical conduction behavior of the ferrites including all the resistances involved in the conduction but in the present work complex electric modulus studies as a function of applied AC field have been provided for the complete understanding of dielectric dispersion and relaxation for the ferrites under study. In physical sense electrical modulus is related to the relaxation of electrical field in the material when displacement remains constant. So it actually reveals the real dielectric relaxation process [19,20].

The purpose of this work is to synthesize $\text{Co}_{1-y}\text{Ni}_y\text{Fe}_{2-2x}\text{Al}_x\text{Cr}_x\text{O}_4$ (where x represents the composition of Al^{3+} and Cr^{3+} and y represents composition of Ni^{2+}) and to investigate the influence of changing Fe:Al:Cr ratio on the structural, electrical and magnetic properties of the cobalt–nickel ferrites. We mainly focused on the AC response of the nanoferrites under study and objectives of present work are to enhance the DC electrical resistivity along with a decrease in dielectric parameters for application in high frequency electronic devices. We are first to report the electric modulus studies of the mixed spinel Co–Ni ferrites co-substituted by Al^{3+} and Cr^{3+} .

2. Experimental

2.1. Synthesis

Precursor samples of aluminum (Al^{3+}) and chromium (Cr^{3+}) substituted Co–Ni nanoferrites [$\text{Co}_{1-y}\text{Ni}_y\text{Fe}_{2-2x}\text{Al}_x\text{Cr}_x\text{O}_4$] with $y=0.0, 0.5$ and $x=0.0, 0.05, 0.1, 0.15, 0.2, 0.25$ were prepared by sol-gel auto-combustion route at temperature of 90°C . All the chemicals purchased were of analytical grade and used as such without further purification steps. Stoichiometric amounts of the salts of Iron nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, aluminum nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and chromium nitrate $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in de-ionized water. Trivalent metal cations to divalent metal cations ratio were kept at 2:1 for whole series of samples. The entire nitrate solutions were mixed and stirred magnetically for 1 h. Citric acid was then added into the mixed nitrate solutions and the mixture was stirred at room temperature for 30 more min. The mixed solution was then neutralized using aq ammonia (NH_3OH) and kept on heating and stirring at 90°C till a viscous gel forms. The gel was kept on heating till burning and combustion. Fluffy powders of synthesized ferrite were obtained as a result of auto-combustion. The synthesized precursor samples were pelletized into 10 mm discs under compression and sintered at 600°C for 4 h for further investigations.

2.2. Characterization

Crystal structure studies of sintered samples were performed using powder X-ray Diffraction (XRD) (STOE-Seifert X'Pert PRO) at room temperature using Cu-K α radiations ($\lambda=1.54060\text{ \AA}$) in 2θ range of 20° to 80° . Morphology, grain size and composition analysis were performed using Scanning Electron Microscopy (SEM) (JEOL-instrument JSM-6490A) and Energy Dispersive Spectroscopy (EDS). DC electrical resistivity was measured using two probe method in a temperature range of 300 K to 573 K. Dielectric parameters, AC conductivity, impedance and electrical modulus studies were performed using LCR Meter Bridge (WANE KERR 6500-B) in a frequency range of 20 Hz–5 MHz. Vibrating Sample Magnetometer (VSM) was used for magnetic characterization of

Al^{3+} and Cr^{3+} substituted cobalt nickel ferrites under a magnetic field of 10 kOe at room temperature.

3. Results and discussion

3.1. Structural analysis

All the XRD patterns of the nanoferrites samples under study are shown in Fig. 1(a) and show a good crystalline structure of pure cubic (fcc) spinel phase of Fd_3m space group. No extra phase of impurity or unconverted oxide is present in the recorded patterns. All the peaks can be indexed according to the pure and substituted cobalt ferrites (JCPDS card nos. 44-1485 and 22-1086). All the crystalline parameters as, crystallite size (D_{311}), strain (ϵ), lattice parameter (a), X-ray density (D_x), porosity (P), and specific surface area (s) have been calculated from data obtained from XRD patterns using standard relations. Crystallite sizes were calculated from the most intense peak (311) using full width at half maximum values (FWHM) by Sherrer's formula,

$$D_{311} = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where β is the FWHM and k is the shape factor. Average crystallite sizes calculated by the above formula lies in the range of 13–21 nm (± 2 nm). A clear decrease in crystallite size has been observed with an increase in $y=0.0, 0.5$ and x from 0.0 to 0.25. Variation of crystallite sizes within small range shows a good control of parameters during synthesis and low sintering temperature. Also Williamson–Hall (W–H) plots were drawn to calculate and compare the average crystallite sizes and lattice strain using FWHM and Bragg angles by following relation [21].

$$\beta \cos \theta = \frac{k\lambda}{D} + 4\epsilon \sin \theta \quad (2)$$

A Gaussian fit to the data provides the crystallite size and lattice strain present in the crystal structure. Fig.1(b) represents the W–H plot for the composition $x=0.05$. Crystallite size by W–H method is slightly greater than calculated by Sherrer's method due to strain effects but lies well in the range with less size distribution. Lattice constant has been calculated by d-spacing (d_{hkl}) using the relation,

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2} \quad (3)$$

Fig.1(c) shows the variation of lattice constants with y (0.0, 0.5) and x (≤ 0.25). The lattice constants are decreasing due to increase in Ni^{2+} , Al^{3+} and Cr^{3+} owing to the small ionic radii of Ni^{2+} (0.69 Å), Al^{3+} (0.51 Å) and Cr^{3+} (0.61 Å) substituting Co^{2+} (0.82 Å) and Fe^{3+} (0.67 Å) respectively. There is a sharp decrease in the lattice constant of pure cobalt ferrite due to inclusions of Ni^{2+} , Al^{3+} and Cr^{3+} cations for the composition $x=0.05$ and $y=0.5$. It has been observed that lattice constants decreases with increase in the concentration of both x and y but this decrease is random as lattice constant decreases sharply to 8.2974 Å for $x=0.05$ but randomly varied for compositions $x > 0.05$. This non-linear behavior is observed for the systems composed of mixed ferrites (not completely inverse or normal) [22]. As the present ferrite system is a combination of ferrite (inverse), aluminates (partial inverse) and chromites (normal), The way lattice constants are changing reveals that the system is inverse spinel for $x=0.05$ and becomes mixed spinel as x increases to 0.25 [23]. X-ray density was calculated from the unit cell volume (a^3) as, $D_x = \frac{8M}{Na^3}$, where M is the molecular weight of the composition and N is the Avogadro's number. Measured density or bulk density of all the samples were calculated using, $D_m = \frac{m}{\pi r^2 l}$. Both D_x and D_m decreases with increase in the doping concentration. Porosity of all the samples

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