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Influence Of Nickel Substitution On The Electrical Transport Properties Of Zn-Nano Ferrites

Srinivas Kondla[1], Gangadhar Thalari[2], K. Chandrasekhara Reddy[3*]
[1]*Department of Physics, Bharathiar University, Coimbatore,Tamilnadu-641046, India*
[2]*Department of Chemistry, Osmania University, Hyderabad, Telangana-500007, India*
[3]*Department of Physics, S.S.B.N Degree College, Ananthapur, A.P-515001, India*

Abstract:
The familiar citrate-gel auto combustion method was used to prepare nano-crystalline materials of $Zn_{1-x}Ni_xFe_2O_4$ (where x=0.0, 0.25, 0.5, 0.75 and 1.0 with 0.25 variation). The AC conductivity and dielectric studies of the synthesized samples was recorded on LCR meter and results were analysed. The AC conductivity (σ_{ac}) and impedance (Z), were calculated and discussed here. The σ_{ac} of the samples enhanced with increasing temperature and dopant concentration. $ZnFe_2O_4$ has shown the lowest conductivity and Ni Fe_2O_4 has shown the highest conductivity in the order of 10^{-3}. The impedance results have given the semi-circular behaviour with decreasing radius. The presence of grains (R_g) and grain boundaries (R_{gb}) in the sample, are the responsible for electrical conductivity and also due to exchange of electron in different sites. The sample containing the highest Ni has given good results among the other samples.

Key words: Citrate gel auto combustion, Ni-Zn nano ferrites, AC conductivity, Dielectric studies

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I. INTRODUCTION

In the recent days, researchers now have a key interest in the synthesis of nano ferrites due to their potential applications in various fields such as electrical, magnetic, and mechanical properties [**1, 2**]. These materials used for wide range of applications like electrical materials, transducers, antenna, transformer cores, digital tapes, and circulators in microwave devices [**3-4**]. The production of microwave materials from ferrites mostly depends on their physical and chemical properties which are influenced by the method of synthesis and the sintering temperature. The material's structural, optical, and electromagnetic properties also depend on the substitution element's (metal's) valence state [**5**]. Ferrites are ferri-magnetic materials with high dielectric permittivity at different temperatures and low dielectric loss [**6**]. These ferrite materials are also used in telecommunication applications in the field of electric needs[**7**]. Especially in nano ferrite materials, grain size and grain boundaries play a significant role in electrical properties. Smaller the grain size materials will have larger grain boundaries. So, electron hopping will not take place between ions, obviously increasing the resistivity and decreasing the loss of the materials. Because of their low cost and high curie temperature, nickel ferrites and Zn doped nickel ferrites are of particular interest to researchers studying synthesis [**8**].

The chemical composition of the ferrite is Fe_2O_3. These are the ceramic magnetic materials and the main component is iron oxide. Basically, ferrites are four types depends on their crystalline structure such as: spinel [**9**], hexagonal ferrites [**10**], ortho ferrites [**11**], and also garnets [**12**]. The spinel ferrites are simple structured materials, composed of tetrahedral and octahedral sites [**13**]. The structure of the spinel contains a face central cubic structure and the co-ordination number is 12. The general formula is AB_2O_4. A indicates the divalent metal ion like Ni^{2+}, Mg^{2+}, Ce^{2+}, Co^{2+}, etc., and B is a trivalent metal ion like Fe^{3+} and Al^{3+} etc,. There are several methods to synthesize ferrites such as citrate gel auto combustion method, sol-gel method [**14**], co-precipitation method, hydrothermal method, and microwave assisted solid-state methods. The present study deals with the synthesis of $Zn_{1-x}Ni_xFe_2O_4$ (x=0.0, 0.25, 0.5, 0.75 and 1.0 with 0.25 variation) nano-ferrites as well as to study electrical transport properties for the suitability for battery applications. It also deals with the mechanism behind the variations of conductivity.

