

CHAPTER 6

A. Conclusions & Future Suggestions

In the present investigation, the selected composition of nickel zinc ferrite is processed by sol-gel method using chelating agents PEG, PVA and subjected to various heat treatments and characterized. The PVA sample showed lower values of crystallite size, particle size and a bit higher values of saturation magnetization for all of the heat treatments as compared to that processed with PEG.

In the process of achieving good end ferrite product, there should be a compromise in the selection of composition, method of preparation, chelating agent, kind and amount of impurity, heat treatment and so on. There is no hard and fast rule that a particular method with a particular chelating agent would turn a particular composition into a useful end product. One should workout various permutations and combinations to process a good material useful for different applications.

Copper substituted nickel zinc ferrites processed with PVA as chelating agent provided good properties as compared to that processed with PEG. The PVA samples exhibit smaller grain size, high initial permeability and quality factors. With increasing of copper content, specific saturation magnetization is slightly decreased and initial permeability increased considerably maintaining the crystallite, particle and grain sizes in nanoregion. The contributions from reduced magnetization, increased permeability and the significant change in grain size favored the critical frequency shift to lower side. This happened because the dc resistivity variation with copper concentration is not high. If the resistivity is changed by 3 or 4 orders in magnitude, the material certainly turns into a wonderful end product, for which the investigation may be continued in future by some researchers.

The processed copper substituted nickel zinc ferrite with high initial permeability is greatly achieved along with fine grains which are primary requirements for the MLCI applications. The processed Ni-Cu-Zn nanoferrite samples exhibited a bit higher saturation magnetization values as compared to similar compositions processed by many others [8]. The

particles are also observed to be small in the processed Ni-Cu-Zn ferrite samples. In our attempt to study the microstructural changes using high resolution SEM the grains/particles are observed to take different shapes (1 D nanoflowers) observed in the micrographs of FESEM. The values of resistivity (10^6 Ohm-cm) are also improved due to the presence of smaller grains.

The attempt to attain fine grains and high initial permeability by altering the chelating agent (PVA) is rightly carried out but the obtained values of resistivities have not been appreciable. Further enhancement in resistivity is possible with proper impurities. Hence it is suggested that not only a good method of preparation in processing nanoferrite, but also the selection of appropriate substitution is highly required so as to meet high frequency for MLCI applications.

To have a comprehensive picture of the copper substituted nickel zinc ferrite processed using PEG, PVA tables 6.1 and 6.2 are given below

Table 6.1 Comparison of the properties of the present studies and the reported.

Ni-Zn ferrite	Crystallite size (nm)	Particle size (nm)	Grain size	M_s (emu/gm)	μ_i	$\rho \times 10^6$ (Ω -cm)
Bulk (reported)	43 [7]		14.5 μ m [6]	73 [1]	100 [2]	10^4 [1]
Nano (reported)	55 [3]		700 nm [4]	29.54 [3]	273 [5]	10^9 [3]
Present (PEG)	70 .2	140 nm	380 nm	71.5	322	3.3
Present (PVA)	22.4	150 nm	209 nm	74.3	125	0.3

Table 6.2 The properties of copper substituted Ni-Zn ferrite processed using (a) PEG, (b) PVA.

Concentration (x)	Crystallite size (nm)		Particle size (nm)		Grain size (nm)		M _s (emu/gm)		μ _i		ρ x 10 ⁶ (Ω-cm)	
	a	b	a	b	a	b	a	b	a	b	a	b
	0.06	40.9	21.2	345	354	420	362	70.9	71	194	160	7.4
0.12	46.9	23.7	488	222	540	337	72	69	318	950	13.7	6.32
0.18	33.6	26.7	500	181	2340	338	69.8	68	2046	2079	19	12.1
0.24	46.9	23.7	511	95	2300	213	69.2	67	1404	2107	15	34.8
0.30	88.1	23.8	538	56	2270	151	69.3	66	1361	2623	1.4	55.5

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1. **“Cation distribution from Fe⁵⁷ infield Mossbauer study of Ni-Cu-Zn nano ferrite”**
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2. **“Magnetic Properties of Ni_{0.65-x}Cd_xZn_{0.35}Fe₂O₄”**
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3. **“Influence of Chelating agent (PVA & PEG) on the Microstructure and Magnetization of Ni-Zn nanoferrites”**
G S V R K Choudary, *P Prameela*, K H Rao, communicated to *Bulletin of Material Science*.
4. **“Contribution to analysis of Co/Cu Substituted Ni-Zn ferrites”**
G S V R K Choudary, *P Prameela*, K H Rao, Communicated to *Bulletin of Material Science*.
5. **“Influence of gadolinium on Magnetization and DC resistivity of Ni-Zn nanoferrites”**
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G S V R K Choudary, *P.Prameela*, M Chaitanya Varma, A.Mahesh Kumar, K.H Rao

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3. **“Analysis of effect of cobalt on The Structural and Magnetic Properties of Ni-Zn Nano Ferrite”**

