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Gadolinium Substitutions Induced Changes in the Magnetic Properties and Dielectric Behavior of Zinc–Magnesium Ferrite Nanoparticles

Deepak Kumar Urmaliya[1]*, Dr. Satish Kumar[2]

[1] Research Scholar, Shri Krishna University, Chhatarpur M.P.

[2] Professor, Shri Krishna University, Chhatarpur M.P.

Abstract - This study examines the structural, magnetic, electrical, and dielectric characteristics of rare earth-doped nanocrystalline gadolinium were introduced to the spinel lattice and the characteristics changed. Comparing sol-gel and co-precipitation-prepared nanocrystalline nickel ferrite's application properties. Magnetic qualities were analyzed by Vibrating Sample Magnetometry (VSM), while electrical and dielectric properties were evaluated using Keithley electrometer and Impedance analyzer. Terbium and gadolinium substitutions expand unit cells, whereas samarium doping decreases nickel ferrite nanoparticle lattice parameter. Gadolinium and samarium doping reduce nickel ferrite particle size, whereas terbium doping increases it.

Keywords - Gadolinium Substitutions, Magnetic Properties, Dielectric Behavior, Zinc–Magnesium Ferrite, Nanoparticles.

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INTRODUCTION

According to reports, nanoferrite characteristics may be modified by adding divalent or trivalent metal ions in precise amounts. Material scientists have studied the properties of mixed ferrites extensively in recent decades. They were able to modify and optimize mixed ferrites. Modern research focuses on trivalent rare earth doped ferrites [1]. Tb3+ ion doping nanocrystalline nickel ferrite induces structural changes and enhances electrical and magnetic properties. Few papers describe rare earth doped nano ferrites. Samarium-substituted Mg-Zn ferrite's dielectric properties and AC conductivity, Nd3+ in zinc ferrite enhances DC resistivity and decreases dielectric loss. Gd3+ doped magnesium ferrite possesses electrical and dielectric properties [2]. The influence of Yttrium doping on ceramically manufactured nickel ferrite. The substitution improved NiFe2O4's structural and transport properties [3]. Minor doping with Gd and Nd ions increases nickel ferrite's dielectric constant and magnetic capacitance.

Recently, structural and optical properties of dysprosium-doped nickel ferrite thin films were characterised. Dy3+ substitution resulted in a wider energy gap, which increased density, grain size, lattice constant, and lattice strain. Auto-combustion-generated gadolinium-doped NiFe2O4 has improved magnetic permeability and decreased magnetic loss. It's crucial to study Gd3+ doped NiFe2O4 nanoparticles systematically [4][5]. The impact of Gd3+ doping on NiFe2O4 nanoparticles and the sol-gel fabrication of NiGdxFe2-xO4.

RESEARCH METHODOLOGY

Material science research requires the synthesis of materials as well as their accurate and detailed characterization. The design of nonmaterial's for diverse applications may be achieved by the use of appropriate preparation procedures and correct investigation of characteristics utilizing various characterization techniques [6]. As a result, a full explanation of the numerous experimental approaches used to prepare and characterization nanoferrite samples is provided. For the characterization and evaluation of properties, various analytical tools such as X-Ray Diffraction (XRD) [7], Fourier Transform Infrared spectroscopy (FTIR), Energy Dispersive X-ray Spectroscopy (EDX), Wavelength Dispersive X-Ray Fluorescence spectroscopy (WD-XRF), Transmission Electron Microscope (TEM), Vibrating Sample Magnetometer (VSM), Impedance analyzer, and Keithley electrometer was used. [8]

NiGdxFe2-xO4 (x=0, 0.1, 0.2, and 0.3) samples were synthesized using the sol-gel method. AR-grade Ferric, Nickel, and Gadolinium nitrate were used with 99.9% pure MERK. The powder was finely milled before being sintered at 400°C for two hours [9]. The samples were compressed at 5 tonnes in a hydraulic press to form 10mm-diameter, 2-3mmthick pellets for DC resistivity and dielectric measurements. [10]

Results and discussion

Structural properties

NiGdxFe2-xO4 (x=0, 0.1, 0.2, 0.3) ferrite X-ray diffraction patterns. All patterns show diffraction peaks compatible with a polycrystalline cubic spine structure, and none show impurity peaks [5]. The d-spacing data determines each composition's lattice constants. Equations can calculate a sample's X-ray density, apparent density, and porosity. Table 1 lists the average lattice constant (a), X-ray density (x), apparent density (a), and porosity of the studied samples, with grain sizes corrected for micro strain.

