High-Temperature Electrical Properties of cerium doped Ni-Zn Nano Ferrites

N. Hari kumar¹, N. Venkatesh², D. Ravinder¹*
Khalid Mujasam Batoo³,
Emad H. Raslan⁴ and Muhammad Hadi⁴

¹Department of Physics, University College of Science, Osmania University, Hyderabad, India.
²Department of Chemistry, University College of Science, Osmania University, Hyderabad, India.
³King Abdullah Institute for Nanotechnology, King Saud University, P.O. Box-2455, Riyadh-11451, Saudi Arabia.
⁴Department of Physics, College of Science, King Saud University, P.O. Box-2455, Riyadh-11451, Saudi Arabia.

Corresponding Author Email: ravindergupta28@rediffmail.com
Email: ravindergupta28@rediffmail.com

Abstract: Rare Earth Ce³⁺ Substituted Nickel-Zinc Nano Ferrite were synthesized Calculated Chemical Formulation Ni₀.₂Zn₀.₈CeₓFe₂₋ₓO₄ (0.000 ≤ x ≤ 0.040) by Citrate-Gel Auto Combustion method at lower temperature. The Single-Phase Cubic Spinel Structure was confirmed by the Characteristic of X-ray diffraction analysis (XRD). The SEM Micrographs confess from typical grain size and surface patterning of the samples is nanometric range confirming the nano crystalline nature. Energy Dispersive Spectrometer (EDS) were used to conduct elemental analysis and elemental parentage. Thermo electric power (TEP) of the prepared samples has been obtained using differential method with high temperature studies carried out in cooling cycle. The electric conductivity at high temperatures using two probe methods. The activation energy in the paramagnetic region (EP) is found greater than the ferrimagnetic region (EF). The carrier concentration(n), charge Carrier Mobility (μ) was carried out by TEP and electric conductivity Studies.

Keywords: Ferrites; Citrate-Gel Auto Combustion method; XRD; Thermo Electric Power; Electrical Conductivity; carrier concentration and Mobility.

1. Introduction:
Nano spinel ferrites having general formula is AB2O4 where in A are divalent and B are tri-valency metallic ions Fe$^{3+}$, Ce$^{3+}$, Al$^{3+}$ etc. it contains a notable category of magnetic substances there having innumerable uses in storages, microwave, magnetic diagnostic equipment’s and magnetic drug delivery etc. [1].

Different types of chemical methods they have used in order to achieve managements of stoichiometry, nitrates homogeneity, low oxidation and formation temperature/time, maximum molecular mixing in ferrites [2-5]. The substances get crystallized to a cubic spinel of O-ion. Cations fill up 2 kinds of interstitial / positions called tetrahedral. A Octahedral B-sites, tenancy of these positions were many times depicted using chemical formula $[A^{2+}_{1-\delta}Fe^{3+}_{\delta}] [A^{2+}_{\delta}Fe^{3+}_{2-2\delta}] O_4^{2-}$ [6].

Generally cubical spinel ferrites show good performance in magnetic and electric properties due to their reason it is commercially important material [7]. Microwave to radio frequencies range from Polycrystalline are excellent dielectric materials and they have more technical applications [8]. They have a high frequency range of applications.

Synthesis of nano spinel ferrites, low size distribution is important characterisation because of its notable electric and magnetic properties. Ferrite materials are a wide range of experimental applications like data storage systems, ferro-fluids, MCR and medical fields [9-10]. Some materials have Attributable dielectric behavior, they are called multiferroics. Used in, many mechanisms such as Transformers, on off systems, resonators, monitors, Televisions and cell phones [11-12]. Ferrites have Excellent electric and magnetic properties and electrical properties depending upon different factors involved in the direction of preparation method, composition with substitution, grain size [13].

