Effect of Ni doping on optical, electrical and magnetic properties of Nd orthoferrite

Sajad Ahmad Mir¹, M Ikram¹ and K Asokan²
¹Solid State Laboratory, Department of Physics, National Institute of Technology, Srinagar, J&K-190006, India.
²Materials Science Division, Inter University Accelerator Centre, New Delhi-110067, India

E-mail: sajadphysics@gmail.com

Abstract. NdFe$_{1-x}$Ni$_x$O$_3$ (NFNO) (x=0.0 and 0.3) perovskite structures were synthesized by ceramic method. The variation of dielectric behavior with frequency at room temperature reveals an order of enhancement in both dielectric constant and dielectric loss with 30 percent Ni substitution. UV-Visible spectroscopy data exhibit that optical energy band gap decreases with Ni substitution from 4.3eV to 4.0eV for the sample with 30% Ni doping. Magnetic disorder over some range between 1.5K and 100K is observed in SFNO samples and is explained in milieu of interaction among Nd and Fe/Ni sub-lattice moments.

1. Introduction:
Perovskite type rare-earth transition metal oxides (RTO) comprise a special place in solid state physics as they provide hefty scope for optical, electronic and magnetic tuning depending on the atoms involved, inter-atomic distances and the bonding strength. Some of these oxides are high dielectric ceramics, some are antiferromagnetic insulators and others are pauliparamagnetic metals etc [1-2]. The varied electric and magnetic properties of RTO render these materials important in advanced technologies such as gas sensors[3], catalysts[4] and solid oxide fuel cells[5] etc. A profound study from last few years has shown that transition metal ion plays an important role in rare-earth transition metal oxides through its electronic ground state and associated magnetic properties. Thus, they have been under thorough investigation over couple of decades. As NdFeO3 and NdNiO3 belongs to RTO family and much emphasis has been given to study their optical, electric and magnetic properties in past few years[6-8].Both these oxides conform to orthorhombically distorted perovskite structure with space group -Pbnm possessing 4 formula units per elementary cell[9-10].

With Pbnm space group, NdFeO$_3$ (NFO) is a room temperature insulator and involves three different interactions which decide the outcome of its several physical properties such as optical, electric and magnetic etc. The strong interaction between Fe-Fe results in long range antiferromagnetic (AF) ordering with a Neel temperature of 690K [11] but weak ferromagnetism (F) is observed due to spin canting. The relatively less strong Nd-Fe interaction causes spin-reorientation transition between 100K and 200K [12] and polarization of Nd$^{3+}$ ion magnetic moments below 25K[9].The weakest of the three interactions between Nd-Nd results in long range AF ordering of Nd$^{3+}$ magnetic moments at 1.5K[13].On the other hand with Pbnm space group, NdNiO3 (NNO) is a room temperature metal but near metal-insulator boundary and exhibits a metal-insulator transition at the same Neel temperature of 200K[14,15] and a metal-semiconductor temperature at 130K[16]. Ni magnetic moments order in such
a way so that quadrupled magnetic unit cell contains same number of ferromagnetically and anti
ferromagnetically coupled nearest neighbors [17].

Thus replacement of Fe in NFO by Ni will develop a new system which lies between two end
members of NFNO series and lend some interesting physical properties like optical, electrical and
magnetic etc. This motivates us to take studies of pure and 30 percent Ni doped NFO and observe how
these properties will evolve and mutate.

2. Experimental Details

NFNO (x=0 and 0.3) samples were prepared by using ceramic method, the details of which our group
have been published elsewhere [18]. X-ray diffraction (XRD) measurements are carried on samples by
Bruker D8 Advanced X-ray diffractometer using Cu Kα radiation for phase identification and analyzed
in the similar way as discussed in detail by our group somewhere else [19]. Optical measurements are
recorded by Perkin Elmer Lambda 950 spectrometer in the wave length range of 200-800 nm. Dielectric
measurements are performed with Agilent 4285A precision LCR meter in the frequency range of 0.02
kHz to 1MHz at room temperature. Temperature dependent zero field cooled (ZFC) and Field cooled
(FC) dc magnetizations are measured using Quantum Design Vibrating sample magnetometer (VSM).

3. Results and Discussion

From X-ray diffraction (XRD) results, the samples are in single phase having distorted orthorhombic
structure and space group $D_{2a}^{5}-Pbnm$. There is an increase in strain and a decrease in unit cell volume
with Ni doping similar to that calculated here [20].