Table 1: Structural parameters of $NiGd_xFe_{2-x}O_4$ ferrite system

Composition (x)	Lattice parameter a (Å)	Crystallite size (nm)	X-ray density (g/cm^3)	Apparent density (g/cm^3)	Porosity(%)
0.0	8.332	18.1±1.2	5.382	3.039	43.53
0.1	8.342	17.2±1.3	5.595	2.790	50.13
0.2	8.331	15.2±0.8	5.850	2.836	51.52
0.3	8.303	13.6±1.1	6.145	3.822	54.07

The table clearly shows that when gadolinium concentration rises, grain size falls. There have been other reports with similar findings. The mobility of grain boundaries is a known to be a crucial factor in the development of grains. The segregation of Gd3+ on or near the grain borders impedes its migration, and this may be a cause of the shrinking grains [6]. Starting at x=0.1, the lattice constant (a) is shown to grow, and then it falls as the gadolinium concentration increases. Due to Gd3higher +'s ionic radius than Fe3(0.0625nm), +'s increasing gadolinium concentration will raise the lattice constant (0.067nm). Gd3+ ions will occupy the octahedral (B) sites, producing internal stress that will deform the lattice and increase the unit cell size [7]. The LiNi0.5GdxFe2xO4 lattice parameter decreases when x > 0.04. This is due to secondary phase lattice compression (GdFeO3). Since our samples are single-phase, this isn't a problem. Higher concentrations of Gd3+ ions may shift Ni2+ ions from octahedral to tetrahedral locations, reducing the lattice constant when x > 0.1. Lattice constant is not exclusively determined by ionic radii. Precise information of the shape and surface structure of the particles, as well as any surface energy [8], is needed to calculate many more parameters, such as the long-range attractive Coulomb force, bond length, etc.

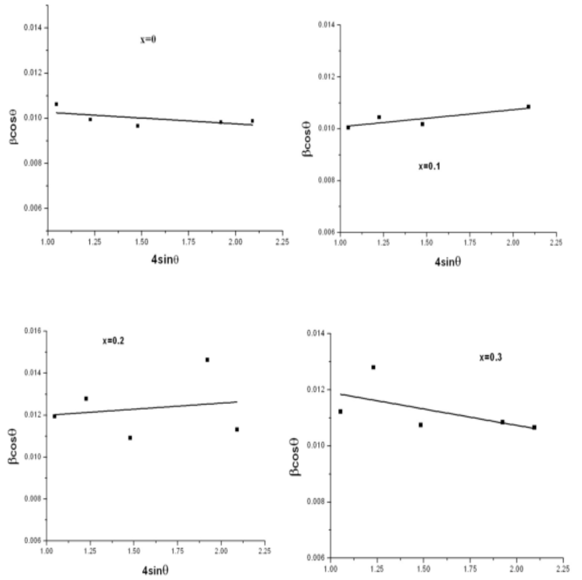

Figure 1: Hall-Williamson plots of gadolinium doped nickel ferrite samples

FTIR analysis

The FTIR spectra of the “NiGdxFe2-xO4 (x= 0, 0.1, 0.2, and 0.3)” ferrite system. Spinel development in ferrite samples may be verified with the use of FTIR analysis. Known IR spectra of ferrites should show two significant absorption bands between 1000 and 300cm-1. Stretching vibrations of the tetrahedral (A) metal-oxygen connection produces the higher frequency band (V1) to be visible between 600 and 550cm-1. The octahedral (B) site vibrations of metal and oxygen cause the lower one (V2), which occurs between 450 and 385 cm-1. The bond lengths and cation types mostly determine the locations of these bands. Band locations acquired for the materials under study are listed in table 2, and they fall within the range previously reported for nickel ferrite.