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Magnetic Properties of $\text{Ni}_{0.65-x}\text{Cd}_x\text{Zn}_{0.35}\text{Fe}_2\text{O}_4$ **P. Prameela^{a*}, P. Appa Rao^b and KH Rao^c**^a*Department of Physics, Dr.Lankapalli Bullayya College, Visakhapatnam, India*^b*Department of Physics, Dadi Institute of Engineering & Technology, Anakapalli, India*^c*Department of Physics, RGUKT, IIIT-Nuzvid, India***Corresponding Author's Email: pra_phd@yahoo.co.in*

Abstract: Ni-Cd-Zn ferrites have been processed through conventional ceramic method. The diamagnetic contribution of cadmium has been investigated by substituting it in place of nickel. Observed variations in saturation magnetization, Curie temperature and initial permeability of the ferrites have been explained on the basis of superexchange interactions among tetra and octahedral sites of spinel lattice and by considering the anisotropy dependent parameters.

Key Words: Spinel structure, superexchange.

Introduction: The fields of application of Ni-Zn bulk ferrites in electronic components for high frequency devices are continuously increasing. The limiting frequency of operation of these ferrites is found to be 100 MHz. Still there is a need to shift its frequency of operation to be applicable up to microwave frequencies for which an improvement in saturation magnetization and dc resistivity is inevitable. Selection of proper impurity, optimization of processing conditions and control over grain size are the necessary parameters in order to improve saturation magnetization and resistivity which in turn enhance the frequency of operation. Improvement in resistivity is possible by controlling grain growth and such small grains would provide more grain boundary area, act as barrier for electron flow. Enhancement in saturation magnetization can be expected by substituting a suitable diamagnetic or paramagnetic impurity occupying tetrahedral site and a ferromagnetic impurity having preference for octahedral site of the spinel lattice. Though a little

quantity of impurity can remarkably influence the electrical and magnetic properties of ferrites, the kind of dopant and its concentration in ferrite system could be decided by the nature of applications intended to design.

An improvement in saturation magnetization is noticed [1] in $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ till $x = 0.5$ with increasing zinc concentration in the spinel lattice. However, an appreciable value of initial permeability is not seen particularly at this composition. A compromise between these two parameters is considerably observed for $\text{Ni}_{0.65}\text{Zn}_{0.35}\text{Fe}_2\text{O}_4$. Suitable diamagnetic impurity having preference for tetrahedral sites similar to zinc is needed to enhance magnetization and initial permeability together. None other than cadmium ions tend to occupy tetrahedral sites due to its electronic configuration with free 5s5p orbitals and able to form covalent bonds with oxygen ions. Hence cadmium ions have been substituted in place of nickel ions in $\text{Ni}_{0.65-x}\text{Cd}_x\text{Zn}_{0.35}\text{Fe}_2\text{O}_4$ exactly till $x = 0.2$ so as to pronounce the diamagnetic content left with $x = 0.5$ without disturbing zinc concentration as described above.

Experimental details: Samples having the general composition $\text{Ni}_{0.65-x}\text{Cd}_x\text{Zn}_{0.35}\text{Fe}_2\text{O}_4$ (x varies from 0.00 to 0.20 in steps of 0.04) were processed through conventional ceramic method. The starting materials were analytical reagent grade nickel, zinc, cadmium and iron oxides. Suitable proportions of these oxides were thoroughly

ground in the presence of acetone into fine homogeneous powder. The resulting mixture was calcined in air for 4 h at 950°C and was further ground for another 2 h to obtain in the form of pellets by adding a small quantity of 15 % polyvinyl alcohol as binder. The pellets were sintered in air for 2 h at 1250°C and subsequently cooled to room temperature. In order to remove any oxide layer formed on the surface of the pellets, necessary grinding of the surface of the pellets was done. The observed single phase structure in basic Ni-Zn ferrite from X-ray diffraction pattern confirmed the procedure adopted for the processing of the series was correct one. X-ray diffraction patterns of all the samples were recorded using Rigaku Miniflex X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). Saturation magnetization for all the samples was measured using Ponderometer method [2]. Curie temperature was determined using Soohoo method [3]. Inductance values were measured using HP4192A LF Impedance analyzer at the small voltage of 1mV at a frequency of 1 kHz, from which the initial permeability was calculated

with the equation
$$\mu_i = \frac{L}{L_0}$$

where $L_0 = 0.4606 N^2 h \log\left(\frac{OD}{ID}\right) \mu H$ [4] is the air core inductance and N is the number of turns.

Results and Discussion: Figure 1 gives the X-ray diffraction patterns of Ni-Cd-Zn ferrites indicating the spinel structure. Accurate estimation of lattice constant is done from X-ray diffraction patterns of Ni-Cd-Zn ferrites using Nelson-Riley function [5], provided the lattice constant for the basic Ni-Zn ferrite as 8.3830 Å which is in agreement with that of the reported [6]. Gradual increase in lattice constant is observed with increasing cadmium concentration (fig.2) following Vegard’s law [7]. Increase in lattice constant is attributed to larger ionic radius of Cd²⁺ ion (0.84 Å) [8] compared to

Ni²⁺ ions (0.69 Å) which suggests the entry of cadmium into the spinel lattice throughout the series by distorting the lattice. As cadmium ions are replacing nickel ions, one can expect the occupancy of cadmium towards octahedral site which is the usual preferential site for nickel in bulk Ni-Zn ferrites. As it is reported [9] that cadmium ions prefers to occupy tetrahedral sites, the vacancy created by the removal of nickel by cadmium ions at octahedral site will be filled by the migration of iron ions from tetrahedral to octahedral sites and hence resulting in increased lattice constant.

