IJST EXPLORE International Journal of Science and Technology
CENTRE OF PROFESSIONAL RESEARCH PUBLICATIONS
ISSN 2049-7318

International Journal of Science and Technology Volume 1 No. 5, May, 2012

Verwey's Hopping Transition Mechanism in relation to Dielectric studies of Zn & Sb substituted Cu ferrites

R.Dhanaraju[a] , M.K.Raju[a] , V.Brahmajirao[b] , S.Bangarraju[a]

[a] Material Science Research Laboratories & Central Instrumentation Facility ,Department of Physics , Andhra University, Visakhapatnam-530005., INDIA

[b]Dept. Of Nano science and Technology, School of Biotechnology, MGNIRSA, D. Swaminathan Research Foundation,[DSRF] , Gaganmahal,HYDERABAD-500029., Andhra Pradesh. INDIA

ABSTRACT

Significant information about the substituted ferrites, in relation to their several applications, is revealed by their Dielectric studies. We present the studies on Zn &Sb substituted Cu ferrites, carried out at Material Science Research Laboratories, Department of Physics, Andhra University, Visakhapatnam-530003, A.P., INDIA. We studied the variation of dielectric constant with substituent concentration, and its frequency dependence .This paper reports the results of those studies and their comparison with very recent similar ones of literature in relation to VHTM. Our findings are in tune with several interpretations for similar works, by a host of other authors cited.

Keywords: *Dielectric studies, substituted spinel ferrites, frequency dependence of electrical property, microwave sintered method, citrate precursor method, Ni-Cu-Zn ferrite, dielectric loss, Verwey's Hopping Transition Mechanism, FTIR studies, Charge ordering , Anderson's correlated electron theory, Saturation magnetization , Sintering aids , Dielectric loss.*

1. INTRODUCTION

The complicated physical phenomena in complex transition-metal oxides (TMO), such as high T_c superconductivity, colossal magneto resistivity, metal-insulator transitions, etc., have long been the focus of intense inquiry and debate in condensed matter science, since they are related to strong electronic correlations and cannot be explained within the 'standard model' of solid state physics. These novel functionalities of the correlated electron systems have a wide range of potential for applications in industry, such as information storage, energy transportation, and so on. The three driving forces for Charge Ordering (CO) in Transition Metal Oxide (TMO)are: magnetic energy, Coulomb interaction, and election-lattice interaction,[1].It is well known that spinel ferrites consist of three types of magnetic structures: normal, inverse and mixed spinel [1]. In normal spinel, the divalent ions locate at tetrahedral sub lattice (A-site) and trivalent ions $\mathbf{Fe}^{3+}$ locate at octahedral sub lattice (B-site). In inverse spinel a half of $\mathbf{Fe}^{3+}$ ions locate at A site and the rest $\mathbf{Fe}^{3+}$ ions together with divalent ions locate at B site. In mixed spinel ferrite, $\mathbf{Fe}^{3+}$ions and divalent ions locate at A and B site. $\mathbf{NiFe_2O_4}$ is inverse spinel ferrite.

Among spinel ferrites, only Zn and Cd ferrites belong to pure normal structure. Mixed Ni-Zn ferrites have extremely high resistivity so that they are widely used as soft magnetic materials suitable for high-frequency applications. Among spinel ferrites, Cd and Zn ferrites are always normal ferrites with Cd and Zn ions locating only in tetrahedral sites [2].The presence of Zn affects lattice parameters, saturation magnetization Ms, Curie temperature, T_c. At highest Zn content, *Tc* reduces to the temperature lower than room temperature and magnetic structure of spins in the octahedral sub lattice should be strongly canted. This is the reason for our choice of dielectric studies, of our specimens. In the Mossbauer studies reported by M.Myndyk [3], on Ba & Sr substituted ferrites, it was pointed out that almost any property in a solid is associated with a particular length scale, and below this length, the property will vary. Mah Rukh Siddiquah [4] in the studies on Spinel ferrite thin film , found that it is useful as a perpendicular magnetic recording material for high density recording because a protective overcoat is not required for it . Introduction of the soft magnetic layer as a back layer is essential to improve recording and reproducing performance of the media. The increase of the storage capacity is being achieved by decreasing the particle size of the magnets (bits).

M.Penchalareddy, et.al.,[5], prepared single phase $\mathbf{(Ni_{0.35}Cu_{0.05}Zn_{0.60}Fe_{1.98}O_4)}$ ferrite, by microwave sintered (MS) method, in which, the sintering temperature and time were significantly reduced to 30 min and 950°C

(from 5hrs and 1250°C for the Conventional Sintering process) . The frequency dependence of the dielectric properties such as dielectric constant (ε'), dielectric loss (tan δ) were studied. These results were compared with the properties of ferrites prepared by conventional sintering method in normal heating, and it was reported that Microwave sintering improves structural as well as electromagnetic parameters measured and thus makes the ferrite more suitable in microwave applications and electromagnetic devices.

P.A. Jadhav et.al.,[6]prepared fine powders of Ni-Cu-Zn ferrite with composition $Ni_{(0.7-x)}Cu_xZn_{0.3}Fe_2O_4$ (where x=0, 0.2, 0.4 and 0.6) by the citrate precursor method and measured Dielectric constant ($\acute{\varepsilon}$) and loss tangent (tan δ) as a function of frequency. The $\acute{\varepsilon}$ and tan δ showed a decreasing trend with increase of frequency for all their samples. Ni–Cu–Zn ferrite materials have been extensively used in multilayer chip inductors because of their remarkable properties at higher frequencies. To design a good microwave device such as isolators and circulators, materials with high dielectric constant are required. Substitution of a suitable cation in the crystalline structure of microwave ferrites like Cu-Zn or Cu-Sb ferrites changes the structure to an inhomogeneous dielectric structured material. Thus, the cations charge deposition on surface layers of grains becomes prominent in changing the dielectric constant and hence the potential of the material might be improved for the application as isolators and circulators.

A series of polycrystalline spinel ferrite nanoparticles of basic composition $\mathbf{Ni_{0.7}Mg_{0.3}AlxFe_{2-x}O_4}$ (0.0 >x >0.5) were prepared by Razia Nongjai et.al. [13],through sol-gel method. The effect of Al^{3+} doping on the structural and electrical properties of the as synthesized ferrite nanoparticles as a function of frequency and composition at room temperature was reported. X-ray diffraction measurements and related details were given. The dielectric constant shows normal behavior with frequency, while the dielectric loss (tan δ) showed an anomalous behavior with frequency for x = 0.3, 0.4 and 0.5. This was explained in the light of Rezlescu model. The variation of dielectric properties , (tanδ)and ac conductivity, with frequency reveals that the dispersion, due to Maxwell-Wagner type of interfacial polarization & in general the hopping of charge between $\mathbf{Fe^{2+}}$ and $\mathbf{Fe^{3+}}$ as well as between Ni^{2+} and Ni^{3+} ions at B-sites. All the dielectric parameters increased up to 10% of $\mathbf{Al^{3+}}$ doping, thereafter, these parameters decreased with further doping. Khalid Mujasam Batoo et.al, [8], Packiaraj G.et.al.,[9], Jogi R. R.et.al.,[10], Panchal N.R.et.al., [11],also reported similar results, all of which are in tune to our reported findings.