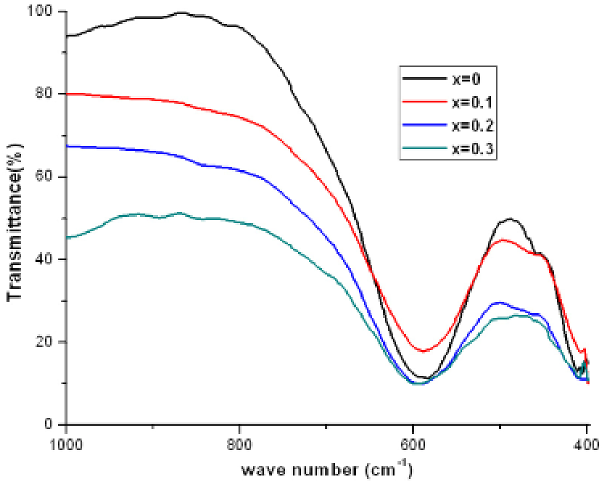

Figure 2: Infrared spectra of $NiGd_xFe_{2-x}O_4$ ferrites

Table 2: Magnetic parameters and vibrational frequency band positions of $NiGd_xFe_{2-x}O_4$system

Composition(x)	M_S (emu/g)	M_R (emu/g)	H_C (Oe)	V_1 (cm^{-1})	V_2 (cm^{-1})
0.0	31.44	3.25	86.87	587.15	410.9
0.1	20.22	13.56	444.84	588.8	407.3
0.2	17.90	6.46	470.90	592.5	409.0
0.3	15.98	13.06	462.30	596.1	410.0

Based on the data in the table, it is clear that for gadolinium doping up to x = 0.1, the frequency band location V1 remains almost same, whereas V2 decreases. It's common knowledge that a larger site radius lowers the fundamental frequency; hence the centre frequency should go down as the radius increases. With the smaller Fe3+ ions being swapped out for the larger Gd3+ ions, an expansion of the octahedral site radius is predicted. It has been found that as the doping concentration is raised, V1 rises while V2 stays the same. When the concentration of dopants, x, is greater than 0.1, it has been observed that the lattice constant decreases. As a result, there is an increase in the positions of vibration frequency bands at smaller sites.

Magnetic Characterization

The magnetic hysteresis curves for NiGdxFe2-xO4 samples at room temperature. The magnetic characteristics MS, HC, and MR. Gadolinium doping affects the magnetic characteristics of nanocrystalline NiFe2O4. Gadolinium boosted terbium-doped nickel ferrite MS values. Gd3+ ions will likely replace Fe3+ ions in octahedral (B) positions due to their large ionic radius. At room temperature, nonmagnetic rare earth metal ions don't contribute to doped ferrite's magnetism. Gd3+ ions in B-sites reduce B sub-lattice magnetization, weakening A-B interactions and lowering MS. Gd3+ doping may increase porosity and decrease particle size, causing MS to drop with increasing gadolinium concentration. Magnetization is inversely proportional to nanoferrite porosity and directly proportional to particle size.

The sample with x = 0.1 shows a significant rise in coercivity, followed by a gradual slowing of the rate of growth and, ultimately, a nearly constant HC. NiFe2O4 lost its soft magnetic nature by gadolinium doping. Micro strain, particle shape and size distribution, anisotropy, porosity, and magnetic domain size have all been linked to changes in the coercivity of ferrite nanoparticles. Doping the NiGdxFe2-xO4 system increases the porosity and reduces the particle size, both of which contribute to the material's higher coercivity. Another possible cause is strain in the nanoparticles brought on by the addition of Gd3+. High value of coercivity together with moderately high magnetization and remanence is desirable for ferrites which are used in magnetic recording and memory devices. The NiFe2O4 nanoparticles may be made acceptable for such applications with just a little amount of gadolinium doping (x = 0.1).

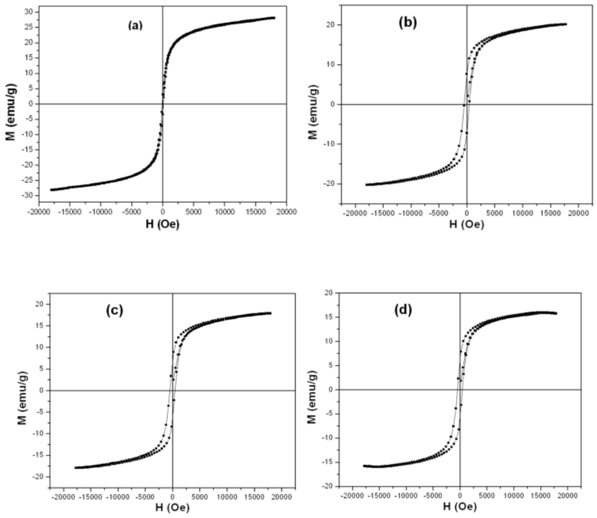

Figure 3: NiGdxFe2-xO4 ferrite nanoparticles at room temperature (a) = 0, (b) = 0.1, (c) = 0.2, and (d) = 0.3

