

AC Impedance spectroscopy study on Nickel doped Cadmium Ferrites Nano particles prepared by sol-gel citrate method

G.N. Chaudhari

Nanotechnology Research Laboratory, Department of Chemistry
Shri Shivaji Science College, Amravati- 444602 (M.S), India

Abstract— In the present work Ni doped CdFe₂O₄ Nanoparticles have been synthesized by Sol-gel Citrate Method. The frequency dependent dielectric dispersion of Ni doped CdFe₂O₄ nanoparticles was investigated by impedance spectroscopy. The dielectric properties and ac conductivity of the samples were measured as a function of frequency. The plots of Z' vs. Z'' (Z' is the real part of impedance and Z'' is the imaginary part) for Ni doped CdFe₂O₄ were recorded. Sample have semicircle arc originating at the origin point, this indicate that Ni doped CdFe₂O₄ can be described by one bulk resistance and one bulk capacitance both connected parallel. The Centre below real axis indicates the relaxation behavior of the system.

Keywords: Ni doped CdFe₂O₄, sol-gel method, impedance spectroscopy, Dielectric properties.

I. INTRODUCTION

Ferrites are characterized by high conductive grains separated by highly nonconductive grain boundaries. The electric properties are mainly controlled by the grain boundaries. The high electrical resistivity of ferrites has been extensively used in many magnetic devices than those of soft magnetic alloys [1, 2] The dielectric behaviors in ferrites were studied with the help of AC conductivity. Ferrites are good dielectric materials and the dielectric properties of ferrites dependent on factors such as method of preparation; hence the study of dielectric behavior became important. The dielectric properties of the ferrites are depending on several factors such as method of preparation [3]. The dielectric behavior of ferrites as a function of frequency is attributed to Maxwell - Wagner polarization. It is been reported that there is a correlation between the conduction mechanism and the dielectric behavior of the ferrites [4]. Small ferri-magnetic oxides, technically known as ferrites have attracted considerable attention not only from a fundamental scientific interest but also from a practical point of view for growing applications in the magnetic, electronic and microwave fields [5-11]. Ferrites are good dielectric materials having low conductivity and have wide applications in the field of micro-wave devices. Nano crystalline ferrites are technologically important materials because of their unique electric, dielectric, magnetic and optical properties, which makes them suitable for many technological applications like microwave devices, transformers, electric generators, storage

devices etc. [12]. These ferrites have provided series of compounds with general formula MFe₂O₄ where M is a mixture of divalent diamagnetic elements [13]. Substituted nickel ferrites have been the subject of extensive investigation because of their microwave applications. Solid solution of the spinel Cadmium Nickel ferrite system have cubic configuration with the unit cell consisting of eight formula units of the form (Cd_{1-x}²⁺Fe_x³⁺)A [Ni_x²⁺Fe_{2-x}³⁺]BO₄²⁻ [14], [15]. Accordingly, a normal spinel ferrites were obtained for x=0, an inverse obtained for x = 1, and intermediate for 0<x<1. In the present work an attempt was being made to synthesis Cd-Ni ferrite with general formula Cd_{1-x}Ni_xFe₂O₄ (where x= 0.1, 0.2, 0.3) by sol- gel method and also the influence of substitution of nickel in cadmium ferrite on structural, electrical and properties are investigated.

II. EXPERIMENTAL

All chemicals and solvents were analytical grade and purchased from commercial sources.

A. Synthesis of Ni doped CdFe₂O₄ nanoparticles

The Ni doped CdFe₂O₄ nano particles prepared by using sol-gel citrate method. The stoichiometry mixture of Cadmium nitrate, Ferric nitrate magnetically stirred with citric acid and ethanol at 80° C for 3hrs to get homogeneous and transferent solution. The solution was further heated at about 130° for 12 hrs. in pressure vessel to form the gel precursor. The prepared product was subjected to 3hrs heat treatment at 350°C in muffle furnace and then milled to a fine powder. The dried powder then calcinated in range of 350°-650°C in order to improve the crystallinity of material.

B. Preparation of pellet

The powders were crushed and ground finally the powder was pressed in the form of pellets of 1cm diameter and 1cm thickness by applying a pressure of 70Mpa. For impedance measurements, the silver coating was done on both sides of the pellet leading to parallel plate capacitor structure.

C. Instrumentation

The powder X-ray diffraction pattern was obtained from Chandigarh(PUNJAB) X-ray diffract meter using Cu-K α radiation. Bonding in Ni doped CdFe₂O₄ obtained from Perkin-Elmer FTIR spectrophotometer (1000). Dielectric

measurements were carried out on this sample using LCR meter (Model HIOKI).