II. EXPERIMENTAL

Synthesis

For the synthesis of $Zn_{1-x}Ni_xFe_2O_4$ (where x=0.0, 0.25, 0.5, 0.75 and 1.0 with 0.25 variation) nano ferrites the most familiar citrate-gel auto combustion method was employed. Stoichiometric amount of metal nitrates such as Ni nitrate, Zn nitrate, Ferric nitrate were dissolved in deionised water individually. Citric acid used as a chelating agent 1:3 ratio then homogeneous solution obtained, ammonia solution added to the homogeneous solution drop wise to maintain P^H -7 neutral, and the solution thoroughly stirred on magnetic stirrer. Initially solution was heated about 80ºC temperature the total solution reduced to one fourth of its initial volume. Then the temperature raised from 80ºC to 150ºC heated an hour viscous gel was formed, then self-ignited happened the resultant ignited powder ground in agate mortar and pestle for minimum 20 min. Later on, under air muffle furnace sample was calcinated for 4 hours at 500ºC temperature residual sample collected from furnace again ground it agate mortar and pestle for 1 hr further powder was given analysis for structure conformation. Citrate-gel method methods citrate gel method was used for the preparation of nano-ferrites because of its low cost, ease of setup, low temperature, good homogeneity, and small particle size obtained [15].

Characterization

The synthesised $Zn_{1-x}Ni_xFe_2O_4$ (where x=0.0, 0.25, 0.5, 0.75 and 1.0 with 0.25 variation) nano ferrites were scanned on LCR meter for the dielectric parameters. Initially, the samples were coated with silver paint for the good access to the electrodes. The temperature range was used from room temperature to 450ºC. The measurements were done with variation of temperature and frequency. The glasses were prepared in the button shape of dimensions 2mm thickness and 10mm diameter for the AC conductivity measurement. After measuring the cross-section area (A) of the glasses, they were coated with silver paste. It enhances the accessibility between the sample and electrodes of the measuring device. The data was recorded in the frequency range 5Hz-35MHz on the LCR meter. The range of temperature was room temperature to 350ºC with 50ºC variation.

III. RESULTS AND DISCUSSION

Formulae of AC conductivity

The AC conductivity is familiar technique to study the transport mechanism of the materials such as ferrites, glasses, polymers etc. at different frequency and at different temperatures. It will give good results for low temperature sintered nano ferrite materials. The following formula helpful in finding the AC conductivity and its related parameters of the nano ferrite compositions.

Determination of AC conductivity was done by the following

$$\sigma_{ac} = \omega\varepsilon^{/}\varepsilon_0 tan\delta \qquad (1)$$

Where, $\varepsilon^{/}$ and ε_0 are the dielectric permittivity in material and also vacuum, respectively.

tan δ- represents the dielectric loss.

The plot of Cole-Cole impedance was drawn by the following;

$$Z' = \frac{G}{(G^2 + \omega^2 C^2)} \qquad (2)$$

$$Z'' = \frac{\omega C}{(G^2 + \omega^2 C^2)} \qquad (3)$$

Where $Z^{/}$ and $Z^{//}$ are the real and imaginary complex impedance, respectively.

The present study deals with variation of ac conductivity with the applied frequency and temperature of the nickel substituted zinc nano ferrites. At low temperatures, the results of conductivity values are in the lower order. Low frequency segment is almost found to be the linear manner, whereas, high frequency region has shown significant enhancement in the σ_{ac}. The results were analysed with the help of different models like quantum mechanical tunnelling (QMT), hopping over barrier (HOB), and correlated barrier hopping (CBH) model.

AC conductivity of nickel substituted zinc nano ferrites: $Zn_{1-x}Ni_xFe_2O_4$

Fig.1. depicts the variation of σ_{ac} with frequency (logf) of pure nickel substituted zinc nano ferrites $Ni_0Zn_1Fe_2O_4$. It was found that the ac conductivity σ_{ac} increased with increasing the applied frequency. In the low frequency region, it almost constant, whereas, suddenly increased. The low frequency domain of the data is almost all considered as DC conductivity region. It may be due to the constant cation mobility at low frequency region. Conductivity $\sigma_{ac}$of $ZnFe_2O_4$ sample varied from 10^{-9}-10^{-7} $\Omega^{-1}cm^{-1}$ for temperatures from 200ºC to 450ºC with stepwise increment of temperature in the low frequency region. In the high frequency domain it varied from 10^{-6}-10^{-4} $\Omega^{-1}cm^{-1}$. It was found that the conductivity varied by two orders in both the segments [16].

