Ferrite remain the best magnetic materials, because they are inexpensive, stable and have a wide range of technological application such as high-quality filters, radio wave circuits and operating devices. Among the ferrites, spinel type ferrites are very important material because of their combined electrical and magnetic properties [1]. An ideal spinel structure is described by the general formula \( \text{M}^{2+}\text{Fe}^{3+}2\text{O}_4 \), where \( \text{M}^{2+} \) is a divalent metallic ion such as \( \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+} \) or mixture of these ions [2-3]. They have been extensively investigated and being the subject of great interest because of their importance in many technological application. The Ni-Cu-Zn spinel ferrite is a soft magnetic material with a completely inverse spinel structure. They have been widely used in multilayer chip inductors, electronic device, mobile phone, notepad computer and video camera and correlative inductive devices due to their low-sintering temperature, high electrical resistivity and most important magnetic materials for multilayer chip inductor (MLCI) applications [4,5].

Different spinel ferrites have been studied for their structural, electrical and magnetic properties by substitution various kinds of ion [6-7]. The rare earth (\( \text{RE}^{3+} \)) ions have unpaired 3f electrons, which play the role of originating magnetic anisotropy because of their orbital shape. The magneto-crystalline anisotropy in ferrite is related to the 4f-3d couplings between the transition metal and rare earth ions; thus
doping rare earth oxides ions into spinel ferrite can improve their structural, magnetic and dielectric properties. In many investigations [8-10], a modification in the structural, magnetic and dielectric properties is obtained due to the addition of rare earth ions however, in some cases conflicting results are also obtained [11, 12]. For these reasons, further studies on rare earth-substituted ferrites are needed.

The effect of doping of various rare earth ions like Gd$^{3+}$, Sm$^{3+}$, Y$^{3+}$, Nd$^{3+}$ on the structural, electrical, dielectric and magnetic properties have been reported in previous chapter. The experimental results on these studies revealed that, among the rare earth doped in Ni-Cu-Zn ferrite Gd$^{3+}$ ion shows better influence on the properties of Ni-Cu-Zn ferrite.

Also to the best of our knowledge, no systematic investigations on the properties of Gd$^{3+}$ ions doped in the pure Ni$_{0.25}$Cu$_{0.20}$Zn$_{0.55}$Fe$_{2-x}$Gd$_x$O$_4$ matrix are reported in the literature.

Therefore, in the present work, the effect of rare earth such as Gd$^{3+}$ on the structural, magnetic, electric and dielectric properties of Ni$_{0.25}$Cu$_{0.20}$Zn$_{0.55}$Gd$_x$Fe$_{2-x}$O$_4$ spinel ferrite is studied. The synthesized samples are characterized as a function of Gd$^{3+}$ concentration, which provides interesting information on various properties.

5.2: EXPERIMENTAL SECTION

Preparation of ferrite sample

Polycrystalline samples of the nominal formula Ni$_{0.25}$Cu$_{0.20}$Zn$_{0.55}$Fe$_{2-x}$Gd$_x$O$_4$ (where $x = 0.00$ to $0.10$ in the steps of $0.02$) were prepared by standard ceramic technique [13-15] using analytical reagent grade oxides (99.99%) materials: NiO, CuO, ZnO, Gd$_2$O$_3$ and Fe$_2$O$_3$. Weighing
of compounds was accurately taken in molecular weight percentage with a single pan microbalance. The mixed powders were ground and presintered at 950°C for 24 h. The solid state reaction for these is as follows

\[ x\text{NiO} + y\text{ZnO} + z\text{CuO} + 1.90\text{Fe}_2\text{O}_3 + 0.10\text{Gd}_2\text{O}_3 \rightarrow \text{Ni}_x\text{Zn}_y\text{Cu}_z\text{Fe}_{0.95}\text{Gd}_{0.05}\text{O}_4 \]

For the perfect iron Stoichiometric composition, the mol ratio of

\( \text{Fe}_2\text{O}_3 + \text{RE}_2\text{O}_3 = 1 \) and \( x + y + z = 1 \)

The sintered powder is again re-ground and pelletized. Polyvinyl alcohol was used as a binder in making disc shape pellets of 10 mm diameter and 3 mm thickness. The pellets were finally sintered in muffle furnace for 1050°C for 24 h and then slowly cooled to the room temperature.

**Characterization**

X-Ray diffraction (XRD) patterns were taken at room temperature to confirm the crystal structure of the prepared samples. The XRD patterns were recorded in the angle 2θ range from 20° to 80° using Cu-Kα as a target having wavelength \( \lambda = 1.54056 \) Å with scanning rate 2° per minute.