Nano-particle ferrites play a significant role in view of their extensive applications. Their physical and chemical properties are remarkably different
from their bulk counterparts making them highly potential for different technical applications. Grain boundaries control their transport properties instead of grain itself [14]. Ferromagnetism is supported by electron spin and the material acts as a powerful magnet. They are widely used in industry and devices like electric motors, generators, transformers, telephone, loudspeakers, magnetic stripe in credit cards. The main advantage of ferrites is its compositional variability of very high degree. Nano-particle ferrites play a significant role in view of their extensive applications. Their physical and chemical properties remarkably differ from their bulk counterparts making them highly potential for different technical applications. Grain boundaries control their transport properties instead of grain itself [15]. In spinel ferrite materials electric and magnetic facets depend upon their ionic radio nature. Nano ferrite materials were used in different preparation synthesized techniques including ceramic method [16], hydrothermal method [17], sole-gel method [18], co-precipitation method [19], and citrate-gel method [20].

The results obtained related to synthesized Ce$^{3+}$ Substituted Ni-Zn Nano Ferrite present work was reports such as XRD analysis, SEM-EDS, Temperature dependence of electrical conductivity, Thermo Electric Power and their properties.

2.Experimental:

Cerium substituted Ni-Zn ferrites of chemical formulation Ni$_{0.2}$Zn$_{0.8}$Ce$_x$Fe$_{2-x}$O$_4$ Synthesized by Citrate-Gel Auto Combustion method. Stoichiometric amounts of metal nitrates of nickel, Cerium, ferric and zinc of 99% purity are dissolved in distilled water and later mixed with citric acid in 1:1ratio. After stirring was heated to 80°C and by adding ammonia the solutions pH value was set to 7 form a sol. The resulting solution was made to form a viscous gel on stirring and heating between 180°C-200 °C to result in ferrite powder. This ferrite powder was grinded and calcined for four hours at 500°C.Added 10% PVA and applied pressure up to 10-ton cm$^{-2}$ form of pellets.
The hopping length at A and B sites were calculated from the formula [21]:

\[ L_A = \frac{a\sqrt{3}}{4}, \quad L_B = \frac{a\sqrt{2}}{4} \]  

(1)

The doping effect always results into the strain in the base matrix. The effect of \( \text{Ce}^{3+} \) doping on the local strain was calculated accorded to the formula:

\[ \varepsilon = \frac{\beta \cos \theta}{4} \]  

(2)

The stress was calculated according to the formula:

\[ \sigma = \frac{15-\varepsilon}{a.t} \]  

(3)

The seebeck coefficient (S) is derived using formula [22]

\[ S = \frac{\Delta E}{\Delta T} \left( \mu V/K \right) \]  

(4)

where the thermo emf is denoted by \( \Delta E \) and \( \Delta T \) denotes the difference of temperature between pellet surfaces.

The carrier concentration values of the prepared samples were calculated using the following relation

\[ n = N \exp \left( -\frac{S_e}{K} \right) \]  

(5)

where \( N \) = concentration of electronic levels involved in the conduction process, \( S \) = Seebeck coefficient, \( e \) = electron charge, \( K \) = Boltzmann constant. Ferrites are low mobility semiconductors having exceedingly narrow bands or localized levels, so value of \( N \) can be taken as \( 10^{22}/\text{mL} \) [23]

Activation energies are derived from slopes of plot between temperature and electrical conductivity using Arrhenius relation.

\[ \rho = \rho_0 e^{E_g/kT} \]  

(6)

where \( E_g \) = activation energy, \( k \) = Boltzmann constant.
Activate Energy of the prepared nano particle samples to paramagnetic [ΔE1] and the ferromagnetic [ΔE2] region are enumerated, the slopes of para and ferromagnetic regions there by using followed condition is [24]

\[ ΔE = 0.198 \times 10^{-4} \times \text{slope} \]  

charge Carrier Mobility (µ) The charge carrier mobility (µ) of mixed Ni-Cd ferrites was calculated from the experimental values of electrical conductivity (σ) and charge carrier concentration (n) using the relation.

\[ σ = neμ \]  
\[ μ = σ/ne \]  

where e is the exchange of electron.

