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Structure and Magnetic Properties of $Ni_{0.7}Mg_{0.3}Cr_xFe_{2-x}O_4$

Dilipkumar V Meshram and Madhav N Rode

Department of Physics, Vaidyanath College, Parli-Vai, Beed

ABSTRACT

In present research work ferrite of composition $Ni_{0.7}Mg_{0.3}Cr_XFe_{2-x}O_4$ with x = 0.0 to 0.3 has been successfully synthesized by conventional standard Ceramic method. The synthesized samples were processed into homogeneous powder form. The single phase cubic spinel structures of the samples were confirmed by X-ray diffraction patterns without any impurity peaks. Lattice constant is found to be decreasing with increase in Cr^{3+} concentration in the composition (x). The X-ray density is found to be decreasing with increase of Cr^{3+} concentration. The particle sizes lies between 300 ^{0}A to 450 ^{0}A. The porosity level is 0.20 to 0.30. The intensities of structure sensitive planes and ratios of intensities for selective places were used to propose the cation distribution. The infrared spectra of present series in range of 200 cm^{-1} to 800 cm^{-1} are taken. The IR spectra showed two absorption bands. The high frequency band v_1 (400cm^{-1}- 530 cm^{-1}) which is assigned to octahedral complex in spinel and low frequency band v_2(290 cm^{-1} – 445cm^{-1}). Thermoelectric power study exhibits that both n-type and p-type of charge carriers are responsible for charge transport and the drift mobility causes the conduction.

Keywords: XRD, Ferrite, Thermoelectric power.

1. INTRODUCTION

The technical demands of magnetic in modern electronics; power conversion, communications, computers, instrumentation and high energy physics requires the circuit engineer to be familiar with the manufacturing techniques of ferrites. Compositions and process steps greatly affect the magnetic properties and shapes that can be generated. In order for the engineer to select the correct material and shape he should be acquainted with the chemistry and manufacturing procedures necessary to produce his required core. With this information the engineer can select the required magnetic device to solve his circuit requirements. Modern electronics demands more sophisticated materials and geometries than are available from the standard catalogue. The important innovations in the field of magnetic oxides took place after Second World War. The development of the magnetic oxides into useful materials has started by the pioneering work of late J.L.Snoek [1]. Since last five decades magnetic oxides have found increasing application in exacting technological requirements due to their controllable and combined magnetic and electrical properties [2]. Mixed magnetic oxides with spinel structure have wide technological applications. These are also known as ferrites if they have M^{2+} Fe_2^{3+} O_4^{2-} composition where M^{2+} is divalent metal ion. These materials are most relevant. The wide usefulness of these materials fascinated the scientists, physicists and engineers to study their basic properties in order to know the controllable parameters to design the suitable material for desired applications [3-4] The new findings with above approach may reveal the reality of controlling parameters and can lead to a breakthrough in the ferrite technology, which may be the most useful development. Thus mixed magnetic materials have been gaining importance in recent times especially in context of devices which can provide necessary infrastructure and flexibility for various human endeavors. Though various technological developments are taking place in fine tuning of these materials for specific attempts are still awaiting to explore the mysteries behind fascinating properties of mixed magnetic oxides.

Initially polycrystalline pure ferrites have been studied to know the controlling parameters behind basic properties. It is found that controllable properties of ferrites provide a wide scope of their technical applications. By suitable mixture of metal cations, ferrites with virtually any specific properties can prepared. Such mixed magnetic oxides are known as mixed ferrites. Many investigat0rs like E.W.Gorter and G.Blass had discovered the importance of mixed ferrites. The magnetic and electrical properties of such mixed

