Effect of Excess Iron Oxide on the Structural, Magnetic and Dielectric Properties of Neodymium Doped Ni-Zn Ferrites

Ratnaiah Kokkanda, N V Krishna Prasad, M.S.S.R.K.N.Sarma, G S V R K Choudary, K Srinivasa Rao

Abstract: Nd-doped Ni-Zn ferrites synthesized by solid state method exhibited extra orthoferrite and \( \alpha-Fe_2O_3 \) phases. The variation of lattice parameters and magnetic properties has been influenced by these extra phases other than spinel structure of Ni-Zn ferrite. Saturation magnetization and Curie temperature have been observed to decrease in with increasing Nd-concentration, but for \( Nd=0.02 \) a slight increase in initial permeability has been observed. These changes have been explained based on the amount of extra phases present and dilution of octahedral sites with Nd ions in place of Fe-ions.

Keywords: Ferrite, orthoferrite, lattice constant and magnetization.

I. INTRODUCTION

Ni-Zn ferrites are one of the versatile materials, which find applications in the fields of high-frequency inductor cores, EMI etc. They have high electrical resistivity in the order of \( 10^5 \) to \( 10^9 \) ohm-cm with moderate magnetization and permeability. These ferrites exhibit low eddy current losses due to high electrical resistivity and hence are used in a high frequency range. To further increase the permeability and magnetization rare earth are being doped in these systems since rare-earth ions have high magnetic moments. Also, incorporation of the rare earth ions may distort the lattice, cause heterogeneity in the structure and generates internal stresses. Another aspect that requires a severe investigation is regarding their site occupancy in spinel lattice. Rare-earth ions with less ionic radius are reported to diffuse into grain boundaries and form an isolating ultra-thin layer around grains. These modifications severely affect the properties of ferrites and demand a careful understanding of the system.

A careful investigation is required to ascertain the above facts, hence it is felt necessary to investigate the influence of neodymium addition on the site occupancy and segregation in Ni-Zn ferrite system.

The present paper provides a detailed explanation of the structural and magnetic properties of neodymium substituted Ni-Zn ferrites with the basic composition \( Ni_{0.65}Zn_{0.35}Fe_2O_4 \). The observed variations in lattice constant, saturation magnetization and coercivity are explained on the basis of iron oxide and orthoferrite additional phases present in samples.

II. EXPERIMENTAL DETAILS

A series of samples having the general composition \( Ni_{0.65}Zn_{0.35}Nd_{x}Fe_{2}O_{4} \) \( (x=0.00 \text{ to } 0.02) \) were prepared by the conventional ceramic method. High purity analytical grade NiO (99.9%), ZnO (99.5%), \( Fe_2O_3 \) (98.5%) and \( Nd_2O_3 \) (99.9%) were taken in nonstoichiometric ratio maintaining an excess of 10 to 15 % excess of iron oxide and crushed finely, mixed thoroughly and ground for 4 hours in acetone media using agate mortar and pestle. A homogeneous powder of this mixer was calcined at 900°C in the air for 2 hours followed by slow cooling. The presintered powder was again crushed and ground thoroughly for 2 hours in acetone media to reduce it to small crystallites of uniform size. The mixer was made into pellets and toroids using 15% polyvinyl alcohol as a binder with a uniaxial pressure of 5 tons/inch\(^2\) and 3 tons/inch\(^2\) respectively. The dimensions of pellets were 4 mm thickness and 3 mm in diameter and toroids having 13 mm inner diameter and 18 mm outer diameter. The pellets and toroids were then finally sintered at 1250°C in the air for 2 hours and cooled naturally. The surfaces of all the samples were polished to remove any oxide layer formed during sintering.

III. RESULTS AND DISCUSSION

The X-ray diffraction studies confirmed the spinel structure. The values of the lattice parameter obtained for each reflected plane are plotted against the Nelson-Riley function \[ F(\theta) = \frac{1}{2} \left( \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right) \] for each composition \( Nd \). The accurate value of lattice constant \( a_0 \) for each composition has been estimated from the extrapolation of these lines to \( F(\theta) = 0 \). The lattice constant \( a = 8.3840 \) Å measured from X-ray diffraction patterns found to be in good agreement with that of the reported [M. Chaitanya Varma et.al.,2012].

Revised Manuscript Received on February 2, 2020.