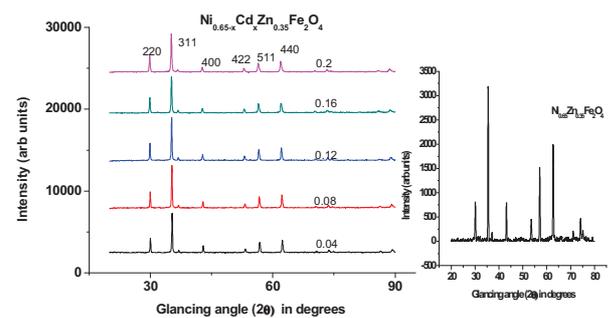
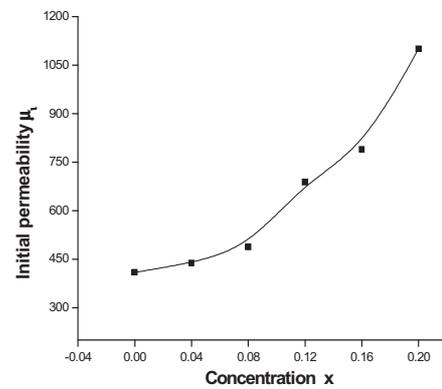
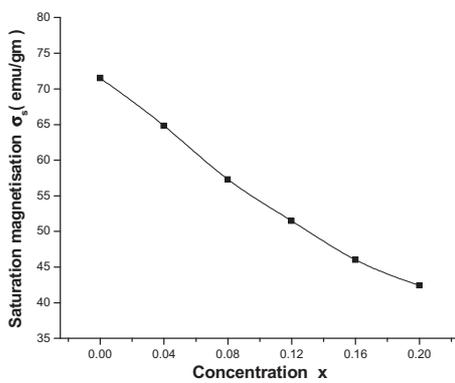
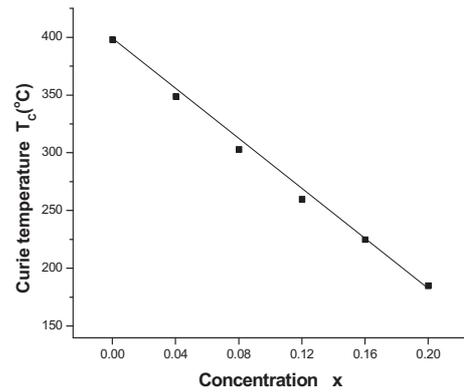
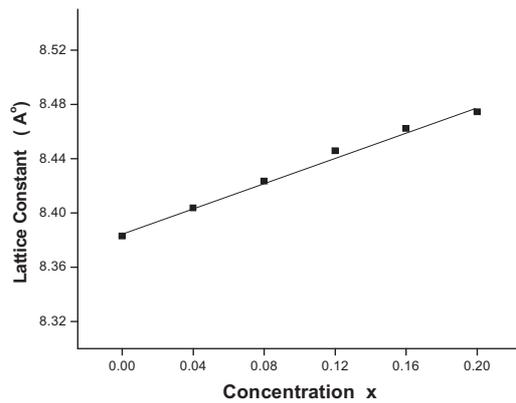


Figure 1: X-ray diffraction patterns of $Ni_{0.65-x}Cd_xZn_{0.35}Fe_2O_4$

Figure 3 shows a systematic linear decrease in room temperature specific saturation magnetization with increasing cadmium concentration, reaching a minimum value of 42 emu/g. The observed decrease in saturation magnetization can be explained on the basis of site occupancy of cadmium ions which in turn modify the exchange interactions between both tetrahedral and octahedral sites of the ferrite lattice. Occupancy of cadmium towards tetrahedral sites results in migration of iron ions from A-site to B-site thereby improving B-sublattice magnetic moment.



Figures 2&3: Lattice constant and Saturation magnetization of $Ni_{0.65-x}Cd_xZn_{0.35}Fe_2O_4$

Figures 4&5: Curie temperature and initial permeability of $Ni_{0.65-x}Cd_xZn_{0.35}Fe_2O_4$

Diamagnetic contribution of cadmium ions thus decreases A-site magnetic moment and consequently the difference between the magnetic moments of A and B sublattices, $M = M_B - M_A$, increases with increasing cadmium content. Contrary to this, the observed magnetization decreases which can be attributed to reduction of A-B exchange interaction due to diamagnetic cadmium and development of B-B interaction due to migration of iron ions. This modification in exchange interactions could tend to decrease the saturation magnetization by the addition of cadmium. Therefore a lesser amount of thermal energy is needed to offset the effect of exchange interactions and the same is reflected through Curie temperature measurements (fig.4).