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ferrites depend upon method of preparation, atomic number and valence of metallic cation, stoichiometry of composition and sintering process (Sintering process includes rate of increase of sintering temperature, sintering temperature, rate of increase of sintering temperature, sintering temperature , rate of cooling after sintering for a certain duration and sintering duration).The nickel ferrite ($NiFe_2O_4$) is an inverse spinel having a collinear ferromagnetic order [5]. The addition of trivalent ion like Al^{3+} and Cr^{3+} for Fe^{3+} in $NiFe_2O_4$ influences the electrical and magnetic properties of the system [6-12]. The investigation done by various worker have shown that the micro-structure [13-15] electric [16-18], dielectric [19] and magnetic [20-22] properties of the basic nickel ferrite are greatly influenced when Ni^{2+} ions or Fe^{3+} ions are partially replaced by tetravalent ions. The most effective means to control saturation magnetization of nickel ferrite is through making substitution for trivalent iron. $NiAl_2O_4$ is a partially inverse spinel in which the ratio of Al^{3+} in the tetrahedral and octahedral site is about 2:3. $NiCr_2O_4$ is normal spinel with a canted ferromagnetic order at octahedral site [22].

The spinel structure seems to be particularly attractive as it allows a variety of magnetic orders from collinear to frustration. This is due to the fact that in spinels intra-sub-lattice interactions are weaker than the inter-sub-lattice interactions and as a result there are unsatisfied bonds increasing magnetic interactions accentuate the competition between the various exchange interactions resulting in a variety of magnetic structure [23]. The negative super-exchange interaction exists in ferrites. The strength of the exchange interaction is specified by exchange integral [24]. The exchange integrals of intra- sublattice interactions follow the order $J_{AB} > J_{BB} > J_{AA}$ in collinear ferrimagentic order. Thus the antiferromagetic A-B super-exchange interaction is the main cause of the cooperative behavior in ferrites [25]. The magnetic order can be controlled by cation substitution [26]. It is found that change in J_{BB}/J_{AB} and M_A/M_B ratios modify the magnetic properties. This inspires to study the properties of ferrites with the substitutions of nonmagnetic and magnetic cations. K.Seshen et al [27] have reported the effect of cation distribution on the properties of some magnesium-nickel ferrites in which the migration rate of Mg^{2+} on tetrahedral site depends upon the cooling rate of heat treatment due to high diffusibility. The substitution of non-magnetic and magnetic cations with different valences on tetrahedral and octahedral sites has been a subject of many researchers in crystal lattice. The structure having collinear ferromagnetic order where degree of inversion depends upon the rate of heat treatment in preparation. Pure nickel ferrite is characterized by excessive losses. Therefore several investigators have proposed the substitutions of order cations. As with other ferrites, the most effective means to control saturation magnetization of nickel ferrite is through making substitution for trivalent iron. $NiAl_2O_4$ is partly inverse, $NiCr_2O_4$ is completely normal. Ni^{2+} cation has a strong octahedral site preference but nickel ferrite has been reported to be 80% inverse. Thus the system $Ni_{1-x}Mg_xFe_2O_4$ is expected to show variation in cation distribution on heat treatment and thereby the magnetization can be modified. Keeping nickel and magnesium in specific ration for which the magnetization will be maximum. The substitution of Al^{3+} as well as the substitution of Cr^{3+} may enhance basic properties of yielded mixed nickel ferrites. In reported works to our knowledge, there is no mention of the studies of basic properties of the mixed magnetic oxides of solid solutions like $Ni_{0.7}Mg_{0.3}Cr_xFe_{2-x}O_4$. Therefore the studies of the basic properties of these mixed magnetic oxides with a view to study the effect of substitution of non magnetic and magnetic trivalent cations on the structural, electric and the magnetic properties have been undertaken for the present investigation.

SYNTHESIS OF THE SYSTEMS

The base system was synthesized to study its magnetization. The maximum saturation magnetization was considered to select the proportion of nickel and magnesium. The eleven samples of the system $Ni_{1-x}Mg_x Cr_x Fe_2O_4$ were prepared with x = 0.0 to 1 in the step of 0.1 using double sintering ceramic technique. The starting materials were of analytical grade high purity oxides such as NiO, MgO and Fe_2O_3 (MERCK). They were taken in stoichiometric proportion by weighing with sensitive balance and were ground thoroughly. The pre-sintering is carried out using a programmable furnace namely Thermolyne (Model-1500, USA made) at 900˚C for 24 hours. The samples then were cooled slowly to room temperature. Pellets of 1 cm diameter of the powder have been made by cold pressing, applying the hydraulic pressure of 5 tones/inch$^{2.}$ The good quality pellets have been obtained by using PVA as binder and maintaining the pressure for about ten

