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Dielectric and Thermal Behaviour of Yttrium Substituted Nickel-Cadmium Ferrites ($Ni_{1-X} Cd_x Y_y Fe_{2-Y}O_4$, x = 0, 0.2, 0.4, 0.6 and y = 0, 0.075) Synthesized Using Sol-gel Autocombustion Method

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Abstract: *Fine powders of Y^{3+} doped $Ni_{1-X} Cd_x Y_y Fe_{2-Y}O_4$ (where x = 0, 0.2, 0.4, 0.6 and y = 0, 0.075) spinel nanoferrite were prepared using a sol-gel autocombustion techniques and sintered at 400 ^oC for duration of 2 hrs. The analysis of XRD patterns revealed the formation of single phase cubic spinel structure. The lattice parameter and crystallite size decreases with increase in Y^{3+} concentration and average grain size was found to be between 12.5 to 34.8 nm. The dielectric properties have been studied as a function of frequency (100 Hz to 5 MHz) at room temperature using LCR meter and shown the normal dielectric behaviour. The value of ac conductivity increases with increase in frequency for all the compositions. TG-DTA analysis of the auto combusted ferrites was carried out with a heating rate of 10 ℃/min in air. These results may be applicable for promising area such as high frequency electrical devices.*

Keywords: *Nanoferrite; Sol-gel autocombustion method; Optical properties; Dielectric constant; Thermal properties;*

I. Introduction

Ferrites are very good dielectric materials which have numerous applications at microwave to radio frequencies and plays a vital role in the technological applications (Chand *et al,* 2011). The study of dielectric properties gives valuable information and can explain the phenomenon of dielectric in the material. Several methods have been used in the preparation of nanoparticles, like the co-precipitation method, sol-gel technique, hydrothermal method, microwave sintering method, spray-spin-heating-coating method and autocombustion method. The ac conductivity increases with increasing in frequency and Cr concentration. The incorporation of Cr^{3+} for Fe^{3+} ions results in a significant impact on the dielectric behavior of the Cr-Zn ferrite system (Lakshmi *et al,* 2016). Out of all these, sol-gel autocombustion method is most convenient and promising technique to synthesize nanoparticles because of its simplicity, inexpensive precursors, short preparation time, better control over crystallite size and other properties of the materials (Srivastava *et al,* 2009). The dielectric properties of ferrites are dependent on several factors, such as the method of preparation, heat treatment, sintering conditions, chemical composition, cation distribution, pH, nature and type of substituent, the ratio of Fe^{3+}/Fe^{2+} ions, frequency and crystallite size (Kharabe *et al,* 2006; Nadeem *et al,* 2014; Huili *et al,* 2014). Y^{3+} substituted in Ni-Cd ferrite powders were synthesized by sol-gel autocombustion technique at low temperatures for different compositions and studied phase crystal structure with magnetic properties (Bhise *et al,* 2015). Ferrites are extremely important magnetic ceramics in the production of electronic components, electrical insulators, torsion sensors and energy storage applications such as anode materials in lithium batteries, fuel cells and solar cells. Yttrium doped cobalt ferrite was prepared using a sol-gel combustion technique and reported the resistivity of the prepared samples increased with increasing yttrium, so that conductivity should decrease with increasing yttrium addition (Shobana *et al,* 2013). The effects of heat treatment on nanocrystalline MnZn ferrite powders could be attributed to an increase in phase formation, crystallinity, microstructure and crystalline sizes (Ping *et al,* 2010). The presence of Zn ions causes appreciable changes in the electrical and dielectric properties of $CoFe_2O_4$ (Rani *et al,* 2013).

The present work investigation on the synthesis of nano-sized Y^{3+} material substituted in Ni-Cd nanocrystalline ferrites by sol-gel autocombustion techniques and characterized by XRD and two probe methods. It reports the consequent changes on their structural, dielectric and thermal properties.

