

Dielectric and Magnetic Properties of Co Substituted Ni-Cd-Ferrite Prepared By Solution Combustion Method

N. D. Patil, N. B. Velhal, N. L. Tarwar, Vijaya R. Puri

Thick and thin film device lab, Department of Physics, Shivaji University, Kolhapur, 416 004, India
Gwangju Institute of Science and Technology, Gwangju. S. Korea

Abstract- In the present paper dielectric and magnetic properties of Co substituted Ni-Cd Ferrite prepared by solution combustion method are reported. The TG-DTA analysis shows weight loss and endo/exothermicity of the reaction during sintering temperature about 900°C. The variation of dielectric constant (ϵ'), $\tan\delta$ and ac conductivity with frequency in the range 20Hz to 1MHz was studied. The saturation magnetization, remnant magnetization, coercivity and magnetic moment were found to increase with Co content in Ni-Cd ferrite.

Index terms-Ferrites, TG-DTA, dielectric properties, magnetic properties.

I. INTRODUCTION

Ferrites are ceramic materials consisting of mixtures of iron oxide divalent metals. Ferrites have gained importance because they possess the combined dielectric and magnetic properties. They are used in advanced electronics because of their multifunctional features and potential applications in transducers, actuators, sensors, microwave and high frequency devices etc. Modifying the chemical composition of the spinel ferrite nanoparticles one can possibly control the dielectric and magnetic properties [1]. The dielectric properties of ferrites are dependent on several factors including the method of preparation, sintering temperature, sintering time and chemical composition [2]. Mixed Cd-ferrite is technically important due to their high resistivity, high permeability and comparatively low magnetic losses. Cd is non-magnetic divalent ions that occupy essentially tetrahedral sites when substituted in ferrites. The magnetic properties of spinel ferrites are governed by the type of magnetic ions residing on the A and B sites [3]. Substituted nickel ferrites have been the subject of investigations because of their microwave applications [4]. Several results of the cobalt and cadmium substituted nickel ferrite has been reported with their excellent electrical and magnetic properties [5]-[7]. A number of physical and chemical techniques have been developed to prepare individual phases of ferrite. The solution combustion synthesis is a self-propagating high temperature synthetic method that has been developed as an alternative to the other methods [8]. Combustion synthesis uses highly exothermic and even explosive reactions to maintain a self-propagating high reaction temperature. All self-propagating high-temperature synthesis reactions are redox reactions. For the reaction to be

self-propagating the heat evolved should be more than the heat required for initiating the combustion. The solution combustion method is easy and fast method that uses simple equipments. Good homogeneity, stoichiometric and high purity product can be obtained by using this method. In this paper, the investigations made on dielectric and magnetic properties of $\text{Ni}_{0.4}\text{Co}_x\text{Cd}_{0.6-x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6$) prepared by solution combustion method are reported.

II. SAMPLE PREPARATION

In the present work, ferrite phase having the general formula $\text{Ni}_{0.4}\text{Co}_x\text{Cd}_{0.6-x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6$) was prepared by solution combustion method. The AR grade nickel nitrate, cobalt nitrate, cadmium nitrate, and iron nitrate were used to prepare the ferrite compositions. The stoichiometric amounts of AR grade nickel nitrate, cobalt nitrate, cadmium nitrate, and ferric nitrate were dissolved in distilled water. To the solution, 10% of polyvinyl alcohol (PVA) and sucrose with oxidant to fuel ratio 1:1 were added. PVA forms a polymer with metal ions trapped in it, while the added sucrose acts as a fuel for combustion process. The whole mixture of solution of metal nitrates, PVA, and sucrose solution was heated and stirred at about 80°C for the evolution of N_2 , CO_2 , and H_2O . This transforms the solution mixture into a gel. The dried, black, and fluffy gel gets burnt out in a self propagating manner. The ash was again calcined at about 900°C for 6 hour. The samples were uni-axially pressed into pellets of thickness about 0.2cm and diameter 1.5cm using hydraulic press by applying pressure of 8 tons/inch² for 10 minutes. The pellets are again sintered at 900°C for 6 hour. The structural analysis was carried out using X-ray diffraction technique (Model PW-1037). The surface morphology of the samples was carried out using scanning electronic microscopy (Model JEOL JSM 6360). The variation of dielectric constant (ϵ'), $\tan\delta$ and ac conductivity with frequency in the range 20Hz to 1MHz (Model HP 4284A) was studied. The magnetic measurement was carried out using vibrating sample magnetometer (Model Lakeshore 7307). XRD patterns reveal the formation of cubic spinel structure without any impurity phase. The decrease in lattice parameter was observed from 8.56Å to 8.36Å with increase in Co content [9]. Scanning electron micrographs indicates decrease in grain size with increase in Co content in Ni-Cd ferrite [9]. The TGA-DTA data is shown in figure 1.