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minutes each time. The presintered pellets were again ground to fine powder. Then the powdered samples were pelletized again using hydraulic pressure machine by applying pressure of 5 tones/inch^{2}and polyvinyl as binder. The pellets were finally sintered at 1050˚C for 30 hours. Then they were cooled to room temperature at its natural rate. The systems $Ni_{0.7}Mg_{0.3}Cr_xFe_{2-x}O_4$ have been synthesized by the same ceramic technique. Six samples of each systems were prepared where x = 0.0 to 0.3 in step of 0.1. Here also AR grade oxides were used. The rest preparation process was similar to that of the base system.

CHARACTERIZATION

The Synthesis samples has been subjected to A.C. Susceptibility, D.C. Resistivity, Thermoelectric power, Dielectric properties etc.

2. RESULTS AND DISCUSSION

A.C. Susceptibility

The plots of relative low field ac susceptibility$\frac{\chi_T}{\chi_{RT}}$indicates room temperature) against temperature T, for all samples are shown in figure [1-2] which exhibit normal ferromagnetic behaviour [19]. The nature of $\frac{\chi_T}{\chi_{RT}}$curves suggeststhe magneticthan thedomainstates in ferrites.The temperature variation of a.c.susceptibility shows that the samples contain multi-domain structure. The Curie temperature of $Ni_{0.7}Mg_{0.3}Cr_xFe_{2-x}O^{2-}_4$ system decreases with an increase of Cr^{3+}concentration in the composition. However, the rate of decrease of the curie temperatures for this is slower than that in case of the first system .The curie system temperatures of all the samples are considerably high which signify good stability of magnetic ordering at high temperature. In all the$\frac{\chi_T}{\chi_{RT}}$ curves, there is peaking behavior near Curie temperature and just before Curie temperature it drops rapidly. The temperature corresponding to peak is called blocking temperature. Near the blocking temperature, the transition of magnetic particle from single domain to multi-domain takes place [20]. This peak could be seen for a magnetic material in multi-domain state. According to Been [21], the susceptibility is inversely proportional to the coercive force, therefore the increase insusceptibility after the isotropic peak is attributed to a decrease in coercive force. The peaking nature of the relative susceptibility indicates that samples contain the multi-domain structure. The Fe-Fe inter action is stronger than the Cr-Cr or Fe-Cr interaction hence there is decrease in magnetization which results in the decrease in the Curie temperature (T_c). The chromium substitution reduces the Fe-Fe link ages and the angels between them therefore the Curie temperature decreases with increase in Cr^{3+}. The decrease in Curie temperatures may also be attributed to decrease in A-B interaction.

