

Structural and Electrical Resistivity Study of Ni doped Orthoferrites GdFe_{1-x}Ni_xO₃ (x ≤ 0.5)

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GdFe_{1-x}Ni_xO₃ (x ≤ 0.3) samples have been prepared using solid state reaction technique and characterized by X-ray diffraction and electrical transport. XRD data suggest orthorhombic structure for both pure and Ni doped compositions with space group Pbnma. However, unit cell dimensions are found to decrease with increase in Ni concentration. Resistivity data have been fitted with the Variable Range Hopping (VRH) model from which different parameters like density of state at Fermi level N(E_f), hopping energy (E_h) and hopping distance (R_h) were estimated. It was observed that the substitution of Ni in the series leads to an increase in conductivity of the samples with conduction being controlled by the disorder induced localization of charge carries. It was observed that all samples exhibit a ferromagnetic behavior at 300K and the saturation of magnetization is decreased with the increase in Ni substitution.

1. Introduction

Orthoferrites have the general formula RFO₃, where R is the large trivalent metal ion. Orthoferrites are well studied materials, but due to the large interest in various applications and the desire to understand the undergoing physical processes make these materials special for modern technology [1-6]. Significant research interests in the study of these materials have attracted much attention over the last few decades because of the profusion of relevant technological applications and for exhibiting a spectacular variety of inspiring physical properties, such as dielectric, magnetic, optical and transport properties, owing to strong electron correlation effect in the system and the discovery of the Metal-insulator Transition (MIT), Colossal Magnetoresistance (CMR), and charge ordering in manganites [3-14]. Orthoferrites are widely studied due to their dynamic properties and the doping can prove a milestone in tailoring the properties of the rare earth perovskites [15-20]. The space group for these compounds is Pbnm and has unit cell dimensions a=5.346 Å, b=5.616 Å and c=7.665 Å and contains four distorted perovskite units. GdFeO₃ has been studied in depth and is found to be a wide gap, high spin Mott insulator and weak ferromagnetic at room temperature. Doping of Ni at the Fe site can change the properties of GdFeO₃.

2. Experimental

The polycrystalline samples of GdFe_{1-x}Ni_xO₃ (x ≤ 0.5) were synthesized using the standard solid-state

reaction technique. The stoichiometric amounts of high-purity Gd₂O₃, FeO and NiO powders were mixed thoroughly and precalcinated for 12h at 1000 °C. The precalcinated materials were again ground and calcinated twice at 1300 °C for 24h, following in-between grinding and pelletization for better homogeneity. Powder x-ray diffraction measurements were performed using Rigaku x-ray diffractometer with Cu Kα radiation at room temperature. The electrical resistivity measurements were carried out using the Four-Probe setup in the temperature range 80-300K. All the measurements were taken in the warm-up cycle.

3. Results and discussions

In order to understand the crystal structure and single phase purity of these compounds the X-ray diffraction is performed. The X-ray diffractograms of powder GdFe_{1-x}Ni_xO₃ (x ≤ 0.5) for crystals are shown in Fig.1. The crystallinity of both pure and substituted crystals is quite clear from diffractograms because of the occurrence of sharp peaks at specific Bragg's angles. From the diffractograms it is clear that the entry of Ni ions in the modified composition brings no change in the internal structure of crystals.

The diffractograms were indexed using CRYSFIRE software. The cell parameters of pure crystals were obtained by selecting seven intense peaks using DICVOL program for pure and Ni doped samples. Calculation of cell parameters reveals that all compounds belong to orthorhombic crystal system having space group Pbnma with unit cell dimensions for pure composition at (x=0) as

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$a=5.4943 \text{ \AA}$, $b=5.610 \text{ \AA}$, $c=7.7935 \text{ \AA}$. The details of lattice parameters are given in Table 1 and Table 2. It is clear from the table that with increasing Ni concentration the unit cell volume decreases.

