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Y^{3+} Doped $Ni_{0.4}$ $Mg_{0.4}$ $Cd_{0.2}$ $Fe_{2-y}O_4$ Spinels Nanoferrite : Structural, Morphological, and Electrical Properties

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ABSTRACT

Structural, morphological, and electrical properties were investigated for Y3+ doped Ni0.4 Mg0.4 Cd0.2 Fe2-y O4 spinel nanoferrite (where y = 0.025 to 0.125) obtained by sol-gel techniques. Nanoscale samples were carried out at low temperature and cost effective method with analytical grade metal nitrate. Citric acid was used as a fuel. The prepared powder were sintered at 400 oC and characterized by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDAX) for structural property andscanning electron microscopy (SEM), transmission electron microscopy (TEM) for morphological studies. Ferrite formation was found to quite sensitive. The particle size was determined using Scherer's formula and it found that it decreases with increase in Y3+content. Also DC resistivity increases with increasing Y3+content and electrical conductivity increases with temperature increases. These results may be applicable for promising area such as high frequency electrical devices.

Keywords : Spinel Ferrite, Sol-Gel Autocombustion Method, Morphological Properties, Electrical Properties

I. INTRODUCTION

The spinel ferrites are interesting materials owing to their wide range of applications in modern science and technology.They have recently attracted considerable research interest on their structural, magnetic and electrical properties [1]. The physical properties such as increase in DC resistivity, low dielectric losses and magnetization characteristics are due to the substitution of tetrahedral cations in the parent crystal structure. The structural variation in the host lattice can be occurred due to proper choice and composition of trivalent cations such as Al^{3+}, Y^{3+}, $Cr^{3+}$and La^{3+}) to replace Fe^{3+} in the parent lattice of cobalt ferrite [2]. Magnetic properties of ferrites depend on their chemical composition, preparation method, sintering time and temperature [3]. The sol-gel method is used for the synthesis of Nickel substituted cobalt ferrite nanoparticles. The result proves that with increase in nickel content magnetic saturation decreases [4]. The sol-gel method is a good combination of combustion and chemical gel process. The advantage of sol-gel method is a good stoichiometric control and results in ultra-fine nanoparticles [5].Infrared spectroscopy (IR) is one of the most powerful techniques, which offers possibility of chemical identification. One of the advantages of IR over other methods for structural analysis is that, it provides useful information about the structure of a molecule rapidly and also without cumbersome evaluation methods. The technique is based upon the simple fact that a chemical substance shows marked selective adsorption in the infrared region. Various bands obtained in IR spectra are corresponding to the characteristic functional groups and bonds present in the chemical substance. The absorption bands in the IR spectra split on the basis of different cations present on tetrahedral (A) and octahedral [B] sites of spinel ferrites [6–8].Nickel ferrites are stable, relatively inexpensive and easily manufactured and have wide applications in electronics and communication industries owing to their interesting magnetic and electrical properties. The coercivity was decreased by increasing Cd content due to the decrease of magneto crystalline anisotropy constant of the samples [9]. Yttrium doped cobalt ferrite was prepared with different concentrations to identify the crystallite size with respect to the yttrium concentration, temperature and changes in the structural and electrical properties and reported that the resistance of the nanostructured yttrium doped cobalt ferrites nanopowder was analysed. The resistance was increased by the addition of yttrium to cobalt ferrites [10].

The present work investigation on the synthesis of nanosize Y^{3+} material substituted in Ni-Mg-Cd

nanocrystalline ferrites by sol-gel autocombustion techniques and characterized by XRD, EDAX, FTIR, SEM and TEM. It reports the consequent changes on their structural, optical, morphological and electrical properties.

II. MATERIAL AND METHOD

The Y^{3+} doped in Ni-Mg-Cd ferrite powders were synthesized by sol-gel auto combustion method at low temperatures for different compositions of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ (where y = 0.025, 0.050, 0.075, 0.100 and 0.125). 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 ($Ni(NO_3)\cdot 6H_2O$), Magnesium nitrate ($Mg(NO_3)\cdot 6H_2O$), 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 [11]. 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 ash convert into powder. Finally get fine powder of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ferrite nanoparticles after auto combustion. Powder was sintered at 400 $^{\circ}$C for 2 hours.

