Chapter 6
Thermal, electrical and magnetic properties of Cr/Co codoped TiO$_2$ nanoparticles

In this chapter, we present the contribution of Cr/Co co-doped ions on the thermal, electrical and magnetic properties of titania nanoparticles with stoichiometric formula Ti$_{1-x}$Cr$_{x/2}$Co$_{x/2}$O$_2$ ($x = 0$, 0.04 and 0.06). The temperature dependent dielectric properties varying in the frequency range of 75 kHz to 5MHz were investigated using LCR meter. Field and temperature dependent magnetic measurements have been done using SQUID magnetometer.
6.1 INTRODUCTION

Over the last couple of decades, oxide based diluted magnetic semiconductors (DMS) like TiO$_2$, ZnO, CuO, and SnO$_2$ have attracted considerable attention worldwide due to their utilization in solar energy conversion, spintronics and many more applications [1–4]. However, doping of cations helps in tailoring the physical properties of these wide band gap oxide semiconductors (E$_g$ ~3.0 to 3.3eV) [5,6]. Though, doping of impurities at the bulk level is not so difficult as at nanoscale due to quantum confinement effect that provides little space for dopants. However, if dopants are properly incorporated, they enhance microstructural, magnetic and optical properties drastically [7,8]. Kennedy et al. [9] reported a significant change in the structural, electrical and thermoelectric properties of ZnO thin films with Al doping. The substitution of suitable ions creates mid band gap electronic states that interact with the host electrons and make changes in the host electronic states. Recently, researchers have made great efforts in searching room temperature ferromagnetism (RTFM) in transition metal doped oxide semiconductors and observed that the doping of transition metals introduces RTFM in these non-magnetic semiconductors [10]. Recent development in this direction has shown that the high Curie temperature (T$_c$) can be achieved in these wide band gap semiconductors when oxygen vacancies are in a dominant state [11]. In transition metal doped DMS, systems are characterized by sp-$d$ exchange interactions between $s$, $p$ free carriers and $d$ state of the transition metal dopant ions. Further, due to these interactions, the carriers become spin polarized and are able to transmit ferromagnetic ordering [12,13]. Magnetic impurities doped TiO$_2$ have been studied extensively after Matsumato et al. [14] who reported room temperature ferromagnetism (RTFM) in cobalt doped TiO$_2$ thin films. When spin is injected into non-magnetic semiconductors, oxygen vacancies behave as an $n$-type dopant and these vacancies deform the structure that might be the reason for enhanced magnetic properties, makes these materials suitable for the applications in spintronic devices. Dietl et al. [15] have predicted the RTFM in several Mn doped oxide based semiconductors like ZnO, SnO$_2$, and TiO$_2$. It has also been observed that codoping strongly affects structural, optical and magnetic properties in a TiO$_2$ system as the dipole moment due to TiO$_6$ octahedra enhances the optical response under the irradiation of visible radiations. Zhang et al. [16] in their research work concluded that even small dipole moment of TiO$_6$ would increase the absorption efficiency in the visible range. Among various oxides, nanocrystalline TiO$_2$ is a member of transparent conducting oxide having potential applications in science and materials engineering like solar cells,
integrated circuits, gas sensors and photocatalyst, owing to its unique properties like high transmittance in visible range, high refractive index ($n \sim 2.52$), low resistivity, high chemical stability, large band gap ($E_g \sim 3.2$ eV), non-toxicity etc. [17–20]