(*Corresponding author)

Ratnaiah Kokkanda, Department of Physics, GITAM School of Science, GITAM University, Bengaluru, India.

N V Krishna Prasad, Department of Physics, GITAM School of Science, GITAM University, Bengaluru, India. dmnvkprasad@gmail.com

M.S.S.R.K.N.Sarma, Department of Physics, GITAM School of Science, GITAM University, Bengaluru, India.

G S V R K Choudary, Department of Physics, Bhavan’s Vivekananda College, Sanikpuri, Secunderabad, India

K Srinivasa Rao, Department of Physics, PBN College, Nidubrolu, India.

Retrieved Number: D1151029420

DOI: 10.35940/ijitee.D1151.029420

129
Effect of Excess Iron Oxide on the Structural, Magnetic and Dielectric Properties of Neodymium Doped Ni-Zn Ferrites

Additional lines are noticed in all the neodymium containing samples and the intensity of the lines observed to be increasing with increasing impurity concentration and are shown in figure 1. The extra lines are identified as lines corresponding to NdFeO₃ second phase [C. Shivakumara, 2006]. Fig.1 shows the diffraction pattern of Ni₀.₆₅Zn₀.₃₅Fe₂-xNdₓO₄ (x=0.02, 0.04, 0.06, 0.08, 0.1) and their structural properties are presented in table 1. Figures 2a and 2b show Rietveld analysis show reasonable goodness of fit (GOF) for all measured samples, as shown in the Table 1. Additional peaks of α-Fe₂O₃[O.M. Lemine,2009] was found to be present due to iron oxide which as stoichiometric conscious introduced into ferrite system to accommodate the high ionic radii of Neodymium (Nd), even higher concentration, which is found to be futile. Rietveld refined XRD spectra are shown in figures 2a and 2b. Lattice parameters and phase contents are presented in Table 1.

Table I: XRD Analysis of Neodymium Doped Ni-Zn-ferrite

| Nd content (x) | Phases present | rwp % | vol % | wt % | cell par. (Å) a | cell par. (Å) b | cell par. (Å) c | Crystallite size (Å) | micro strain | 2 Theta (degrees) |
|---------------|----------------|-------|-------|------|----------------|----------------|----------------|-------------------|-------------|------------------|
| 0.00          | Ni-Zn          | 86.550| 85.711| 8.4135| 2082.766        | 1023.386        | 1.7356 e-5      | 1.4001 e-4        | 2 Theta (degrees) |
|               | Iron(III) Oxide| 13.449| 14.288| 5.4292| 2260.582        | 55.284          | 1.4098 e-4      | 9.2617 e-6        | 2Theta (degrees) |
| 0.02          | Ni-ZnNd1       | 4.000 | 82.000| 8.4158| 2026.847        | 55.305          | 1.0519 e-4      | 3.2412 e-6        | 2 Theta (degrees) |
|               | Iron(III) Oxide| 17.999| 17.854| 5.4284| 1000.120        | 4.2091          | 6.0 e-4         | 1.4001 e-4        | 2 Theta (degrees) |
| 0.04          | Ni-ZnNd2       | 4.713 | 75.563| 8.4164| 2026.847        | 55.293          | 6.0 e-4         | 3.2504 e-4        | 2 Theta (degrees) |
|               | NdFeO₃         | 3.0863| 3.9968| 5.5878| 1000.000        | 5.448           | 1.7356 e-5      | 1.4001 e-4        | 2 Theta (degrees) |
|               | Iron(III) Oxide| 21.350| 20.855| 5.4305| 1016.348        | 5.448           | 6.0 e-4         | 3.2504 e-4        | 2 Theta (degrees) |
| 0.06          | Ni-ZnNd3       | 4.299 | 80.239| 8.4147| 2283.188        | 55.311          | 5.411 e-4       | 1.7356 e-5        | 1.4001 e-4        | 2 Theta (degrees) |
|               | NdFeO₃         | 4.2092| 5.3917| 5.5878| 1000.000        | 5.448           | 6.0 e-4         | 3.2504 e-4        | 2 Theta (degrees) |
|               | Iron(III) Oxide| 15.531| 15.050| 5.4267| 1538.281        | 55.309          | 6.0 e-4         | 3.2504 e-4        | 2 Theta (degrees) |
| 0.08          | Ni-ZnNd8       | 4.167 | 74.590| 8.4155| 1983.952        | 55.309          | 7.479 e-6       | 1.4001 e-4        | 2 Theta (degrees) |
|               | NdFeO₃         | 7.6932| 9.7122| 5.5878| 1000.000        | 5.448           | 6.0 e-4         | 3.2504 e-4        | 2 Theta (degrees) |
|               | Iron(III) Oxide| 17.715| 16.887| 5.4278| 1000.017        | 55.309          | 6.0 e-4         | 3.2504 e-4        | 2 Theta (degrees) |
| 0.10          | Ni-ZnNd10      | 4.142 | 80.420| 8.4119| 3168.210        | 55.284          | 4.2091 e-6      | 3.7252 e-4        | 2 Theta (degrees) |
|               | NdFeO₃         | 8.8989| 11.087| 5.5845| 1000.000        | 5.452           | 6.0 e-4         | 3.7252 e-4        | 2 Theta (degrees) |
|               | Iron(III) Oxide| 10.681| 10.067| 5.4274| 1020.876        | 55.284          | 6.0 e-4         | 3.7252 e-4        | 2 Theta (degrees) |
Abnormality values observed in strain, crystallize size and weight percentages, as shown in the table suggests that uniform distribution of Nd in ferrite lattice is difficult to achieve and it is dependent on synthesis or sintering conditions. Non-uniform distribution of Nd can cause slight deformation in cubic spinel structure, higher particle size, localization near grain boundaries and occurrence of secondary phases such as α-Fe$_2$O$_3$ or REFeO$_3$ phase. This could dilute the net contribution to magnetic or dielectric properties which are dependent on distribution of ions in octahedral or tetrahedral sites or grain size.