The Fourier Transform infrared (FTIR) spectral data was collected using α-FTIR Bukar spectrophotometer in the wave number range 400 cm\(^{-1}\) to 1100 cm\(^{-1}\) by KBr pellet method.

The magnetic properties were studied using pulse field hysteresis loop technique at room temperature. a. c. susceptibility measurement was carried out by instrument supplied by Magenta Company (Mumbai).

D. C. electrical resistivity measurements were carried out using two-probe method in the temperature range 300-600 K in the steps of
10 K. For electrical measurement, surface of the pellets were well polished and coated with silver paste for good electrical contact. The samples were placed between two electrodes inside of silica tube which was supported with a furnace. The temperature of the samples was controlled and measured using chromel-alumel thermocouple with an accuracy of ±5K.

The dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and dielectric loss tangent (tan$\delta$) all the samples in the pellet form were measured using a Hioki 3532-50 (JAPAN) impedance analyzer in the frequency range 100 Hz to 1 MHz at room temperature.

### 5.3: RESULTS AND DISCUSSIONS

#### 5.3.1: Structural characterization

**X-ray diffraction**

Figure 5.1(a, b and c) represents the X-ray diffraction (XRD) pattern of all the sample of Ni$_{0.25}$Cu$_{0.2}$Zn$_{0.55}$Gd$_x$Fe$_{2-x}$O$_4$, ($x = 0.00 - 0.10$ in steps of 0.02) spinel ferrite system. The presence of the strong diffraction peaks corresponding to the planes (220), (311), (222), (400), (422), (511/333), (440), (533) indexed using Bragg’s law that the presence of cubic spinel structure. Miller indices (hkl) and interplaner spacing (d) for Ni$_{0.25}$Cu$_{0.2}$Zn$_{0.55}$Gd$_x$Fe$_{2-x}$O$_4$ ferrite system are listed in Table 5.1. The single phase cubic spinel structure is observed for $x = 0.00$ to 0.04, indicating that introducing an appropriate amount of Gd$^{3+}$ ions into ferrite can replace the Fe$^{3+}$ ions on the octahedral sites, which obeys Vegard’s law [16]. An additional (secondary phase) peak $2\theta = 32.84^0$ (indicated * in Fig.5.1 (b, c)) Bragg diffraction angle was also observed in the XRD data which belongs to GdFeO$_3$ (gadolinium iron oxide) phase from $x = 0.06 - 0.10$. The additional peak of GdFeO$_3$ well matched with
the JCPDS Card No. 78-0451. It is observed from XRD pattern that peak intensity of GdFeO$_3$ increased with increasing Gd$^{3+}$ contents $x$. The presence of the secondary phase in the Ni$_{0.25}$Cu$_{0.2}$Zn$_{0.55}$Gd$_x$Fe$_{2-x}$O$_4$ ferrite indicates that the substituent’s Gd$^{3+}$ content have a solubility limit in the spinel lattice. It is known that the degree of replacement of the Fe$^{3+}$ ions by the other ions in the spinel lattice depends on the cationic radius of the substituent. The ionic radius of Gd$^{3+}$ (0.938 Å) is larger than that of the Fe$^{3+}$ ions (0.67Å) the amount of Fe$^{3+}$ ions substituted by Gd$^{3+}$ ions have a limit, consequently redundant Gd$^{3+}$ form the GdFeO$_3$ on the grain boundaries [17-19].

**Lattice constant**

Figure 5.2 shows the variation of lattice parameter as a function of Gd$^{3+}$ substitution in Ni$_{0.25}$Cu$_{0.2}$Zn$_{0.55}$Gd$_x$Fe$_{2-x}$O$_4$ ferrite. It is observed that all Gd$^{3+}$ substituted samples have larger values of the lattice parameter than that of pure Ni$_{0.25}$Cu$_{0.2}$Zn$_{0.55}$Fe$_2$O$_4$ ferrite. This is because of the larger Gd$^{3+}$ ions replace Fe$^{3+}$ ions on the octahedral sites, leading to the expansion of the spinel lattice. The lattice parameter initially increased from 0.00 ≤ 0.04 and thereafter it decreases up to $x=0.10$. The possible explanation for the decrease in the lattice parameter can be the compression of the spinel lattice induced by secondary phases because of the difference in the thermal expansion coefficients [20]. The values of lattice parameter are tabulated in Table 5.2; similar behavior of lattice parameter was also reported is the literature [21-23]. Table 5.2 also includes the values of molecular weight (M), unit cell volume (V). Similar type of behaviour of lattice constant as a function of Gd$^{3+}$ content was reported in the literature [17].
X-ray density