The general chemical reaction for the synthesis of sample can be presented as;

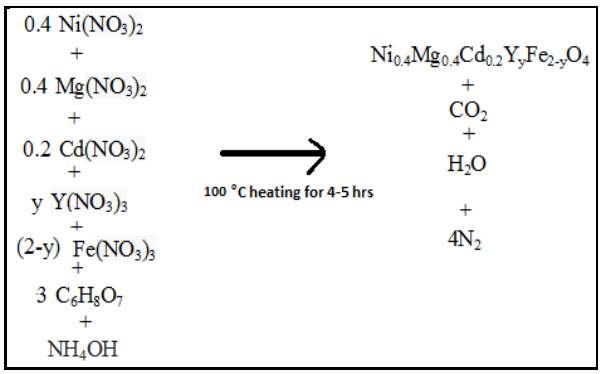

Figure 1. Structural properties of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ by XRD

Various analytical tools like X-ray diffraction (XRD), Energy dispersive x-ray spectroscopy (EDAX), Fourier transformation infrared (FTIR), Scanning electron microscopy (SEM), and Transmission electron microscopy (TEM) were used for the characterization and evaluation of properties. The structural characterization was done 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 microstructure investigations were carried out on the fracture surfaces of the samples using thermal field emission scanning electron microscope (SEM, JSM-7600F) equipped with an energy dispersive x-ray spectroscopy (EDAX).The optical characteristics was studied using Fourier Transformation Infrared (FT-IR) of Bruker 3000 Hyperion microscope with vertex 80 single point detector performing images resolution ranging between 7500 to 450 cm^{-1}. The particle morphology was studied using Scanning electron microscopy (SEM) of JEOL JSM-7600F combines two proven technologies operating at 0.1 to 30 kV with high resolution and Transmission electron microscopy (TEM) of PHILIPS CM-200 operating at 20-200 kV with resolution 2.4 A^0. The temperature dependence of DC resistivity of samples was recorded at different temperature 200 ^{0}C and 300 ^{0}C with USB computer interface through SES-CAMM module using electrometer (TPX-600C having resolution 1 pA to 100 nA) in two probe method. Further investigations of the electrical properties are under way to elucidate the effective role of inter particle interactions in these samples.

III. RESULTS AND DISCUSSION

3.1 Structural Studies

a) XRD analysis : The resulting powder $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ (where y = 0.025, 0.050, 0.075, 0.100 and 0.125) nanocrystals were characterized by XRD pattern. The XRD pattern of sintered Y^{3+} doped the nickel-magnesium-cadmium ferrite nanocrystals as shown in figure-2. Obtained XRD pattern and crystalline phases were identified and it conforms the formation of a homogeneous well-defined spinal cubic structure with put any impurity. The broad peaks in the XRD pattern

indicate a fine particle nature of the particles. The particle size was determined using Scherer's formula,

$$t = \frac{0.9\,\lambda}{\beta Cos\theta}$$

Where, λ = wavelength of X-ray used, 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 1.9228 to 2.1300 A^0. The deviation in lattice parameter can be attributed to the cations rearrangement in the nanosize prepared ferrites. 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-Mg-Cd ferrite.

Table 1. The particle size of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ by XRD

Composition y	Average grain size (t) nm	Lattice constant (a) A^o
0.025	23.092	8.3597
0.050	24.352	8.3716
0.075	20.534	8.3603
0.100	21.984	8.3585
0.125	17.02	8.3624

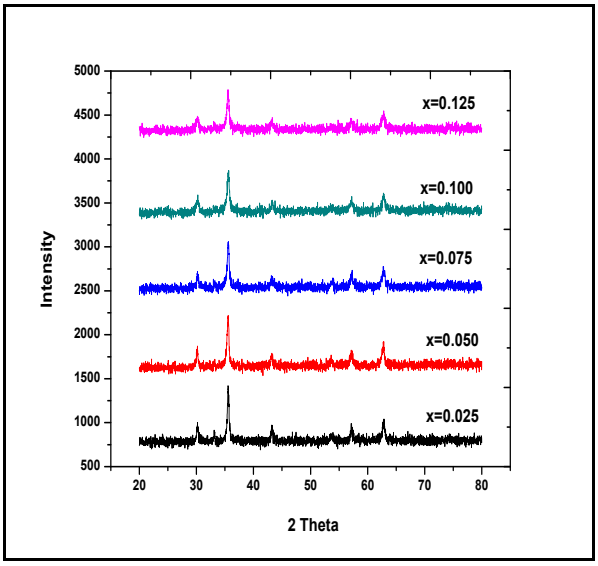

Figure 2. Structural properties of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ by XRD

