Structural, Dielectric and Conductivity Studies of Ni-Cu-Cd Ferrite Nanoparticles

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***Abstract*- In this study, the nanoparticles (NPs) of $Ni_{0.6}Cu_{0.1}Cd_{0.3}Fe_2O_4$ (NCCF) ferrite was successfully synthesized by sol-gel auto combusted process. The effects of temperature and size on the structural, dielectric and conductivity properties of NCCF ferrite nanoparticles were investigated. X-ray diffraction (XRD) analysis of the NPs annealed at 550 and 700 °C displayed the single phase cubic spinel structure with the particle size of 11 and 17 nm, respectively. The surface morphology of the annealed NCCF ferrite nanoparticles was studied by using field emission scanning electron microscopy (FESEM). Dielectric constant of larger particles shows higher values at low frequency as well as lower dielectric loss tangent. Ac conductivity shows conventional trend with size effects.**

Keywords—Sol gel process, NCCF ferrite nanoparticles, dielectric properties, ac conductivity.

I. INTRODUCTION

Nanocrystalline forms of ferrites are being considered as most significant materials in the scientific point of view owing to their wide range of uses specially in high frequency devices and biomedical applications. Ferrite nanoparticles display better dielectric properties because of its size and surface effects which remarkably reduce the formation of Maxwell-Wagner interfacial polarization and dielectric loss tangent [1] and their properties can be defended by various things, such as preparation circumstances, heat treatment, microstructure, substituent or dopants and the synthesis techniques. Spinel ferrite nanoparticles have gained great attraction from researchers due to their extensive applications in various sectors, like as microwave gripping equipments, aerial stick, computer elements, magnetic recording media, drug delivery, cancer cure, hyperthermia treatment and magnetic resonance imaging [2, 3]. Nickel based spinel ferrites are becoming the subject of interest mainly due to their high frequency applications.

In comparison with bulk materials, ferrite nanoparticles display excellent physical, electric and dielectric properties. These nanoparticles are composed of low resistive grains alienated by high resistive grain boundaries and low resistive grain contribution decreases due to the increase of the volume ratio between grain and grain boundary. The dielectric behavior of ferrite particles are influenced significantly by this hetero-structure of the materials [4] and it is important to get low dielectric losses for the fabrication of high frequency devices. Although the magnetic properties of nickel based ferrites have already been explored, the electrical and dielectric properties are rarely reported. The structural and electromagnetic properties of Cd containing Ni-ferrites were studied by Nath et al. [5]. Belavi et al. [6] also investigated $Ni_{0.95-x}Cd_xCu_{0.05}Fe_2O_4$ and reported that saturation magnetization (M_s) increased with Cd substitution up to x = 0.3. Batoo et al. [7] synthesized single phase $Ni_{0.2}Cd_{0.3}Fe_{2.5-x}Al_xO_4$ NPs successfully through sol-gel technique. To the best of author's knowledge, the size dependent electric and dielectric properties of NCCF ferrite nanoparticles were not explored earlier. Hence, the aim of the present work is to study the structural, dielectric and electric behaviors of NCCF ferrite nanoparticles for high frequency applications.

II. MATERIALS AND METHOD

A. Synthesis of NCCF Ferrite Nanoparticles

The $Ni_{0.6}Cu_{0.1}Cd_{0.3}Fe_2O_4$ nanoparticles were synthesized by sol-gel auto combusted technique. The stoichiometric mixtures of $Ni(NO_3)_2.6H_2O$, $Cu(NO_3)_2.3H_2O$, $Cd(NO_3)_2.4H_2O$ and $Fe(NO_3)_3.9H_2O$ were dissolved into deionized water (DI) and a few drops of ethanol were added with the mixtures to make homogeneous solution. A magnetic stirrer was used to stir the solution continuously at constant temperature of 70 °C until the gel was formed and required amount of liquid ammonia was used to maintain pH value of the mixtures fixed at 7. The resulted gel was then heated at 200°C for 5 h and self-ignition occurred to burn out it into fluffy powder form. Afterwards, the fluffy powder was annealed at 550 and 700 °C for 5 h to eliminate any raw materials present in the composition and finally the NCCF ferrite nanoparticles of two different sizes were formed. The resultant powders were then ground to make them nanopowders and pressed into disc shaped without any binders. The both side of the discs was coated with silver paste to make them desired parallel plate capacitor geometry for characterizations. The synthesized samples were then used to study their structural, dielectric and ac conductivity properties.