The X-ray density ‘d_x’ of Ni_{0.25}Cu_{0.2}Zn_{0.55}Gd_xFe_{2-x}O_4 have been calculated from the molecular weight and volume of the unit cell and the values are given in Table 5.2. X-ray density depends upon the molecular weight of the composition as well as the lattice constant of the composition. The density increases from 5.41 to 5.61 g/cm^3 with the increase in Gd^{3+} content x. because of the replacement of larger Gd^{3+} (0.938Å) for Fe^{3+} (0.67Å) and the molecular weight has more increment when compared to the volume of the unit cell, therefore, the X-ray density increases with the Gd^{3+} content x. The variation of X-ray density with Gd^{3+} content x is depicted in Figure 5.3.

Bulk density

The bulk density (d_B) of the samples was measured by using Archimedes principle [24]. Table 5.2 gives the values of X-ray density as a function of Gd^{3+} content x. The relation between Bulk density and composition x is clearly observed in the samples and is shown in Figure 5.4. The bulk density increases with increase in Gadolinium (Gd^{3+}) content x.

Porosity

Using X-ray density and Bulk density data, the percentage porosity ‘p’ of the sample is calculated using the relation [25].From Figure 5.5, it is seen that, the percentage porosity decreases with increase Gd^{3+} content x. possible explanation on X-ray density and Bulk density both are increases; therefore porosity is decrease with increase Gd^{3+} content x and the values are present in Table 5.2.
**Particle size**

The crystallite size of all the samples was estimated from the full width at half maximum (FWHM) of the most intense peak (311) and by using Scherer's relationship [26].

The value of crystallite size for all the samples are listed in Table 5.2. It is observed from Figure 5.6 that crystallite size decreases as increases Gd$^{3+}$ content in Ni-Cu-Zn spinel ferrite. Our results on crystallite size are in good agreement with that reported in the literature [27]. The decrease in crystallite size can be explained on the basis that Gd$^{3+}$ ions may diffuse to the grain boundaries and have a segregation effect for the grains during the sintering process. This segregation process will inhibit the grain growth by limiting grain mobility. On the other side, due to the larger bond energy of Gd$^{3+}$-O$^{2-}$ as compared to that of Fe$^{3+}$-O$^{2-}$, it is obvious that more energy is needed to make Gd$^{3+}$ ions enter to lattice and from the bond of Gd$^{3+}$-O$^{2-}$. Therefore, all Gd$^{3+}$ substituted ferrite have higher thermal stability relative to pure ferrite, and hence more energy is needed for the Gd$^{3+}$ substituted sample to complete crystallization and grow grains [28, 29].

**Hopping length**

The hopping length for A-site ($L_A$) and B-sites ($L_B$) are calculated using the values of lattice constant. Hopping length analysis by using the relation discussed elsewhere [30]. The values of $L_A$ and $L_B$ are tabulated in Table 5.3. The dependence of the hopping length ($L_A$ and $L_B$) for the A- site and B-site on the Gd$^{3+}$ content $x$ is shown in Figure 5.7. It is observed that the lattice parameter $a$, $L_A$ and $L_B$ increase at $x = 0.04$ because the Gd$^{3+}$ ions replace the Fe$^{3+}$ ions on the B-sites in the spinel lattice, while these decrease with the Gd$^{3+}$ ions from the GdFeO$_3$
phase along the grain boundaries and inhibit the grain growth. This behavior of hopping length with content x is analogous with the behavior of lattice constant with Gd$^{3+}$ content x.

**Tetrahedral bond, octahedral bond, tetra edge and octa edge**

The values of the tetrahedral and octahedral bond length ($d_{AL}$ and $d_{BL}$), the tetrahedral edge ($d_{AE}$), and the shared and unshared octahedral edge ($d_{BE}$ and $d_{BEL}$) can be calculated according to equations [31] using the values of the lattice constant ‘a’ and oxygen parameter ‘u’. The edge and the bond length of the tetrahedral and octahedral sites as a function of the Gd$^{3+}$ content ‘x’ are shown in Table 5.3, respectively. It is seen that $d_{BL}$ and $d_{BE}$ increase with Gd$^{3+}$ content x, which may be because of the fact that Fe$^{3+}$ ions are substituted by larger Gd$^{3+}$ ions on the octahedral sites, resulting in the increase of $d_{BE}$ and $d_{BL}$ along with the expansion of the B sublattice; meanwhile the A sublattice is compressed by the B sublattice, resulting in the decrease of $d_{AL}$ and $d_{AE}$. $d_{BEL}$ exhibits similar behavior as the lattice parameter.