III. RESULT AND DISCUSSION

A. Structural Characterizations

Fig 1. X-Ray Diffraction Pattern of 1 wt % Ni doped $CdFe_2O_4$ calcined at $550^\circ C$ reveals crystalline nature of sample. It exhibit major diffraction peak 2θ value, 24.17° , 30.30° , 35.62° , 43.39° , 49.47° and 57.47° at 650 C Corresponds to d values 3.681,2.949,2.520,2.085,1.842 and 1.603 respectively which was attributed to the formation of $CdFe_2O_4$ spinel structure and no peak corresponds to NiO is observed.

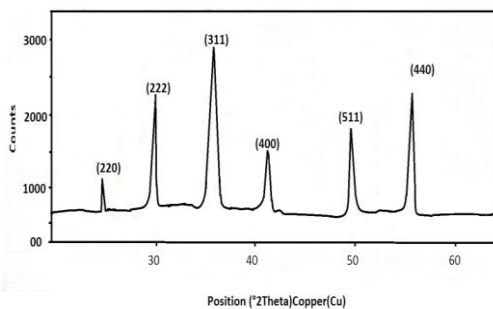


Fig 1. X-Ray Diffraction Pattern of 1% Ni doped $CdFe_2O_4$

The average crystalline size was 80nm obtained from FWHM of peak corresponding to 2θ calculated by Debye-Scherrer formula which is given by, $L = k \lambda / \beta \cos\theta$ Where, L is the average size of crystal, $K=0.9$ particle diameter, the λ (0.154 \AA) is wavelength of X-Ray, β is full width at half maximum (FWHM) of the diffraction peak and 2θ is the diffraction angle of diffraction. FWHM is calculated by warren's formula

$$B_2 = (B_{m_2} - B_{s_2})$$

Where B_m is full width at half maximum of the sample and B_s the full width at half maximum of standard quartz. FTIR spectra were recorded in range of $400-4000 \text{ cm}^{-1}$. Fig 2. Shows the FTIR spectra of 1 wt % Ni doped $CdFe_2O_4$ calcined at $550^\circ C$. It is observed that most intense band of spectrum, splitted in 1410 cm^{-1} and 455 cm^{-1} , due to stretching of Cd-O-Fe bond of tetrahedral building units forming the structure. The wide absorption in the high energy region of spectrum, centered at 3431 cm^{-1} , resulting from -OH stretching is associated to the vibration of water molecule Coordinated to ferrite structure that is a broad band at 3431 cm^{-1} that assigned to absorption of H_2O from the atmosphere or OH group of alcohol. Very small band at 2342 cm^{-1} is due to adsorbed or atmospheric CO_2 . The characteristics small band at 1628 cm^{-1} is assigned to both asymmetric and symmetric C-O respectively. Two small peaks at 455 and 545 cm^{-1} that are characteristics of poorly crystalline $\alpha-Fe_2O_3$.

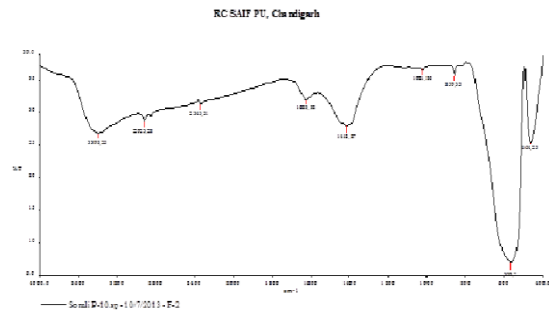


Fig 2. FTIR OF 1 wt% Ni doped Cadmium Ferrite

B. AC Conductivity

The response of the real components of impedance (Z') with frequency for Ni (1wt %) doped $CdFe_2O_4$ sample at different temperature is shown in fig.3 (a). The value of Z' is higher at lower frequency region and as frequency increases the value of decreases. The decrease in the Z' values as frequency increases in all compounds indicate conductivity of these compound increases with.

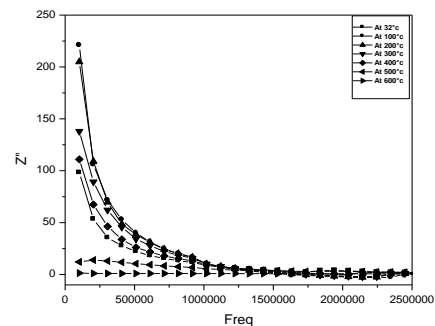
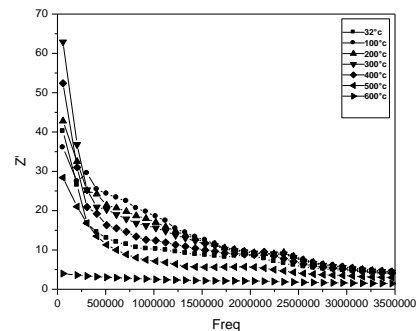