2. MATERIAL AND METHODS

2.1 Brief Analysis of Methods Used by Other Workers

The conventional ceramic method [12, 14& 15] is used for the preparation of the sample, after a thorough analysis of the evens and odds of the methods used by different workers. A suitable temperature is required to perform solid state reaction among constituent oxides of the mixed ferrite to be formed. Also the mechanical grinding cannot give particles of uniform size and shape the homogeneity, & morphology and microstructure of the material are affected. R.K.Singh et.al.,[16] prepared a set of $\mathbf{Ni_{0.5}Zn_{0.5}Fe_2O_4}$ samples by citrate precursor route to investigate the growth mechanism and its effect on cationic distribution. A.C.F.M.Costa et.al.,[17] reported data of $\mathbf{Ni_{0.5}Zn_{0.5}Fe_2O_4}$ prepared by combustion synthesis using urea fuel. They found that the large quantity of gas developed inhibited particle aggregation and yielded soft powders .They used the condition of (1200^0C/2hrs) for sintering. Uzma Gazanfar[34], reported studies on $\mathbf{[(£)_x\ Zn_{(1-x)}Fe_2O_4]}$for (x=0.66, 0.77, 0.88, 0.99), with **(£ = Ni, Mn** and **Cu**).These specimens were prepared by conventional double sintering method, using a locally available low cost Iron oxide. Also U. Gazanfar[19] claims (without any estimation) that the presence of Silicon in the Iron oxide as an impurity improved the properties of the ferrites produced .$\mathbf{Zn^{2+}}$ is used to improve electromagnetic properties as well as densification in the ferrite. It also lowers magneto striction and anisotropy in ferrites [20]. Goev et al. [21] stated that initial permeability increased and hysteresis loss decreased with increasing Zn concentration in $\mathbf{(Ni_{0.85-y}Cu_{0.15}Zn_y)\ Fe2O4}$ ferrite. An improved set of electromagnetic properties were obtained by Low et.al. [22] at high **Zn** content of $\mathbf{(Ni_{0.02x}Cu_{0.02y}Zn_{0.02z})Fe_2O_4}$; where (x+y+z = 50) .Both saturation and remancence magnetization had maximum at (y = 0.4). P.K.Roy[23] investigated ferrites represented by $\mathbf{[(Ni_{0.8-x}Cu_{0.2}Zn_x)Fe_2O_4\ ]}$ with $\mathbf{(0.45\leq x\leq 0.60)}$, along with the effects of $\mathbf{Mg^{2+}}$ substitution for $\mathbf{Ni^{2+}}$ and $\mathbf{La^{3+}}$, $\mathbf{Sm^{3+}}$ substitutions for $\mathbf{Fe^{3+}}$ on the electromagnetic properties of optimized **Ni-Cu-Zn** ferrite and also the effects of sintering aids like $\mathbf{V_2O_5}$, $\mathbf{Bi_2O_3}$ and $\mathbf{MoO_3}$ on the densification kinetics and electromagnetic properties of the ferrite. These were synthesized by nitrate-citrate sol-gel auto combustion process.

2.2 Details of Our method of preparation

We have chosen two series in our studies.

(1) First series, of samples having general formula $Zn_{1-x}Cu_xFe_20_4$ (with x=0, x=0.2, x=0.4, x=0.6, x=0.8) ,

(2) Second series of copper zinc & copper antimony ferrites with basic compositions **:[$Cu_{(1-x)}Zn_x$ Fe_2 0_4]**, & **[$Cu_{(1-x)}Sb_xFe_20_4$],** in which, x varies from x = [0.0- to- 1.0] in steps of 0.2., have been synthesized by the method described elsewhere as per the flow chart shown. Highly pure (analytical reagent grade) **CuO, ZnO,Fe_2 0_3** and **Sb_2 0_5** chemicals were used. Nabertherm Furnace with Eurotherm controller was used to ensure perfect temperature control. These samples were used to systematically obtain the data in (1) Morphological studies using **SEM, of JEOL, make model JSM-840** (2) Structural studies using **XRD Philips Diffract meter (model PW-3710)** Setup, (3) Resistivity studies and (4)Dielectric studies using **Hewlett Packard Impedance analyzer model 4192 A** , (4)Magnetic Hysteresis and permeability studies using **Imagetronics-Loop Tracer** . The Photographs of all the equipment, used in the Material Science Research Laboratories at Andhra University, are presented In our relevant publications. Relevant conclusions along with Morphological, And Electrical Resistivity data and FTIR data, obtained by us appear elsewhere [15,24 ,25]. Details of the estimated Ferrous and Ferric content in various samples analysed is given in Table 1.

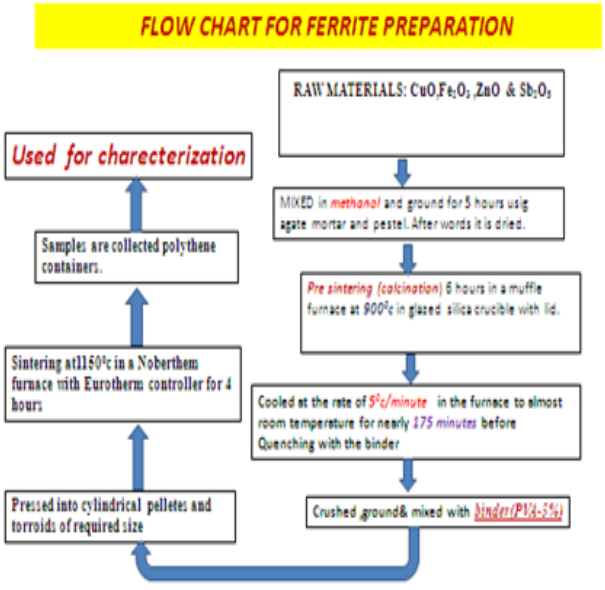


Table 1: Ferrous$^+$ and Ferric$^+$ Ionic content (%) with substituent concentration'x'

Substituent concentration 'x'	Zinc		Antimony	
	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}
0.00	0.446	53.700	0.446	53.700
0.10	1.004	34.840	1.116	30.230
0.20	1.620	21.110	0.446	25.264
0.30	2.680	12.310	1.004	23.744
0.40	2.568	11.780	0.670	19.675
0.50	2.345	6.348	0.558	16.074

3. DIELECTRIC STUDIES

3.1 Instruments and formulae

Dielectric studies of samples and their variations with frequency in the range of frequencies from 5KHZ to 13 MHZ were performed by measuring the capacitance with Hewlett Packard 4192A impedance analyzer (photo shown elsewhere in our other related publications) .