An appreciable increase in the room temperature initial permeability and a gradual decrease in magnetic loss have been noticed throughout the cadmium concentration studied (fig 5). The value of initial permeability for the basic Ni-Zn composition found to be 430 which is in close agreement with that of the reported [10, 11]. The increase in initial permeability is attributed to increase in grain size with increasing cadmium content through the relation $\mu_i \propto D^{1/3}$. In addition to this, initial permeability of ferrites intimately depend on anisotropy constant according to the relation $\mu_i \propto M_s^2 / K_1^{1/2}$. Substitution of cadmium replacing nickel would reduce the small negative anisotropy contribution of Ni^{2+} ions thereby causing an increase in the initial permeability. Increase in grain size would cause increase in

density and contain more number of domain walls exhibiting no hindrance to the domain wall motion.

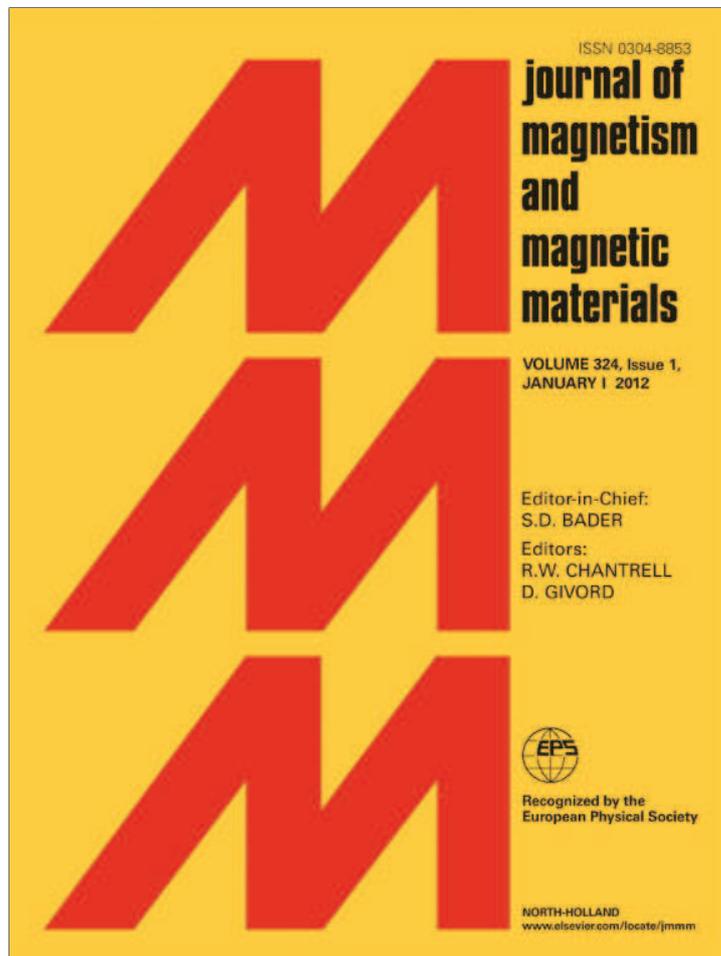
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Conclusion: Spinel structure of ferrites has been confirmed in Ni-Cd-Zn ferrites. They exhibited a linear decrease in saturation magnetization and Curie temperature which is attributed to the diamagnetic nature of cadmium. A gradual increase in initial permeability was noticed which might be due to the increased grain size and lowered anisotropy constant of the ferrite throughout the series.

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Influence of gadolinium on magnetization and DC resistivity of Ni–Zn nanoferrites

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ABSTRACT

The study of gadolinium substitution in small amounts on the saturation magnetization and DC resistivity of nickel–zinc nanoferrite has led to the understanding of the degree of formation of a secondary orthoferrite GdFeO_3 phase, the generation of cationic and oxygen vacancies and the dilution of gadolinium in the lattice. The role of secondary phase in modifying the electromagnetic properties has been stressed by making further investigations on the Curie temperature and the activation energies.

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1. Introduction

Research on nanoparticles has opened an avenue for various potential applications due to their novel properties. Efforts are being continued in bringing out good quality of magnetic cores suitable for ultra-high frequency (microwave) applications. The critical frequency of operation of a ferrite core, in general, is proportional to square of saturation magnetization and DC resistivity and inversely proportional to grain size and initial permeability [1]. An extensive investigation on bulk mixed ferrite systems reveals that Ni–Zn ferrite with high saturation magnetization (73 emu/g) coupled with high resistivity ($10^6 \Omega \text{ cm}$) is a suitable core up to 100 MHz. Selection of proper impurity dopant, optimization of processing conditions and control over the grain size are necessary to improve the saturation magnetization, DC resistivity and hence the frequency of operation. Saturation magnetization can be improved by substituting either a suitable diamagnetic or paramagnetic impurity occupying tetrahedral sites or a ferromagnetic impurity having preference for octahedral sites of the spinel lattice. Improvement in resistivity is possible by synthesizing the material in the form of nanoparticles with innumerable grain boundaries [2] and with the elimination of intragranular domain walls.