II. Material And Method

The Y^{3+} doped in Ni-Cd ferrite powders were synthesized by sol-gel autocombustion method at low temperatures for different compositions of $Ni_{1-x} Cd_x Y_y Fe_{2-y} O_4$ (Where x = 0, 0.2, 0.4, 0.6, and y = 0.0 and 0.075). The AR grade nitrate of Merck company (purity of 99%) are used in the experiments such as Yttrium nitrate ($Y(NO_3).6H_2O$), Nickel nitrate ($Ni(NO_3)\cdot 6H_2O$), Cadmium nitrate ($Cd(NO_3)\cdot 6H_2O$), Ferric nitrate

($Fe(NO_3)_3.9H_2O$). These nitrates and citric acid are using stoichiometric ratio proportion to obtain the final product and the citric acid ($C_6H_8O_7$) is used as a fuel in the ratio 1:3. The proportion of each reagent was defined according to its respective molar amounts. All chemicals are dissolved in distilled water and were stirred till to obtain the homogeneous solution. To maintain pH equal to 7 by adding drop by drop ammonium hydroxide (NH_4OH) during the stirring process. This solution was stirred continuously with 80 $^{\circ}$C for about 4-5 hours to obtain sol. After 4-5 hours, gel converts into ash and finally ash convert into fine powder of $Ni_{1-x}\, Cd_x\, Y_y\, Fe_{2-y}\, O_4$ ferrite nanoparticles after autocombustion. The powder was sintered at 400 $^{\circ}$C for 2 hours.

The structural characterization was done by using XRD analysis. The X-ray diffractometer with Cu-Kα radiation of wavelength 1.5405 A^0 at 40 kV performed a scanning from 20 to 80 degree at a step size of 0.02 degree per second for each prepared sample and determined crystal structure, lattice parameter and crystallite size. The capacitance (Cp) and loss tangent (tan δ) were measured by two probe method in the frequency range 100 Hz to 5MHz at room temperature using precision LCR meter (HIOKI Model L2000). The variation of dielectric constant, dielectric loss and loss tangent with frequency were studied. The frequency dependent AC conductivity was calculated from dielectric constant and loss tangent data. The DC resistivity measurements of the samples were performed by means of a four probe method. Thermo gravimetric and differential thermal analysis (TG-DTA) of the auto combusted ferrites was carried out with a heating rate of 10 ℃/min in air.

III. Results And Discussion

Structural Studies: The resulting powder $Ni_{1-x}\, Cd_x\, Y_y\, Fe_{2-y}\, O_4$ (Where x = 0, 0.2, 0.4, 0.6, and y = 0.0 and 0.075) nano crystals were characterized by XRD pattern. The XRD pattern of sintered Y^{3+} doped the nickel-cadmium ferrite as shown in figure-1. Obtained XRD pattern and crystalline phases were identified and it conform the formation of a homogeneous well-defined spinal cubic structure. The broad peaks in the XRD pattern indicate a fine particle nature of the particles. The particle size was determined using Scherer's formula,

$$t = \frac{0.9\,\lambda}{\beta\, Cos\, \theta} \qquad \ldots\ldots\ (1)$$

Where, λ = Wavelength of X-ray, θ = Peak position and β = FWHM of the peak θ and it is corrected for instrumental broadening. The average particle sizes of nanoparticles are given in Table-1. The particle size decreases as the concentration of Y^{3+} increases. Lattice parameter obtained for prepared sample is ranging between 8.3399 to 8.3665 A^0. The deviation in lattice parameter can be attributed to the cations rearrangement in the nano sized prepared ferrites. The value of lattice constant for Ni-Mg-Cd doped yttrium ferrite shows the expansion of unit cell with rare earth doping when compared with pure yttrium ferrite. This is expected due to substitution of large ionic radius of Y^{3+} ions (0.9 A^0) with small ionic radius Fe^{3+} ions (0.645 A^0). This result in Y^{3+} substituted ferrites to have higher thermal stability relative to Ni-Cd ferrite. Yttrium doped Ni-Cd nanoferrites were synthesized with average grain size ranging between 12.5 to 34.8 nm which will give great effect on its dielectric and thermal properties.