$$\varepsilon = [\frac{d}{\varepsilon_0 A}]C$$

Using the expression, Where ε is dielectric constant, A is the area of the cross section, is thickness of the sample, and ε_0 is the permittivity of the free space (ε_0 =8.854 x 10^{-12} Fm^{-1}).The dissipation (D) was measured directly from the impedance analyzer. The angle 'δ' between the vectors for the amplitude of the total current, and that for the charging current is called the loss angle (less than{π/2}). The dielectric loss factor or dissipation factor (tan δ), measures the dielectric loss.
It is also obtained by the formula:

$$\tan\delta=\left[\frac{loss\ current}{charging current}\right] = [\frac{(\varepsilon'')}{(\varepsilon')}]$$

The *activation energy* is given by : {$\rho=\rho_\infty \exp [E_\rho/kT]$ }, in which: 'ρ' is resistivity, 'ρ_∞' is resistivity extrapolated to (T=∞), 'E_ρ' is the activation energy, 'k' is Boltzmann's constant and 'T' is absolute temperature .The activation energy data determined for our samples is presented elsewhere [52]. In the shown plots: (ε') is the real part of dielectric constant, and (ε") is the imaginary part of Dielectric constant. For the variations in Dielectric constants (ε' and ε") and dielectric loss tangent (tan δ) with the frequency, we find that: in the low frequency region the variation is conspicuous, only at lower concentrations of substituents.

4. RESULTS AND DISCUSSION

4.1 Our Graphical Results

The variation of (ε') and (ε") with frequency (f) that is obtained for our specimens is shown in the Eleven plots, (presented below). The salient evident observations from the plots are given in the Tables 2 &3. Dielectric relaxation process is understood in terms of dielectric constant components i.e. real (ε') part and imaginary (ε") part, with frequency (f). The dispersion was reported by Ravinder [26] in an earlier study of (Cu-Zn) ferrite. At higher frequencies and for higher substituent concentrations no variation in 'ε' is observed. Loss tangent (tan δ) dispersion is exhibited till 100 kHz and remains practically constant at higher frequencies. The structural and magnetic properties of $(Ni_{0.5}Zn_{0.5}Fe_2O_4)_x(SiO_2)_{(100-x)}$ ($6 \leqslant x \leqslant 78\%$) nanoparticles embedded in SiO_2 fabricated by a sol–gel processing, were investigated by A.S. Albuquerque et.al.,[27]. The samples were characterized by X-ray diffraction, Mössbauer spectroscopy (MS) and vibrating sample magnetometry. The results showed the formation of stoichiometric NiZn-ferrite in the SiO_2 matrix, for x<41%.Samples with higher ferrite fraction have small amounts of Fe_2O_3. The data reported by U. Gazanfar [19] is limited to five frequencies(100,300,500,700,900kHz), & the ε' and tanδ are found to decrease with increasing Ni content and decreasing Cu content which was taken as a characteristic of the spinel behavior. Ahmed et al. [28] investigated the influence of zinc ion substitution on densification in **Ni-Zn** ferrite. They found rapid densification with increased Zn^{2+} concentration. Also with the increase in the Ni content ,the presence of Fe^{2+} ions is enhanced giving rise to more polarization and creation of heterogeneity in the spinel structure[29] .Since Fe^{2+} ions are easily polarizable ,the larger the number of them ,the higher would be the dielectric constant. Though the composition is the same for all three samples, the results of these characterizations are found to be different for different synthesis methods and also much different from their corresponding bulk counterpart. However, the magnetic performance of these nanoparticles is primarily determined by their respective particle size in all three samples. The results are analyzed in terms of the microstructure and magnetic performance. A. Mahesh Kumar et.al., [34] achieved the highest value of saturation magnetization (80 emu/g) ever reported, in $Ni_{0.65}Zn_{0.35}Fe_2O_4$ at lower sintering temperatures through sol-gel synthesis. The observed highest value of saturation magnetization has been explained on the basis of core-surface magnetic interactions facilitated through low temperature and in-field Mossbauer investigation of the system. Cation distribution for this composition has also been proposed and verified quantitatively by calculating the intensity of each peak of x-ray diffraction and estimating the lattice constant.

Table 2: Observations from Dielectric Data from the Plots for ε' and ε'', for Cu -Zn Ferrite Specimens

Formula of the specimen	**Observed Variation in ε' with 'f'**	**Observed variation in ε'' with 'f'**
$ZnFe_2O_4$	Reduced up to 100KHz and constant later	Almost constant with frequency
$Cu_{0.8}Zn_{0.2}Fe_2O_4$	Constant up to 10Khz and decreased later	Increased upto1.1KHz and later recorded fall
$Cu_{0.6}Zn_{0.4}Fe_2O_4$	Constant almost throughout	Recorded Maximum at 30KHz
$Cu_{0.4}Zn_{0.6}Fe_2O_4$	Decreased up to 100KHz and constant later	Almost constant with frequency
$Cu_{0.2}Zn_{0.8}Fe_2O_4$	Decreased up to 10KHz and constant later	Almost constant with frequency

Table 3: Observations from Dielectric Data from the Plots for ε' and ε'', for Cu -Sb ferrite Specimens

Formula of the specimen	**Observed Variation in ε' with 'f'**	**Observed variation in ε'' with 'f'**
$Cu\ Fe_2O_4$	Reduced up to 50KHz and constant later	Minute Increase upto 500 KHz and later constant
$Cu_{0.8}\ Sb_{0.2}\ Fe_2O_4$	Reduced up to 10KHz and constant later	Remained Constant with 'f'
$Cu_{0.6}\ Sb_{0.4}Fe_2O_4$	Reduced up to 20KHz and constant later	Remained Constant with 'f'
$Cu_{0.4}\ Sb_{0.6}Fe_2O_4$	Reduced up to 11KHz and constant later	Remained Constant with 'f'
$Cu_{0.2}Sb_{0.8}Fe_2O_4$	Reduced up to 11KHz and constant later	Remained Constant with 'f'
$Sb\ Fe_2O_4$	Reduced up to 10KHz and constant later	Remained Constant with 'f'