b) EDAX analysis: The typical EDAX spectra taken from the ferrite grain and grain boundary of a typical sample $Ni_{0.4}$ $Mg_{0.4}$ $Cd_{0.2}$ $Y_{0.125}Fe_{1.875}O_4$to know the chemical constituents present in the materials and it reveals that the ferrite grain contain amount of Y^{3+} supporting indirectly the entering of yttrium ions into the sub lattice of ferrites. The EDAX spectrum shows the content of Y^{3+} is less than that of its normal composition due to segregation of yttrium ions into the grain boundaries and evaporation at high temperature. Also it is found that grain sizes of the samples decreases with increasing in doping of Y^{3+} ions because more cations vacancies, closed pores exist and grain boundary movement when large amount of Y^{3+} ions exist in the samples.

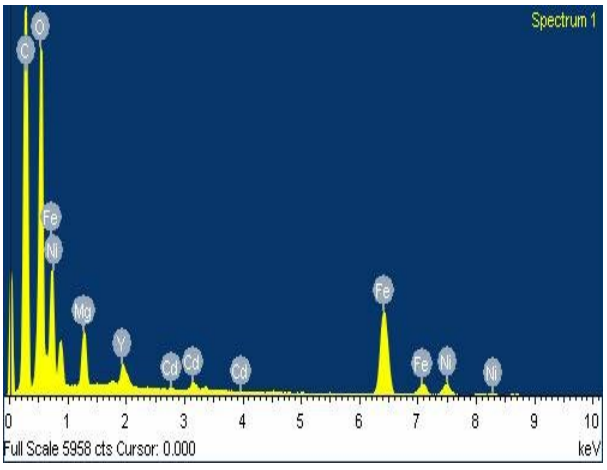

Figure 3. Structural properties of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_{0.125}Fe_{1.875}O_4$ by EDAX

3.2 Morphological Studies:

a) SEM analysis: The SEM images of Ni-Mg-Cd nanocrystalline ferrites by sol-gel auto combustion method as shown in figure-4. The SEM image of the prepared $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_{0.075}Fe_{1.925}O_4$ sample is composed of nanocrystals and shows the distribution of nanoparticles. The calculated ferrite gain sizes of the corresponding Yttrium doped Ni-Mg-Cd ferrite samples from these graphs are presented in table1. It is observed that the grain sizes of the ferrites in the samples decreases with increase in doping of Y^{3+} ions that indicates increase in grain size is not liquid-phase sintering. The melting point of Y^{3+} is 1522 ^{0}C which is much larger than the sintering temperature (400 ^{0}C) of the ferrites.

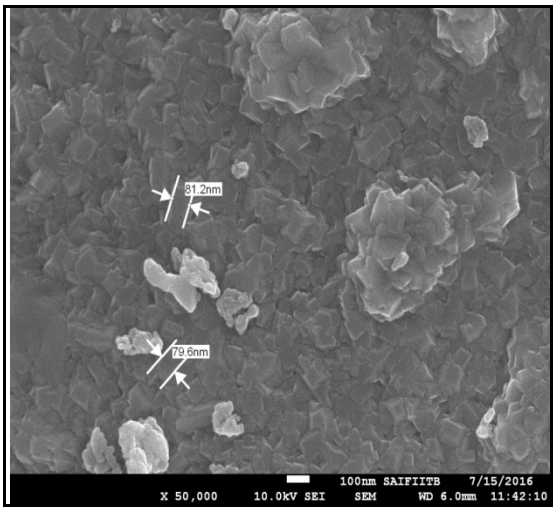

Figure 4. Morphology of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_{0.075}Fe_{1.925}O_4$by SEM

b) TEM analysis: The particle size was estimated using TEM analysis. The reduction in particle size with rare earth doping is evident from TEM images. Average particle sizes measured are given in table 1. Figure 5(a) and (b) show the TEM images of$Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$nanoferrite by using sol-gel autocombustion method. The most of nanoparticles are in spherical shape and agglomerated due to the tendency of nanoparticles.