Electrical Properties

DC resistivity

Absolute temperature against the reciprocal of the temperature in gadolinium-doped NiFe2O4, In terms of dc resistivity fluctuation, it is quite close to terbium doped nickel ferrite. Similarly to terbium doped samples, gadolinium doped nickel ferrite showed an increase in resistivity with increasing temperature in the 300-330K range. All the samples became semiconducting above 330K, as expected for ferrite. The resistivity of the samples is shown to rise naturally when gadolinium content rises. The increase in resistivity from 24.2Mcm at ambient temperature to 60.5Mcm by substituting 15% gadolinium is not very noticeable, but the increase to 125Mcm at 330K is rather noticeable. The activation energy is found to rise from 0.487eV (for x=0.3) to 0.593eV (for x=0.3) when gadolinium is substituted. Charge carrier drift mobility and the hopping conduction mechanism explain ferrites' temperature and composition-dependent resistivity. Another possible explanation for the higher resistivity is that gadolinium doping has increased porosity and reduced particle size in the samples. In high frequency applications, ferrite with a high resistivity is preferred because it results in less eddy current loss.

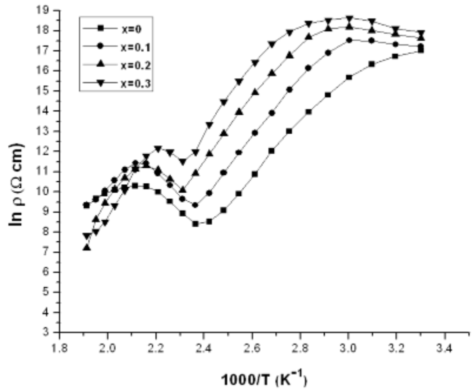

Figure 4: the relation between dc resistivity and absolute temperature for Ni-Gd system

Dielectric Constant

From 100Hz to 20MHz, all of the samples' dielectric constants are shown in Figure 5 as a function of frequency at ambient temperature. Normal dielectric behaviour was seen in all of the formulations. Dielectric constant values are highest at low frequencies, dropping off precipitously as the frequency rises, and levelling out at constant values; this is a universal property of ferrites. Electric conduction and dielectric polarisation have a same process, as is well known from studying ferrites. Local electron displacement in the direction of an applied electric field results in dielectric polarisation due to electron hopping between Fe2+ and Fe3+ ions on octahedral sites, which facilitates electrical conduction. Koop's phenomenological theory, which interprets the ferrite's dielectric structure as a Maxwell-Wagner heterogeneous medium, explains its dielectric dispersion.

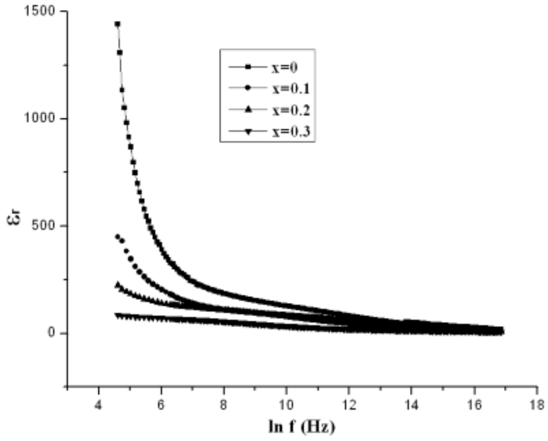

Figure 5: Variation of dielectric constant with frequency

Dielectric constant frequency-temperature dependence for x = 0.1 sample. All compositions behave similarly. The dielectric constant drops between 300 and 340K, then rises with a peak at 430K.