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The magnetic properties of ferrites are governed [3] by super-exchange interactions among the cations in the spinel lattice. By introducing rare-earth (RE^{3+}) ions into ferrite lattice, the $\text{RE}^{3+}-\text{Fe}^{3+}$ interactions also appear besides 3d–4f coupling, which could lead to small changes in the magnetization and the Curie temperature. It is well known that the rare-earth ions play a vital role in determining the anisotropy of 4f–3d intermetallic compounds [4]. The $\text{RE}^{3+}-\text{RE}^{3+}$ interactions are very weak as compared to $\text{RE}^{3+}-\text{Fe}^{3+}$ interactions since they mainly arise from the indirect 4f–5d to 5d–4f mechanism [3]. Possibility of $\text{Ni}^{2+}-\text{RE}^{3+}$ interactions can never be ignored if B–B interactions can prevail. Out of the available rare-earths ions, gadolinium and samarium exhibit higher magnetic moments relative to others and the electrical resistivity is found [5] to increase for all the rare-earth ion substitutions barring samarium. Enhancement of saturation magnetization and DC resistivity through the knowledge of exchange interactions has been described in the current investigation as an extension of our earlier study [6] by substituting ferromagnetic gadolinium in place of iron in $\text{Ni}_{0.65}\text{Zn}_{0.35}\text{Fe}_2\text{O}_4$.

2. Experimental details

Ferrites having the general composition $\text{Ni}_{0.65}\text{Zn}_{0.35}\text{Fe}_{2-x}\text{Gd}_x\text{O}_4$ (x varies from 0.00 to 0.20 in steps of 0.04 or 0.00 to 5 mol % in steps of 1 mol %) were processed through the sol–gel synthesis described elsewhere [6]. Powder X-ray diffraction analysis of all the ferrites has been done using a calibrated Philips (PW-3710) X-ray diffractometer coupled with PW-1800 software

using Cu K α ($\lambda=1.5406 \text{ \AA}$) radiation. Vibration sample magnetometer 115 PAR-EG&G model has been used to carry out room temperature saturation magnetization measurements. Curie temperature measurement has been performed by the Soohoo method [7]. DC resistivity was estimated using the two-probe method by measuring current accurately with the help of a Keithley electrometer 614. Temperature dependence of DC resistivity was studied for all the ferrite samples at temperatures below the Curie temperature of respective compositions.

3. Results and discussion

3.1. Lattice constant

X-ray diffraction signatures correspond to the formation of Ni–Zn ferrite, exhibiting the spinel structure besides additional peaks ($2\theta=32.95^\circ$ and 47.5°) as shown in Fig. 1. A gradual increase in the intensity of the additional peaks is noticed with increasing gadolinium concentration and the peaks are identified to be corresponding to GdFeO $_3$ (orthoferrite phase). Accurate estimation of lattice constant from X-ray diffraction patterns is done using the Nelson–Riley function [8] and for the basic Ni–Zn ferrite (8.3738 \AA), it is in agreement with that reported [9]. An increase in lattice constant is noted from 8.3738 \AA to 8.3904 \AA for 1 mol% of gadolinium beyond which the increase is insignificant (Fig. 2). This suggests the entry of gadolinium in minute quantities into the spinel lattice. The observed slight increase in lattice constant is attributed to larger ionic radius of gadolinium ion (0.91 \AA) [10] compared to that of Fe $^{3+}$ ion (0.65 \AA). Though little quantity of gadolinium enters into the lattice initially, the rest of the content produces GdFeO $_3$ second phase. While the amount of gadolinium entering into the lattice remains fixed, the iron content decreases gradually with increasing gadolinium concentration (as indicated in formulae of compositions). The depleted iron content promotes the lattice shrinkage, which might be a cause for the observed insignificant variation in lattice constant beyond 1 mol%. Such a slight lattice shrinkage in the case of gadolinium substituted Ni–Zn ferrites has been reported [3] earlier.

The formation of orthoferrite secondary phase suggests that only some of the nickel, zinc, iron and gadolinium oxides are expected to participate in producing stoichiometric Ni–Zn–Gd ferrite. If this is true, the unreacted oxides should exist to some extent either independently or in the form of their compounds like Gd $_2$ O $_3$, Fe $_2$ O $_3$ and GdFeO $_3$ as extra phases. If the extra phase present in