Table-1: The particle size of $Ni_{1-x}\, Cd_x\, Y_y\, Fe_{2-y}\, O_4$ by XRD

Obs. No.	Composition	Average grain size (t) nm	Lattice constant (a) A^o
1	$\mathbf{Ni\, Fe_2\, O_4}$	**34.7791**	**8.3399**
2	$\mathbf{Ni_{0.8}\, Cd_{0.2}\, Fe_2\, O_4}$	**25.158**	**8.3455**
3	$\mathbf{Ni_{0.8}\, Cd_{0.2}\, Y_{0.075}\, Fe_{1.925}\, O_4}$	**20.762**	**8.3591**
4	$\mathbf{Ni_{0.6}\, Cd_{0.4}\, Y_{0.075}\, Fe_{1.925}\, O_4}$	**16.052**	**8.3635**
5	$\mathbf{Ni_{0.4}\, Cd_{0.6}\, Y_{0.075}\, Fe_{1.925}\, O_4}$	**12.498**	**8.3665**

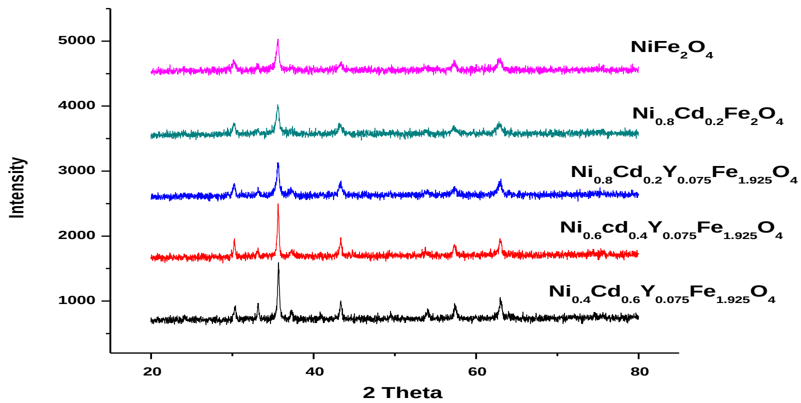

Figure1: Structural properties of $Ni_{1-x}\, Cd_x\, Y_y\, Fe_{2-y}\, O_4$ by XRD

Dielectric Studies: Dielectric measurements were carried out at room temperature over a wide frequency range from 100 Hz up to 5 MHz. The value of dielectric constant is calculated by using the following relation:

$$\acute{\varepsilon} = \frac{Cp\ d}{\varepsilon 0\ A} \qquad \text{............ (2)}$$

Where, ε_0 is the permittivity of free space, d is the thickness of the pellets, A is the area of cross-section of the pellet and Cp is the measured value of the capacitance of the pellet.
The variation of dielectric constant and dielectric loss tangent with frequency for the as-prepared ferrites doped with different amounts of yttrium ions are shown in figure-2 and figure-3 respectively.