**Cation distribution**

The cation distribution in spinel ferrite can be obtained from the analysis of X-ray diffraction pattern. In the present work, the Bertaut method [32] is used to determine the cation distribution. In the present work (220), (400) and (440) were used to calculate intensity ratio. These planes are assumed to be sensitive to the cation distribution. The temperature and absorption factors are not taken in to account in our calculations as they do not affect the intensity calculation. If an agreement factor (R) is defined as in relation discussed [33], the best-simulated structure which matches the actual structure of the sample will lead to a minimum value of R.
For a given spinel compound the analyzed sub-lattice expand or contract on varying oxygen parameter ‘u’ until A-site and B-site volumes match the ionic radii of constituent cations. The cation distribution determined using X-ray diffraction method is presented in Table 5.4. In this table, the fraction of Fe\(^{3+}\) ions in either site is listed. The results demonstrate that Zn\(^{2+}\) ions distributed over tetrahedral A sites. Gd\(^{3+}\) preferentially replaces Fe\(^{3+}\) from octahedral sites. Further, Ni\(^{2+}\), Cu\(^{2+}\) and Gd\(^{3+}\) ions predominately occupy the octahedral sites, which is consistent with the preference for large octahedral site energy. With the increasing Gd\(^{3+}\) content, the fraction Gd\(^{3+}\) ions in octahedral sites increased, whereas the fraction of Fe\(^{3+}\) ions in octahedral sites decreased linearly. The intensity ratio corresponding to these cation distribution data is presented in Table 5.5. It can be observed the results of cation distribution is good agreement each other.

**Tetrahedral radius**

In spinel ferrite cations are distributed at tetrahedral (A) and octahedral [B] site. The radius of tetrahedral sites (r\(_A\)) can vary, depending upon the nature and ionic radii of the constituent ions [34]. The tetrahedral radius (A-site) can be calculated using the values of lattice constant ‘a’ and oxygen positional parameter ‘u’ (u =0.381Å). Table 5.6 gives the values of tetrahedral radius r\(_A\). The value of ‘r\(_A\)’ slightly increases with increase in Gd\(^{3+}\) content x ≥ 0.04 and thereafter decrease in tetrahedral radius is attributed to increases in Gadolinium content into Ni-Cu-Zn ferrite.

**Octahedral radius**

The octahedral radius ‘r\(_B\)’ of all the samples was calculated using the values of lattice constant ‘a’ and oxygen parameter ‘u’. Octahedral
radius ‘r_B’ found to increase in between concentration of x=0.00-0.04 and thereafter decrease attribute to Gd^{3+} content x. The values of octahedral radius for each sample were found to be greater than tetrahedral radius are given in Table 5.6. The cations of higher ionic radii like Fe^{3+} (0.67Å) and Gd^{3+} (0.938Å) prefer to occupy octahedral B site. The increase in tetrahedral and octahedral radius is due to the doping of Gadolinium content in place of ferric ions in Ni-Cu-Zn ferrite.

**Fourier Transform Infrared Spectroscopy**

The Fourier Transform Infrared (FTIR) Spectroscopy spectra as shown in Figure 5.8 (a, b and c) were recorded at room temperature in the frequency range 400 cm\(^{-1}\) to 1000 cm\(^{-1}\). The study of infrared absorption spectrum is an important tool to get information about the positions of the ions in the crystal through the crystal’s vibrational modes. The absorption bands are in the expected range which confirms the formation of the spinel structure. In spinel ferrites, it is observed from Figure 5.8 (a, b and c) and Table 5.7 that, there are two main frequency bands, namely, high frequency band (\(\nu_1\)) is observed at 585–590 cm\(^{-1}\) whereas the lower frequency band (\(\nu_2\)) is observed at 411-462cm\(^{-1}\). The third vibrational frequency band (\(\nu_3\)), is observed in the range of 464–493 cm\(^{-1}\), is associated with the divalent octahedral metal ion and oxygen complexes [35, 36]. The higher frequency band \(\nu_1\) is nearly constant for all investigated compositions. The lower frequency band \(\nu_2\) slightly shifted to higher frequency side and broadening of the spectral band is also observed with increasing Gadolinium content. The broadening of the spectral band and shift in \(\nu_2\) to higher frequency side be attributed to the occupancy of Gadolinium ions on octahedral (B) sites due to its higher atomic weight and larger ionic radius than iron.
ions which affect Fe$^{3+}$-O$^{2-}$ distances on B-sites. Similar observations were reported by elsewhere [6, 37]