Stable RTFM can be achieved in semiconducting oxide materials when doped with few percent of transition metal ions and researchers predicted RTFM property in rutile and anatase phase TiO$_2$ keeping the semiconducting property preserved. Shinde et al. [21] found that Co islands are responsible for the ferromagnetism in anatase phase of the TiO$_2$ thin films whereas trivalent Cr$^{3+}$ ions exhibit $3d^3$ high spin configuration in Cr doped TiO$_2$ system which helps in generating large magnetic moments while Kim et al. [22] explained the presence of oxygen vacancies as the source of RTFM in Mn doped TiO$_2$ thin films. Waseem et al. [23] reported no evidence of FM in rutile TiO$_2$ pallets whereas Hong et al. [24] reported 2.6 μ$b$/Cr for the Cr doped anatase TiO$_2$ thin films. Park et al. [25] studied the electronic structure of Ti$_{1-x}$Co$_x$O$_2$ and suggested that the magnetic properties get influenced by the oxygen vacancies created near the Co site and Santara et al. [26] reported RTFM in Co doped TiO$_2$ nanoparticles prepared by ball milling due to bound magnetic polaron (BMP) and oxygen vacancies. But still, there is ambiguity in the origin of RTFM in these diluted magnetic semiconductors. However, Wang et al. [27] also reported that the Cr ions possess high magnetic moment (2.9 μ$b$/Cr) and $pd$ hopping interactions between Cr$^{3+}$ ions are responsible for the origin of ferromagnetism in these systems. Some researchers have reported that codoping of different elements in TiO$_2$ can further narrows the band gap and enhances electronic, optical and photocatalytic activity. For example, Dashora et al. [28] investigated the electronic and optical properties of Cu/N codoped anatase TiO$_2$ whereas Shi et al. [29] reported the photocatalytic activity of Fe$^{3+}$ and Ho$^{3+}$ ions codoping in TiO$_2$. However, Zou et al. [30] explained the structure and source of room temperature ferromagnetism in Mo-N codoped TiO$_2$ anatase nanotube thin films. These explanations made it more exciting and convincing to investigate the microstructural and ferromagnetic origin roots, and changes in the properties on account of simultaneous incorporation of Cr and Co ions in TiO$_2$ lattice. In this work, we have synthesized (Cr,Co) codoped TiO$_2$ nanoparticles by microwave assisted sol-gel method and analyzed the thermal, electrical and magnetic properties of (Cr,Co) codoped TiO$_2$ nanoparticles. We have doped equal concentration of both chromium and cobalt ions in TiO$_2$, motivated from earlier reports on single ion doping of Cr and Co.
6.2 EXPERIMENTAL DETAILS

Synthesis process of undoped and codoped TiO$_2$ has already been discussed in Chapter 5 and details of further characterization are given below:

Thermal properties measurements were performed through Differential thermal analysis (DTA) technique by a STA-8000 (Perkin Elmer) thermal analyzer in the temperature range of 30 to 800 °C at the heating rate of 20 °C/min. The temperature dependent dielectric properties have been measured in the temperature range of 35 to 300 °C using a LCR meter (Agilent 4284A) in parallel plate capacitor geometry in the frequency range 75 kHz to 5 MHz. The dc resistivity as a function of temperature was measured using two probe method by Keithley 6517B electrometer. Magnetic behaviour of the samples was observed through superconducting quantum interference device (SQUID) magnetometer.

6.3 RESULTS AND DISCUSSION

6.3.1 Thermal Analysis

DTA plots of undoped, 2% and 3% Cr/Co-TiO$_2$ samples as a function of temperature were recorded in a controlled nitrogen atmosphere for the temperature range of 30-800 °C (Fig. 6.1). These plots depict the heat flow in and out of the system associated with the endothermic and exothermic reactions taking place with the variation of temperature.

![Fig. 6.1. Heat flow as a function of temperature for undoped and Cr/Co codoped TiO$_2$ nanoparticles.](image-url)
We have observed endothermic peaks at temperatures 64.39, 240.61, 311.67 and 548.83 °C whereas exothermic peaks are found at 492.45 and 631.71°C in the case of pristine TiO$_2$. However, on doping with Cr/Co simultaneously, a slightly different behaviour is observed. The endothermic peaks appear at temperatures 31.64 °C, 271.67 °C and 585.30 °C for 2% Cr/Co doped sample, while for 3% these peaks shifted to 34.68, 267.28 and 590.18 °C respectively, whereas exothermic peaks have disappeared. The endothermic peaks originated below 100 °C are due to desorption of the physically adsorbed water and residual alcohol [31]. However, the endothermic peak at ~ 240.61 °C is attributed to the heat required for the combustion of organic substances [32]. The exothermic peak in pristine TiO$_2$ at 492.45 °C is ascribed to the phase transformation of TiO$_2$ to an anatase phase [33]. Moreover, the endothermic peaks at higher temperatures might be due to the structural transition in an exchange interaction of the Ti-O and Ti-Cr$^{3+}$-Co$^{2+}$ depending on the bond length and bond angles [32]. We have also noticed the signature of magnetic transition in pristine and codoped TiO$_2$ samples. An endothermic peak at around 312 °C in undoped sample is the indication of the Curie temperature ($T_C$) and by the doping of Cr/Co this value of $T_C$ decreases systematically. These results are quite consistent with earlier reported results.