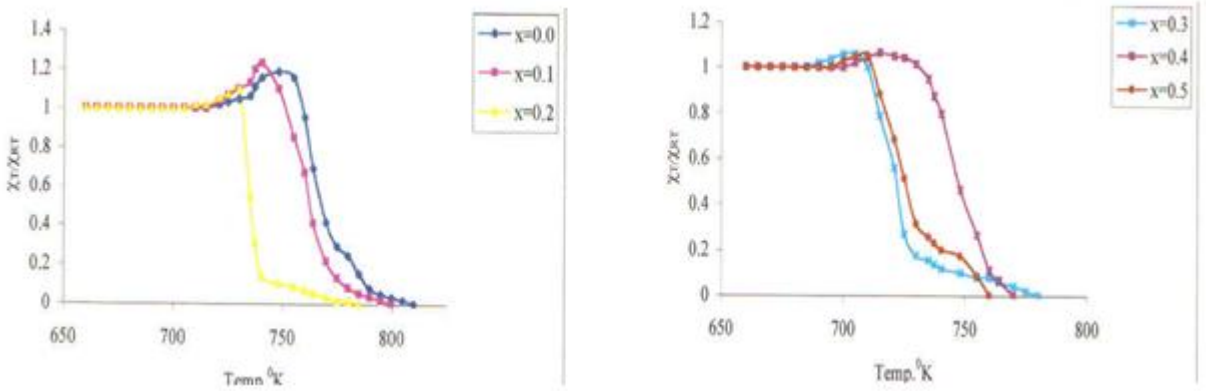

Figure-1 & 2: Variation of Susceptibility Nio.7Mg0.3CrxFe2$_{-x}O^{2-}_4$

5.5 D.C. Resistivity

The variation of d. c. resistivity with respect to temperature has been studied for all the samples. The d. c. resistivity of the system for all the samples decreases within crease in Cr^{3+}concentration in the compositions. The plots of log $\rho_{d.c}$. Versus1000/T as shown in figure (3) indicate the variation in d. C .resistivity. The d. c. resistivity of all the six samples decreases within crease in temperature and obey the Arrhenius relation [22]

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$$\rho_{d.c.} = \rho_0 \exp\left(\frac{\Delta E}{k_B T}\right) \quad \text{.....(5.8)}$$

The plots of log $\rho_{d.c}$. Versus 1000/T show kinks near the Curie temperature where the magnetic phase changes from ferrimagnetic region to the paramagnetic region due to thermal energy. The activation energy, in ferrimagnetic and paramagnetic region, has been calculated using above relation (4.7) and tabulated in the table (5.6). The activation energy values indicate that there exists the hopping type of conduction mechanism.

Figure-3: Variation of $Log_{\rho d.c.}$ with 1000/T for $Ni_{0.7}Mg_{0.3}Cr_xFe_{2-x}O_4$

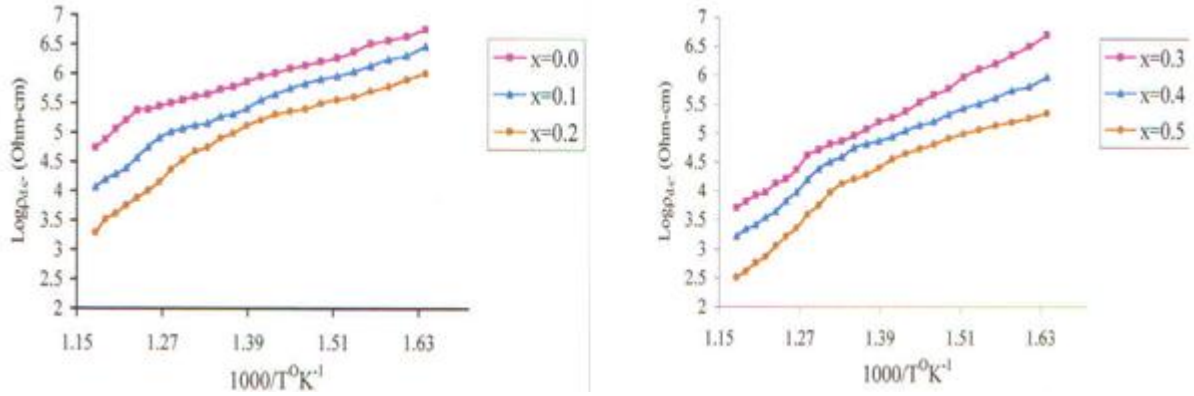

Table-1: ρ_{dc} at fixed temperature and activation energy with composition for $Ni_{0.7}Mg_{0.3}Cr_xFe_{2-x}O_4$ system

Composition (x)	ρ_{dc} at 600^0K x 10^6 Ω-cm^{-1}	Activation energy	
		Ferri-magnetic region (eV)	Paramagnetic region (eV)
0.0	10.16	0.31	0.36
0.1	6.86	0.38	0.47
0.2	6.69	0.35	0.43
0.3	6.25	0.33	0.41
0.4	6.07	0.30	0.39
0.5	5.90	0.31	0.35