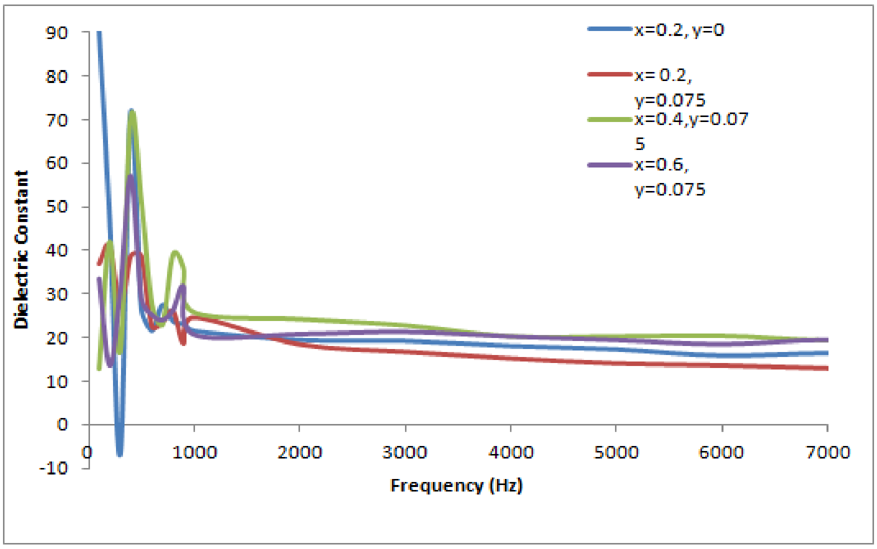

Figure 2: Variations of dielectric constant with frequency of $Ni_{1-x} Cd_x Y_y Fe_{2-y} O_4$ nanoferrites

Figure-2 shows the variation of dielectric constant as a function of frequency at room temperature from 1 kHz to 5MHz. It is observed that for each sample the dielectric constant decreases with an increase of frequency and a normal dielectric behaviour of spinel ferrites. This can be explained on the basis of mechanism of polarization process which is similar to that of conduction process. The whole polarization in ferrites is mainly contributed by space charge polarization, the conductivity in materials and hopping exchange of the charges between two localized states.
The value of dielectric loss tangent is calculated by using the following relation:

$$\varepsilon'' = \acute{\varepsilon} \tan \delta \qquad \text{............ (3)}$$

From figure-2 it is observed that the small variation of dielectric constant occurs up to 1000 Hz frequency and from the frequency 5000 Hz it becomes stable.

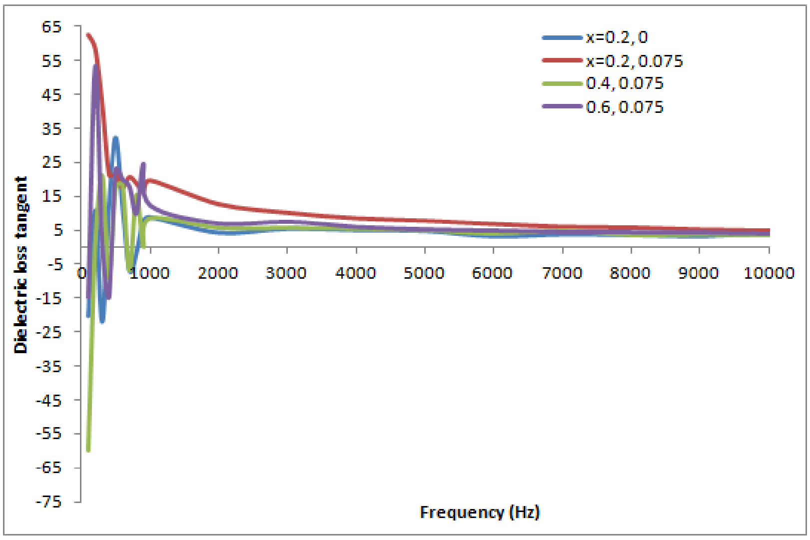

Figure3: Variations of dielectric loss with frequency of $Ni_{1-x} Cd_x Y_y Fe_{2-y} O_4$ nanoferrites

Figure-3 shows the frequency dependence of dielectric loss in Ni_{1-x} Cd_x Y_y Fe_{2-y} O_4 nanoferrites. The value of dielectric loss tangent is very low in the present work indicating that the samples are structurally prefect. From figure-3 we conclude that the dielectric loss tangent is very low and varies up to 1000 Hz and above that it becomes stable. The AC conductivity of the sample can be evaluated from the dielectric permittivity (ϵ_0) and the loss factor (tan δ) using the equation

$$\sigma_{AC} = 2\pi\epsilon_0 f \tan\delta \qquad \ldots\ldots\ldots\ldots\ldots (4)$$

Where, *f* is the frequency. The AC conductivity increases with increasing frequency at low temperatures.

