

# Curie Temperature of Ti<sup>4+</sup> Ions Doped Ni-Ferrite by Different Techniques

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**Abstract**— In the present study,  $Ti^{4+}$  doped Ni-ferrite with generic formula  $Ni_{1+x}Ti_xFe_{2-2x}O_4$  (x= 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7) samples were prepared by solid-state reaction method using high purity oxide. The X-ray diffraction pattern showed the presence of all planes, no extra peak has been observed. The analysis of the XRD pattern revealed the formation of the single-phase cubic spinel structure of the samples.

We also report the variation in Curie temperature by using different techniques, such as ac susceptibility, dc electrical resistivity, and the Loria technique. The values of Curie temperature found from these methods are in good agreement with each other. The Curie temperature decreases with Ti4+ ions substitution. The decrease in Curie temperature is related to the decrease in magnetic linkages associated between the tetrahedral (A) and octahedral [B] site. Due to the substitution of nonmagnetic titanium ions, the magnetic linkages are reduced, and hence Curie temperature decreases with titanium substitution.

**Keywords**— X-ray diffraction, Curie temperature, dc electrical resistivity, ac susceptibility Loria technique

#### I. INTRODUCTION

Ferrites are magnetic ceramics of great importance in the production of electronic and other components. They have a wide range of applications from a small permanent magnet to sophisticated devices for the electronic industry. Some interesting applications are in computer peripherals, telecommunication equipment, permanent magnets, electronic and microwave devices [1], etc.

Nickel ferrite is a magnetic material of great scientific and technological interest because of its high electrical resistivity moderate saturation magnetization, high Curie temperature, excellent chemical stability, etc. Nickel ferrite is an inverse spinel ferrite in which Ni ions occupies the octahedral B site and Fe<sup>3+</sup> ions are equally distributed at the tetrahedral (A) and octahedral [B] site.

Nickel- ferrite and substituted nickel ferrite has been the subject of many workers [2-5]. The addition of tetravalent ion in nickel ferrite influences the electrical and magnetic properties.  $Ti^{4+}$  substituted nickel ferrite has been studied by several researchers to understand their structural, electrical, and magnetic properties [6-8]. These studies have not reported any information about Curie temperature. Curie temperature is the temperature at which the substance can change its phase properties. Curie temperature is determined by A–B exchange interactions, the weakening of the  $Fe^{3+}(A)-O_2-Fe^{3+}(B)$  interaction results in a decrease in the values of Curie temperature, when the concentration of  $Ti^{4+}$  ions increases in the nickel ferrite system. So Curie temperature is most important in the study of phase transition of the materials.

Here also literature survey does not study in detail about the Curie temperature by various methods. Considering these facts and it has been decided to study the Curie temperature of Ti substituted nickel ferrite by different techniques.

#### II. EXPERIMENTAL

The polycrystalline samples of  $Ni_{1+x}Ti_xFe_{2-2x}O_4$  (x= 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7) were prepared by using solidstate reaction method [9]. The A.R. grade oxides (SD fine) of corresponding ions (NiO, TiO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub>) are mixed in stoichiometric proportion. Grinding using agate mortar for 4 hours was carried out for each sample. The samples were presintered in a muffle furnace at 900°C for 12 hours. After that, the powder was reground and compressed into a pellet form using a hydraulic press with a pressure of 6 tons. The pellets were sintered at  $1200^{\circ}$  C in the air for 24 hours. The samples were furnace cooled to room temperature.

X-ray diffraction patterns (XRD) were taken at room temperature to confirm the single-phase cubic spinel structure. The XRD patterns were recorded in the  $2\theta$  range  $20^{\circ}$  to  $80^{\circ}$ . dc. Electrical resistivity measurements were carried out using two probe techniques in the temperature range 300 K to 800 K, a silver paste was applied on both the surfaces of the pellet to ensure good electrical contact. AC susceptibility measurements study and Loria method are also used to measure the Curie temperature of the prepared samples.

### III. RESULTS AND DISCUSSION





system.

X-ray powder diffraction patterns of  $Ni_{1+x}Ti_xFe_{2-2x}O_4$ ; where  $x = 0.0 \le x \le 0.7$  are obtained by X-ray diffractometer at scanning rate in the 2 $\theta$  range  $20^0$  to  $80^0$  at room

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temperature. Fig.1 shows the XRD pattern of the typical sample x=0.6. XRD pattern shows the reflections (220), (311), (222), (400), (422), (511), (440), and (533). All the XRD reflections are sharp, clear, and intense. These reflections are an indication of the presence of a cubic spinel structure. The diffraction line corresponding to a cubic spinel-type and crystalline phase provides clear evidence of the single-phase formation of a Ni<sub>1+x</sub>Ti<sub>x</sub>Fe<sub>2-2x</sub>O<sub>4</sub> spinel ferrite.

## 3.2. AC Susceptibility Measurements

The variation of ac susceptibility as a function of temperature for all compositions x is studied. The temperature dependence of ac susceptibility is plotted for typical sample x=0.6. The variation of Curie temperature is depicted in Fig.2 for x=0.6 of the prepared system.