The force constant is the second derivative of the potential energy with respect to the site radius with the other independent parameters kept constant. The force constant for tetrahedral site ($K_t$) and octahedral site ($K_o$) were calculated employing the method suggested by Waldron [38]. According to Waldron the force constant $K_t$ and $K_o$ for respective sites are given by relation [39]. The values of force constants $K_t$ and $K_o$ are listed in Table 5.7.

**5.3.2: Magnetic properties**

The magnetic properties of Gd$^{3+}$ substituted Ni-Cu-Zn spinel ferrite were studied using pulse field hysteresis loop technique method. The hysteresis curve recorded at room temperature for all the samples were shown in Figure 5.9, Using the M-H plot the saturation magnetization (Ms), coercivity (Hc), remenence ratio (Mr/Ms) were obtained as a function of Gd$^{3+}$ content ‘x’ and their values are given in Table 5.8. It can be seen from Figure 5.10 that the saturation magnetization decreases with Gd$^{3+}$ content ‘x’. The magnetic moment of rare earth ions generally originate from localized 4f electrons. Magnetic moment of Gd$^{3+}$ ions is 7.94 µB, and Gd$^{3+}$ is the only rare-earth element that the Curie temperature $T_c$ (293.2 K) is close to room temperature [40] their magnetic dipolar orientation exhibits disordered form at room temperature. Hence, it may be reasonable that Gd$^{3+}$ ions are considered as non-magnetic ions, and make no contribution to the magnetization of doped ferrite at room temperature. Furthermore, the deformity of the spinel lattice produces due to Gd$^{3+}$ substitution for Fe$^{3+}$, nonlinear antiferromagnetic coupling between A and B sub-lattice increases and
the magnetic dilution of secondary phase (GdFeO$_3$) becomes stronger with Gd$^{3+}$ content, consequently, saturation magnetization of samples decreases. Similar result reported in literature [23, 41-43].

The coercivity values of the Gd$^{3+}$-doped samples are lower than that of pure Ni$_{0.25}$Cu$_{0.2}$Zn$_{0.55}$Fe$_2$O$_4$ ferrite. It is seen that the coercivity decreases in the Gd$^{3+}$ content $x = 0.00 - 0.06$, then increases up to $x = 0.08$, and thereafter decreases. The coercivity is influenced by factors such as magneto-crystallinity, microstrain, magnetic particle morphology, size distribution and domain size.

The magnetic moment per formula unit ($n_B$) was calculated from Neel’s sub-two lattice model. The magnetic moment in ferrite is mainly due to the uncompensated electron spin of the individual ions and the spin alignments in the two sub-lattices, which are arranged in an antiparallel fashion. In a spinel ferrite, each ion at the A site has 12 B-site ions as nearest neighbors. According to Neel’s molecular-field model [44], the A-B super-exchange interaction predominates the intra sublattice A-A and B-B interactions. Therefore, the net magnetic moment is given by the sum of the magnetic moments of the A and B sub-lattices. The magnetic moment per formula unit ($n_B$) was calculated from Neel’s sub-two-lattice model using the relation,

$$n_B (\text{cal.}) = M_B(x) - M_A(x)$$

where, $M_B$ and $M_A$ are the B and A sub-lattice magnetic moments in B. The $n_B$ cal.(B) values were calculated using cation distribution (Table 5.8) and ionic magnetic moment of Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Gd$^{3+}$ and Fe$^{3+}$. The observed magnetic moment $n_B$ (Obs.) per formula unit in the Bohr magneton ($\mu_B$) was calculated using a relation [45],

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[146]
It is obvious from Figure 5.11 that the observed values of the magneton number decreases with the increase in Gd$^{3+}$ content x. In the present ferrite system the Fe$^{3+}$ ions of 5µ$_B$ ions are replaced by Gd$^{3+}$ of 7.94 µ$_B$ ions, leading to a decrease in the B-site sub-lattice magnetization. This placement leads to a decrease of the magnetic moment of the A and B site and thus the magneton number $n_B$ decreases with Gd$^{3+}$ substitution x. The values of observed magnetic moment listed in Table 5.8. Remenant magnetization Mr is observed that pure ferrite 17.54emu/g and amount of Gd$^{3+}$ substituted in ferrite Mr is 0.86 then increases in Gd$^{3+}$ increases remenance magnetization up to 2.939 emu/g. it is observed from Table 5.8 also include the values of remenant magnetization (Mr), Coercivity (Hc), Remenance ratio (Mr/Ms).