![Figure 1. Variation of $\varepsilon'$ and tan$\delta$ as a function of frequency at room temperature for NdFeO$_3$
and NdFe$_{0.7}$Ni$_{0.3}$O$_3$.](image-url)
Figure 1 (a,b) represent the frequency dependent dielectric constant ($\varepsilon'$) and figure 1(c,d) the dielectric loss (tan$\delta$) of NFNO samples over the frequency range from 0.02 kHz-1 MHz at room temperature. High $\varepsilon'$ in these samples of the order of $10^3$ - $10^4$ is observed. The high $\varepsilon'$ in Ni-Zn ferrites of the order of $10^3$ prepared by ceramic method has been already reported in literature [21, 22]. The high $\varepsilon'$ in NFNO structure may possibly be attributed to the local charge accumulation which takes place at the interface between grain and grain boundary under the effect of external field. This leads to polarization which results in a decrease in dielectric constant with increase in frequency and is in accordance with Maxwell-Wagner type of polarization [23-24]. However, $\varepsilon'$ decreases till it attains some constant value. It is because local charge is made available through electronic charge exchange between Fe$^{2+}$ and Fe$^{3+}$ and after certain frequency limit the charge exchange between Fe$^{2+}$ and Fe$^{3+}$ cannot follow the alternating nature of field. It is evident from Fig. 1(b,d) that 30 percent Ni doping can change the $\varepsilon'$ and tan$\delta$ of NFO significantly. For example, the $\varepsilon'$ of NdFe$_{0.7}$Ni$_{0.3}$O$_3$ [(NFNO)$_{0.3}$]
measured at 100 Hz is about ten times larger than that of NFO. The other possible reason of the large $\varepsilon'$ of (NFNO)$_{0.3}$ corresponds directly to the small resistivity at $x = 0.3$, suggesting that the increase in the $\varepsilon'$ may be ascribed to the leakage current caused by Ni doping. The tan$\delta$ data presented in figure 1(b-d) is also in accordance to this notion. The tan$\delta$ decreases with increasing frequency without indication of loss peak. Similar demeanor was reported in Bi-Cr ferrites by F. Chang et al [25].

Figure 2 shows the absorption spectrum of NFNO over the wavelength range from 200-800nm at room temperature. The value of absorption is high between 200-234nm in case of NFO and 202-237 nm in case of (NFNO)$_{0.3}$. The absorption coefficient for these materials is calculated by Tauc relation [26]:

$$\mu h\nu=A(h\nu-E_g)^n$$

Where, $\mu$ is absorption coefficient, $A$ is constant different for different transitions, $h\nu$ is energy of incident photon, $h$ is the planks constant, $n$ is the index which assumes the different values 1/2, 3/2, 2 and 3 corresponding to direct allowed, direct forbidden, indirect allowed and indirect forbidden electronic transitions respectively responsible for reflection and $E_g$ the optical band gap. Using Tauc plot (not shown here), $(\mu h\nu)^{1/2}$ versus $h\nu$ by extrapolating linear portion of the curve to $(\mu h\nu)^{1/2}=0$ axis yields $E_g$ values for NFO and (NFNO)$_{0.3}$ as 4.3 eV and 4.0eV respectively. One of the possible reasons for this red shift observation in $E_g$ with Ni doping could be orthorhombic distortion [27].

In any RTO family there are two magnetic sublattices namely T and R. In NFO family the Fe$^{3+}$ sublattice is $G_z$ type AF ordered below 100K with a small $F_x$ type F component due to spin canting structure of Fe$^{3+}$ sublattice [28-30] and Nd$^{3+}$ sublattice changes from disordered state at higher temperature to AF ordered state at lower temperature of 1.5K [14,31]. It is in-between these two temperatures (1.5K and 100K) under 1T magnetic field an anomalous mode of magnetization is observed. ZFC and FC modes of magnetization as a function of temperature in 1T field for NFO and (NFNO)$_{0.3}$ are shown in figure 3. It is evident from the figure 3 that there is hardly any bifurcation seen between ZFC and FC magnetizations at higher and lower temperatures. However, as shown in inset of figure 3 in case of NFO the bifurcation is evident from 10-40K and in (NFNO)$_{0.3}$ from 14-72K which suggests a disorder state arises due to intricate interaction between Fe$^{3+}$/Ni$^{3+}$ and Nd$^{3+}$ moments. Another possible reason may be the heterogeneous mixture of F and AF order instead of distinct F or AF order. Similar explication was reported in Pr ferrites by A. Bashir et al [19]. Also, as rare-earth ion subsystem acquires magnetization due to an interaction with iron subsystem, so the shift of disordered state in the temperature range with the Ni doping at Fe site may likely be due to weaker AF exchange between rare earth and transition metal sub-lattices [32].

4. Conclusions
In conclusion, the present study confirms colossal room temperature dielectric constant and dielectric loss of ceramically synthesized NFNO with an order of increase in these quantities at 30% Ni doping. A decrease in optical energy band gap is observed with Ni doping that we propose is related to an orthorhombic distortion. At 1T it is clear ZFC and FC magnetization curves of NFNO within the temperature range of 10-40K [in case of NFO] and 14-72K [in case of (NFNO)$_{0.3}$] have not overlapped.
indicating the existence of disordered or inhomogeneous mixture of F and AF ordered state over these temperature ranges.

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