3. Result and Discussion:

3.1 XRD:

The single phase cubic spinel structure was confirmed by XRD diffraction peaks were indexed as (111), (220), (311), (222), (400), (422), (511) and (440) which matches with standard pattern JCPDS file number-48-0489. Ce\(^{3+}\) substituted Ni-Zn ferrite sample XRD patterns was displayed in Fig 1. Structural parameters of the preparation of all samples shown on Table 1. It is clearly indicated that the crystallite size ranges between 12.8 nm to 22.7 nm.

The crystallite size will gradually increase with increased Ce\(^{3+}\) substitution into the single-phase cubic spinel Structure. Since Ce\(^{3+}\) ionic radio (1.03 Å) is larger than Fe\(^{3+}\) ionic radio (0.64 Å), it should be occupying an enormous area B than A sites. Finally conclude that curtailment of grain improvement and also crystallite size consequence’s increase of Ni\(_{0.2}\)Zn\(_{0.8}\)Ce\(_x\)Fe\(_{2-x}\)O\(_4\) (x ≤ 0.000 ≤ 0.040) nano crystalline particles [25].

Lattice parameters decreased and XRD density was increased with increase Cerium concentration obeying the Vegard’s law.

From the Table1, the values of Hopping length A and B-site to be decreased with increase in the Ce\(^{3+}\) composition (except x=0.000) because of lattice parameters and hopping length of the A, B-sites were directly proportional to it. Cerium composition with variation of lattice parameter (Å) and hopping length of B-sites were shown in Fig 2 and 3 receptively.
3.2 SEM:

Scanning Electron Microscopy (SEM) resulted in Micro structural analysis of the prepared sample. These representations were shown from the fig 4. SEM all micrograph images are present grain size, these are having maximum homogeneous dispersion and agglomeration between inter particles. Finally conclude from the below micrographs of the ferrite all samples the grain size was nano meter range with shape of spherical and inter partials have narrow size dispensation.

SEM image revealed that with increasing in the Ce concentration, when the increased Ce\(^{3+}\)substitution randomly in Ni-Zn ferrites then the grain size was inconsequence’s increased except pure sample of the series its authentication from the XRD analysis.

3.3 EDS:

Analyse for the elemental percentage of Ce\(^{3+}\)substituted Ni-Zn ferrites by ED- spectroscopy. Their series existence of elements (Ce, Zn, Ni, Fe and O) was detected without precipitating cations. Elemental percentage for all the prepared ferrites were communicated in fig 5. From Table 2 Elements of each sample composition analysed by (%weight) obtained by EDS Spectra.

3.4 Thermoelectric Power studies:

Thermo electrical power of Ni\(_{0.2}\)Zn\(_{0.8}\)Ce\(_x\)Fe\(_{2-x}\)O\(_4\)Nano ferrites samples has been obtained using a differential method with high temperature studies between the 200\(^{0}\)C -600 \(^{0}\)C. The thermo emf for all samples is carried out in a cooling cycle. Seebeck coefficients for these nano-ferrites are derived from observed thermo e.m.f values and are tabulated in Table 3

Table 3 indicates that Seebeck coefficients for all Ni\(_{0.2}\)Zn\(_{0.8}\)Ce\(_x\)Fe\(_{2-x}\)O\(_4\) samples positive indicates that majority of charge carriers to be holes. Then assumed that, randomly increasing Ce\(^{3+}\) concentration, its position at B – Sites
and exchange to A-site of Fe $^{3+}$ ions, finally Fe$^{3+}$ ions will be decreasing in B-site [26]. This stipulates Fe$^{2+}$ions. Seebeck coefficient for cubicle spinal system as

\[ S = \frac{\text{Total number of Fe}^{3+} \text{ ions on B-sites}}{\text{Total number of Fe}^{2+} \text{ ions on B-sites}} \]

When substituted Ce$^{3+}$ concentration increases then the opponent of B-sites Fe$^{2+}$ decreases due to this reason Seebeck coefficient will be increased. when the charge carrier’s concentration will be more produced