5.3.3: A.C. Susceptibility

A.C. susceptibility primarily depends upon the magnetic ordering present in the compound which varies as a function of method of preparation, chemical composition. The variation of AC susceptibility as a function of temperature and composition x is studied in the present work. Thermal variation of A.C. susceptibility of all the samples is shown in Figure 5.12. All the samples exhibit ferrimagnetic behavior, which decreases as Gd$^{3+}$ content x increases. The plots of $\chi_T/\chi_{RT}$ are used to determine the Curie temperature (Tc) and the values are given in Table 5.9. It is clear from Table 5.9 that Curie temperature goes on decreasing with the addition of Gd$^{3+}$ content. Gadolinium is the only rare-earth element that the Curie temperature (293.2 K) is close to room temperature. Hence, it may be reasonable that Gd$^{3+}$ ions are considered as non-magnetic ions. The non-magnetic Gd$^{3+}$ ions are
replacing the Fe$^{3+}$ ions having magnetic moment of 5 $\mu_B$. Therefore, a decrease in the density of magnetic ions is observed and the magnetic moment of the sublattice is expected to decrease.

5.3.4: D.C. Resistivity

The temperature dependence of D.C. electrical resistivity of all the samples were carried out on disc shaped pellets of 10 mm diameter and about 3 mm thickness using two probe technique and in the temperature range 300K to 600K with step of 10 K. The electrical resistivity was estimated by measuring the resistance ‘R’ of the samples. Figure 5.13 shows the variation of resistivity log $\rho$ against with reciprocal of temperature (1000/T) for all the composition of the $\text{Ni}_{0.25}\text{Cu}_{0.2}\text{Zn}_{0.55}\text{Gd}_{x}\text{Fe}_{2-x}\text{O}_4$ (0.00-0.10 in the steps of 0.02) ferrite system. Resistivity decreases continuously with the increasing temperature, revealing the semiconducting nature of the prepared samples [46]. The plot is divided into two distinct regions corresponding to the ferrimagnetic and paramagnetic region. The slope is observed to change at a particular temperature and this temperature corresponds to the Curie temperature of the sample. Curie temperature decreases with increase Gd content x.

Curie temperature decreases with increase in Gd$^{3+}$ content x. The decrease in Curie temperature can be explained on the basis of magnetic linkages due to the doping of Gd$^{3+}$ ions. Curie temperature determined from A.C. susceptibility, Loria and D.C. electrical resistivity decreases with increase in Gadolinium concentration x and their values are tabulated in Table 5.9. Figure 5.14 shows different methods used in measurement of Curie temperature of samples goes on decreasing with
the addition of Gd$^{3+}$ content $x$. From Table 5.9 value good agreement each other.

**Activation Energy**

The activation energies were calculated from the slope of Arrhenius plot and are plotted in Figure 5.15. It has been noted that the activation energy and the electrical resistivity show similar behavior with composition. The sample with higher resistivity has higher values of activation energy and vice versa [47]. Since the resistivity has been found to increases with Gadolinium concentration, a rise in activation energies with Gadolinium content is expected. The higher values of activation energy at higher Gadolinium concentration show the strong blocking of the conduction mechanism between ferrous and ferric ions due to the presence of Gadolinium ions at B-site. A possible reason for the increases behavior of activation energy can be attributed to the increases in lattice constant. In ferrites, the interionic distance increases with the increases in the values of lattice constant. This gradual increases in inter ionic enhances the barrier encountered by the charge carriers. The result as a function of Gd$^{3+}$ content $x$ is listed in Table 5.10.