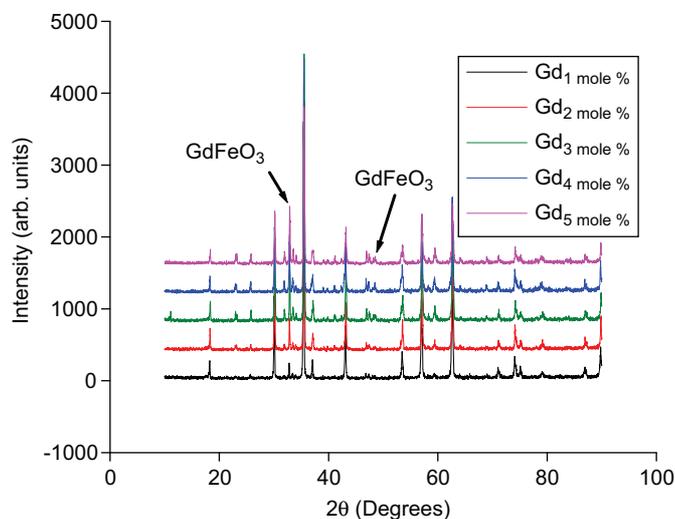


Fig. 1. X-ray diffraction patterns of Ni $_{0.65}$ Zn $_{0.35}$ Fe $_{2-x}$ Gd $_x$ O $_4$ ($x=0.00$ –5 mol%).

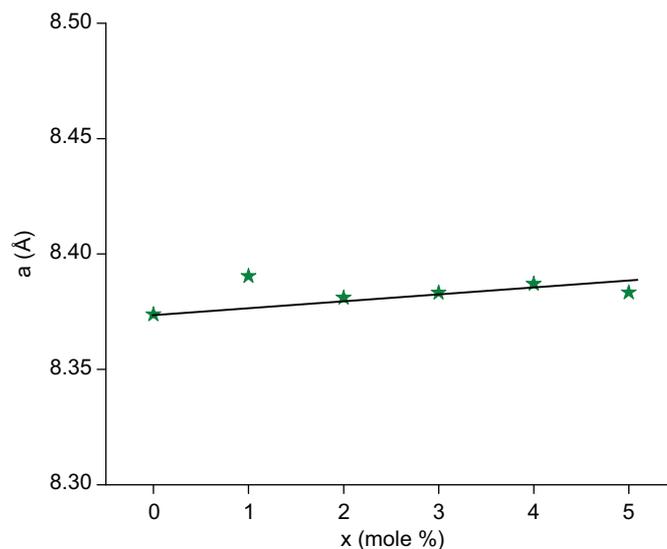


Fig. 2. Lattice constant as a function of concentration of gadolinium.

the compound is more than 5 mol%, it is known to be reflected through X-ray diffraction measurements. No such information about the formation of additional oxide phases except GdFeO $_3$, however, has been noticed from the X-ray diffraction patterns.

3.2. Saturation magnetization and Curie temperature

Fig. 3(a) shows room temperature hysteresis loops with increasing gadolinium concentration. The specific saturation magnetization initially falls rapidly up to 2 mol% of gadolinium and decreases slightly at higher concentrations. The observed decrease in magnetization (Fig. 3(b)) can be understood on the basis of the Neel model [11] in which A–B exchange interaction in ferrites is stronger and more effective than B–B and A–A superexchange interactions and the net magnetic moment of the ferrite lattice as a whole is equal to the difference between the magnetic moments of A and B sublattices, i.e. $M=M_B-M_A$.

If ferromagnetic gadolinium (7 μ_B) has its preference for A sites only, an improvement in A site magnetic moment is expected as it replaces tetrahedral iron ion having less magnetic moment (5 μ_B). Thus the difference in the net magnetization, M_B-M_A , decreases with increasing gadolinium concentration and is reflected in magnetization measurements. As the available tetrahedral site radius ($\sim 0.4 \text{ \AA}$) is too small to accommodate large gadolinium ion (0.91 \AA), further examination in this regard is essential.

If ferromagnetic gadolinium prefers to occupy only B-sublattices, an increase in saturation magnetization is expected with the replacement of octahedral Fe $^{3+}$ ion. The gadolinium entry at B-sites at lower concentrations may be expected as the available octahedral site radius is in the order of the substituent ion. In such a case, the observed decrease in magnetization might be attributed to some factors other than the magnetic moments of the ions and the superexchange interactions among them. Continuous increase of non-magnetic GdFeO $_3$ phase with increasing gadolinium content might be a responsible factor for the observed decrease in the saturation magnetization. In case gadolinium ions enter both the A and B sites, a meager decrease in overall saturation magnetization should be noticed. Hence, the possible entry of gadolinium into both the sites is ruled out at lower concentrations of gadolinium as the decrease in net magnetization is rapid. Similar observations with rare-earth ion substitution in Ni–Zn ferrites have been reported earlier by Rezlescu et al. [12]. As an appreciable decrease in saturation magnetization (25 emu/g) is noticed with increasing gadolinium,