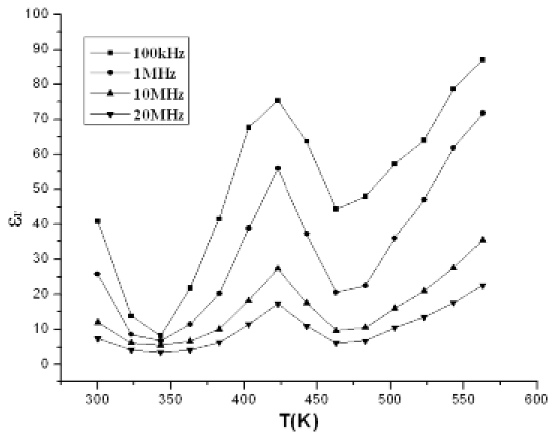

Figure 6: Variation of dielectric constant with temperature at selected frequencies for $NiGd_{0.1}Fe_{1.9}O_4$ sample

Due to rare earth ion scattering, the dielectric constant decreases. Pure nickel ferrite lacks this effect. Because charge carriers can wander more as temperature rises, hopping rate and dielectric constant rise. It's well known that ferrites' dielectric constant is directly related to their resistivity. The temperature dependence of the dielectric constant is opposite to the DC resistivity, as shown in the study. Low nickel ionisation potential may explain the 430K transition, as we saw in the last chapter.

Figure 6 shows that the dielectric constant of NiFe2O4 has decreased as a consequence of gadolinium doping. When stable valence ions like Gd3+ replace Fe3+ in the octahedral sites, the hopping rate drops and the dielectric constant drops with composition. The decline is most pronounced at low levels of doping, and its pace decreases with increasing doping concentration.

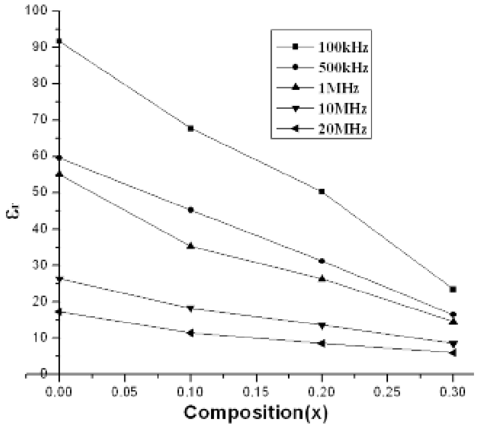

Figure 7: Variation of dielectric constant with composition at different frequencies

Dielectric loss (ε”)

The dielectric loss (shown by ε”) at room temperature, as a function of frequency, Figure 8 shows gadolinium-doped nickel ferrite samples. All mixes are dielectric. Low frequencies reduce dielectric loss. As frequency increases, rate of reduction decreases, and “becomes frequency independent. Koop's phenomenological theory describes such behavior. Low-frequency electron hopping requires more energy due to weakly conducting grain boundaries. High-frequency conductivity in grains reduces hopping energy. Gadolinium concentration increases resistivity, which reduces dielectric loss. Yttrium-doped nickel ferrite and gadolinium-doped magnesium ferrite show similar results.

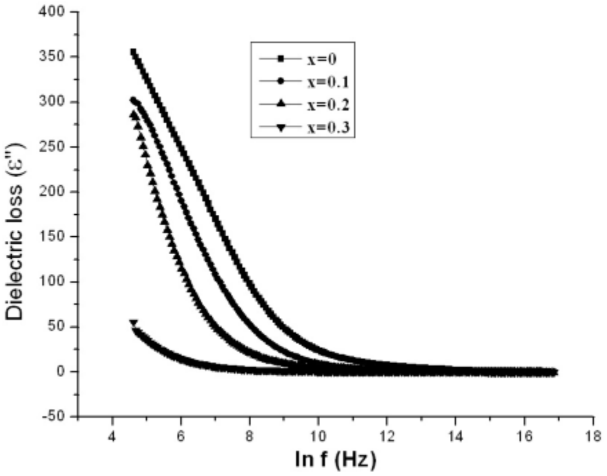

Figure 8: ε” versus ln *f* graphs of $NiGd_xFe_{2-x}O_4$ ferrite system

AC Conductivity

AC conductivities of all the compositions are computed from the dielectric values. Figure 9 shows each sample's room-temperature AC conductivity frequency dependence. Frequency increases AC conductivity. Maxwell-two-layer Wagner's model of polycrystalline ferrites describes AC conductivity frequency dependence. Grain boundaries are more active and, as a result of their high resistance, conductivity is lower in the low frequency range. Similar outcomes are reported. Conductive grains become active in the high frequency range, leading to increased conductivity in this area. Almost linear character of the AC conductivity maps indicates the conduction owing to minor polaron hopping in the examined gadolinium doped nickel ferrite samples.