### 6.3.2 Dielectric studies

Temperature dependent dielectric response of pristine and (2%, 3%) Cr/Co codoped TiO$_2$ nanoparticles have been studied using LCR meter at frequencies 100 kHz, 500 kHz, 1 MHz, 1.2 MHz and 1.4 MHz respectively. Under these varying field, dielectric constant is a complex quantity and can be expressed as

\[ \varepsilon^* = \varepsilon' - j\varepsilon'' \]

where real part of dielectric constant $\varepsilon'$ describes the energy stored while imaginary part of dielectric constant $\varepsilon''$ represents the dissipated energy. The dielectric constant ($\varepsilon'$) is obtained using the relation

\[ \varepsilon' = \frac{C_p t}{\varepsilon_o A} \]

Here $C_p$ gives the measured capacitance, $A$ is the cross section area, $t$ is the thickness of the sample and $\varepsilon_o$ is the permittivity of free space. Imaginary part of dielectric constant ($\varepsilon''$) is calculated using the following equation
\[ \varepsilon' = \varepsilon' \tan \delta \]

where \( \tan \delta \) is the dielectric loss. The temperature dependent real part of dielectric constant (\( \varepsilon' \)) at particular frequencies for pristine and (2\% & 3\%) Cr/Co codoped samples is illustrated in Fig. 6.2. It is evident that \( \varepsilon' \) is increasing with the increase in temperature suggesting semiconducting nature of the sample.

Fig. 6.2. The variation of real part of dielectric (\( \varepsilon' \)) with temperature at selected frequencies for \( \text{TiO}_2 \), (2\% & 3\%) Cr/Co codoped samples.

In general, different types of polarizations are responsible for the dielectric behaviour in nanomaterials. The interface of nanostructured material has a large number of defects either because of negative or positive space charge distribution. Under the application of electric field, space charge move and get trapped giving rise to dipole moments. This phenomenon is known as space charge polarization [34]. As temperature increases, more dipoles will orient and hence lead to enhanced the value of electric dipole moment. Because of this, value of dielectric constant increases with the increase in temperatures at a particular frequency. At the lower temperatures
magnitude of $\varepsilon'$ falls with the increase in frequency because dipoles freeze throughout the relaxation mechanism and polarization decreases with respect to applied electric field. However, at the higher temperatures, the rate of polarization is high. Therefore, it is evident that the $\varepsilon'$ is increasing with the increase in temperature and dielectric dispersion occurs for Cr/Co codoped samples as the frequency increases. This happens owing to space charge polarization and can be explained in the light of Maxwell-Wagner model [35,36]. When mobile charge carriers are impeded in poorly conducting grain boundaries that inhibit charge relocation then space charge polarization occurs. This resulted in piling up of charges at grain boundaries and produces localized polarization within grains. Therefore, space charge polarization becomes sufficiently larger with the increase in temperature. Temperature dependent dielectric constant at selected frequencies shows that the value of dielectric constant initially increases with temperatures and then attains a maximum value which can be explained on the basis of Rezlescu model [37]. This model states that the contribution of two types of charge carriers in the polarization depends on temperature [38]. The rapid enhancement in dielectric permittivity with temperature may be attributed to the increase in molecular ability, lattice expansion and charge carrier excitation present in nanostructures. At low temperature, mobile charge carriers do not orient with the applied field direction and hence acquire a weak contribution to the polarization while as temperature increases, bound charge carriers get thermally excited and follow the external electric field change easily that enhances their contribution in polarization resulting to increase in dielectric behaviour. Consequently, as we increase the concentration of dopant i.e. Cr/Co, defects are introduced in TiO$_2$ which assist the grain boundary formation acting as physical barrier that stops the flow of charge carriers. Hence high temperature is required for charge carrier hopping mechanism and resonance takes place when the frequency of localized electron becomes nearly equal to the external ac electric field. All samples show high dielectric constant which increases with the increase in Cr/Co co-doping in TiO$_2$. In 3% Cr/Co doped sample, giant dielectric constant attributed to the oxygen vacancies created during the compensation of charge due to substitution of Ti$^{4+}$ with Cr$^{3+}$/Co$^{2+}$. As introduction of Cr$^{3+}$/Co$^{2+}$ may result in the distortion of TiO$_6$ octahedra and weakening of sublattice bond interaction that allows less resistance to polarization and thus enhances the dielectric constant. However, our results are well in agreement with earlier reported work [39]. There are some polarizations like electronic, dipolar, interfacial and ionic polarization playing important role for dielectric properties in prepared samples.
Interfacial and dipolar polarizations are temperature dependent. Among these, dipole polarization decreases and interfacial polarization enhances as temperature increases because of generated crystal defects. Therefore, rapid increase in dielectric constant with temperature suggests that the temperature plays an effective role in interfacial than in dipolar polarization. At high frequencies, ionic and electronic polarizations are the main cause of polarization inside dielectric material while temperature dependence becomes immaterial [40]. The dielectric polarization in various metal oxides like TiO$_2$, SnO$_2$ and NiO takes place through conduction mechanism. Due to temperature, charge carrier exchange occurs instead of displacement of charge carriers leading to the increase in $\varepsilon'$ in various Cr/Co codoped TiO$_2$ samples.