From fig.1 it is seen that three distinct weight loss regions are observed at temperature 50°C, 270°C and 300°C with losses of weights 2.051%, 1.919% and 1.547% respectively. The first weight loss is observed due to the humidity, physisorbed and lattice bound water loss and combustion of some organic substances [10]. The second and third weight loss is observed due to the decomposition of the nitrate precursor in the material. In this way many NO₂ and CO₂ gases are released from the sample. After that a sharp and minute weight loss is observed at 600 °C which is due to formation of intermediate spinel ferrite phases. Similar way in the DTA one exothermic peak one endothermic peak is observed at 294°C and 950°C which indicate that the decomposition of organic salts and the endothermic peak shows that there is no further decomposition of the precursor and which confirms the phase temperature so from the weight loss and thermal decomposition of the temperature the 800°C temperature chosen for the calcinations of the sample to obtain pure Co-Ni-Cd-Ferrite powder [11].

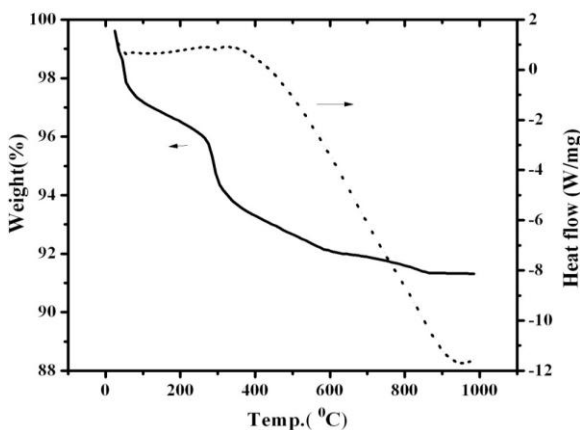


Fig. 1. TG-DTA of as prepared Ni_{0.4}Co_{0.2}Cd_{0.4}Fe₂O₄

III. RESULTS AND DISCUSSION

The variation of dielectric constant and loss tangent for different frequencies at room temperature is shown in fig. 2.

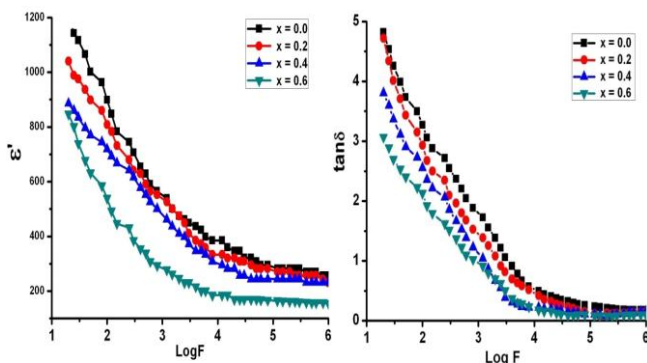


Fig. 2 Variation of Dielectric constant (ϵ') and loss tangent ($\tan\delta$) with frequency of Ni_{0.4}Co_xCd_{0.6-x}Fe₂O₄ (x = 0.0, 0.2, 0.4, and 0.6)