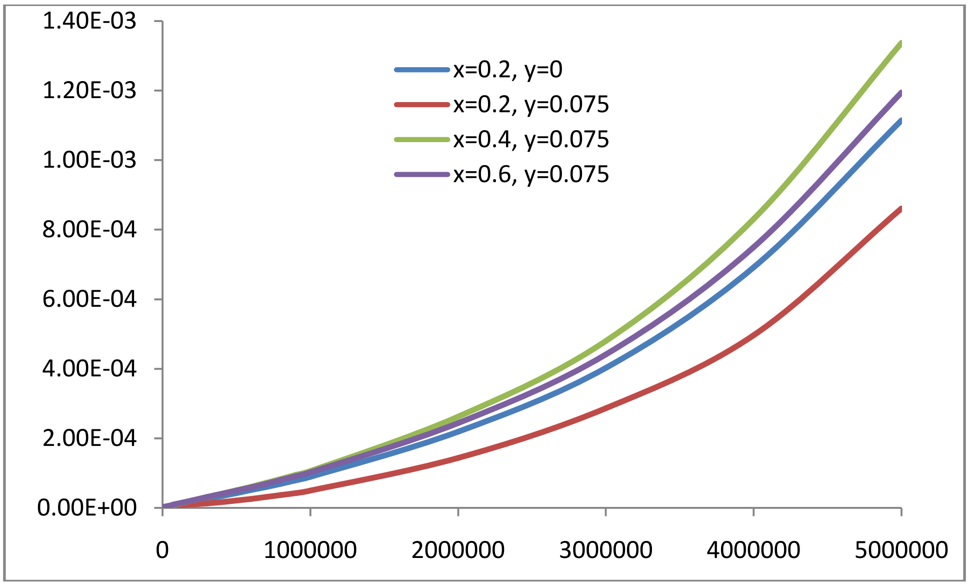

Figure4: Variations of AC Conductivity with frequency of Ni_{1-x} Cd_x Y_y Fe_{2-y} O_4 nanoferrites

Figure-4 shows AC conductivity increases linearly with the frequency.

Thermal Studies:

In order to investigate the mechanism of the Y^{3+} doped Ni-Cd ferrites autocombustion, Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) was carried out with a heating rate of 10 ℃/min in air and the results are shown in Figure-5 and Figure-6 respectively.