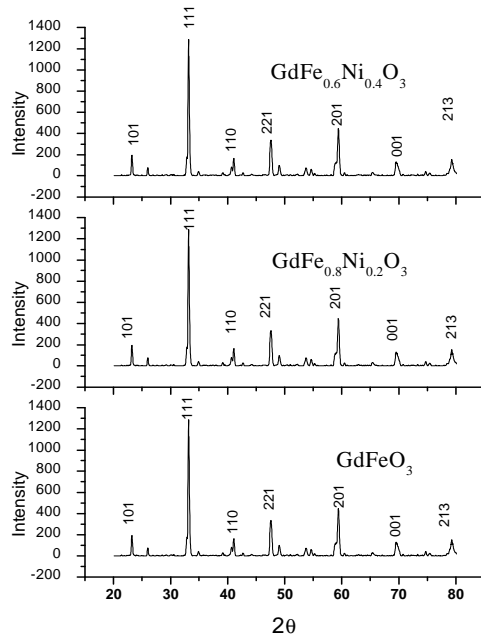


Fig. 1: X-Ray diffraction patterns of $GdFe_{1-x}Ni_xO_3$ ($x \leq 0.5$) samples.

The electrical Resistivity, as a function of temperature, for all the samples ($x=0.0, 0.2, 0.4$) is shown in Fig.2. All samples show semiconducting behavior. It is clear from the plots that the Resistivity at room temperature is decreasing with Ni substitution and for (0.2) Ni doping it drops to $11.52m\Omega cm$ at room temperature, as compared to the $228.93\Omega cm$ (for $x=0.0$). Generally, at higher temperatures, the carriers are thermally activated to extend states with higher mobility. In order to examine the electrical conduction mechanism of $GdFe_{1-x}Ni_xO_3$ ($0 \leq x \leq 0.5$), $\rho(T)$ is compared to

$$\rho = \rho_0 \exp(W/k_B T) \quad (1)$$

which represents simple thermally activated electrical conductivity [21], where an electron or hole (as the charge carrier) moves from one localized state to another due to an exchange of energy between the charge carrier and phonon (the localization is not a consequence of interaction with a phonon, but could occur due to a random electric field or disordered arrangement of atoms). In Eq. (1), ρ_0 is the electrical resistivity at

extremely high temperatures, W is the thermal activation energy (or simple activation energy) of the electron or hole, and k_B is the Boltzmann constant. Realizing that the specimens are polycrystalline, only general statements will be made here regarding the electrical conduction mechanism. The electrical resistivity of $GdFe_{1-x}Ni_xO_3$ ($0 \leq x \leq 0.5$) is plotted as $\ln \rho$ versus $1/T$ in Fig.2. Since the data does not exhibit linear behavior through the entire temperature range, we conclude that Eq. (1) is an inadequate description. However, this equation can provide a rough idea of thermal activation energies in narrow temperature regions where the data can be fitted.

It is well established that the Ni substitution in the $GdFeO_3$ is leading to carrier doping, which consequently decreases the energy gap and hence the resistivity of the composition. However, carrier doping by chemical substitution generally brings disorder in the system, which may tend to delocalize the carriers at the doping site. The carriers in the localized states move by a phenomenon known as variable-range-hopping (VRH) [22]. So, in order to understand the effect of disorder induced localization on the electrical transport properties in this system, we have fitted our data with Mott's variable range hopping (VRH).

According to Mott's variable range hopping (VRH), the expression for electrical resistivity in a three dimensional system is given by:

$$\rho = \rho_0 \exp(T_0/T)^{1/4} \quad (2)$$

where T_0 is the Mott's characteristic temperature related to the density of states at Fermi level $N(E_f)$ and the localization length (α) as shown below

$$T_0 = 18\alpha^3/N(E)k_B \quad (3)$$

The mean hopping distance $R_h(T)$ and hopping energy $E_h(T)$ as function of temperature are given below

$$R_h(T) = 3/8 \alpha (T_0/T)^{1/4} \quad (4)$$

$$E_h(T) = 1/4 k_B T^{3/4} T_0^{1/4} \quad (5)$$

The fitted data are plotted and shown in Fig.3. It has been observed that the data fit by VRH model to limited range of temperature of measurement. This is consistent with the reported results of a similar system and suggests that the conduction is governed by the disorder induced localization of charge carriers [23].

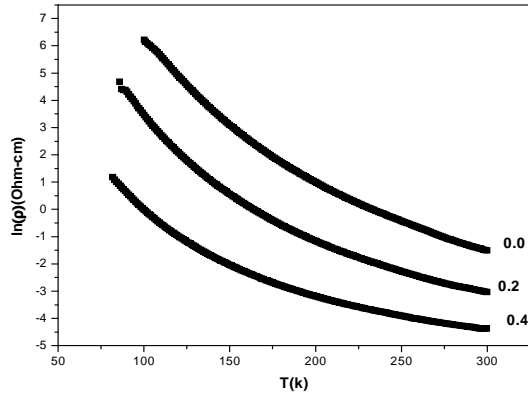


Fig. 2: Shows the variation of resistivity with temperature of $GdFe_{1-x}Ni_xO_3$ ($x= 0.0, 0.2, 0.4$) for these compositions.