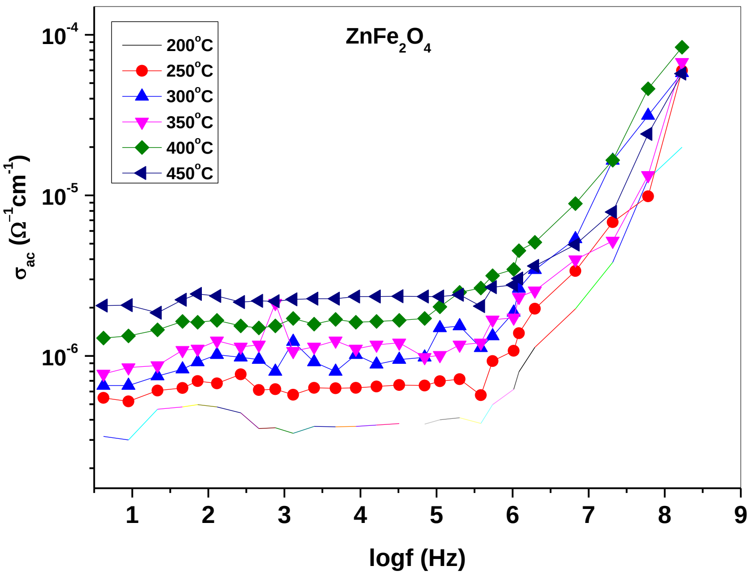

Figure.1.Variation of σ_{ac} with applied frequency of pure sample

Temperature is also playing an important role in the study of conductivity. In the present study, conductivity found in the 10^{-6} $\Omega^{-1}cm^{-1}$ order initially at 200°C. Further, it was linearly increased as a function of temperature. σ_{ac} found to be the maximum for pure sample at 400°C.

Conductivity σ_{ac} of nickel (Ni) dope zinc nano ferrites NFs showed dispersion behaviour at lower temperatures. Sample impurities of the synthesized ferrites are the reasons for such type of behaviour. $\sigma_{ac}$of $Ni_{0.25}Zn_{0.75}Fe_2O_4$ sample has shown in Fig.2 and it found to vary from 10^{-7} to 10^{-5} $\Omega^{-1}cm^{-1}$ in the lower applied frequency region, whereas, at high frequencies it varied from 10^{-6}-10^{-4} $\Omega^{-1}cm^{-1}$. The conductivity $\sigma_{ac}$is enhanced up to three orders in between the low and high frequency segments.