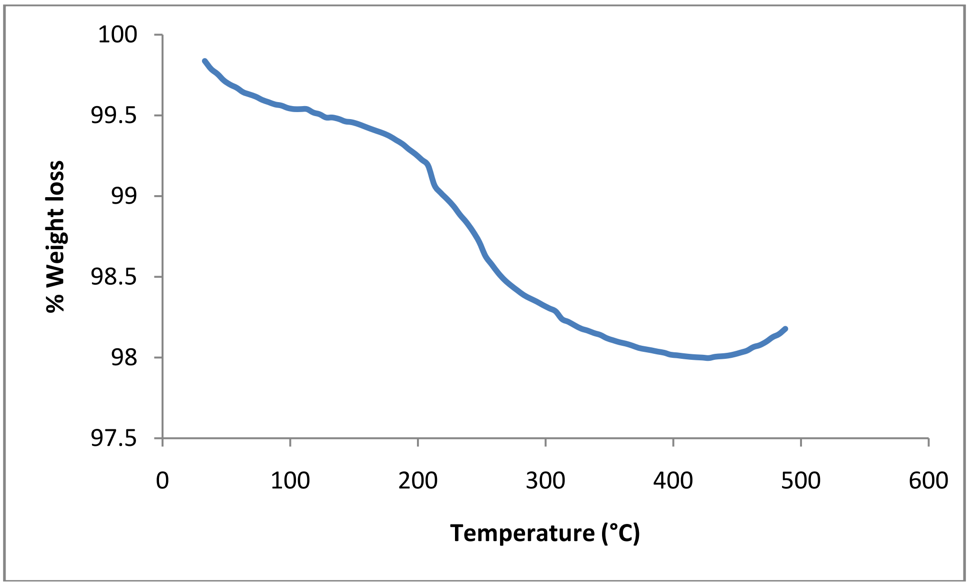

Figure 5: TGA curve for $Ni_{0.8}$ $Cd_{0.2}$ $Y_{0.075}$ $Fe_{1.925}$ O_4 nanoferrites

From TGA analysis it is observed that as the temperature increase the percentage weight loss decreases.

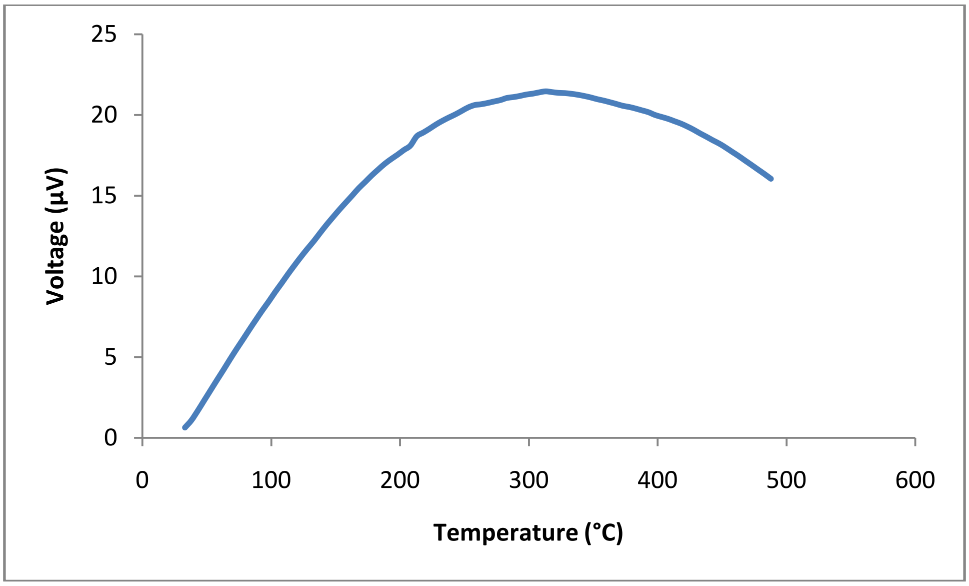

Figure 6: DTA curve for $Ni_{0.8}$ $Cd_{0.2}$ $Y_{0.075}$ $Fe_{1.925}$ O_4 nanoferrites

From DTA analysis we observe that with increase in the temperature the voltage increases up to 308 ^{o}C and it decreases with the increase in temperature.

IV. Conclusions

Nanostructured Ni_{1-x} Cd_x Y_y Fe_{2-y} O_4 (Where x = 0, 0.2, 0.4, 0.6, and y = 0.0 and 0.075) powder were successfully prepared by sol-gel autocombustion method and the conclusions can be summarized as followings;

1) The XRD pattern shows that nanoparticles decreases with the increase in Y^{3+} content.
2) A dielectric study indicates that for each sample the dielectric constant decreases with an increase of frequency and a normal dielectric behaviour of spinel ferrites. The value of dielectric loss tangent is very low in the present work indicating that the samples are structurally prefect. The AC conductivity increases with increasing frequency at low temperatures.
3) From TGA analysis it is observed that as the temperature increase the percentage weight loss decreases and from DTA analysis we observe that with increase in the temperature the voltage increases up to 308 ^{o}C and it decreases with the increase in temperature.

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