Fig. 6.3. The variation of dielectric loss (tan$\delta$) with temperature at selected frequencies for all prepared NPs.

The dielectric loss factor (tan$\delta$) represents the dissipation of power in dielectric material and came into consideration when the polarization lags behind the applied electric field due to impurities, defects and imperfections in the crystal lattice.
Fig. 6.3 shows the temperature dependent dielectric loss of undoped and Cr/Co codoped TiO$_2$ nanoparticles for particular frequencies. The dielectric loss for undoped TiO$_2$ is found lower as compared to Cr/Co codoped samples. This rapid increase in dielectric loss at the lower frequencies and high temperatures is attributed to the space charge polarization which can be explained on the basis of Shockley-Read mechanism [41]. A relaxation peak for undoped sample is observed in Fig. 6.3 associated with the thermally activated process and Maxwell-Wagner model [42,43]. The disappearance of relaxation peaks for other samples of Cr/Co codoped TiO$_2$ may be due to relatively high resistivity. Dielectric loss decreases for the low doping of Cr/Co while increases for 3% Cr/Co which leads to decrease in the ac conductivity for low doping and increase in conductivity for 3% Cr/Co at higher frequencies. Hence one can conclude that these materials show capabilities to be used in high frequency devices.

In order to explore the effect of temperature and frequency on the conductivity of undoped and Cr/Co codoped TiO$_2$ nanoparticles, ac conductivity ($\sigma_{ac}$) was studied over the temperature range of 35 to 300$^\circ$C. Fig. 6.4 shows the variation of $\sigma_{ac}$ as a function of temperature at selected frequencies. The electrical conductivity occurs due to the hopping of electrons between ions of the same element present in valence state randomly distributed over the entire crystal. The increase in conductivity with increase in temperature ascribed to the semiconducting nature of the nanoparticles. Therefore, relaxation model states that the hopping conduction phenomena of charged particles do not get disturbed by the applied electric field at high temperature and low frequencies. The ac conductivity increases with temperature which can be explained as pumping force of applied frequency resulting to the charge carrier hopping between localized states and liberates the trapped charge carriers from trapping centers. Therefore, these mobile charge carriers taking part in conduction mechanism jointly with electrons evolved from the valence exchange between different metal ions.

Pollak et al. [44] explained conductivity is an increasing function of frequency in case of conduction by hopping process, while it is decreasing function of frequency in the case of band conduction [45].
Fig. 6.4. The variation of ac conductivity with temperature at selected frequencies for all prepared NPs.