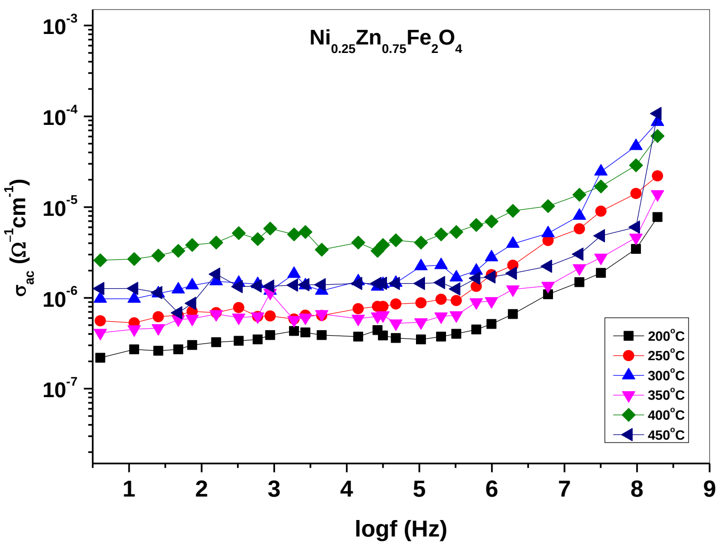

Figure.2.Variation of σ_{ac} with applied frequency

σ_{ac} of $Ni_{0.5}.Zn_{0.5}.Fe_2O_4$ sample also shown the similar results. Conductivity of $Ni_{0.5}.Zn_{0.5}.Fe_2O_4$ varied from 10^{-7}-10^{-5} $\Omega^{-1}cm^{-1}$ for the variation of temperatures from 200°C to 450°C in the low frequency region as shown in Fig.3 and two orders of conductivity changed in both the segments. Fig.4. depicts the variation of ac conductivity with the applied frequency of $NiFe_2O_4$ nano ferrite sample in which dopant Ni content is the highest. In the high frequency range it lies between 10^{-5}-10^{-3} $\Omega^{-1}cm^{-1}$. The conductivity is increased up to two orders in the high frequency domain. The increment in the conductivity may be due to the exchange of electron from octahedral site to tetrahedral site when dopant content increased.

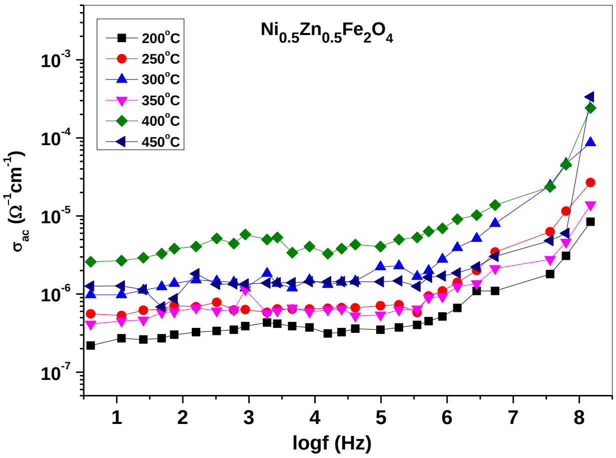

Figure.3.Variation of σ_{ac} with applied frequency of $Ni_{0.5}$.$Zn_{0.5}$.Fe_2O_4

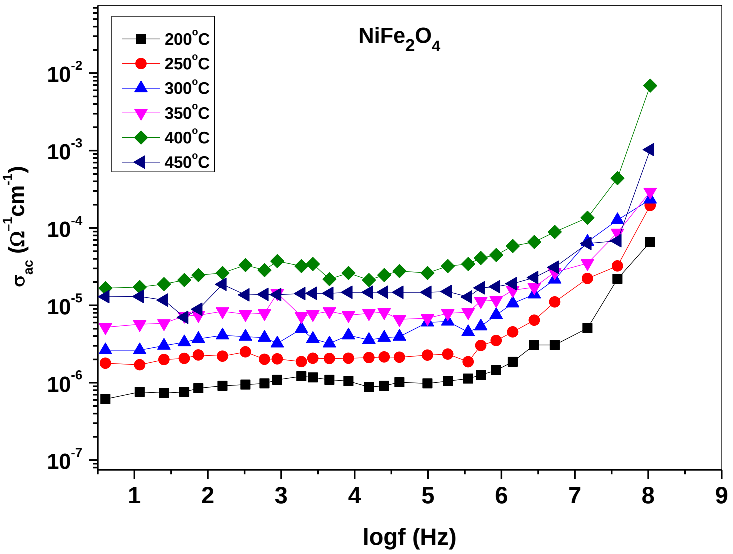

Figure.4.Variation of σ_{ac} with applied frequency of Ni.Fe_2O_4

Impedence behavior ($Z^{/}$ vs $Z^{//}$ Cole-Cole plots) of Ni substituted Zinc nano ferrites:

Dielectric behaviour of synthesized Nickel doped zinc nano ferrites were studied at different temperatures like 200°C, 250°C, 300°C, 350°C, 400°C and 450°C. Impedance was discussed in terms of real and imaginary complex components $Z^{/}$ and $Z^{//}$. Plots of both the real and imaginary parts were shown single semicircle at high and low temperatures. It may attribute to the small polarons hopping mechanism and also bulk effects. Cole-Cole Impedence plots of pure zinc nano ferrites were shown semi-circular curves.