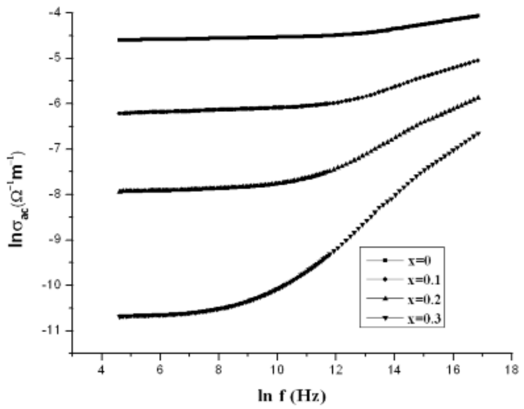

Figure 9: Plots showing frequency dependence of AC conductivity of$NiGd_xFe_{2-x}O_4$ ferrite system

Figure 9 shows how the AC conductivity of the sample with x = 0.1 varies with the absolute temperature for a range of frequencies. All samples behave similarly. Since ferrites' dielectric constant is proportional to conductivity's square root, their variations make sense. According to the equation, conductivity depends on frequency more at low temperatures and less at high temperatures. High-temperature conductivity was less pronounced, and low-temperature dispersion was observed. Lower temperatures reduce charge carrier drift mobility. This means that as the temperature rises, the hopping frequency rises as well, leading to a rapid increase in mobility and, consequently, conductivity.

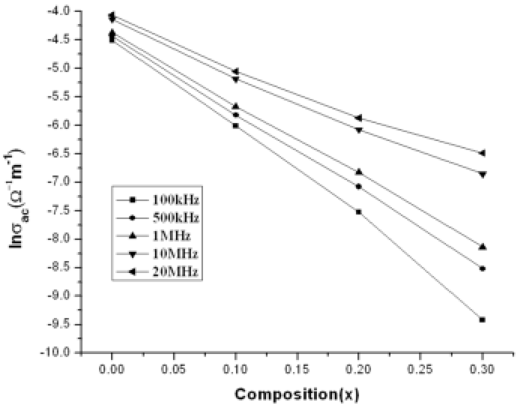

Figure 10: Variation of AC conductivity with gadoliniumcontent for $NiGd_xFe_{2-x}O_4$ system

In the high temperature zone, massive lattice vibrations are caused by enormous amounts of thermal energy, and it is predicted that the dispersion of charge carriers owing to their collisions with the vibrating lattice would reduce mobility and make conductivity less temperature dependent. Increasing gadolinium doping concentration results in decreasing conductivity. This is to be expected, since the hopping conduction is suppressed when Gd3+ ions replace Fe3+ ions on the octahedral sites. Decrease rates are found to be proportional to gadolinium concentration.

CONCLUSION

Sol-gel technique integrates gadolinium ions into NiFe2O4 without disturbing spinel structure or introducing impurity phase. Gadolinium added to nickel ferrite changes its structure and improves its electrical and magnetic characteristics. Gadolinium causes Ni-Gd ferrite grain size to decrease. Lattice parameter increases with gadolinium content because to Gd3large +'s ionic radius, however this effect is mitigated at greater doping concentrations. Gadolinium increases X-ray density and porosity. Gadolinium substantially changed nickel ferrite nanoparticles' magnetic characteristics. Gadolinium increases decrease saturation magnetization. Doping degraded the soft magnetic characteristics of nickel ferrite. High coercivity, mild magnetism, and remanence make Ni-Gd ferrites ideal for magnetic recording and memory systems. The linearity of AC conductivity vs frequency graphs showed tiny polaron type hopping conduction in the Ni-Gd ferrite system. Gadolinium doping reduces nickel ferrite nanoparticle dielectric loss.

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Corresponding Author

Deepak Kumar Urmaliya*

Research Scholar, Shri Krishna University, Chhatarpur M.P.