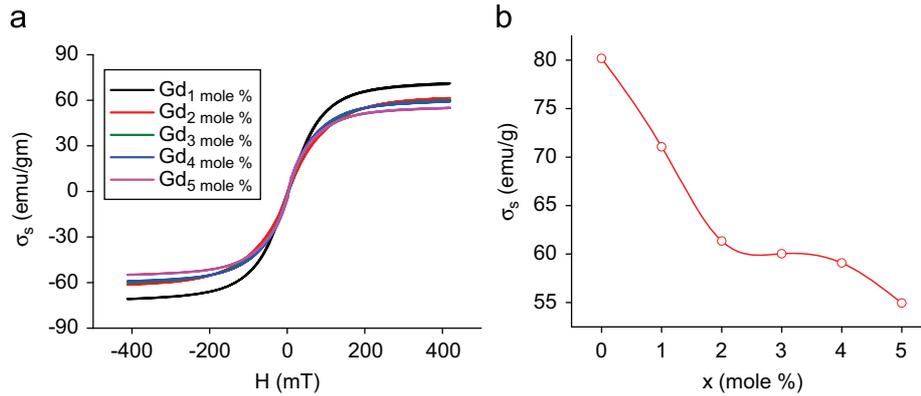


Fig. 3. (a) Room temperature hysteresis loops and (b) specific saturation magnetization of gadolinium substituted Ni-Zn ferrites.

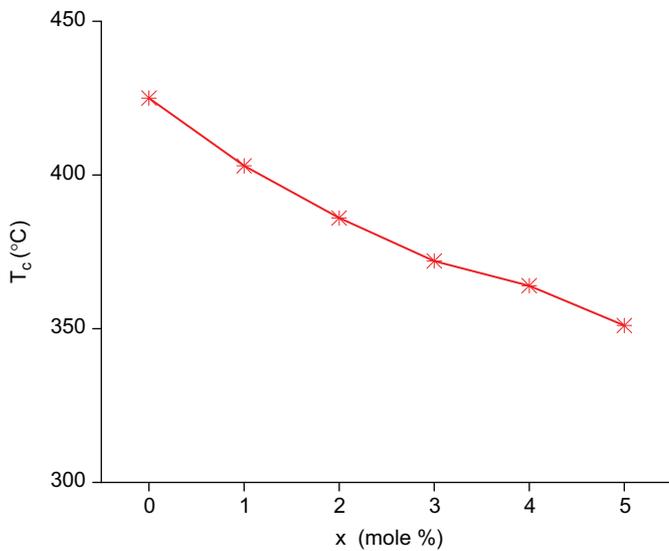


Fig. 4. Curie temperature variation with gadolinium concentration.

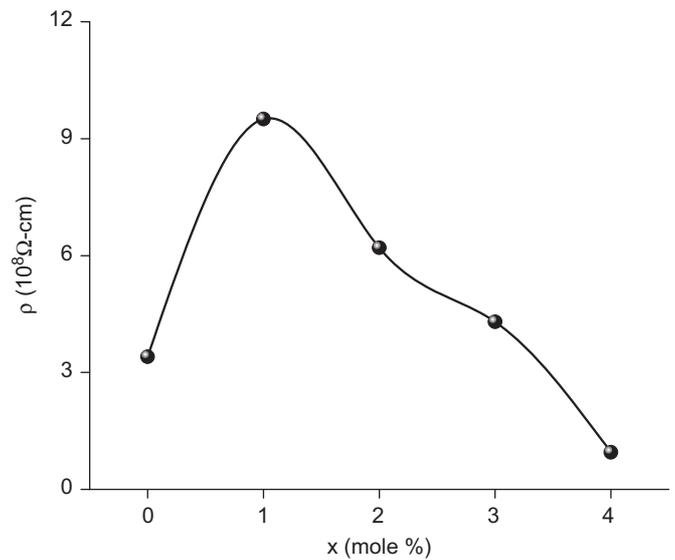


Fig. 5. Variation in resistivity as a function of concentration of gadolinium.

there is no question of B–B interactions among the cations in the ferrite lattice and the same has been evidenced from Curie temperature observations, where the decrease is not so rapid (75 °C).

If a fixed quantity of gadolinium enters into the lattice and segregation of more GdFeO_3 as a secondary phase is noticed with increasing gadolinium content, the observed gradual reduction in the Curie temperature (Fig. 4) might be a combination of both these contributions together. The decrease in Curie temperature in rare-earth substituted ferrites is due to weaker Fe–RE interactions than Fe–Fe interaction when Fe^{3+} ions are replaced by RE ions. However the observed decrease is not so rapid in the current study as RE concentration is low, indicating that the Fe–Fe interactions still exist and play a predominant role in understanding the magnetic mechanism [13] of the Ni–Zn ferrite system. Therefore a greater amount of thermal energy is needed to offset the effect of exchange interactions. If gadolinium ions tend to occupy A sites only, a rapid fall in the Curie temperature should be observed due to the large decrease in A site magnetic moment, M_A . As such the effect is not noticed, and entry of gadolinium at B sites is considered only in understanding the magnetic and electrical properties.

3.3. DC resistivity

A gradual decrease in room temperature DC resistivity is noticed on increasing gadolinium concentration except at 1 mol % (Fig. 5).