A. Magnetic properties:

Fig.3 shows the hysteresis curves for Ni$_{0.65}$Zn$_{0.35}$Fe$_{2-x}$Nd$_x$O$_4$ (x = 0.02, 0.04, 0.06, 0.08, 0.1) and their magnetic properties such as Coercivity($H_c$), Remanence ($M_r$) and Saturation Magnetization($M_s$) are shown in Fig.3. Dilution of magnetic properties are expected for rare-earth doping may disturb the Fe$^{3+}$-Fe$^{3+}$ along with 3d-4f interaction [Yehia, M et.al., 2014], which can be seen from Fig.3. $M_s$ and $H_c$ show variform behaviour for Nd doping in Ni-Zn ferrites with maximal values obtained for x=0.10 and x=0.08. Remanence ($M_r$) showed improvement from x=0.04 indicating moderation in exchange interactions.
Effect of Excess Iron Oxide on the Structural, Magnetic and Dielectric Properties of Neodymium Doped Ni-Zn Ferrites

The extent of Nd doping not only causes changes in the magnetic moment but also changes in a cubic structure. It is expected that not all Nd may enter into ferrite lattice and some may reside at the grain boundaries. The presence of further α-Fe2O3 or REFeO3 phase can arise at grain boundaries at lower or higher concentrations of rare-earth-doped samples, hence it is expected to show some variance in magnetic properties. Since there is evidence of such a phase in current investigating samples, dilution of magnetic properties can be expected due to infinite effects, shown in our diffraction studies in the earlier section. It is interesting to observe that current samples show the NdFeO3 phase from a concentration of x=0.04 and the same point also reflects a mark of improvement in remanence or lowest state of Ms among the investigating samples. The initial decrease in saturation magnetization (figure 4) is due to dilution of octahedral sites by Nd3+ ions, whereas increase in saturation magnetization for higher content of Nd may be attributed to excess iron entering to spinel lattice. The variations of coercivity (figure 5) and remanent magnetization (figure 6) with increase in neodymium content can also be attributed to the above affects.

B. Curie Temperature:

Figure 7 shows permeability variation with temperature for Ni0.65Zn0.35Fe2-xNd_xO4 (x=0.0, 0.02, 0.04, 0.06, 0.08, 0.1). Permeability is found to be maximum for x=0.02 and showed versatile behavior for the rest of the samples investigated. It is found that Curie temperature shifted to a lower temperature side for measured samples, indicates the dilution of exchange interaction among Fe3+-O-Fe3+ ions in ferrite lattice as additional phases such as NdFeO3 phase or α-phase Fe2O3 is present, as observed from diffraction studies. Samples are found to be stable up to Curie temperature point, indicating the deformation in spinel structure rather than the presence of impurities.