Ravinder observed relaxation for 'ε' from 10 kHz and for 'tan θ' from 100 kHz. Rezlescu and Rezlescu [35] records close and similar variations as those obtained in our studies for spinel ferrites. Using Verwey's Hopping Transition Mechanism (VHTM),[36]. Eugenio Coronado

et.al.,[37]and Joaqu´ınGarc´ıa et.al.,[37]in their reviews VHTM and on Ferromagnetic Conductors &Insulators (sections 4 &5 of therein) pointed about the magnetic ordering being responsible ,for destroying possible superconducting state. Also Ginzburg.V. L., [51], showed first that coexistence between superconductivity and ferromagnetism was impossible. Other factors could be relevant in this regard, such as the structural incommensurability of phases .Mott [38] assuming the ordering of an ionic charge state, the metal-insulator transition of the mixed valence compounds was explained. In spite of investigations of several types, this transition is still a matter of discussion, and X-Ray scattering experiments by Gracia J et.al.,[39] clearly indicate the confirmation to the Anderson condition[40],including the Verwey model. The variation of 'ε' depends on number of ferrous and ferric ions available in particular and also on the cation distribution at the A and B sites of the mechanism. The decrease of 'ε' beyond a certain value of 'f' occurs when the electronic hopping between ferric a ferrous ions fails to follow the applied alternating field. The dielectric loss tangent (tan θ) decreases continuously without showing any peak with the frequency (f), contrary to the usual behavior of spinel ferrites. Materials having high relative densities do not show increase of 'tan θ' that will lead to a peak with 'f'. Substituted Mg-Mn ferrites have a low porosity ranging from 0.25 to 8.00 % [41]. Similar results were obtained earlier in lithium and other ferrites [42, 24]. The possibility of occurrence of a peak for tan θ beyond the frequency range studies i.e. 12 MHz is not ruled out. A.Verma et.al.,[43] reported several parameters of Ni-Zn Ferrites prepared by citrate precursor method and sintered around 1400^0C.They reported much lower values of (**ε'**) and 'tan δ' for their samples than for those obtained by conventional ceramic method. They attribute this to better compositional stoichiometry, single phase spinel structure and uniform microstructure.

4.3 Our Findings

There is very little variation of real part (**ε'**) with frequency. However a very slight dispersion has been found from (x = 0.2) onwards for Sb substituted ferrites while imaginary part shows a clear dispersion. For Sb substituted ferrites also similar observations have been found for both real and imaginary parts except at x = 0.2 for materials with these concentration a peak is observed. High valence cations accumulating at grain boundary increase grain boundary width and thus insulating property increases. This enhances dielectric behavior of the material. Variation of dielectric constant (ε) as a function of substituent concentration (x), frequency (f) has been studied for Sb/Zn substituted Cu ferrites. Probing the materials in different ways will enhance the knowledge about substituents' influence on the basic ferrite (**$CuFe_2O_4$**). At room temperature, dielectric constant (ε) variation as a function of substituent concentration (x) is depicted in Fig. at a frequency of 1 kHz. In Sb ferrites 'ε' minimum is obtained at x=0.1 and 'ε' increase for x > 0.1. The 'ε' variation with 'x' confirms the expected variation of resistivity and 'ε' increases for x ≥ 0.3 of molybdenum. Iwachi [44] reported a strong correlation between the conduction and dielectric behavior of ferrites. The variation of 'ε' (real part) is ascribed to orientation of dipoles in the direction of applied electric field causing the polarization of ferrites [44]. Substitution of high valence cations impede hopping mechanism by forming stable bonds as $\mathbf{2Fe^{3+} \leftrightarrow Zn^{2+}}$ and $\mathbf{2Fe^{3+} \leftrightarrow Sb^{5+}}$. Hence, mobility of cation increases through the vacancies. The deposition of charge on heterogeneous grain boundaries increases the resistivity. Thus 'ε' decreases. At higher concentrations of substituents, the increase of ε is explained on the basis of exchange interaction of electrons, and valence fluctuations of substituents which results in decreased resistivity. The microstructural property like grain-to-grain boundary thickness ratio plays an important role in correlation of dielectric data with resistivity data [45]. The real part of dielectric constant is directly proportional to the root mean square value of the dc conductivity. Sb substituted ferrites have higher values of ε compared to Zn substituted ferrites. This is attributed to resistivity and microstructural parameters.

4.4 Frequency Dependence

Dielectric constant (ε) and dielectric loss tangent (tan δ) with the frequency in the low frequency region has been observed only at lower at concentrations of substituents. The dispersion was reported in an earlier study of Cu-Zn ferrite [46, 47]. At higher frequencies and for higher substituent concentrations no variation in 'ε' is observed. Loss tangent (tan δ) dispersion is exhibited till 100 kHz and remains practically constant at higher frequencies. This reveals according to VHTM ,that hopping of electrons and holes ,a part of the conduction mechanism[48] ,leads to the result that when the hopping frequency is nearly equal to that of the applied external field ,a maximum loss is recorded .Sun et. al.[49] reported the initial permeability and relative loss factor increased while the cut off frequency decreased with increasing Zn content in $\mathbf{(Ni_{(1-x)}\ Zn_x)Fe_2O_4}$ ferrite.

Mott, D.M.[38],in his focused investigation of the synthesis and characterization of metal nanoparticles and supported catalysts, obtained preliminary results using computational modeling to elucidate some of the surface binding and energy properties of nanoparticles providing some guidelines to experimental measurements, and also

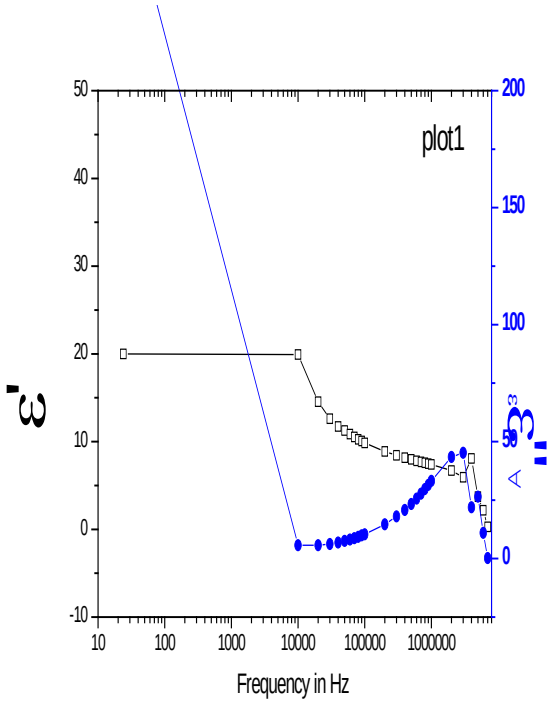
helped in the explanation of the complex experimental data, later obtained .These findings and results have provided new insights into the fundamental factors governing the physical and chemical properties in the synthesis and application of metal nano particles.The synergistic properties of multi metallic nanoparticles were analyzed by monitoring the CO absorption on bimetallic gold-platinum nanoparticles using infrared spectroscopy. N.Chau et.al.,[2]studied magnetic and magneto caloric characteristics of mixed spinel ferrites $\mathbf{Ni_{(1-x)}Zn_xFe_2O_4}$ (with x = 0.60, 0.65, 0.70, 0.75) The authors' similar published work on IR Studies using ***BRUKER (ALPHA)FT-IR*** with software ***OPUS 6.5 (version),*** is available elsewhere [25].

Wojciech Tabis [50],in his structural studies as a tool to interpret VHTM in Magnetite(Fe_3O_4),investigated ,whether 'electronic' and 'structural transitions' are simultaneous; and whether structural changes drive electronic transitions , or vice-versa .This point was suggested by Verwey(1939) and Anderson(1956),who described the transition as a freezing out of strongly correlated electrons .W. Tabis [50],established that the structure was not stable after the sample quenching to 110K. It was also pointed out that the structural domains created at the transition have strong reorganization tendency, which fact is strongly supported by all our studies reported so far , in our specimens .