B. Characterization

The X-ray diffractometer (Philips X'Pert PRO XRD system) with with Kα radiation (λ=0.154 nm) was used to determine the phase of the prepared samples. To detect the diffracted X-rays, an electronic detector was placed on opposite side of the samples from the X-ray tube and X-ray data were recorded over a 2θ range of 15–60° using a step size 0.01° in units of counts/sec which were sent to the attached computer. The 2θ for each diffraction peak was then converted to

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d-spacing, using the Bragg's law; $n\lambda = 2dSin\theta$ and the lattice parameter of the synthesized ferrite sample was calculated using the following equation

$$a = d_{hkl}\sqrt{(h^2 + k^2 + l^2)} \tag{1}$$

The morphology of NCCF ferrite nanoparticles were carried out by using FESEM (JEOL JSM-7600F, Japan). As the samples were non-conducting, a thin layer of platinum was coated using a sputter coater to get clear images. The average grain sizes of the samples were determined using the linear intercept method from FESEM nanographs.

The complex dielectric constant was studied using Wayne Kerr Impedance Analyzer (6500B) by two probe method over frequency range varying from 20 Hz to 15 MHz. The real part of dielectric constant is estimated by

$$\varepsilon' = C_p t / \varepsilon_0 A \tag{2}$$

where ε_0 is the permittivity of free space with value of 8.854×10^{-12} F/m, t is the thickness of the pellet, C_p is the capacitance of the pellet and A is the area of cross section of the pellet. The dielectric loss can be determined by imaginary part

$$\varepsilon'' = \varepsilon' tan\delta \tag{3}$$

Here $tan\delta$ is the dielectric loss tangent.

The *ac* conductivity of the nanoparticles is measured by the equation

$$\sigma_{ac} = \varepsilon' \varepsilon_0 \omega \, tan\delta \tag{4}$$

where ω is the angular frequency.

III. RESULTS AND DISCUSSION

A. *X-ray Diffraction Analysis*

Fig. 1 shows XRD pattern of $Ni_{0.6}Cu_{0.1}Cd_{0.3}Fe_2O_4$ ferrites annealed at both 550 and 700 °C using sol-gel method. The studied sample exhibits fundamental reflections coming from different crystal planes of (220), (311), (222), (400), (422), (511) and (440) with showing no secondary picks, thereby confirming the single phase cubic spinel structure of the composition. The well defined diffraction peaks are observed in Fig. 1 and the peaks' position in XRD patterns match well with the literature value [8]. It is clearly visible that the diffraction peaks get sharper and wider at higher annealing temperature, thereby enhancing the crystallinity of ferrite nano powders. The narrow size distribution of the nanocrystalline ferrites is confirmed by broadness of the diffraction peaks. The most intense diffraction peak (3 1 1) of XRD patterns is used to estimate the average crystallite size of the ferrite composition using Scherrer formula [9]. The average crystallite size of NCCF ferrite nanoparticles measured from XRD data are 11 and 17 nm at 550 and 700 °C, respectively. The lattice constant was calculated using equation (1), where d_{hkl} is the observed inter planar spacing for (h k l) planes and they were calculated from the diffraction peaks using Bragg's law and the analysis revealed that the lattice constant lies in the nano scale range i.e., 0.845 and 0.847 nm at 550 and 700 °C, respectively. The lattice constant is found to be increased a little bit with increasing the temperature, may be due to the structural stability factor of the crystal as well as the ionic radius variation of Ni^{2+} (0.0069 nm) and Cu^{2+} (0.0072 nm).