Ac conductivity ($\sigma_{ac}$) described using power law having $s$ exponent ($s<1$) can be expressed as

$$\sigma_{ac}(\omega) = K(\omega)^{s}$$

where $s$ is dimensionless frequency exponent and $K$ depends on temperature. It was concluded that the conductivity ($\sigma_{ac}$) occurs due to the presence of small number of free charges, which leads to leakage or conduction current and polarization or displacement current arises ascribed to the displacement of bound charges in solid dielectric. It is observed that the ac conductivity increases with the increase in frequency that can be attributed to the transfer of charge carriers between localized states. This happens due to driving force generated from an applied field that easily liberates the trapped charges [46]. Therefore, these electrons and charge carriers generated due to exchange interaction of different metal ions collectively participated
in the conduction mechanism. A strong dependence of conductivity on temperature is attributed to the increase in drift mobility and hopping frequency of charge carriers. Moreover, hopping of charge carrier increases between Cr$^{3+}$ ↔ Co$^{2+}$ ↔ Ti$^{4+}$ in addition to free charges from different ion centers that also influence conductivity. Therefore, slight decrease in conductivity observed on Cr/Co codoping that can be explained on the basis of replacement of Ti with Cr/Co simultaneously.

**Fig. 6.5.** Variation in exponent $s$ with temperature for undoped and Cr/Co doped TiO$_2$ NPs.

At higher temperatures, linear increase in conductivity with frequency is exhibited by different type materials i.e. $\sigma \propto \omega^s$, where $s$ is the UDR parameter ($0 < s \leq 1$). Exponent $s$ varying with temperature is shown in Fig. 6.5. The calculated value of $s$ from slope of $\log(\sigma_{ac})$ and $\log(\omega)$ for undoped and Cr/Co codoped TiO$_2$ nanoparticles. It is observed that with the increase in temperature, exponent $s$ value increases which is ascribed to the barrier hopping model [47]. Free movement of charge carrier through localized states leads to decrease in exponent $s$ value at high temperature. Different theoretical models were proposed for the explanation of conduction mechanism of ac conductivity having $s$ exponent as a function of temperature. Therefore, if $s$ increases with temperature, predominant mechanism is small polaron instead of large overlap polaron which is characterized by a minimum followed by increase of $s$ with increase in temperature [48]. Therefore, one can say that associated barrier hopping conduction is leading mechanism for the studied samples.
6.3.3 Electrical Resistivity

The variation in dc resistivity with temperature of pristine and Cr/Co codoped TiO$_2$ nanoparticles is shown in Fig. 6.6. It exhibits that the electrical resistivity reduces with the increase in temperature confirming the semiconducting nature of the samples. Electrons trapped in atoms gain adequate energy to become free from the valence band on increasing the temperature. This evolution of effective density of electrons and holes in the conduction and valence bands respectively resulted increase in conductivity [49]. However, on increasing Cr/Co concentration in TiO$_2$ lattice resistivity of the prepared samples increases. The increase in resistivity of the sample is mainly due to free electron scattering in the conduction band [50]. On increasing the concentration of Cr/Co in host lattice, surface defects such as oxygen vacancies increases in crystalline material that interrupt the conduction of electrons by scattering of electrons. Moreover, replacement of Ti$^{4+}$ by Cr$^{3+}$/Co$^{2+}$ in TiO$_2$ lattice leads to the increase in the carrier concentration to rapidly increase the resistivity of samples.

![Graph showing variation in dc resistivity as a function of temperature for undoped and Cr/Co co-doped TiO$_2$ NPs.](image)

**Fig. 6.6.** Variation in dc resistivity as a function of temperature for undoped and Cr/Co co-doped TiO$_2$ NPs.
Temperature dependent dc electrical resistivity ($\rho_{dc}$) follows Arrhenius equation [51] which is as follows

$$\rho_{dc} = \rho_0 e^{\frac{E_A}{K_BT}}$$

here $E_A$ is activation energy, $T$ is the temperature and $K_B$ is Boltzmann constant. Fig. 6.7 shows the $\ln\rho$ versus 1000/T Arrhenius plot of pristine and Cr/Co codoped TiO$_2$ whose slope gives the activation energy. It is observed that activation energy increases from 26 to 254 meV with the increase in concentration of Cr/Co in TiO$_2$ which is in good agreement with the values reported in result. The increase in activation energy is attributed to the hopping of electrons leading to conduction mechanism in the prepared samples. Formation of defects due to dopant ions which leads to reduced transportation ability of ions [52]. Therefore, values of activation energy give an idea that conduction mainly occurs by activated motion of strongly localized electrons.