The activation energy in ferrimagnetic region is lower than that in paramagnetic region. The conduction in ferrites can be explained on the basis of hopping mechanism. It is observed that under the normal conditions the electron hopping between B-A sites is very small as compared to that of B -B hopping. Hopping between A-A sites does not exist because most of the Fe^{3+} ions occupy A site and Fe^{2+}ions, which are formed during sintering process, preferentially occupy B-site only. The hopping probability depends upon the separation between the ions involved and the activation energy. The conduction mechanism for the present system may be given as,

$Fe^{3+} – Fe^{2+}$

$Ni^{3+} + Fe^{2+}$

$Ni^{2+} + Fe^{3+}$

Both Ni and Fe ions having two different valances may be providing conductivity mechanism. The d. c. resistivity is observed to be decreasing with increase in Cr^{3+} concentration. The conduction in the ferrites is mainly due to the electron hopping among Fe^{2+} and Fe^{3+} on B-site [23] (phonon induced transfer mechanism). As the chromium has strong B-site preference it replaces $Fe^{3+}$from B-site which results in reducing the population of Fe^{3+}. This reduction of Fe^{3+}on B-site causes generally increase in the resistivity. The chromium ions do not participate in the conduction process but limit the degree of Fe^{2+}-Fe^{3+}conduction

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by blocking up the Fe^{2+}-Fe^{3+} pairs. The decrease in the resistivity can be attributed to following reason [24]. Fe^{2+} or Ni^{2+}may shift to tetrahedral site for higher concentration of chromium [25]. The conduction process between Fe^{2+}-Fe^{3+} takes place at tetrahedral site, which results in an increase of conduction. Therefore, there is decrease in d. c. resistivity for higher Cr^{3+} ions content. The spin state in mixed magnetic oxides is also a cause for decrease in the resistivity the chromium ions exist in low spin state which cause the decrease in the resistivity (26-27).

5.6 Thermoelectric power

The thermoelectric power measurement of all the samples have been carried out from 350 ^{0}K to 850 ^{0}K temperature. The values of Seebeck coefficient (α) have been determined by using the following relation, [28]

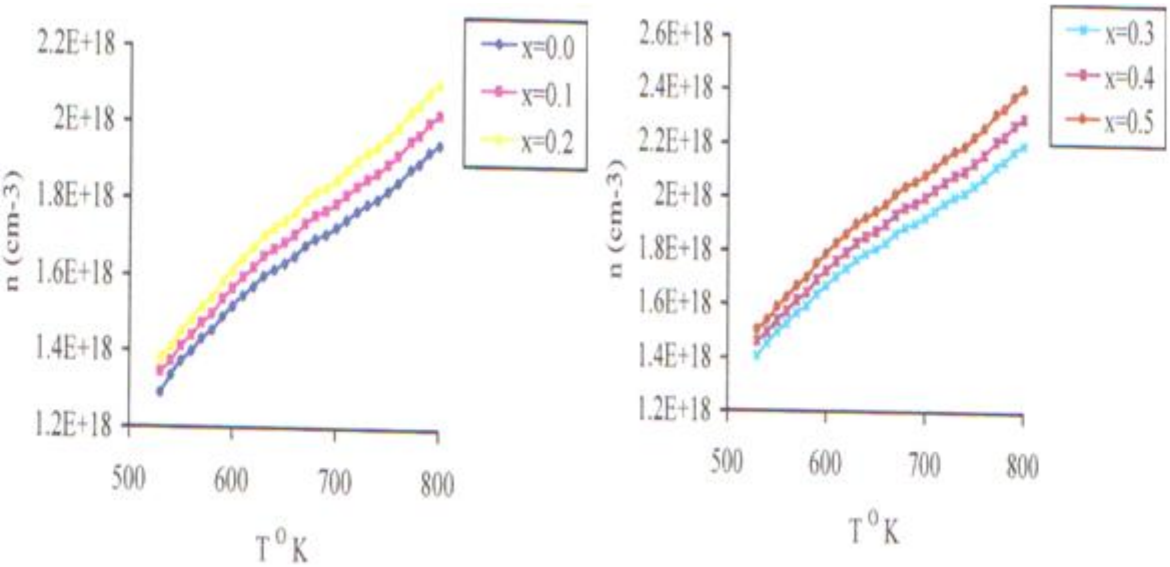
$$\alpha = \frac{thermo\ emf}{Temperature\ difference\ across\ the\ sample} \quad \ldots\ldots (1.1)$$