**Room Temperature Resistivity**

The room temperature D.C. resistivity of Ni$_{0.25}$Cu$_{0.20}$Zn$_{0.55}$Fe$_{2-x}$Gd$_x$O$_4$ was measured by two probe method. The results as a function of Gd$^{3+}$ content are listed in Table 5.10. It is observed that the room temperature resistivity increases with increase of Gd$^{3+}$ content from $0.124 \times 10^6 \, \Omega\text{cm}$ to $9.68 \times 10^6 \, \Omega\text{cm}$, this behavior is attributed to the field effect. Owing to large ionic radius of Gd$^{3+}$ (0.938Å) as compared to
Fe\(^{3+}\) (0.67Å), it has been reported that Gd\(^{3+}\) ions occupy octahedral sites [43]. The concentration of Fe\(^{3+}\) ions gradually decreases at B-site when Gd\(^{3+}\) is substituted in place of iron. The hopping rate of electron transfer will decrease with the decrease of Fe\(^{3+}\) ions concentration. As a result, it enhances the D.C. resistivity increase with the increase of Gd\(^{3+}\) content x. The Fe\(^{2+}\) an ion concentration is a characteristic property of a given material and it depends upon the several factors namely amount of substituent, sintering temperature, atmosphere, time and grain size etc. [48]. Another possible reason for increase in resistivity on increasing Gd\(^{3+}\) is due the fact that the occupation of Gd\(^{3+}\) ions at B-sites will increase the separation between Fe\(^{3+}\) and Fe\(^{2+}\) ions in proportion to its ionic radius which is consistent with the variation of lattice constant vs. Gd\(^{3+}\) content. Since the hopping of electrons between ferrous and ferric ions is restricted hence both resistivity and activation energy increases. These results are consistent with the results reported by various authors [46, 49]. Possible conduction mechanism in the present samples may be due to hopping of electrons from present samples may hole transfer from Fe\(^{2+}\) to Fe\(^{3+}\) and hole transfer from Ni\(^{3+}\) to Ni\(^{2+}\) ions.[50,51]:

\[
\begin{align*}
\text{Fe}^{2+} & \leftrightarrow \text{Fe}^{3+} + e^- \\
\text{Ni}^{3+} + e^- & \leftrightarrow \text{Ni}^{2+}
\end{align*}
\]

Combining the above two equations,

\[
\text{Ni}^{2+} + \text{Fe}^{3+} \leftrightarrow \text{Ni}^{3+} + \text{Fe}^{2+}
\]
5.3.5: Dielectric properties

Compositional dependent dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$)

The variation of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) determined at the frequency in kilohertz at room temperature are shown in Figure 5.16 (a, b) respectively. Both ($\varepsilon'$) and ($\varepsilon''$) decreases with the increase of Gadolinium concentration as the mechanism for the electrical conduction is similar to that of the dielectric polarization. It was observed that the electronic conduction is similar to that of the dielectric polarization. It was observed that electronic exchange between

$$\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$$

results in local displacements, determining the polarization of the ferrite. Thus, it is the number of ferrous ions on octahedral sites that play a dominant role in the processes of conduction as well as dielectric polarization. Due to its larger ionic radius, Gd$^{3+}$ ions will prefer to occupy octahedral sites [43]. The concentration of Fe$^{3+}$ ions at B-sites decreases gradually with increasing concentration of Gd$^{3+}$. The reduction in the values of dielectric constant and complex dielectric constant with increasing concentration of Gd$^{3+}$ is due to depicting concentration of iron ions at B-sites which play a dominate role in dielectric polarization. The electron transfer between Fe$^{2+}$ and Fe$^{3+}$ ions

$$(\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} + \text{e}^-)$$

hindered the hopping process and hence polarization decreased. Consequently, both dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) decrease with increasing Gd$^{3+}$ contents $x$. 
**Frequency dependent dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$)**

The Figure 5.17(a, b) shows the variation of the dielectric constant and dielectric loss as a function of frequency range from 100 Hz to 1 MHz at room temperature for all the samples. It is clear from the Figure 5.17 that both dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) show dispersion with frequency. Table 5.11 observed that all values of ($\varepsilon'$) and ($\varepsilon''$) are high at low frequency and then decreases rapidly with increase in frequency for all the composition. Ultimately, it attains a constant value which is the general trend for all the ferrite samples [4]. This general behavior depicts the dispersion due to the Maxwell-Wagner type interfacial polarization, in agreement with Koop's phenomenological theory. The phenomenon of electron exchange between Fe$^{2+}$ and Fe$^{3+}$ ions gives local displacement of electrons in the direction of an applied electric field, which subsequently determines the polarization. The polarization decreases substantially with increase in frequency and reaches a constant value due to the fact beyond a certain frequency of external field, the electron exchange between Fe$^{2+}$ and Fe$^{3+}$ ions cannot follow the alternating field. Moreover, the higher values of dielectric constant observed at lower frequencies are due to the predominance of species like Fe$^{2+}$ ions, due to which interfacial dislocation piles-up oxygen vacancies and grain boundary defects etc. The decrease in both ($\varepsilon'$) and ($\varepsilon''$) with frequency is due to the fact that any lagging behind in the applied field at higher frequencies [53-55].