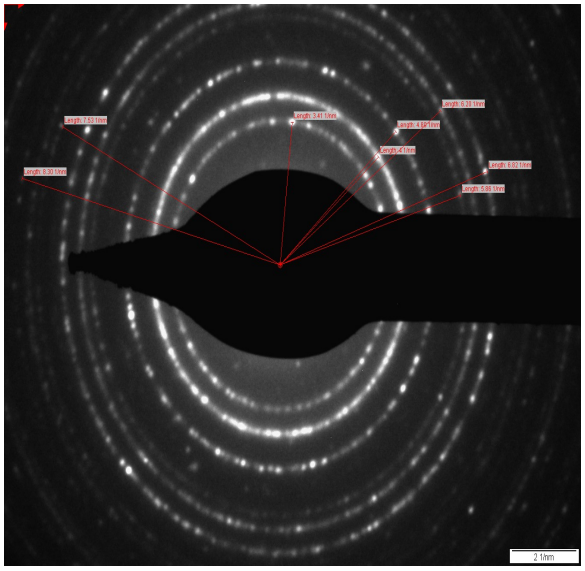

Figure 5(a). Morphology of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_{0.100}Fe_{1.900}O_4$ by TEM

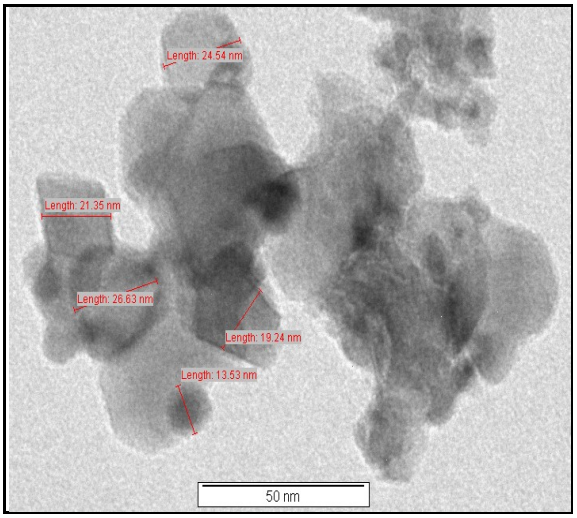

Figure 5(b). Particle size using morphology of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_{0.100}Fe_{1.900}O_4$ by TEM

3.3 Electrical studies:

Table 2. The resistivity and conductivity of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$

Composition	Resistivity (ρ) (ohm-m)		Conductivity (σ) (mho)	
	at 200 °C	at 300 °C	at 200 °C	at 300 °C
y=0.025	212746.14	4660288.79	5.1221 x 10^{-6}	2.1457 x 10^{-7}
y=0.050	1251638.44	244406.46	7.8677 x 10^{-7}	4.0915 x 10^{-6}

y=0.075	2122939.87	300018.62	4.7008 x 10^{-7}	3.3331 x 10^{-6}
y=0.100	914634.77	104424.91	1.2796 x 10^{-6}	9.5763 x 10^{-6}
y=0.125	3292097.63	256715.18	3.4270 x 10^{-7}	3.8954 x 10^{-6}

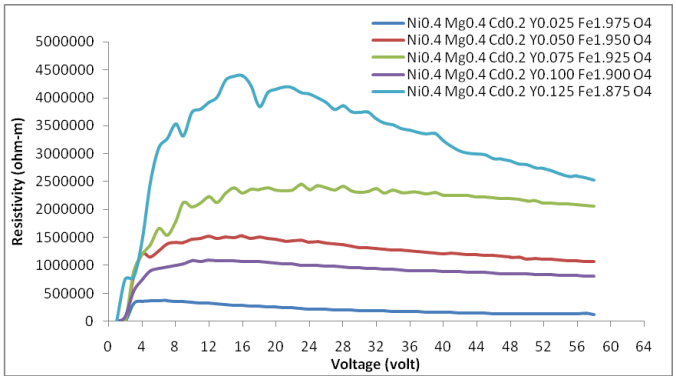

Figure 6(a). Electrical behaviour of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ at 200 ^oC

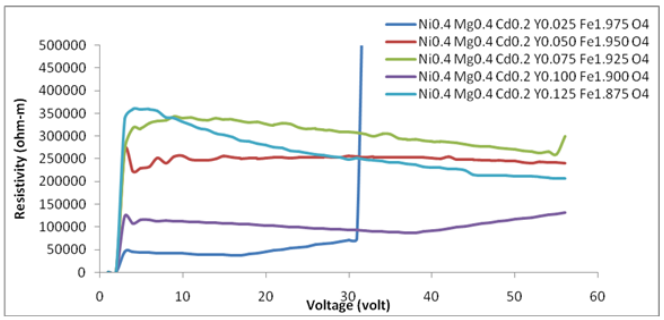

Figure 6(b): Electrical behaviour of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ at 300 ^oC