IV. CONCLUSIONS

The Ni0.65Zn0.35Fe2-xNd_xO4 (x = 0.02, 0.04, 0.06, 0.08 & 0.1) were synthesized via the conventional solid state reaction method. The X-ray diffraction patterns indicated the formation of cubic spinel phases along with the secondary phases associated with the NdFeO3 and α-Fe2O3 phases. Furthermore, the primary and secondary phases were evidenced from the Rietveld refinement analysis of Ni0.65Zn0.35Fe2-xNd_xO4. The M-H curves of x = 0.1 content revealed the highest saturation magnetization (M_s) of 49.1 emu/g.
The maximum value of magnetic permeability of 42.5 was achieved for \( x = 0.02 \) composition. In addition, the magnetic permeability versus temperature plots of \( \text{Ni}_{0.65}\text{Zn}_{0.35}\text{Fe}_2\text{O}_4\) samples established the decreasing trend of magnetic Curie transition temperature from 382 to 330°C as a function of Nd-content from \( x = 0.0 \) – 0.1. This report concluded that the magnetic exchange interactions were decreased between tetrahedral (A) and octahedral (B) sites upon substituting the Nd-element.

**REFERENCES**

1. J B Nelson and D P Riley “An experimental investigation of extrapolation methods in the derivation of accurate unit-cell dimensions of crystals” Proc. Phys. Soc. 57 (1945) 160
2. M. Chaitanya Varma etal., “Effect of particle size on saturation magnetization and magnetic anisotropy of \( \text{Ni}_{0.65}\text{Zn}_{0.35}\text{Fe}_2\text{O}_4\) nanoparticles” International Journal of Nanosci 11 (2012) 1240003
3. C.Shivakumara “Low-temperature synthesis and characterization of rare earth orthoferrites LnFeO3 (Ln=La, Pr and Nd) from molten NaOH flux” Solid State Communications 139 (2006) 165–169
4. O.M. Lemine “Microstructural characterization of G-Fe2O3 nanoparticles using, XRD line profiles analysis, FE-SEM and FT-IR”Superlattices and Microstructures 45 (2009) 576-582
5. Yehia, M., Ismail, S.M. &Hashhash, A. “Structural and Magnetic Studies of Rare-Earth Substituted Nickel Ferrites” J Supercond Nov Magn 27 (2014) 771-774

**AUTHOR PROFILE**

**Kokkonda Rathnaihah** was born on 28-01-1973. He pursued graduation with Mathematics, Physics and Electronics as major Subjects in Arts and Science College, Subedari, Hanamkonda, Kakatiya University. Later he completed M.Sc. in Physics with Electronics as specialization from Osmania University in 1997.

He started his career as Lecturer in degree college affiliated to Kakatiya University. I am pursuing PhD on Ferrites under the supervision of Dr. N.V. Krishnaprasad, HoD, Dept of Physics, GITAM University, Bengaluru.

**N.V.Krishna Prasad** was born in Visakhapatnam, Andhra Pradesh, India on 14 September 1969. He received his Ph.D Degree in Physics from Andhra University, Visakhapatnam, India in 2004. From 1993 to 2001 he worked as a Lecturer in Electronics at G.V.P.Degree College, Visakhapatnam, India. Since 2001, he is working as Assistant Professor, Department of Physics, School of Physics, GITAM University, Visakhapatnam upto 2012. and presently working as Professor since 2012. His current area of research activities include Lower and Middle Atmospheric studies. He is a member of Indian Science Congress Association, Indian Physics Association and IETE.  
Tel: (+91) 8971199913  
E-mail: dmvkprasad@gmail.com

**MSSRKN Sarma** born in Visakhapatnam, India on 30th April 1978, received his PhD Degree from Department of Physics, Andhra University in 2009. He started his career as Assistant Professor in the Department of Physics, GITAM (Deemed to be University), Visakhapatnam campus just after awarding of doctorate and presently working in GITAM, Bengaluru campus. During his PhD, he constructed HF Doppler radar to study the E and F regions of ionosphere with an operating frequency of 5.5 MHz with digital data receiving system. Later his studies are extended to lower atmospheric dynamics like studying stratospheric ozone and air pollution of different cities over India using PM2.5 index.