The variation of Seebeck Coefficient with temp for all ferrite samples was shown in Figure 6 which indicated positive value between low to high temperature but pure Ni-Zn ferrite is negative to positive with increasing temperature. Seebeck was positive value for all ferrite samples under study. These samples exhibit the characteristics of p type semiconductor in high temperature region accepting pure Ni-Zn ferrites. Pure samples at low temperatures behave like n-type semiconductor. With increase in temperature, it behaves like p-type semiconductor due to predominant conduction mechanism. Figure 6 indicate that measurements of thermo electric power carried out between 200°C-600°C using differential method. Thermoelectric power exhibits a clear transmission at Curie temperature just like magnetic properties. Minimum value of Seebeck coefficient at Tc indicate the influence of magnetic ordering on thermoelectric power of current samples under investigation [27]

Ce+3 substituted Ni-Zn ferrites when temperature Increases then the electrons behave like p-type semiconductors by conduction mechanism. This nature of conductivity is imputing to the trip of electrons allying Fe $^{2+}$ and Fe $^{3+}$ at octahedral sites. Then the conduction mechanism

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + 1 \text{e}^- \]
By the graphical representation observed that the Seebeck coefficient and temperature values are increasing then greater p-type carriers are liberated. Gradually increasing in temp, the Seebeck coefficient instantaneously decreases at specific temp and again moderately increases, this is known as Transition temperature (Tc).

Cerium Substituted Nickel-Zinc Nano Ferrite samples was carried out by Charge Carrier concentration calculated Temperature at 400K. Calculated Curie Temperature (500k to 800k) and Charge Carrier concentration (0.645x10$^{22}$ to 0.890x10$^{22}$) values are observed from the Table 4. From the tabular form plated Variation of charge carrier concentration with temperature shown in Fig 7. That among all the Cubical spinel ferrites, gradually Cerium composition substitution in Ni-Zn ferrites the Charge carrier concentration was increases due to number of mixed ferrites as greater p-type carriers are liberated from the Seebeck coefficient property. Observed compositions Ni$_{0.2}$Zn$_{0.8}$Ce$_{0.040}$Fe$_{1.96}$O$_4$ was having the highest values of carrier concentration.

3.4.2 Curie temperature:

The varying of Curie temperature with Cerium composition in the Chemical composition Ni$_{0.2}$Zn$_{0.8}$Ce$_x$Fe$_{2-x}$O$_4$ nano ferrites was shown in fig 8. From this figure one can conclude that the decreasing Curie temperature with increased the Cerium composition may be understood depending on the number of magnetic ions currently in the constant sub-lattices and their simultaneity interaction. An increasing Ce$^{3+}$ at the octahedral site substituted the Fe$^{3+}$ at this site leading to decreasing A and B interaction of the type Fe$^{3+}$A-O-2 - Fe$^{3+}$B (28)

3.5 DC electrical Conductivity:

DC electrical conductivity of the prepared samples from under room temperature to 530$^0$C was reported. It reduces with enhanced temperature for
every sample indicating semiconducting nature. From Fig 9 the plot of Log ($\sigma T$) vs 1000/T indicating a curve from which samples thermal activation energy can be derived from slope.

As per the plot electrical conductivity of Ce substituted Ni-Zn nano ferrites show discontinuity having two different regions located in different value of activation energies resulting in paramagnetic and ferrimagnetic regions. As per magnetic semiconductor theory, ferrimagnetic and paramagnetic represent ordered and disordered regions. Hence extra energy is required for conduction in the paramagnetic region rather than ferromagnetic region. The activation energy values in the paramagnetic region and ferromagnetic region with Curie temperature values are tabulated in Table 5.

3.5.1 Activation energy:

$\text{Ce}^{3+}$ concentration(x) was increases from 0.000 to 0.040 similarly the value of activation energy also increased from 0.024ev to 0.067ev. as evident from Variation of Activation of energy of hopping with Ce composition of Ni$_{0.2}$Zn$_{0.8}$Ce$_x$Fe$_2$O$_4$ (0.000 ,0.020 and 0.040) Fig 10. Hence, the activation energy in the paramagnetic region (EP) is found greater than the activation energy in the ferrimagnetic region (EF) for these reason that the ferrimagnetic state is an ordered compare to the paramagnetic state.