Fig.3: Frequency dependence of (a) real part of impedance (Z') and (b) imaginary part of impedance (Z'')

Increase of frequency due to the increase of hopping of charges between the localized ions. At low frequency, the value of Z' for these compounds decreases with the increase of temperature and these values merge at high frequency region due to the increase of ac conductivity. Fig 3(b) shows the imaginary part of impedance (Z''). At low temperatures below $150^\circ C$, the value of Z'' is high at low frequency and decreases with the increase of frequency indicating that electric relaxations are absent. Such results are not obtained in undoped and (0.5 and 1.5 wt %) Ni doped $CdFe_2O_4$

samples. Fig. 4 shows Nyquist plot of Ni (1 wt %) substituted CdFe₂O₄ with different temperatures. These plot allow resistances related to grain interiors (bulk), grain boundaries and

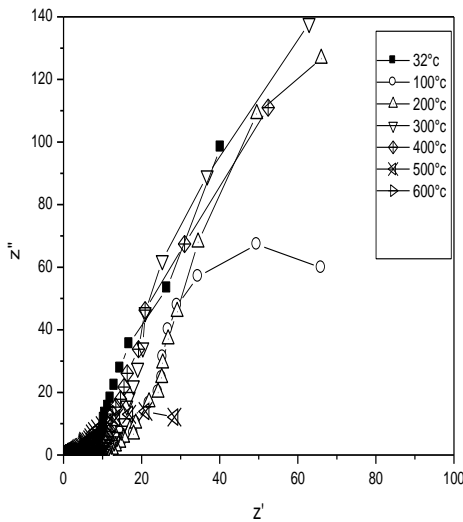


Fig 4. Nyquist Plot

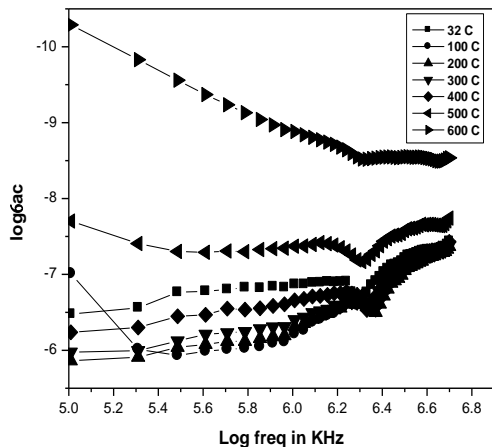


Fig 5. Ac conductivity of Ni (1 wt %) doped CdFe₂O₄

Sample/electrode interfaces to be separated because each of them has different relaxation times, the analysis of these semicircular arcs gives, from the high frequency side, the grain-bulk, the grain-boundary. All these semicircles are not perfect semicircles, but inclined with their centers below the Z' -Axis by an angle, which is different for each case. Fig 5 shows variation of log σ_{ac} with frequency the curve at different frequency appear to merge at lower temperature on high frequency side ac conductivity increases with temperature and it shows little frequency dependence Figure 6 and 7 shows the dielectric properties of Ni(1 wt%) doped CdFe₂O₄ calcined at 550°C. The variation of ϵ' with frequency explains relaxation phenomena of the material, which are associated with a frequency-dependant orientation polarization. The value of dielectric constant ϵ' decreases to a constant value with increase in frequency in the compound, which may be attributed to the fact that, at lower frequency

region the permanent dipoles align themselves along the direction of the field and contribute to the total polarization of the dielectric material. On the other hand, at higher frequency the variation in field is too rapid for the dipoles to align themselves in the direction of field, i.e., dipoles can no longer follow the field, so their contribution to the total polarization and hence to the dielectric constant become negligible. Therefore the dielectric constant (ϵ') decreases with increase in frequency. The increasing value of ϵ' at frequencies below 500 Hz may arise due to space charge polarization.