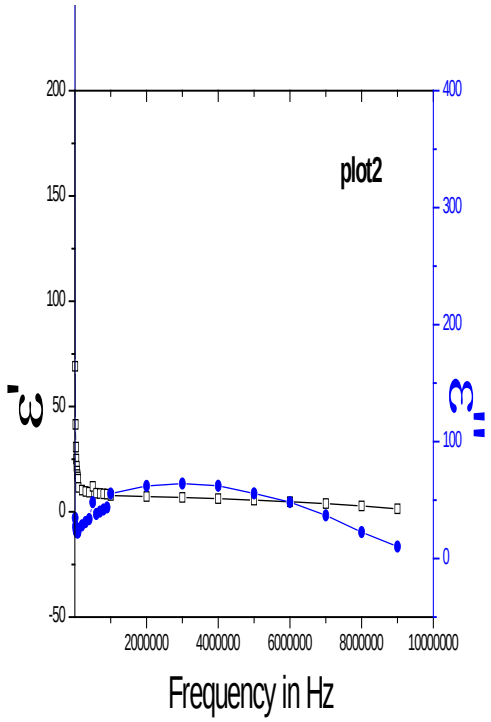
ACKNOWLEDGEMENTS

The author [a] records his thanks to Dr. Malivel Raja, Scientist, DMRL, of DRDO,, HYDERABAD,A.P., INDIA, for several valuable discussions and suggestions during the course of the work. The authors [a,b,c] also thank Dr. N.S.Naidu, and Dr. K.Trinadh, Scientists of Naval Science and Technological Laboratories, Visakhapatnam,A.P., INDIA, for their valuable help and suggestions in providing help to use their facility and planning the work to take measurements .One of the authors (R. Dhanaraju), records thanks to UGC , for the fellowship with which this work could be done,in the Physics Dept , of Andhra University ,Visakhapatnam-500003,A.P., INDIA.

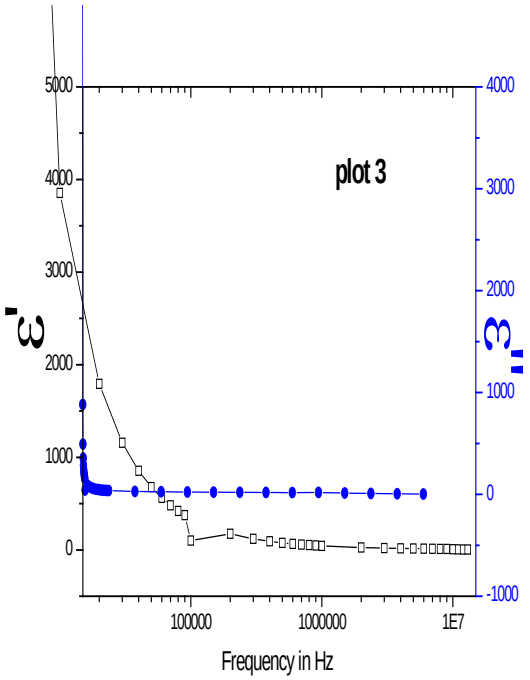
Plots (1) to (11) : of Frequency Versus (ε' and ε'') for the Zn and Sb Doped Ferrites



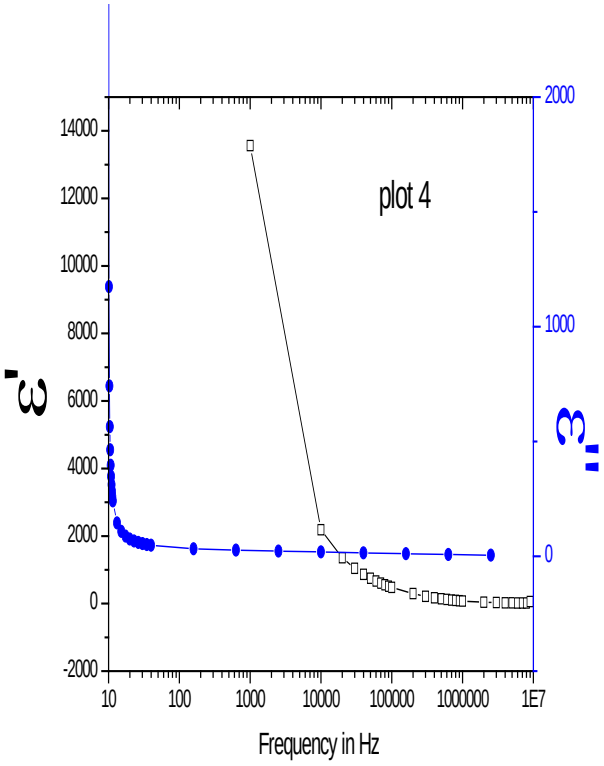
Plot 1 for sample $Cu_{0.8}Zn_{0.2}Fe_2O_4$



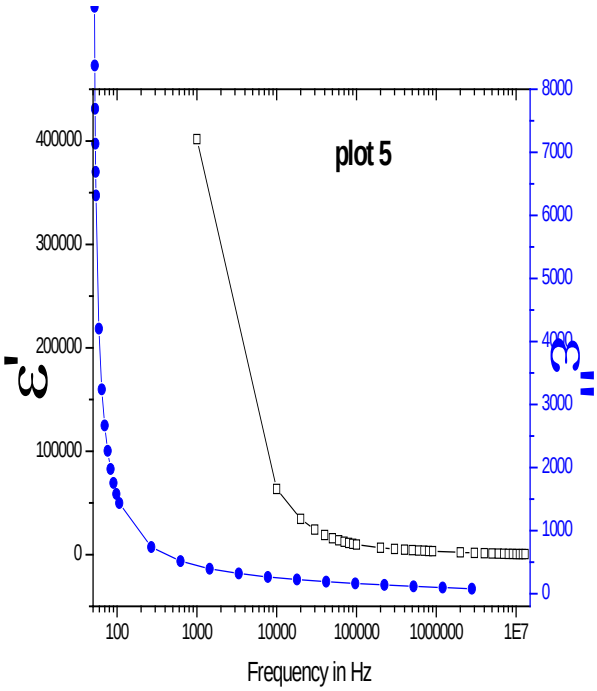
Plot 2 for sample$Cu_{0.6}Zn_{0.4}Fe_2O_4$