The dielectric constant decreases with increase in frequency showing dispersion in lower frequency region and attains constant value at higher frequencies. Dielectric

dispersion in ferrite can be explained on the basis of space charge polarization which is the result of the presence of higher conducting phase (grains) in the insulating matter (grain boundaries) of a dielectric causing localized accumulation of charges under the influence of electric field. Dispersion in lower frequency region is due to Maxwell-Wagner type interfacial polarization in agreement with Koop's phenomenological theory [12]. The polarization mechanism in ferrite is similar to conduction mechanism in ferrite. Due to the presence of Fe³⁺ and Fe²⁺ ions, ferrite ions are referred to as dipolar. The orientation polarization arises due to the rotation displacement of the dipoles. In ferrites at the low frequency region rotation of Fe³⁺-Fe²⁺ dipoles may be visualized as the exchange of electrons between the ions so that the dipoles align themselves in response to the alternating field gives the maximum polarization. The polarization decrease with increase in frequency and reaches a certain value due to the fact that beyond certain frequency of external field the electron exchange between Fe³⁺ and Fe²⁺ ions cannot follow the alternating field [13]. Due to substitution of cobalt in Ni-Cd ferrite, Fe³⁺ ions moves towards A-site and this reduces the concentration of Fe³⁺ at B-site. Due to decrease in concentration of Fe³⁺ at B-site electron transfer between Fe³⁺ and Fe²⁺ ions will be slowed down i. e. polarization decreases. Accordingly dielectric constant decreases with increase in cobalt content. The dielectric properties also depend on porosity of the materials. In the present ferrites the porosity decreases with increase in cobalt content in Ni-Cd ferrites. Decrease in number of pores decreases accumulation of charges which decreases the permittivity of the material. The variation of loss tangent with frequency shows similar kind of dispersion. At lower frequency tanδ is large and then decreases with increase in frequency [14]. The high value of loss tangent corresponds to high value of resistivity due to grain boundaries. Therefore, more energy required for electron exchange between Fe³⁺ and Fe²⁺ ions resulting high value of energy loss. At higher frequency small amount of energy is required for electron exchange between Fe³⁺ and Fe²⁺ ions resulting small value of energy loss and low value of resistivity [15].

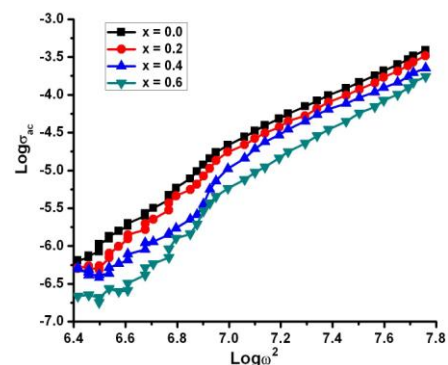


Fig. 3 Variation of ac conductivity with frequency of Ni_{0.4}Co_xCd_{0.6-x}Fe₂O₄ (x = 0.0, 0.2, 0.4, and 0.6).

Fig. 3 shows the variation of ac conductivity with frequency at room temperature. All the samples show increase in ac conductivity with increase in frequency, which is the

normal behavior of ferrites. As mentioned above the conduction in ferrites mainly due to exchange of electrons between Fe^{3+} and Fe^{2+} ions. The increase in frequency of the applied field increases the hopping of charge carriers resulting in increase of conductivity and decrease of resistivity. From the fig. 3, it is also observed that ac conductivity decreases with increase in cobalt content in Ni-Cd ferrite. The ac conductivity is proportional to dielectric constant and dielectric loss of the material. The decrease in dielectric constant and loss tangent is responsible for decrease in ac conductivity with increase in cobalt content in Ni-Cd ferrite [16]. Fig. 4 shows variation in saturation magnetization, retentivity, coercivity and magnetic moment are found to increase with increase in cobalt content in $Ni_{0.4}Co_xCd_{0.6-x}Fe_2O_4$.