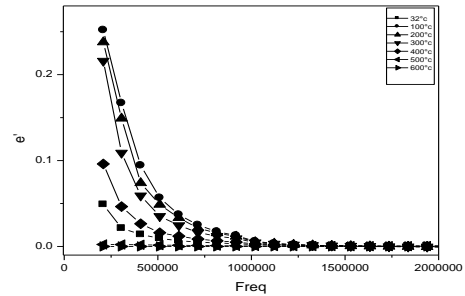


Fig. 6 Dielectric properties of Ni (1 wt %) doped CdFe₂O₄

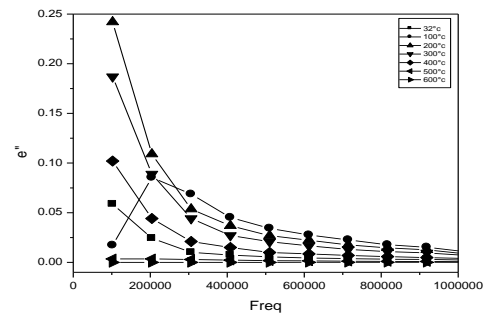


Fig. 7 Dielectric properties of Ni (1 wt %) doped CdFe₂O₄

Dielectric loss is the electrical energy lost as heat in the polarization process in the presence of an applied ac field. The energy is absorbed from the ac voltage and converted to heat during the polarization of the molecule. The dielectric loss is a function of frequency and temperature and is related to relaxation polarization, in which a dipole cannot follow the field variation without a measurable lag because of the retarding or friction forces of the rotating dipoles. Also, due to the change in polarization of the dielectric, a polarizing current flowing in the dielectric is induced by the relaxation rate. This current induces dielectric loss in the material. It is well known that in high frequency alternating fields there is always a phase difference between polarization and field, which gives the dissipation factor and is proportional to the energy absorbed per cycle by the dielectric from the field.

IV. CONCLUSION

Polycrystalline Ni (1 wt %) doped CdFe₂O₄ nano particles ceramics were prepared successfully by a sol gel method. XRD patterns analysis showed that all the ceramics crystallize in a structure. Impedance analysis indicated the presence of grain and grain boundary effect in. The value of Z' is higher at lower frequency region and as frequency increases the value of decreases. The value of Z'' is high at

low frequency and decreases with the increase of frequency indicating that electric relaxations are absent. The frequency dependent ac conductivity at different temperatures indicated that the conduction process is thermally activated process. Long range mobility of charge carrier are playing effective role in conduction process at elevated temperature. The Nyquist plot suggest oxygen vacancies/ions or defects are responsible for long range motion of charge carriers.

REFERENCES

- [1] B. K. Bommannavar, L. R. Naik and R. B. Pujar MSAIJ, 4(3), 160 (2008)
- [2] M. K. Shobana, S. Sankar Journal of magnetism and magnetic materials 321, 3132 (2009).
- [3] R. G. Kharabe, R. S. Devan, C. M. Kanamadi and B. K. Chougule Smart Mater. Struct. 15, N36 (2006)
- [4] D. Ravinder, K. Latha Materials Letters 4, 247 (1999)
- [5] I. Anton., I. D. Dabata and L. Vekas, "Application Orientated Researches on Magnetic Fluids," and Journal of Magnetism Magnetic Materials, Vol. 85, No. 1-3, 1990, pp. 219-226.
- [6] R. D. McMichael, R. D. Shull, L. J. Swartzendruber, L. H. Bennett and R. E. Watson, "Magneto caloric Effect in Super paramagnets," Journal of Magnetism and Magnetic Materials, Vol. 111, No. 1-2, 1992, pp. 29-33.
- [7] D. L. Leslie-Pelecky and R. D. Rieke, "Magnetic Properties of Nanostructures Materials," Chemistry of Materials, Vol [1. 8, No. 8, 1996, pp. 1770-1783.
- [8] T. Hirai, J. Kobayashi and I. Koasawa, "Preparation of Acicular Ferrite Fine Particles Using an Emulsion Liquid Membrane System," Langmuir, Vol. 15, No. 19, 1999, pp.6291-6298.
- [9] R. H. Kodama, "Magnetic Nanoparticles," Journal of Magnetism and Magnetic Materials, Vol. 200, No. 1-3,1999, pp. 359-372.
- [10] K. V. P. M. Shafi, Y. Kolytyn, A. Gedanken, R. Prozorov, J. Balogh, J. Lendvai and I. Felner, "Sonochemical Preparation of Nanosized Amorphous NiFe₂O₄ Particles,"
- [11] The Journal of Physical Chemistry B, Vol. 101, No. 33, 1996, pp. 6409-6414.
- [12] D. Niznansky, M. Drillon and J. L. Renspinger, "Preparation of Magnetic Nanoparticles (γ -Fe₂O₃) in the Silica Matrix," IEEE Transaction on Magnetics, Vol. 30, No. 2, 1994, pp. 821-823.
- [13] S. Gubbala, H. Nathani, K. Koziol and R. D. K. Misra, "Magnetic Properties of Nanocrystalline Ni-Zn, Zn-Mn, and Ni-Mn Ferrites Synthesized by Reverse Micelle Technique," Physica B: Condensed Matter, Vol. 348, No. 1-4, 2004, pp. 317-328.
- [14] E. Wolska, W. Wolski, J. Kaczmarek Solid State Ionics 51, 231 (1992)
- [15] N. A. Eissa and A. A. Bhagat and M. K. Fayek Hyperfine Interactions 5, 137 (1978)
- [16] B. D. Cullity, Elements of X-ray diffraction, Addison-Wesley Publications (1956)