DC resistivity measurement has not been carried out at 5 mol % of gadolinium as cracks occurred repeatedly in the pellets during the heat treatment. Increase in electrical resistivity is expected in general when gadolinium ions replace iron ions at octahedral sites. Because of its large ionic radius (0.91 Å) compared to the ionic radius of iron (0.65 Å), entry of gadolinium into B sites increases the distance between the lattice sites and decreases the hopping probability at B-sites by blocking the conduction mechanism among $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ pairs. Formation of Fe^{2+} ions occurs due to volatilization of zinc at higher sintering temperatures (~ 1100 °C) [14] when heated in air atmosphere. The decrease in resistivity might be understood as due to the formation of secondary phase, GdFeO_3 along with the Ni–Zn ferrite.

Gd_2O_3 and Fe_2O_3 have to be reacted together in stoichiometric proportions to form GdFeO_3 . The formation of Gd_2O_3 decreases the amount of iron oxide required for the formation of stoichiometric gadolinium containing Ni–Zn ferrite. The deficiency of iron and oxygen leads to the creation of some vacancies in the material. In order to balance the total charge of the ferrite lattice, the electrons have to hop among the available Fe^{3+} and Fe^{2+} ions and holes have to hop from Ni^{3+} and Ni^{2+} [15]. It has been noticed from the X-ray diffraction measurements, segregation of GdFeO_3 phase increases with increasing concentration of gadolinium, which produces more number of vacancies in the material. A gradual reduction in Fe^{3+} ions decreases hopping among Fe^{3+} and Fe^{2+} ions and the hopping among the Ni^{3+} and Ni^{2+} ions

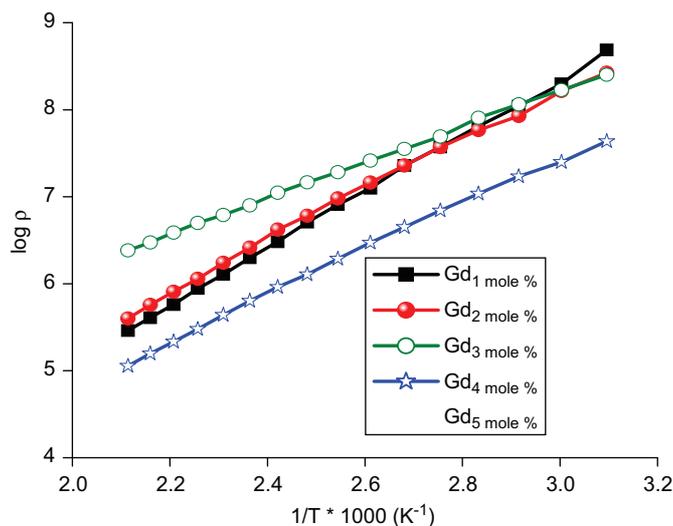


Fig. 6. Temperature dependence of resistivity of $\text{Ni}_{0.65}\text{Zn}_{0.35}\text{Fe}_{2-x}\text{Gd}_x\text{O}_4$ ($x=0.04-0.16$) for an applied field of 1 V/m.

Table 1
Activation energy values (in eV) of gadolinium substituted Ni–Zn ferrites.

x	0	0.04	0.08	0.12	0.16	0.20
E_A (eV)	0.50	0.64	0.57	0.43	0.52	–

still existing and thus leading to continuous decrease in the resistivity. The predominance of Ni^{3+} and Ni^{2+} hopping is evidenced from the activation energies of these ferrites (discussed later). The change in the oxygen content also influences the resistivity of the ferrite as cations at the tetrahedral sites are surrounded by four oxygen ions whereas at the octahedral sites by six neighboring oxygen ions.

Activation energies of Ni–Gd–Zn ferrites are determined from the slope of log of resistivity ($\log \rho$) against reciprocal of absolute temperature ($1/T$) plot (Fig. 6) and are presented in Table 1. The observed changes in activation energies are in accordance with the observed changes in the resistivity values of these ferrites. In general, in ferrites, the activation energy is decided by the hopping probability of electrons and holes among $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ and $\text{Ni}^{3+} \leftrightarrow \text{Ni}^{2+}$ pairs, respectively.

Activation energy required for conduction due to electron hopping in ferrites is found to be around 0.4 eV [16]. Still higher energies are needed for hole hopping as compared to that of electron hopping. The observed higher values of activation energies (> 0.4 eV) in the current study suggest that both the hopping

processes are responsible for electrical conduction. Similar inferences regarding the higher activation energies of nanoferrites have been reported [17–19] earlier.

4. Conclusions

The observed decrease in resistivity and magnetization of gadolinium substituted Ni–Zn ferrites have been elucidated on the basis of the formation of non-magnetic secondary phase GdFeO_3 (orthoferrite) besides spinel structure. The entry of gadolinium into B-sites has affected Fe–RE interactions by distorting the ferrite lattice and is evident from the large reduction in magnetization and appreciable variation in Curie temperature. The influence of GdFeO_3 phase in creating vacancies in the lattice hence promoting both electron and hole hopping. A support for this contention has been evidenced from the higher activation energies (> 0.4 eV) needed for electrical conduction. High magnetic moment ferromagnetic ions which strengthen A–B interactions and avoid secondary phase formation might be suitable substituent ions in improving the saturation magnetization of the Ni–Zn nanoferrite to the maximum possible extent.

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