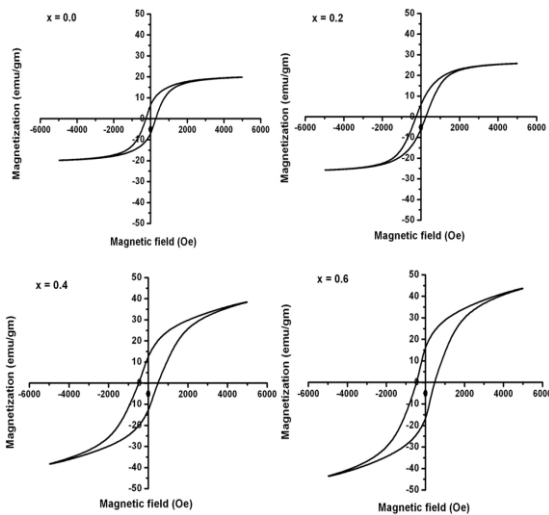


Fig. 4 Magnetic hysteresis loops of $Ni_{0.4}Co_xCd_{0.6-x}Fe_2O_4$ ($x = 0.0, 0.2, 0.4, \text{ and } 0.6$).

Table I Data on saturation magnetization, coercivity, retentivity and magnetic moment for $Ni_{0.4}Co_xCd_{0.6-x}Fe_2O_4$ ($x = 0.0, 0.2, 0.4, \text{ and } 0.6$).

Composition, x	Saturation magnetization (emu/gm)	Coercivity (Oe)	Retentivity (emu/gm)	Magnetic moment (μ_B)
0.0	19.95	259.13	5.58	0.95
0.2	25.85	275.02	6.07	1.18
0.4	38.22	483.11	12.56	1.67
0.6	43.38	485.14	16.11	1.82

The magnetic properties of ferrites depend on chemical composition, grain size, porosity and interaction between tetrahedral and octahedral sites. In ferrites, the variation in saturation magnetization has been attributed to both surface spin effect and cation distribution on A and B sites. In this case, the net magnetization comes from the Ni^{2+} moments in the B-sites alone as the Fe^{3+} moments from the A and B sites cancel each other. As the cobalt content increases in Ni-Cd ferrite, the inverse spinel Ni-Cd ferrite converts in to mixed spinel ferrite. Generally, for magnetic particles the size has

significant influence on their magnetic properties. For relatively larger grains, magnetic domains are formed to reduce the static magnetic energy. The number of domains diminishes with decreasing grain size. The particles turn into single domain ones with their size under a critical radius, resulting in the increasing coercive force [17]. In the mixed spinel type structure, some Ni^{2+} ions may occupy tetrahedral sites and hence the net magnetization should be higher than that for inverse spinel structure. The higher value of saturation magnetization in the present work shows the mixed spinel structure is likely to be in our case. The addition of Co ions displaces non-magnetic Cd ions to A- sites. Thus weakening the A-site moment and Fe^{3+} ions from now have parallel moment in the B-sites, because of strong AB interaction [18]. Cobalt which have strong magnetic anisotropy & replaces nonmagnetic cadmium ions in the octahedral sites and affects its magnetic properties. Cobalt ion doping causes the pinning of the domain walls due to an increase in anisotropy and has an impact on the coercivity and saturation magnetization. Further in present case of bulk and thick film Ni-Co-Cd ferrites, the variation in saturation and coercivity with increase in cobalt concentration may be attributed to the decrease in porosity of the ferrite. The porosity of the material decreases with increase in Co content. The saturation magnetization of ferrite is given by the formula [19].