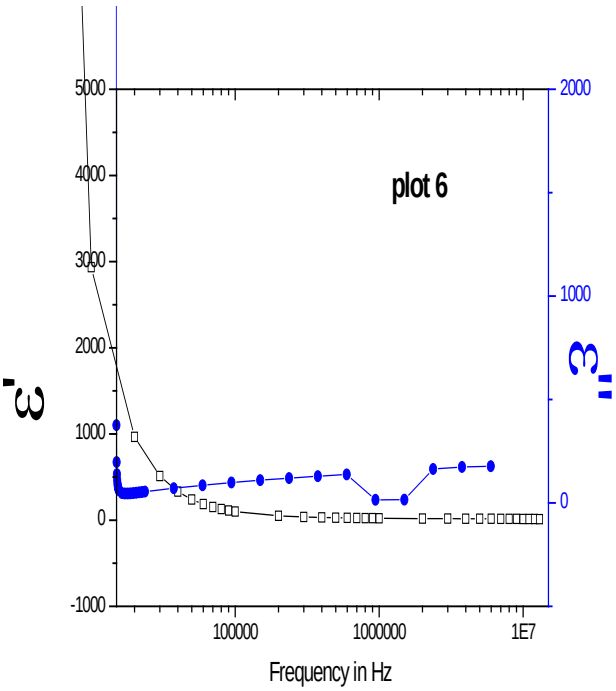
Plot 3 for sample $Cu_{0.4}Zn_{0.6}Fe_2O_4$



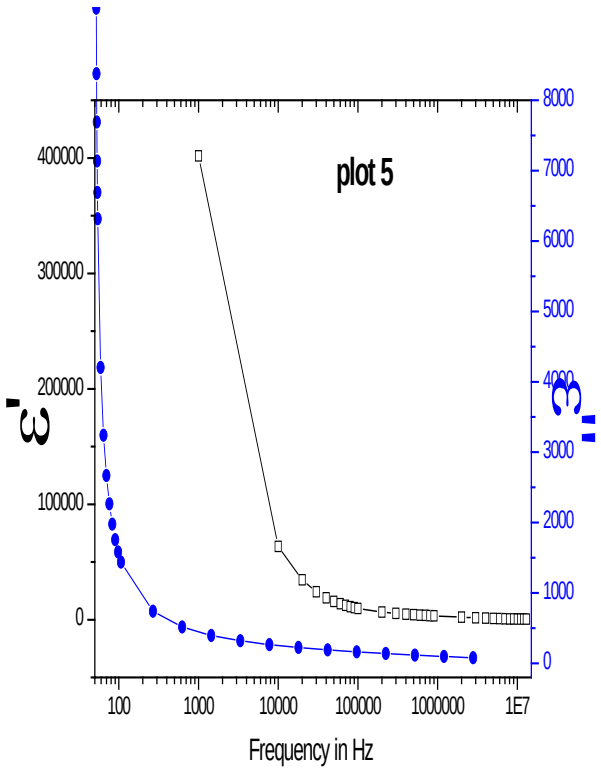
Plot 4 for sample $Cu_{0.2}Zn_{0.8}Fe_2o_4$