Cole-Cole plots of Nickel doped zinc nano ferrites has shown in the Fig.5 and was observed the semi-circular behaviour for different temperatures. Bulk resistance (R_b) of the samples was decreased with increasing temperatures and also increase of Ni content. It may be due to the dispersion of the Rb of nickel dope zinc nano ferrite samples [17-19]. The radius of semi-circular arcs has been decreasing with increasing temperature as well as dopant content.

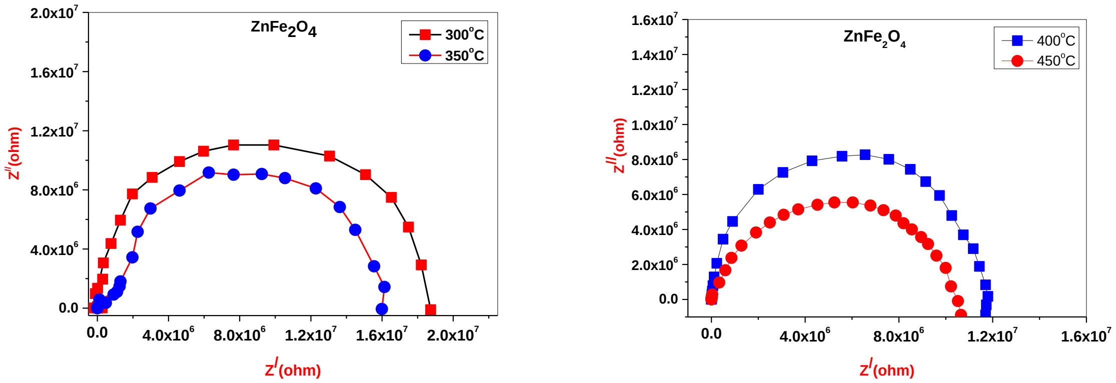

Figure.5. Cole-Cole plots of pure $ZnFe_2O_4$

Cole-Cole Impedence plots of nickel dope zinc nano ferrites were studied at 300°C, 350°C, 400°C and 450°C and were shown in the figures from Fig.5 to Fig.8. These plots in are almost equivalent to the Resistor-Capacitor (R-C) network of the electric circuit. These plots also showed the similar behaviour as compared with kel doped zinc nano ferrites. Bulk resistance R_b of all the samples decreased with the increasing temperature. It is also due to the sample bulk resistance of ferrite sample [20-22].