$$M_s = 16\mu_B / Na^3 \quad (1)$$

Where M_s = saturation magnetization, μ_B = Bohr magnetron = 9.27×10^{-24} A/m², W = molecular weight of the sample, N_a = Avogadro's number, a = lattice parameter. As we keep on increasing the Co^{2+} doping, there is an increase in the saturation magnetization. The anisotropy energy for a cubic lattice is given by

$$E_k = K_1 (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_1^2 \alpha_3^2) + K_2 (\alpha_1^2 \alpha_2^2 \alpha_3^2 + \dots) + \dots \quad (2)$$

Where $\alpha_1, \alpha_2, \alpha_3$ are direction cosines of the magnetization vector relative to the crystallographic axis. The increase in saturation magnetization with increase in Co content is due to relatively high orbital contribution to the magnetic moment of Co^{2+} ions, which are known to give large induced anisotropy. Hence, the coercivity values increases with increase in Co content. An increase in coercivity with increase in Co content may be attributed to the increase in anisotropy field, which in turn decreases the domain wall energy.

The dependence on anisotropy constant K on the Co^{2+} concentration by the following relation [20].

$$K = H_c M_s / 2 \quad (3)$$

As Co^{2+} is highly magnetically anisotropic therefore as we keep on increasing the Co^{2+} doping in nickel cadmium ferrites, there's a rise in the coercivity as seen from the fig. 4. The data on saturation magnetization, coercivity, retentivity and magnetic moment for $Ni_{0.4}Co_xCd_{0.6-x}Fe_2O_4$ ($x = 0.0, 0.2, 0.4, \text{ and } 0.6$) is given in table 1. An increase in remnant magnetization and magnetic moment of these ferrites may be attributed to the facts that increase in saturation magnetization with increase in Co content in Ni-Cd ferrite.

The magnetic moment of the samples was calculated by the formula

$$n_B = M_S W / \mu_B N_A \quad (4)$$

Where M_S = saturation magnetization, W is molecular weight of the samples, μ_B is Bohr magneton and N_A is Avogadro's number. Here, μ_B and N_A are constants. From the table 2, it is seen that magnetic moment of ferrite increases with Co concentration in Ni-Cd ferrite due to increase in saturation magnetization of the samples.

IV. CONCLUSION

Cobalt substituted Ni-Cd ferrites were successfully prepared using solution combustion method. The dielectric constant and loss tangent are found to decrease with increase in frequency and Co substitution in Ni-Cd ferrites and it shows dielectric dispersion at lower frequencies attains constant value at higher frequencies. The small polaron type of conduction was confirmed by the ac conductivity measurements. Saturation magnetization, retentivity, coercivity and magnetic moment are found to be increase with increase in cobalt content in $Ni_{0.4}Co_xCd_{0.6-x}Fe_2O_4$.

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AUTHOR'S PROFILE

N. D. Patil has done his M.Sc. in Department of Physics, Shivaji University. At present he is pursuing Ph.D. His area of interest is Materials for microwave devices. He is fellow of UGC-BSR India.

N. B. Velhal has done his M.Sc. in Department of Physics, Shivaji University. At present he is pursuing Ph.D. He is fellow of DAE-BRNS India. His area of interest is Material for microwave devices.

N. L. Tarwar has done his PhD from Department of Physics Shivaji University. At present he is working as post doctoral fellow at Research Institute of Solar and sustainable energies, Gwangju Institute of Science and Technology, Gwangju. S. Korea.

Vijaya R. Puri is a UGC research scientist "C" in the Department of Physics, Shivaji University, Kolhapur, India. She is engaged in research of thick and thin film microstrip components with special emphasis on metallization aspects and overlay technique. She is also working on bio materials, thermistors, ferrites, conducting polymer composites and carbon nanostructures for use in planar form with microwave components. Dr Vijaya Puri is a member of IEEE (USA), MTT, CHMT, Magnetic and AP-S societies, and life member of IMAPS India. Vijaya Puri is the corresponding author and can be contacted at: vijayapuri1@gmail.com.