Similar results were reported by others in Ni-Zn ferrites. It shows that the activation energy was more in the paramagnetic region than in the ferromagnetic region It may be justified due to the decrease to increases in conductivity with the increase in $\text{Ce}^{3+}$ composition concentration (29).

3.5.2 Curie temperature:

Curie temperature (Tc) verses as a function of dopant Ce composition was exposed in fig 11. From The plot the Curie temperature was found to be decreasing to a small range of increasing from the range of 516 to 488 K with increasing Cu Composition. This kind of manner was attained as a
result of the depletion of magnetic exchange reciprocity between the cations at the octahedral site [30].

3.5.3 Charge Carrier Mobility (μ):

Charge Carrier mobility (μ) for the samples of Ce³⁺ substituted Ni-Zn (0.000, 0.020 and 0.040) nano ferrites system have been calculated Curie temperature and carrier mobility Tabulated in Table 6. From the table 6 values evident from fig 12, it was decrease in carrier mobility (4.49X10⁻³ to 3.59X10⁻³) with increase in Ce content (x=0.000 to 0.040) at variation of high temperature.

We can observe that the Nano ferrite crystallites with lower conductivity have low to negative carrier mobility. For this difficult results behavior of the carrier mobility vs temperature, that Carrier mobility increases by increasing the temperature in degree Celsius. The carrier mobility in ferrites formed at high temperature are comparatively low. This is due to composition with variation of carrier mobility behavior was reported in number of mixed ferrite systems Ni-Zn Cerium and Zr-Mg Cobalt ferrite [31], and increase in crystallinity and also stoichiometry of the ferrites.

4. Conclusions:

The single phase cubic spinel structure was confirmed by XRD diffraction peaks which matches with standard pattern JCPDS file number-48-0489. the crystallite size ranges between 12.8 nm to 22.7 nm. Lattice parameters decreased and XRD density was increased with increase Cerium concentration. the values of Hopping length A and B-site to be decreased with increase in the Ce³⁺ composition (except x=0.000) because of lattice parameters and hopping length of the A, B-sites were directly proportional to it. Micrographs of the ferrite all samples the grain size was nano meter range with shape of spherical and inter partials have narrow size dispensation. Elements of each sample composition analysed by (%weight) obtained by EDS Spectra. Ce+3 substituted Ni-Zn ferrites when temperature Increases then the electrons behave like p-type semiconductors by conduction mechanism. all the Cubical spinel ferrites, gradually Cerium composition substitution in Ni-Zn ferrites the Charge carrier concentration was increases due to number of mixed ferrites as greater p-type carriers are liberated from the Seebeck coefficient property. In S coefficient the decreasing Curie temperature with increased the Cerium composition may be understood depending on the number of magnetic ions currently in the constant sub-lattices and their simultaneity interaction. electrical conductivity of Ce substituted Ni-Zn nano ferrites show discontinuity having two different regions
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REFERENCE