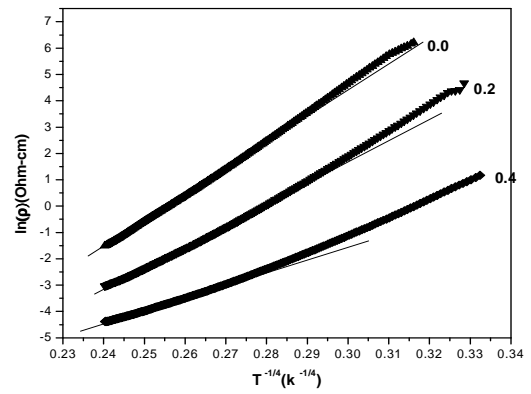


Fig. 3: Shows fitting by Mott's 3D VRH model of $GdFe_{1-x}Ni_xO_3$ ($x= 0.0, 0.2, 0.4$).

Table 1: Calculated Lattice parameters and unit cell volume of $GdFe_{1-x}Ni_xO_3$ ($x=0.0, 0.2, 0.4$).

x	A(Å)	B(Å)	C(Å)	Cell volume(Å ³)
0.0	5.4943	5.61024	7.79395	240.24
0.2	5.48283	5.6096	7.78676	239.49
0.4	5.49130	5.5442	7.7655	236.41

Table 2: Physical parameters of $GdFe_{1-x}Ni_xO_3$ ($x= 0.0, 0.2, 0.4$) obtained from *dc* conductivity data.

Samples	ρ (mΩ-cm)	ρ_0 (mΩ-cm)	$N(E_f) \times 10^{19}$ (eV ⁻¹ cm ⁻³)	R_h (Å) (300K)	E_h (meV) (300K)
x=0.0	1531.401	15.13	1.440	1.26	182.23
x=0.2	1213.635	8.73	1.623	1.12	179.22
x=0.4	945.22	4.39	2.321	0.99	165.23

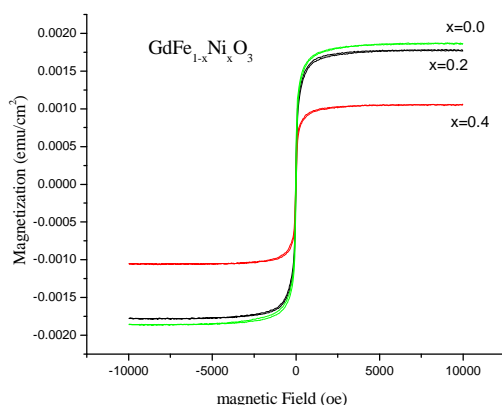


Fig. 4: Shows Hysteresis curves of $\text{GdFe}_{1-x}\text{Ni}_x\text{O}_3$ ($x=0.0, 0.2, 0.4$).

In the matrix of GdFeO_3 , Fe ions experience an internal magnetic field. The Fe ions are arranged at two sub lattices coupled antiferromagnetically. As the Ni concentration increases in the system the strength of antiferromagnetic interaction decreases, which causes a decrease in the internal magnetic field. Fig.4 shows the isothermal hysteresis loops of $\text{GdFe}_{1-x}\text{Ni}_x\text{O}_3$ ($x \leq 0.5$) at 300K. It is clearly evident from the figure that the samples show ferromagnetic behavior above room temperature and the value of saturation magnetization is found to decrease with the increase in Ni concentration.

4. Conclusions

Single-phase polycrystalline $\text{GdFe}_{1-x}\text{Ni}_x\text{O}_3$ ($x \leq 0.3$) have been prepared using the solid-state reaction method. The structural analysis (XRD) for all compositions suggest the decrease in unit cell volume on increasing Ni concentrations, however, no change is observed in unit cell structure and space group on doping GdFeO_3 by Ni. Electrical resistivity measurements reveal semiconducting behavior for all compositions, while their resistivity values decrease with increase in the Ni concentration in the composition due to decrease in energy gap. The resistivity behavior fits well for all the samples with the VRH model at low temperatures signifying that the conduction is controlled by the disorder-induced localization of charge carriers at intermediate temperature. The DC magnetization study infers that all samples exhibit ferromagnetic behaviour at room temperature and saturation of magnetization decreases with increasing concentration of Ni ions.

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