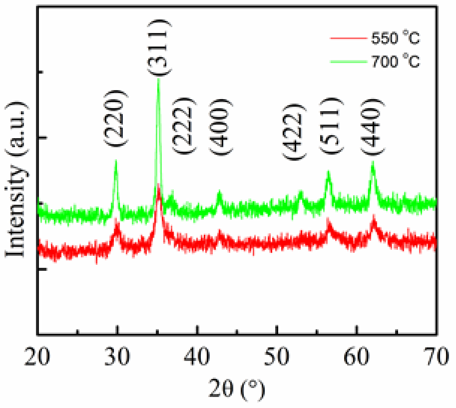

Fig. 1 XRD patterns of NCCF ferrite nanoparticles annealed at 550 and 700 °C, respectively.

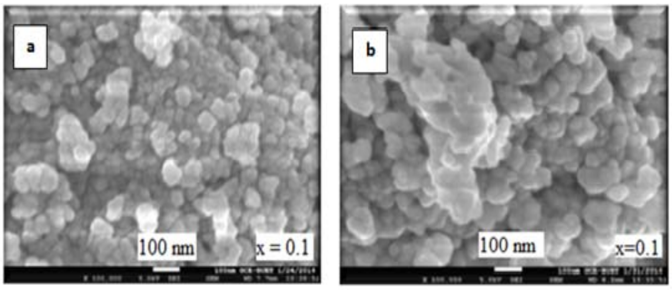

Fig. 2 FESEM nanographs of NCCF ferrite nanoparticles annealed at temperatures (a) 550 and (b) 700 °C, respectively.

B. *Surface Morphology and Nanostructure*

Fig. 2 shows the FESEM nanographs of the NCCF composition annealed at temperatures 550 and 700 °C, respectively. From Fig. 2, it can be observed that the formation of spherical shaped grains separated by grain boundaries illustrating narrow size distribution. The average grain sizes of ferrite nanoparticles are estimated by linear intercept technique from FESEM nanographs, which provide values of 13 and 20 nm at 550 and 700 °C, respectively. These values are very comparable to the average crystallite sizes (11 and 17 nm) measured from XRD data. The particles' size increases a little bit with increasing temperature since thermal energy enhances the grain growth.

C. *Dielectric Studies*

The change in complex dielectric constant of NCCF ferrite nanoparticles annealed at both 550 and 700 °C with frequency is illustrated in Fig. 3. It can be observed that both $\varepsilon^{/}$ and $\varepsilon^{//}$ exhibited usual dispersion behavior in the lower frequency region (20 Hz-1 kHz), whereas they decrease sharply in the frequency domain (1 kHz-1 MHz) and thereafter they become almost frequency independent at both temperatures. The $\varepsilon^{/}$ shows higher values slightly than that of $\varepsilon^{//}$ which gives the indication of having low dielectric loss and it is crucial for selecting materials for fabricating high frequency devices. In the low frequency side, the dominance of $\varepsilon^{/}$ is due to the contribution of interfacial polarization which is supported by Maxwell-Wagner's space charge polarization in accordance with Koop's phenomenological theory [10]. The maximum values of dielectric constant are found at low frequencies because of availability of space charge polarization at the grain boundaries. The dielectric constants display higher values at low frequencies and decrease very slowly after 10 kHz, furthermore become almost frequency independent beyond 1 MHz. This may be due to the fact that disappear of space charge polarization at higher frequencies i.e., the frequency of electron exchange between the ferrous and ferric ions cannot follow the alternating field. The effects of temperature also play a significant role for variation in dielectric values depending on space charge polarization. Hence, accommodation of charge carrier decreases which reduces the dielectric constant. The possible reasons for showing higher values of dielectric constant at lower frequency regime also include the predominance of Fe^{2+} ions, interfacial dislocation pileups, oxygen vacancies, grain boundaries and defects[11].