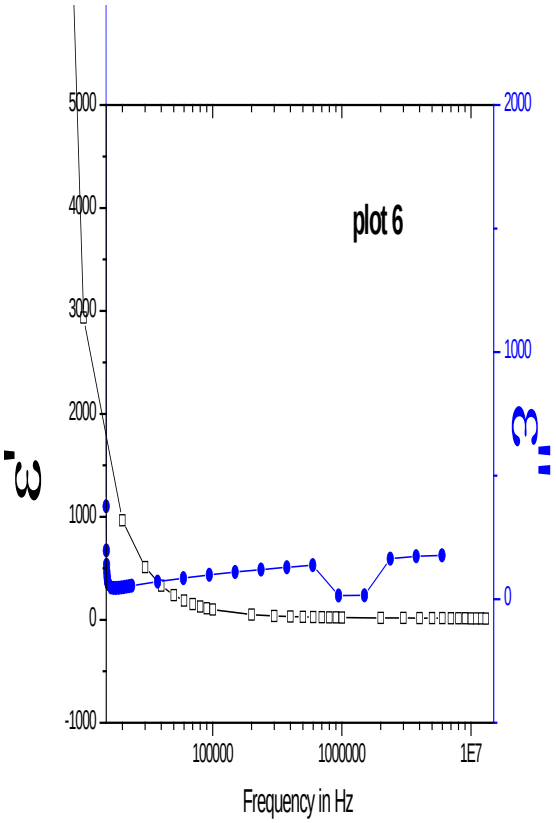
Plot 5 for sample $ZnFe_2O_4$



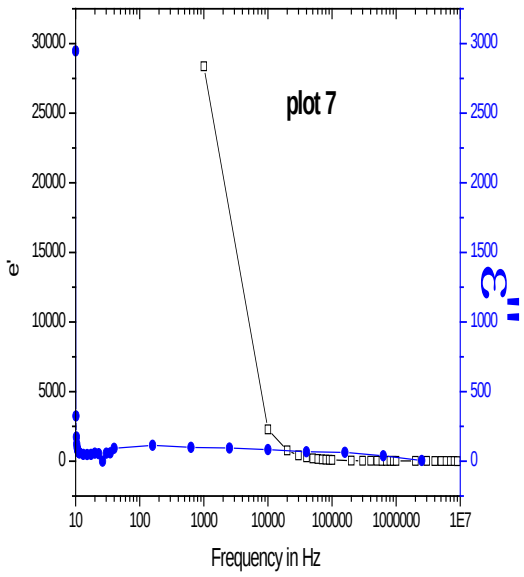
Plot 6 for sample $CuFe_2O_4$



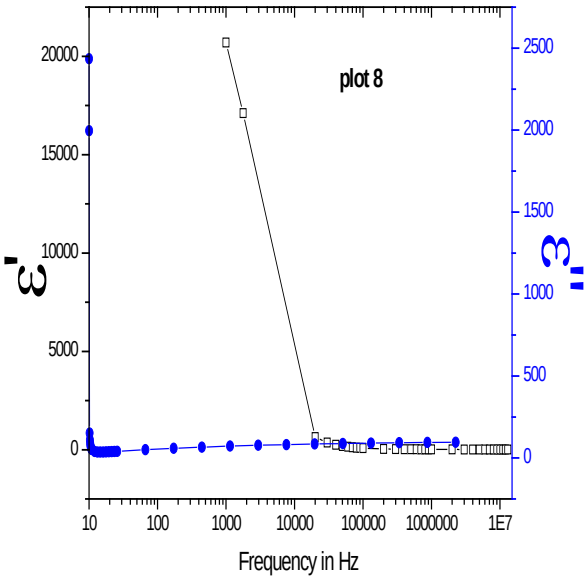
Plot 5 for sample $ZnFe_2O_4$



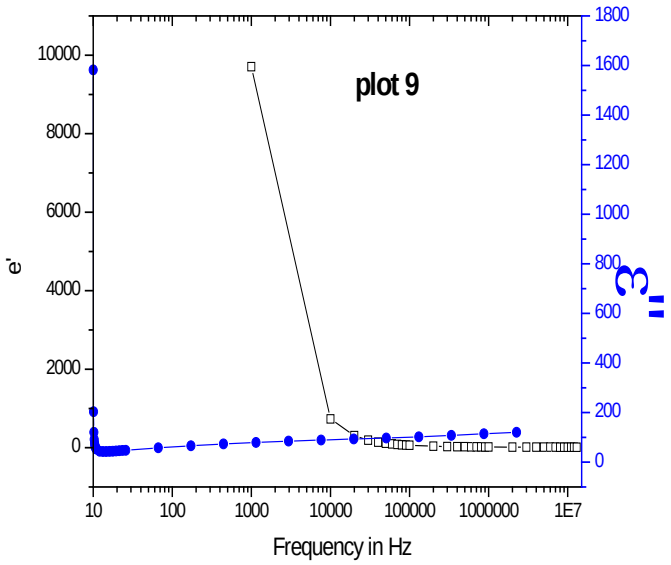
Plot 6 for sample $CuFe_2O_4$



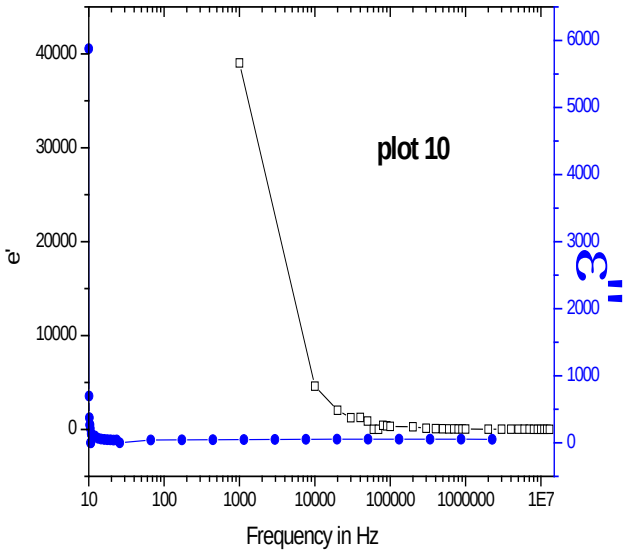
Plot 7 for sample $Cu_{0.8}Sb_{0.2}Fe_2O_4$



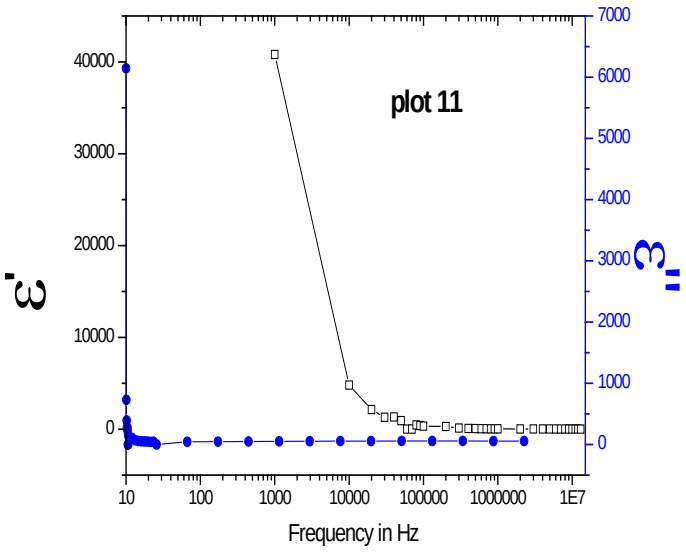
Plot 8 for sample $Cu_{0.6}Sb_{0.4}Fe_2O_4$



Plot 9 for sample $Cu_{0.4}Sb_{0.6}Fe_2O_4$



Plot 10 for sample $Cu_{0.2}Sb_{0.8}Fe_2o_4$



Plot 11 for sample $Sb\ Fe_2O_4$

REFERENCES

[1] Jie Ma **(2010)** :Ph.D. Thesis entitled: ‘‘Neutron scattering study of charge-ordering in $R_{1/3}Sr_{2/3}FeO_3$(R = La, Pr, Nd, Sm, and Y) ’, submitted to : Iowa State University,U.S.A

[2] N. Chauet.al.,**(2008),** ‘Effects of Zn content on the magnetic and magneto caloric properties of Ni-Zn ferrites’, VNU Journal of Science, Mathematics - Physics 24 (2008) 155-162

[3] MksymMyndyk **(2010)**, in his Ph.D. Thesis entitled ‘Nano crystalline oxides prepared by Mechano chemical reactions’: submitted to TechnischenUniversitätBraunschweig, Ukraine

[4] MahRukhSiddiquah**(2008),**Ph.D. Thesis entitled , ‘Effect of Doping of Various Metal Cations on Structural Electrical and Magnetic Properties of Nano Cobalt Ferrites’ submitted to: Quaid-I-Azam University, Islamabad, PAKISTAN

[5] M.Penchalareddy et.al.,(**2011**),[Modern Physics Letters B (MPLB)(2011), **25(3)**,pp. 211-222]

[6] P.A.Jadhav et.al.,**(2009),** J. Phy.&Chem. of Solids, 70(2), , pp. 396-400.

[7] RaziaNongjai et.al.**(2010)**‘Influence of Al^{3+} doping on the structural and electrical roperties of Nano crystalline $Ni_{0.7}Mg_{0.3}Al_xFe_{2-x}O4$ ferrites’**,** Int. J. Syst.Biology, 2(1), p3 Copyright © 2010, Bio infoPublications,ISSN: 0975–2900 & E-ISSN: 0975–9204.

[8] Khalid MujasamBatoo et.al.**(2010)** ‘Dielectric and ac impedance properties of $NiFe_{2-x}Cu_xO_4$ ferrite nanoparticles through citrate gel method’, Int. J. Syst.Biology, 2(1), p4 Copyright © 2010, Bioinfo Publications,ISSN: 0975–2900 & E-ISSN: 0975–9204.

[9] Packiaraj G. et.al, **(2010)** ‘Synthesis and Characterization of Barium Hex ferrite Particles by Sol – Gel Auto Combustion Method’, Int. J. Syst.Biology, (2010), 2(1), p5, Copyright © 2010, Bio info Publications,ISSN: 0975–2900 & E-ISSN: 0975–9204.

[10] Jogi R. R. et.al,**(2010)**‘Tatiana nanoparticles used as a self-cleaning material’**,** Int. J. Syst.Biology, (2010), 2(1), p5, Copyright © 2010, Bio info Publications,ISSN: 0975–2900 & E-ISSN: 0975–9204.

[11] Panchal N.R.et.al.,**(2010)**‘Cobalt Ferrite Nano Particles by Micro emulsion Route’, Int. J. Syst.Biology, (2010),2(1), p5, Copyright © 2010, Bio info Publications, ISSN: 0975–2900 & E-ISSN: 0975–9204.

[12] R.F. Saohoo: **(1960)** ‘Theory and application of ferrites’, Engle wood cliffs. N.J., Prentice Hall (1960)

[13] RaziaNongjai et.al.**(2010)**‘Influence of Al^{3+} doping on the structural and electrical roperties of Nanocrystalline $Ni_{0.7}Mg_{0.3}Al_xFe_{2-x}O4$ ferrites’**,** Int. J. Syst.Biology, 2(1), p3 Copyright © 2010, Bio infoPublications,ISSN: 0975–2900 & E-ISSN: 0975–9204.

[14] D.L. Fresh, **(1956)** Proc. IRE, 49, pp1303.