[1]. M.Pardavi-Horvath, J Magn Magn Mater 215/216, 171 (2000)
[2]. P.K.Roy and J.Bera, J Magn Magn mater 298,38,(2006)
[3]. P.D.Thang, G.Riginders and D.H.Blank, J Magn Magn mater296,251(2005)
[4]. M.F.F.lelis , A.O.Porto, C.M.goncalvers, and J.D.Fabris, J J Magn Magn mater278,263 (2004)
[5]. M.K.Kumar, P.K.Singh, P.Kishan, N.kumar, S.L.N.Rao, P.K.Singh, and S.L.Srivathsava J.Appli Physics,63,3780 (1998 )
[6]. T. Abbas, Y.Khan,M.Ahmed,S.Anwer, solid state communi 82 (1992)701
[7]. P.V. Reddy and T.S. Rao."Dielectric behavior of mixed Li-Ni ferrites at low frequencies.” Journal of less common metals.Vol.86.1982. PP. 255-26
[8]. Kharabe R G, Devan R S, Kamadi CM and Chougule B K, Smart Material Structures. 15 N, 36 (2006).
[9]. A.K. Giri. E.M. Kirkpartrick, P. Moongkhamllang, S.A. Majetich, Journal of Applied
[10]. Physics Letters. 80, 2341(2002).
[11]. A.K. Giri, K. Pellerin, W. Pongsakswad, M. Sorescu, S. Majetich, IEEE Transctions on Magnetics. 36, 3029 (2000)
[12]. J. Smit, H.P.G. Wijn, Ferrites. 136 (1959).
[13]. M. Sugimoto, Journal of Ceramic American Society, 82, 2, 269 (1999).
[14]. K. Kondo, T. Chiba, S. Yamada, Journal of Magnetism and Magnetic Materials 541, 254(2003).
[15]. KaleA,Gubbala,S, Misara RDK:magnetic behavior of nanocrystallite nickel ferrite synthesized by the reverse micelle technique. J Magn Magn mater 2004,3:350-35DOI:10.1016/0022-5088(82)90211-9
[16]. El-Sayed Ahmed M, Hamzawy Esmat MA. Structure and magnetic properties of NickeleZinc ferrite nanoparticles prepared by glass crystallization method. Monatsh fu´r Chemie/Chemical Mon 2006;137:1119. http://dx.doi.org/10.1007/s00706-006-0521-1.
[17]. Hu Chaoquan, Gao Zhenghong, Yang Xiaorui. One-pot low temperature synthesis of MFe2O4 ( M¼Co, Ni, Zn) superparamagnetic nano crystals. J Magn Magn Mater 2008;320:L70.
[18]. Batoo Khalid Mujasam, Kumar Shalendra, Lee Chan Gyu, Alimuddin. Finite size effect and influence of temperature on electrical properties of nano crystalline NieCd ferrites. Curr Appl Phys 2009;9:1072.
[19]. Soibam I, phanjoubam S, Prakash C. Magnetic and Mössbauer studies of Ni substituted LieZn ferrite. J Magn Magn Mater 2009;321:2779.

[20]. Raghasudha M, Ravinder D, Veerasomaiah P. Characterization of chromium substituted cobalt nano ferrites synthesized by citrate-gel auto combustion method. Adv Mater Phys Chem 2013;3:89e96.

[21]. M.C. Varma, G.S.V.R.K. Choudary, A.M. Kumar, K.H. Rao, Phys. Res. Inter. 1, 579745 (2014)

[22]. B.K. Bammannavar, L.R. Naik, R.B. Pujar, B.K. Chougule, Indian J. Eng. Mater. Sci.14 (2007) 381

[23]. ] Morin FJ, Geballe TH. Electrical conductivity and seebeck effect in Ni0.8Fe2.2O4. Phys Rev 1955;99:467.

[24]. Abbas.T,Khan.Y,Ahmed.M,Anwer 1992 Solid state communi 82 701

[25]. G. Dixit, J. Pal Singh, R.C. Srivastava, & H.M. Agrawal, 2012, 324, 479– 483.

[26]. A.A.Samokhavalov, A.G.Rustamov,Soviet PhysSolid State,6 (1964) 749.

[27]. Srinivasan, G., C.M Srivastava: Electrical conductivity mechanism in zinc and copper substituted magnetite. Phys. Status Solidi B 108, 665– 671 (198

[28]. Chandra Babu.B,Naresh. V, Jayaprakash. B, Buddhudu. S, Ferro Electrics letter.38, 124 (2011).

[29]. M. Raghasudha , D. Ravinder , P. Veerasomaiah , K.M. Jadhav , Mohd Hashim, Pramod Bhatt , Sher Singh Meena: Electrical resistivity and Mossbauer studies of Cr substituted Co nano ferrites 2016 Published by Elsevier http://dx.doi.org/10.1016/j.jallcom.2016.10.028

[30]. Raghasudha, M.;Ravinder, D.; Veerasomaiah, P. Thermoelectric powerstudies of Co–Cr nano ferrites.Journal of Alloys and Compounds2014, 604, 276–280, https://doi.org/10.1016/j.jallcom.2014.03.097
[31]. Muhammad Javed Iqbal, Mah Rukh Siddiquah, J. Magn. Magn. Mater. 320 (2008) 845.