![Fig. 6.7. $\ln(\rho)$ vs 1000/T plots for undoped and Cr/Co co-doped TiO$_2$ NPs.](image)
6.3.4 Magnetic properties

Magnetic behaviour of the 2% and 3% Cr/Co-TiO₂ synthesized nanoparticles were studied as a function of temperature and applied magnetic field. Fig. 6.8 shows the field dependent magnetization ($M$-$H$) plots at room temperature after subtracting the background contribution from the data. The $M$-$H$ plots illustrate the ferromagnetic nature of the prepared samples with the significant value of saturation magnetization ($M_s$), remanent magnetization ($M_r$) and coercive field ($H_c$) as tabulated in Table 6.1. The anisotropy constant ($K$) and magneton number ($n_B$) have been calculated for the codoped samples using the equations, $H_c = (0.96 \times K)/M_s$ and $n_B = (M. wt \times M_s)/5585$ as shown in Table 6.1. It is observed from the Fig. 6.8 that the value of saturation magnetization increases with the increase in Cr and Co codoping simultaneously in TiO₂ lattice that may be attributed to the oxygen vacancies and magnetic impurities (Cr³⁺ and Co²⁺). The origin of room temperature ferromagnetism in transition metal doped TiO₂ is still a controversial topic. Therefore, to explain the intrinsic ferromagnetic ordering several theoretical models were proposed like double and super-exchange interactions, carrier mediated Rudeman-Kittel-Kasuya-Yashida (RKKY) and bound magnetic polarons (BMP). In order to know which model is applicable to our system, various structural characterizations were performed but we could not find any other magnetic impurity phase.

![Magnetization vs Magnetic Field](image)

**Fig. 6.8.** Hysteresis loops for codoped Ti₁₋ₓCrₓCoₓO₂ (x=0.04 and 0.06) samples at room temperature. Inset shows a magnified view of the same at lower fields.
Despite of all, the structural analysis confirms the proper incorporation of Cr/Co in TiO$_2$ lattice and replacement of Ti$^{4+}$ by Cr$^{3+}$ and Co$^{2+}$ ions that leads to the formation of oxygen vacancies in order to maintain charge neutrality in the system. Due to charge imbalance, O$^{2-}$ ions are needed to escape the lattice creating oxygen vacancies. Therefore, these oxygen vacancies play an important role in trapping unpaired electrons located near to the dopant ions. Coey et al. [53] have suggested BMP model to explain room temperature ferromagnetism in diluted magnetic oxides whereas Kim et al. [54] reported that the oxygen vacancies induced lattice distortion of TiO$_2$ makes it ferromagnetic. In these materials, the exchange interactions among the oxygen deficiencies and Cr$^{3+}$/Co$^{2+}$ align all the Cr$^{3+}$ and Co$^{2+}$ spins around the oxygen vacancies. A BMP is formed when an electron gets trapped in oxygen vacancies or defects and they get coupled with the moments of cobalt and chromium within their hydrogen like orbit around the oxygen vacancies or defects. BMP theory states that when defect concentration exceeds the percolation threshold, dopant ions moment and oxygen vacancies overlap for BMP that resulted in the ferromagnetism coupling between two Co$^{2+}$ and Cr$^{3+}$ ions via oxygen vacancies (O$_v$) and give rise to the room temperature ferromagnetism [55]. Depending on the dopant concentration, interaction between ions and oxygen vacancies can be either double exchange or superexchange that imparts either ferromagnetism or antiferromagnetism in the doped TiO$_2$ system.

**Fig. 6.9.** Temperature dependent magnetization for Ti$_{0.96}$Cr$_{0.02}$Co$_{0.02}$O$_2$ and Ti$_{0.94}$Cr$_{0.03}$Co$_{0.03}$O$_2$ samples.
Table 6.1 Variation in room temperature coercivity ($H_c$), remanent magnetization ($M_r$) and saturation magnetization ($M_s$) for Ti$_{1-x}$Cr$_x$Co$_{0.5}$O$_2$ ($x = 0.04$ and $0.06$) samples.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$H_c$ (Oe)</th>
<th>$M_r$ (emu/gm) $\times 10^6$</th>
<th>$M_s$ (emu/gm) $\times 10^5$</th>
<th>Anisotropy Constant, $K$ (erg/gm) $\times 10^4$</th>
<th>Magneton number $n_B$ ($\mu_B$) $\times 10^7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$<em>{0.96}$Cr$</em>{0.02}$Co$_{0.02}$O$_2$</td>
<td>212</td>
<td>1.45</td>
<td>1.62</td>
<td>35.78</td>
<td>2.32</td>
</tr>
<tr>
<td>Ti$<em>{0.94}$Cr$</em>{0.03}$Co$_{0.03}$O$_2$</td>
<td>36</td>
<td>1.12</td>
<td>2.22</td>
<td>8.33</td>
<td>3.17</td>
</tr>
</tbody>
</table>