[15] Dhanaraju R., et.al, **(2011),** ‘SEM and XRD studies on Sb substituted Cu ferrite Nanomaterial’, Science &Society,9(2),pp97-102.(ISSN0973-0206).

[16] R.K.Singhet.al., (**2010)** ,‘Cation distribution of $Ni_{0.5}Zn_{0.5}Fe_2O_4$nanoparticles’International Journal of Engineering, Science and Technology, 2(8), 2010, pp. 104-109

[17] A.C.F.M.Costa et.al**.,(2003),** ‘Synthesis, microstructure and Magnetic properties of Ni-Zn Ferrites’, *J. Magn. Mag. Mater.* Vol. 256, pp. 174-182.

[18] UzmaGazanfar**(2005),** Ph.D. Thesis : ‘Preparation and ChrecterizationofFerriteMaterials for Practical applications’, Centre of Excellence in Solidstate Physics ,The University of Punjab,Lahore, Pakistan.

[19] Ibid (2005),Ph.D Thesis,

[20] A. Goldman**,(1990):** “Recent Advances in Ferrite Materials Technology,” in Modern Ferrite Technology, Van Nostrand Reinhold, New York, (1990).

[21] G. Goev, et.al**.,(2003),** Proceedings of the fifth General Conference of the Balkan Physical Union BPU-5 (2003) 687.

[22] K.O. Low,et.al**.,(2003),** J. Magn. Magn.Mater.**256** (2003) p221.

[23] P.K.Roy**(2009),**Ph.D .Thesis : ‘*Influence of substitutions and sintering aids on Structural and Electromagnetic properties of NiCuZn*

Ferrite',Dept. of Ceramic Engg.,N.I.T.,Rourkela, Odisha, INDIA.

[24] Dhanaraju R. et.al.**(2011),** '*Measurements of Electrical charecteristics of Zn &Sb Substituted Cu ferrites, and the frequency dependence of resistivity for Zn Substituted Cu ferrite'*, Science &Society,9(2),pp103-108. (ISSN0973-0206).

[25] R.Dhanarajuet.al.,**(2011), '***Graphical traits about VHTM in the lightof FTIR Studies on Zn &Sb substituted Cuferrites'*, International Journal of Engineering Science and Technology (IJEST) ISSN : 0975-5462,**3(11),**pp8069-8075.

[26] **Ibid (2012),** '*Hysteresis and related magnetic studies on Zn & Sb substituted Cu ferrites in relation to Verwey's Hopping Transition Mechanism*', [communicated to IJMS-Manuscript ID **ijms-15753/D 2012-02-18]**D. Ravinder, **(1992)** , Phys. Stat. Solidi (A) 129 , p549.

[27] A.S. Albuquerque et.al**.,(1999) ,** 'A study of nanocrystalline Ni-Zn-ferrite–SiO_2 synthesized by sol–gel', J. of Magnetism and Magnetic Materials, **192(2)** ,pp 277-280.

[28] M. A. Ahmed,et.al**.,(2005),** Mat. Chem. Phys. 92 (2005),p310.

[29] A.Vermaet.al.,**(2005),** Material Science and Engineering B,116(1), pp1-6,

[30] P. Kishan. et.al, **(1985)**, J. Less-common Metals, 108, p 345.

[31] M.G. Reddy .et.al, **(1991),**J.Phys.D, **24**, p975.

[32] D. Ravinder, **(1993)**, phys. Stat. Sol. (a) 139, k69.

[33] B. ParvatheeswaraRaoet.al.,**(2007),**'Soft chemical synthesis and characterization of **$Ni_{0.65}Zn_{0.35}Fe_2O_4$** nanoparticles', J.Appl.Phys.101, 123902 (2007), (4 pages).

[34] A. Mahesh Kumar et.al.,(**2009**),'Mössbauer investigation on Ni–Zn nanoferrite with the highest Saturation magnetization',J. of Appl.Physics , 105(7):Magnetism and Superconductivity(*5 pages*).

[35] N. Rezlescu and R. Rezlescu, **(1974),** Phys. Stat. Sol (a) 23, p575

[36] E. J. W. Verwey, **(1939),** Nature **144**, pp. 327-328; Verwey, E. J. W., and de Boer, (**1936)** J. H., *Rec.Trav. chim.*, **55**,p 531 ;de Boer, J. H., and Verwey, E. J. W. (**1937**), *Proc. Phys. Soc.*, **49**, extra part, 57; Schottky.W.(**1938**)., *Z. tech. Phys.*, **19**, 611 ; Verwey, E. J. W., (**1935**) *Z.Krist.*, **91**, 65; Hägg, G., and Söderholm, G., **(1935)***Z. phys.Chem.*, (B), **29**, , p 95;Van Arkel, et.al, (1936), *Rec. Trav. chim.***55**, 337(1936).

[37] Eugenio Coronado, et.al. (**2004),** Chem. Rev.**,** 104, pp5419-5448.Joaquin in Garcia.et.al.,**(2004),**J. Phys.: Condens. Matter **16,** R145–R178.

[38] Mott. N.F.(1980), Phil.Mag B42, p327.Mott, Derrick.M**(2008),**Ph.D. Thesis , **'**Synthesis, characterization, and catalysis of metal nanoparticles',submitted to State University of New York, At Binghamton, U.S.A.(227 pages; 3311499).

[39] Joaquin in Garcia. et.al.,**(2004),**J. Phys.: Condens. Matter **16,** R145–R178.

[40] Anderson P.W. **(1956),** Phys.Rev.,**B102**, p1008.

[41] L.G. Nanuttert, **(1956)**, Proc., IRE, 44, p1294.

[42] D. Ravinder, **(1993)**, phys. Stat. Sol. (a) 139, k69.

[43] A.C.Verma et.al.,**(1999),** 'Material Science and Engineering',(1999),B60,pp156-162.

[44] K. Iwachi, **(1971)** , J. Appl. Phys. 10, p1520

[45] L.I. Rabinkin, and Z.I. Novikova, **(1960)**, "*Ferrites"*, Minsk, p. 146.

[46] R. Satyanarayana, **(1983),** Ph.D. Thesis, Osmania University

[47] R.Narayana, & others (Eds), **(1989),** *"Advances in ferrites"* (Oxford and IBH pub Co.), p. 267.

[48] A.M.Abdeen**(1999),**J.of Mag and Mag Materials,192,pp121-129.

[49] G. L. Sun,et.al., **(2004)** J. Magn. Magn.Mater. 281,p173.

[50] WojciechTabis**,(2010),**Ph.D Thesis :'Structural changes ….in the vicinity of verwey transition observed with various X-Ray diffraction methods' ,submitted to AGH University of Science and Technology, Krakow,Grenoble(2010).

[51] Ginzburg, V. L. **(1957)**, *Sov. Phys. JETP*, **4**, p153.

[52] R.Dhanarajuet.al.,**(2011),** 'Activation energies of Zn & Sb substituted Cu ferrites' (being communicated).