The plots of Seebeck coefficient (α) against the temperature a. The Seebeck coefficients have been observed to be negative up to 530°K and later on for higher temperature positive for all samples. This indicates that both types of charge carriers are present in the system. The α decreasesnonl in early with increase in temperature. The decrease of oxygen vacancies gives rise to decrease α [29]. The charge carrier concentration has been determined by using the following relation,

$$n = N\ exp(\frac{-\alpha}{k}) \quad \ldots\ldots (1.2)$$

where N is the density of the state and k is Boltzmann constant .The concentration of the charge carriers increases with the increase in temperature. The variation of charge concentration with temperature is shown in figure (4). The mobility for all the samples has been calculated by the following relation,

$$\mu_d = \frac{\sigma}{ne} \quad \ldots\ldots (1.3)$$



where σ is de conductivity ,n is the concentration of charge carriers and is electronic charge. The variation of drift mobility with temperature is shown in figure (4). The drift mobility increases within crease in temperature and decreases withCr^{3+}content. This clearly indicates that the conduction in the systems depends on the temperature dependent drift mobility and not on the temperature dependent charge carrier concentration. The decrease in dc resistivity with Cr^{3+}can also be explained on the basis of drift mobility.

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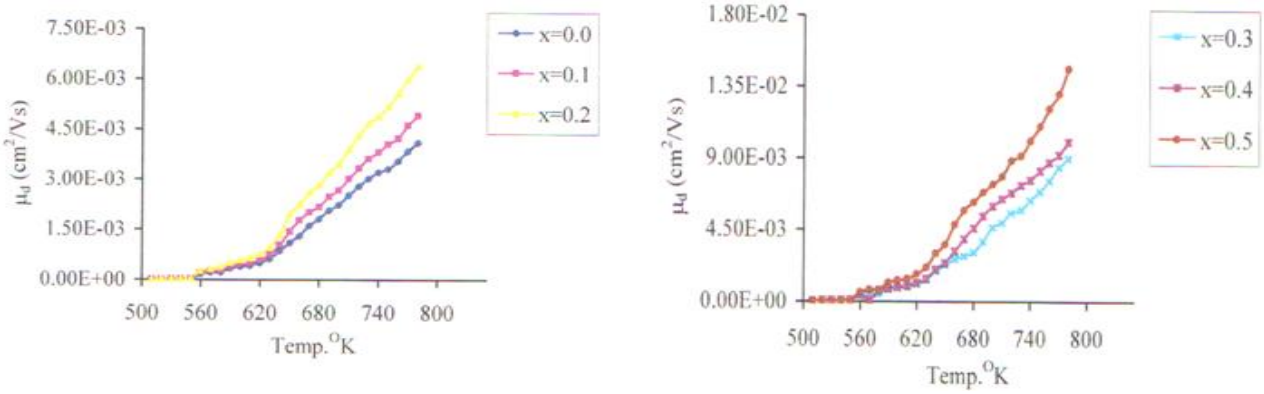

Figure-4: Variation of charge carrier's concentration with temperature for with $Ni_{0.7}Mg_{0.3}Cr_xFe_{2-x}O_4$

The Seebeck coefficient for the present series show that initially n type of charge carriers are predominant and later on from500°K onwards, p-type of charge carriers are predominant. The conduction in n-type region is due to electron hopping $Fe^{2+} \leftarrow > Fe^{3+}$and that in p-type region is due to hole transfer between the two different valence states of the cation [30]. The Ni^{2+} may be playing certain role in controlling the resistivity along with Fe^{2+}-Fe^{3+} pair. From the thermoelectric power, the conduction is observed to be dependent on the temperature dependent drift mobility and not on the temperature dependent charge carrier concentration.