The change in dielectric loss tangent ($tan\delta$) of NCCF at 550 and 700 °C with frequency are illustrated in Fig. 4. From this Fig. 4, it is apparent that the $tan\delta$ exhibited higher values in the lower frequency zone than that of high frequency zone exhibiting the peaking behavior. According to Rezlescu model, if the frequencies of hopping charge carriers exactly equal to the frequency of the applied frequency, a maximum in $tan\delta$ is appeared showing peaks. In both cases, the $tan\delta$ is found to be very low at higher frequencies and with increasing the size of nanoparticles the $tan\delta$ goes down. This property makes them ideal for high frequency applications. The $tan\delta$ increases at low frequency regions because the phase lags between the applied field frequency and natural hopping frequency. The $tan\delta$ shows little lower values for larger size nanoparticles synthesized at higher temperature due to the hopping frequency cannot follow the applied field exactly and there exists the lag between them.

D. AC Conductivity Study

Fig. 5 shows the change in σ_{ac} with respect to the frequency ranging from 20 Hz to 15 MHz at room temperature. The σ_{ac} is found to be increased with frequency for both temperatures. The rate of hopping electrons between ferrous and ferric ions increases with increase the applied frequency which ultimately increases the ac conductivity [10]. While the conductivity in higher frequency side is due to conduction through grains the conductivity in the lower frequency domain is responsible for conduction through grain boundaries. The conduction mechanism occurs predominantly due to the grains contribution at higher frequencies.

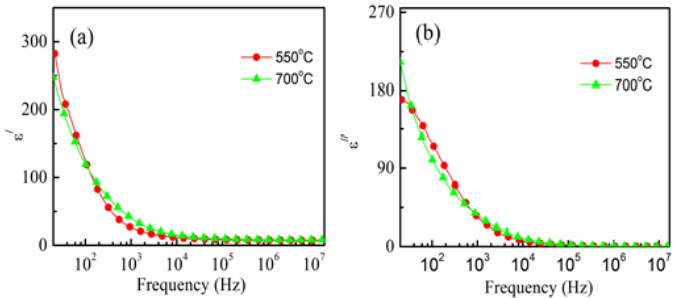

Fig. 3 Variation of (a) $\varepsilon^{/}$ and (b) $\varepsilon^{//}$ of NCCF ferrite nanoparticles annealed at 550 and 700 °C, respectively.

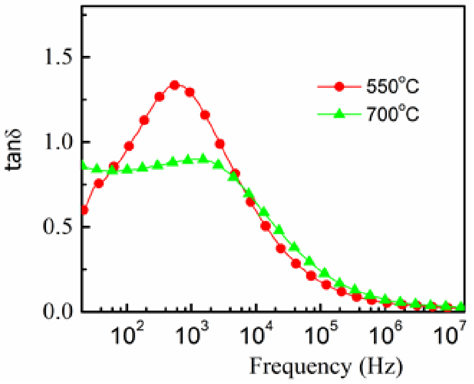

Fig. 4 Variation of $tan\delta$ in NCCF ferrite nanoparticles annealed at 550 and 700°C, respectively.

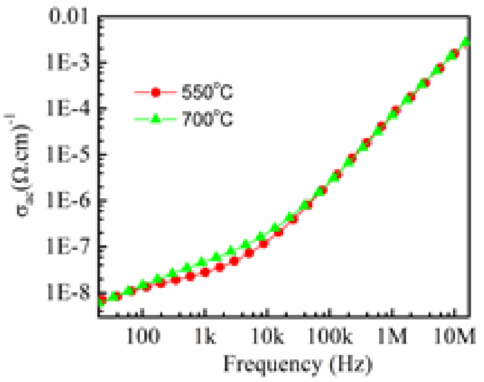

Fig. 5 Variation in ac conductivity of NCCF ferrite nanoparticles annealed at 550 and 700 °C, respectively

IV. CONCLUSIONS

The sol-gel auto combusted method was used for the synthesis of NCCF ferrite nanoparticles without adding any reagents. The particle size obtained from XRD analysis lies in the nano scale range, which are 11 and 17 nm at 550 and 700°C, respectively. The crystallite size increases slightly at higher annealing temperature. The increasing trend of ac conductivity with applying frequency occurs due to the translation from a long range to the short-range charge motion and the conduction takes place predominantly through the grains at higher frequencies. The dielectric loss and dielectric loss tangent values are found very low which makes the studied NCCF ferrite nanoparticles suitable for high frequency applications.

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