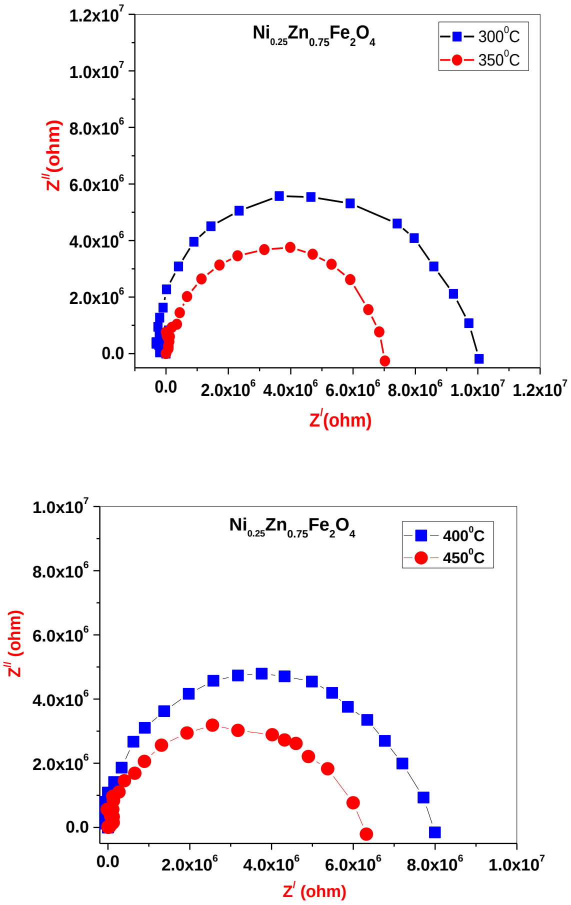

Figure.6. Cole-Cole plots of $Ni_{0.25}Zn_{0.75}Fe_2O_4$

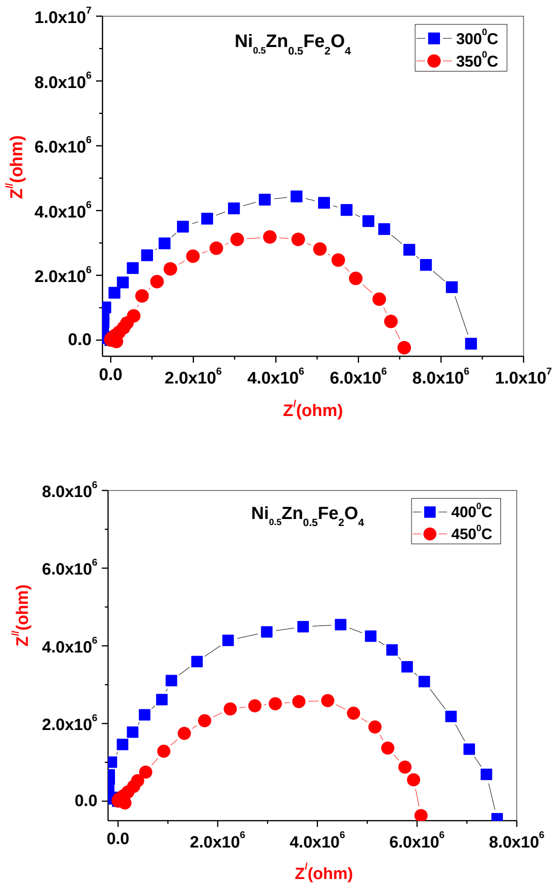

Figure.7. Cole-Cole plots of $Ni_{0.5}Zn_{0.5}Fe_2O_4$

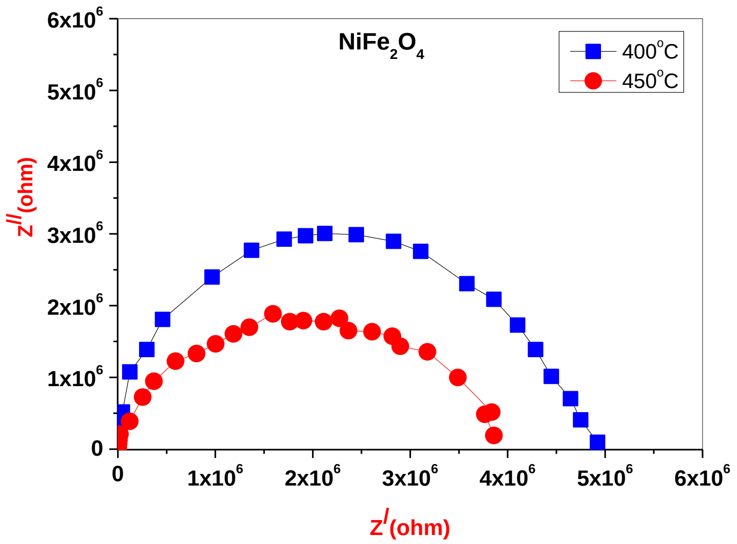

Figure.8. Cole-Cole plots of nano ferrite $NiFe_2O_4$

IV. Conclusions

- Citrate Gel auto combustion technique was used to obtain homogeneous nano sized mixed Ni-Zn ferrites of compositions $Ni_xZn_{1-x}Fe_2O_4$.
- The process involves no impurity pickup and material loss. It is a very simple and economical method where no specific heating or cooling rate is required. It is a low temperature processing technique and requires shorter sintering duration.
- In $Ni_xZn_{1-x}Fe_2O_4$ (x=0.0,0.25,0.5,0.75,and 1.0) nano ferrites all the samples behave as n –type semiconductor
- In Ni- Zn nano ferrite systems it is observed that conductivity increased with increase in temperature and frequency
- The Cole-Cole impedence plots were shown semi-circular behaviour
- The highest value of conductivity observed for $NiFe_2O_4$ in the order of 10^{-3}.

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