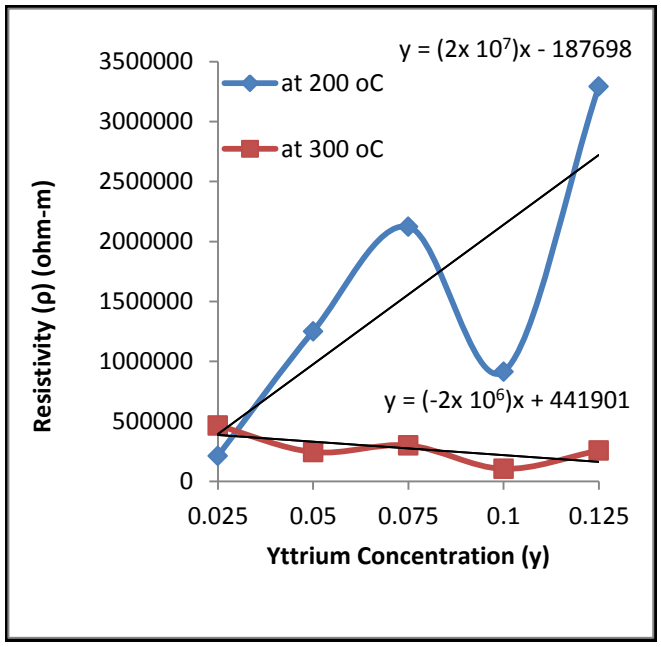

Figure 6(c). Variation of resistivity of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ spinal ferrite with yttrium content (y)

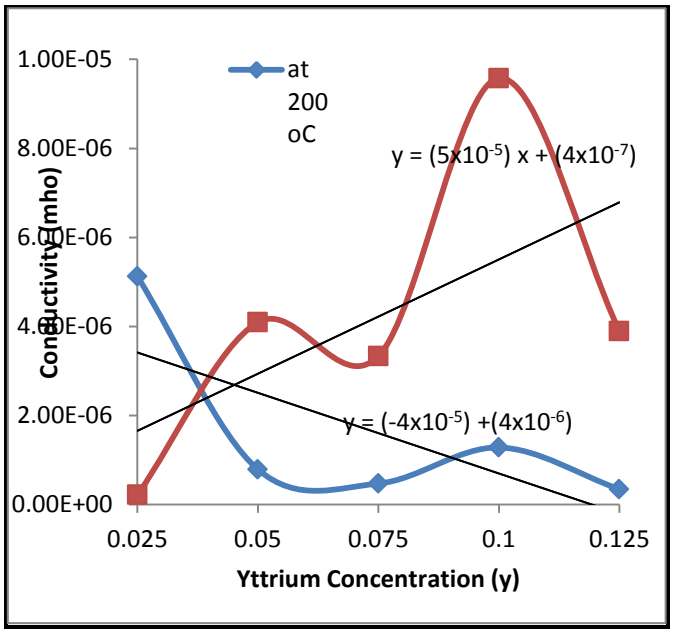

Figure 6(d). Variation of DC conductivity of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ spinal ferrite with yttrium content (y)

Changes inresistivity and DC conductivity of $Ni_{0.4}Mg_{0.4}Cd_{0.2}Y_yFe_{2-y}O_4$ spinal ferrite with yttrium content (y) is shows in figure 6 (c) and (d). Actually conductivity in ferrites are collectivelly contributed by electron hopping between Fe^{2+} and Fe^{3+} ions and holes hopping between Y^{2+} and Y^{3+} ions and depends on availability of charge

carriers with mobility. Hence increase in conductivity explains increase in hopping pairs.

IV. CONCLUSIONS

Yttrium doped $Ni_{0.4}Mg_{0.4}Cd_{0.2}Fe_{2-y}O_4$ (where y = 0.025 to 0.125)powder have been successfully synthesized using sol-gel method. The formation of the ferrite powders has been confirmed by XRD, EDAX, SEM and TEM. The XRD pattern shows that nanoparticles decreases with the increase in Y^{3+} content and lattice parameter is ranging between **8.3585** to **8.3716**A^0 and average grain size ranging between 17 to 24.3 nm which will give great effect on it electric properties. It is also observed that the most of nanoparticles are in cubical shape and agglomerated due to the tendency of nanoparticles. The optical property of prepared samples was also investigated and shows the characteristic bond of spinel structure. The electrical property indicates that conductivity increases with the increase in temperature. It results the doping of Y^{3+} in Ni-Mg-Cd nanoferrite produces consequent changes on their structural, morphological, electrical properties and it applicable for high frequency electrical devices.

V. ACKNOWLEDGEMENTS

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