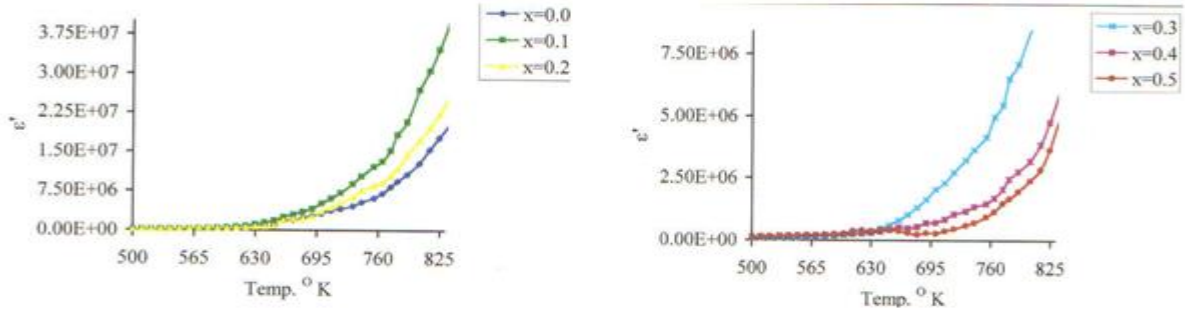

Figure-5: Variation of $\mu_{d.c.}$ with temperature for Ni0.7Mg0.3CrxFe2-xO4

5.7 Dielectric properties

The variation of dielectric constant as a function of temperature at 1KHz frequency for all the six samples, containing different Cr^{3+} concentration, (i.e.for x = 0.0 to 0.5) has been shown in the figure (5). The dielectric constant varies slowly at the beginning and after the temperature 650° K it increases rapidly within crease in temperature. This behaviour of the ε'could be explained on the basis of Maxwell Wagner interfacial polarization [31-33]. The origin of the interfacial polarization is attributed to the distribution of electrical resistivity in the ferrites which is considered to be caused by the non- uniform distribution of oxygen ions induced by the sintering process. The variation of ε' can be understood with the mechanisms of dielectric

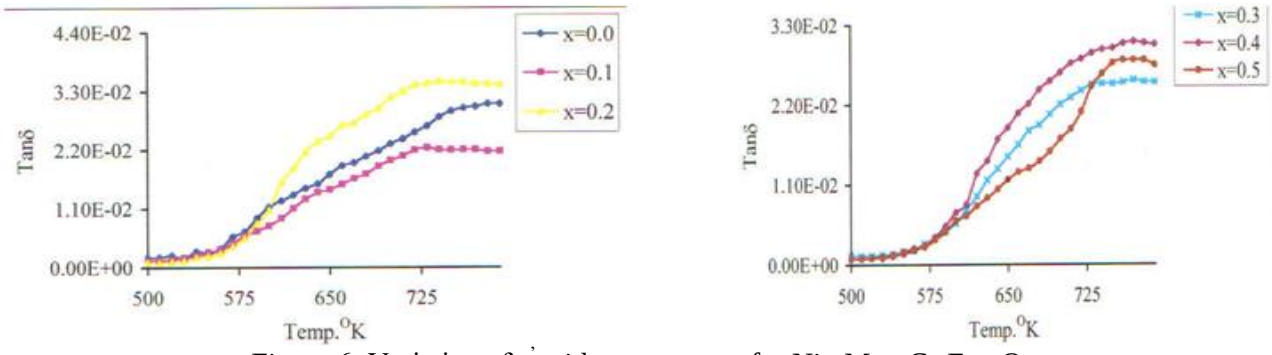

Figure-6: Variation of ε' with temperature for $Ni_{0.7}Mg_{0.3}Cr_xFe_{2-x}O_4$

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polarization and the electronic exchange which results in the displacement of the electrons in the direction of the electric field that determine the polarization in the ferrites [34].The exchange of electron in conduction mechanism may be responsible for space polarization. Thus mechanism of dielectric polarization is similar to that of conduction [35-37].

As the conductivity increases with increase in temperature, the dielectric constant also increases with increase in temperature [38]. With the rise in temperature the number of carriers increases resulting in an enhanced build up of space charge polarization and hence increases in the dielectric constant. As the concentration of Cr^{3+}increases the conductivity, the dielectric constant obviously increases with increase in Cr^{3+}.