Fig. 2: Variation of ac susceptibility  $\chi_T / \chi_{RT}$  with temperature for the samples x = 0.6 of the system  $Ni_{1+x}Ti_xFe_{2-2x}O_4$ 

TABLE 1: Values of Curie temperature 'Tc' (K) by ac Susceptibility, dc Resistivity and Loria technique of  $Ni_{1+x}Ti_xFe_{2-2x}O_4$  (x=0.0  $\leq x \leq 0.7$ ) system

Ti	Curie temperature $T_c^{\prime}(K)$		
content	A.C.	D.C.	Loria
х	Susceptibility	Resistivity	technique
0.0	854	853	859
0.1	813	813	811
0.2	782	773	793
0.3	741	733	729
0.4	665	673	690
0.5	556	563	560
0.6	530	543	532
0.7	471	483	455

The plots of  $\chi T/\chi RT$  versus temperature are used to determine the Curie temperature. The value of Curie temperature with Ti<sup>4+</sup> ions content X is represented in Table 1 and represented graphically in Fig.4. The susceptibility plots exhibit normal ferrimagnetic behavior which decreases with Ti substitution. The behavior of susceptibility indicates the existence of a multi-domain structure. It is observed from Curie temperature value that, Curie temperature decreases with Ti<sup>4+</sup> ions substitution. The decrease in Curie temperature is related to the decrease in magnetic linkages associated between the tetrahedral (A) and octahedral [B] site. Due to the

substitution of nonmagnetic titanium ions, the magnetic linkages are reduced, and hence Curie temperature decreases with titanium substitution [10].

The decrease in Curie temperature is almost linear. It is well known that when magnetic ions are replaced by paramagnetic or diamagnetic ions, Curie temperature falls. Non-magnetic  $Ti^{4+}$  ions are replacing the  $Ni^{2+}$  ions having a magnetic moment (2µB). The decrease in Curie temperature can also be explained based on the strength of the exchange interactions. Since Curie temperature is determined by an overall strength of the A–B exchange interactions, the weakening of the Fe<sup>3+</sup>(A)–O<sub>2</sub>–Fe<sup>3+</sup>(B) interaction results in a decrease of the Curie temperature, when the concentration of  $Ti^{4+}$  increases in the nickel ferrite. The Curie temperature decreases with the number of the non-magnetic tetravalent ions per molecule bearing a complex relationship with the distance between magnetic ions.

### 3.3. DC Electrical Resistivity Measurements

The variation of logarithm of resistivity versus reciprocal of temperature is depicted in Fig.3 for typical simple x=0.6 of the  $Ni_{1+x}Ti_xFe_{2-2x}O_4$  (x=0.0  $\le$  x  $\le$  0.7) system.



Fig. 3: Variation of log  $\rho$  Vs 1000/ T of the  $Ni_{1+x}Ti_xFe_{2\cdot 2x}O_4$  system for x=0.6.

The plot exhibits two regions with changes in slope. These regions are namely ferrimagnetic and paramagnetic region. The temperature at which slope changes may corresponds to the Curie temperature ( $T_c$ ) of the samples. The resistivity plots obey the exponential relation given by,

$$\rho_{\rm DC} = \rho_{\rm o} \exp\!\left(\frac{\Delta E}{kT}\right)$$

Where,  $\Delta E$  -is the activation energy in electron volt (eV), need to release an electron from one ion to the neighboring ions giving rise to the electrical conductivity. k-is the Boltzmann constant and T is the absolute temperature.

Using the above relation and the values of the slope from resistivity plots, the activation energy corresponds to the ferrimagnetic region, and the paramagnetic region is calculated. The point at which phase changes called Curie point represents the Curie temperature. The values of Cure

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temperature obtained from dc resistivity plots are as given in Table 1 and represented graphically in Fig.4. Higher the values of activation energy for the paramagnetic region compared to that of the ferrimagnetic region. The activation energy in the present case is below 0.2 eV which suggests that the conduction mechanism in the present case is due to the hopping of electrons (Fe<sup>3+</sup>  $\longrightarrow$  Fe<sup>2+</sup>, Ni<sup>2+</sup>) [11]. During the sintering process, some of the Fe<sup>2+</sup> ions have been transformed to Fe<sup>3+</sup> ions and generated electrons which take part in the conduction mechanism. The presence of Fe<sup>2+</sup> and Fe<sup>3+</sup> on the equivalent lattice site (octahedral B-site) may cause low surface resistivity.

#### 3.4. Loriea Method



Fig. 4: Variation of Curie temperature 'T' (K) using different technique versus Ti content x for the system Ni<sub>1+x</sub>Ti<sub>x</sub>Fe<sub>2-2x</sub>O<sub>4</sub> with x=0.0 to 0.7

The Loria technique is the most simple and versatile technique to measure Curie temperature of magnetic materials. The temperature of the sample is measured using a calibrated chromel-alumel thermocouple. A ferrite sample in the form of a pellet is fixed to the soft iron piece and introduced into the furnace. The position of the pellet is confirmed with the help of the mirror. The temperature of the sample is increased slowly by gradually increasing the current in the heating coil with the help of a dimmer stat. The temperature at which the ferrite sample loses its magnetization and drops is measured with the help of a thermocouple. The procedure is repeated for other pellets of the same sample an average value of Curie temperature is determined. The values obtained by this technique are given in Table 1 and represented graphically in Fig. 4.

#### IV. CONCLUSIONS

The influence of non-magnetic Ti substitution in  $Ni_{1+x}Ti_xFe_{2-2x}O_4$  ferrite system with increase x=0.0 to 0.7

represents a single cubic spinel structure. The dc electrical resistivity decreases with temperature showing the semiconductive nature of the samples. Curie temperature decreases with the substitution of non-magnetic Ti ions. The behavior of susceptibility indicates the existence of a multi-domain structure. It is observed from the Curie temperature value that, Curie temperature decreases with an increase in Ti<sup>4+</sup> ions substitution. The decrease in Curie temperature is related to the decrease in magnetic linkages associated between the tetrahedral (A) and octahedral [B] site. The Curie temperature obtained from ac susceptibility, dc resistivity, and by Loria technique is in good agreement with each other.

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