**Dielectric loss tangent**

The variation of dielectric loss tangent ($\tan\delta$) vs. frequency is shown in Figure 5.17 It is clear from the figure that $\tan\delta$ decreases with
increases Gd$^{3+}$ concentration. This can be attributed to the increases in resistivity which causes reduction in tanδ [55].

When the frequency of the applied ac electric field is much smaller than hopping frequency of electrons between Fe$^{2+}$ and Fe$^{3+}$ ions at adjacent octahedral sites, the electron follow the field and hence the loss is maximums. At higher frequency of the applied electric field, the hopping frequency of the electron exchange between Fe$^{2+}$ and Fe$^{3+}$ ions cannot follow the applied field beyond certain critical frequency and the loss is minimum [52]. At low frequency, tanδ is high and decreases rapidly at high frequency. The values are shown in Table 5.11. Ferrites consist of well conducting grain boundaries while thin insulated grain boundaries are more effective at low frequency, however well conducting grain boundaries are more effective at the high frequency region. Hence, it is expected that energy loss is high at the low frequency region while it is low at the high frequency region. Therefore tanδ is high in the low frequency region because more energy is required for the hopping process of charge carriers, whereas it is low in the high frequency region because little energy is required for the hopping process of charge carriers in this region [53, 54].
The Ni$_{0.25}$Cu$_{0.20}$Zn$_{0.55}$Fe$_{2-x}$Gd$_x$O$_4$ (x= 0.00 - 0.10 in steps of 0.02) spinel ferrite system have been synthesized successfully using slandered ceramic method. The conclusion is summarized given follows:

- The XRD analysis showed that all Gd$^{3+}$ substituted ferrite had major spinel phase and a single spinel phase was obtained in the range of x=0.00-0.04. An additional (secondary phase) peak was also observed in the XRD data which belongs to GdFeO$_3$ (gadolinium iron oxide) phase from x = 0.06 - 0.10, the addition of Gd$^{3+}$ ions to the system leads to a better applicable ferrites with high resistivity.

- The lattice parameter of Gd$^{3+}$ substituted samples were larger than those of pure Ni-Cu-Zn ferrite and increases with the Gd$^{3+}$ content x=0.00-0.004 and then decreases up to x=0.10, because of the formation of the secondary phase.

- The X-ray density and bulk density increases with Gd content increase in Ni-Cu-Zn spinel ferrites; however, decreasing trend in porosity was attributed to the substitution of Gd$^{3+}$ thereby making all samples denser.

- The particle size decreases with increase of Gd$^{3+}$ content due to hindrance of grain boundary mobility.

- XRD analysis cation distribution of present system which suggest that the Fe$^{3+}$ ion occupies tetrahedral (A) and octahedral [B] sites. Gd$^{3+}$, Ni$^{2+}$ and Cu$^{2+}$ ions showed a strong preference for the occupied only octahedral [B] site, whereas Zn$^{2+}$ ions occupy tetrahedral A-site.

- FTIR spectra show that the substitution of Gd$^{3+}$ ions broadened the v$_2$ band and also shifts the band suggested the occupation of Gd$^{3+}$ ions on octahedral B-site.
The saturation magnetization and the observed magneton number decreases with increase of Gd$^{3+}$ content of Ni-Cu-Zn spinel ferrite.

Coercivity lower as camper to pure Ni-Cu-Zn ferrite, Low coercive field suggest that these ferrites can be used in magnetic shielding devices.

The Curie temperature determined from different method are finely agree with each other.

The variation of dc resistivity with temperature confirms semiconducting nature of the sample. It is observed that the samples having high resistivity have activation energy and vice versa.

The activation energy in paramagnetic region is more than that of ferrimagnetic region. The variation of DC resistivity with temperature shows change in conduction behavior at Curie temperature.

The room temperature resistivity increases with increases Gd$^{3+}$ content, dependent resistivity for all samples Arrhenius equation.

The dielectric constant, dielectric loss and dielectric loss tangent decreases with the increase of Gd doped Ni-Cu-Zn Ferrites.

The decreases in dielectric constant and increase resistivity is required for high frequency application

The experimental results obtained are of interest for the research and growth of compositionally modified soft ferrites for multilayer chip inductor application.