Figure (6) shows the variation of dielectric loss tangent (tanδ) with temperature for all the samples. The loss tangent increases with increase in temperature. The compositional dependence shows that the dielectric loss tangent (tanδ) decreases with increase in the Cr^{3+} concentration. The variation of dielectric loss ($\varepsilon^{/}$) as a function of temperature for all the samples at frequency1KHz is shown in the figures (7). The dielectric loss initially increases very slowly up to 750°K temperature and later on it increases rapidly with the increase in temperature. The dielectric loss decreases within crease in Cr^{3+} concentration in the system. Chromium minimizes the dielectric losses. The dielectric constant is found to be appreciably high.

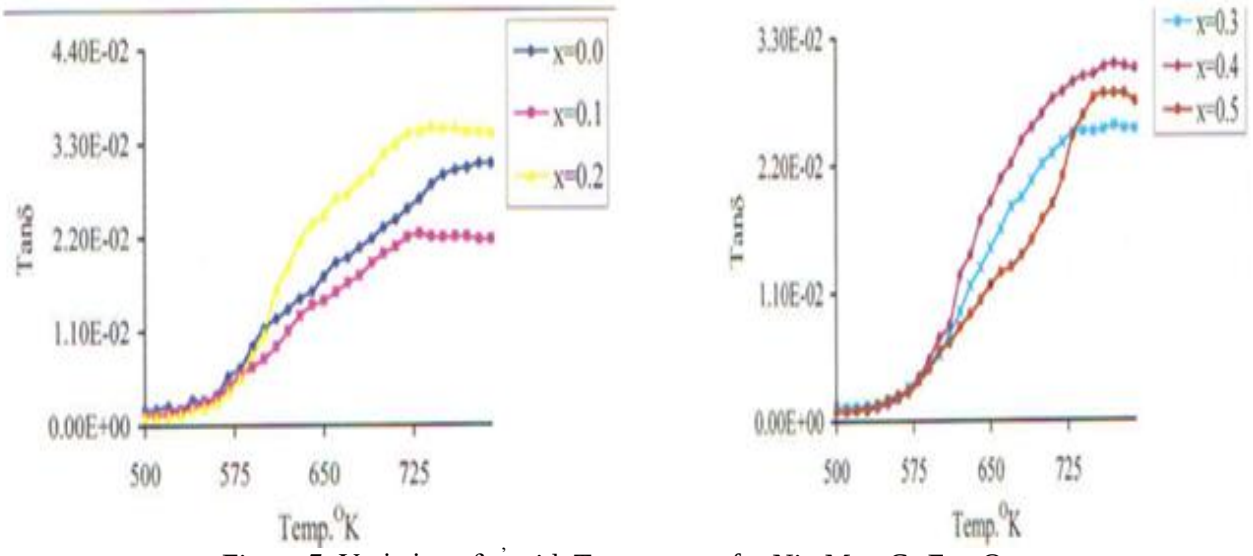

Figure-7: Variation of $\varepsilon^{'}$ with Temperature for $Ni_{0.7}Mg_{0.3}Cr_xFe_{2-x}O_4$

5.8 CONCLUSION

Thus from the above results and discussion the following conclusions can be drawn.

- The variation of ac susceptibility with increase in temperature indicates the normal ferrimagnetic behaviour of the system. The system has multi-domain structure.
- The Curie temperature decreases with increase in the Cr^{3+} in the composition.
- The de resistivity decreases with increase in Cr^{3+} content in the composition.
- The behaviour of the system changes from ferrimagnetic to paramagnetic at a particular temperature.
- Thermoelectric-power study exhibits that both n-types and p-types of charge carriers are responsible for charge transport and the drift mobility causes the conduction.
- The dielectric constant increases with Cr^{3+}content initially and later on decreases whereas the dielectric loss factor increases with increase in the Cr^{3+}content initially and decrease with increase in Cr^{3+}content. Both tanδ and dielectric loss increase with increase in the temperature.

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