The increase in dopant concentration creates an ionic charge imbalance between Cr$^{3+}$, Co$^{2+}$ and Ti$^{4+}$ that produces more oxygen vacancies as also confirmed by XPS and PL spectroscopy measurements. This increases the probability of more BMP and their overlapping and hence room temperature ferromagnetic (RTFM) ordering is enhanced on increasing the concentration of Cr/Co in TiO$_2$. Further, to explore the RTFM nature of the nanoparticles, temperature dependent magnetization (M-T) i.e. field cooled (FC) and zero field cooled (ZFC) magnetization were measured in the presence of 500 Oe magnetic field. The combined plots of ZFC and FC are shown in Fig. 6.9 for the 2% and 3% Cr/Co-TiO$_2$ samples and that give the evidence of enhancement in the magnetization with the decrease in temperature. The MT behaviour can be explained in the light of polaron percolation theory that mentions the ferromagnetism in disordered systems is due to the strong localization of the carriers [56,57]. The temperature dependence on the average radius of polarons is given by the equation [58], $R_p(T) = (a_p/2) \ln((sS|J|(a_o/a_p)^3)/[K_bT])$, here $a_p = \varepsilon(m*/m)a_o$, $a_p$ is the confinement radius, $J$ stands for the exchange constant, $s$ and $S$ are the spins of the defects and magnetic ions respectively. The sharp increase in magnetization at lower temperatures is attributed to the expansion in polaron size (increases logarithmically with the decrease of temperature) and due to the occurrence of percolation of more polarons. However, this phenomenon induces high ordering of polaron magnetic moments which is a property of diluted magnetic semiconductors. ZFC and FC plots do not show magnetic blocking phenomenon which predicts the absence of any magnetic impurity or secondary phase in the prepared samples as confirmed from XRD, Raman and XPS results too.

6.4 Conclusions

In summary, we have successfully synthesized undoped and codoped Ti$_{1-x}$Cr$_{0.5}$Co$_{0.5}$O$_2$ ($x = 0.04$ and $0.06$) nanoparticles by microwave assisted sol-gel method. DTA plots
depicted the peaks associated with the endothermic and exothermic reactions taking place with the variation of temperature and also noticed the signature of magnetic transition in pristine and codoped TiO$_2$ samples. The dielectric properties as a function of frequency (75 kHz $\leq \nu \leq$ 5 MHz) and temperature were explored by employing the complex impedance spectroscopy. Temperature dependent dielectric constant at selected frequencies shows that the value of dielectric constant increases with temperature and dielectric dispersion occurs for the doped samples due to space charge polarization which can be explained in the light of Maxwell Wagner model. Although rapid increase in dielectric loss at low frequencies and high temperatures is attributed to the space charge polarization and explained on the basis of Shockley-Read mechanism. Dielectric loss increases in the doped samples that lead to the increase in ac conductivity, while it gradually decreases in the higher frequency region for all samples. A strong dependence of conductivity on temperature was observed which is attributed to the increase in drift mobility and hopping frequency of the charge carriers. Therefore, incorporation of Cr/Co in TiO$_2$ enhances dielectric behaviour and decreases ac conductivity of the synthesized nanoparticles which has the advantage in device fabrication from the nanomaterials. The electrical resistivity and activation energy have been investigated using two probe method and found that the resistivity decreases with the increase in temperature and hence confirms the semiconducting nature of the samples. The activation energy is found to increase from 26 to 254 meV with the cooping in TiO$_2$. The increase in activation energy is attributed to the hopping of electrons leading to the conduction mechanism in the prepared samples. Room temperature ferromagnetic nature of the nanoparticles enhances with the increase in the dopants concentration that attributed to the rise in oxygen vacancies related defects and explained on the basis of BMP theory. Temperature dependent magnetization ($M-T$) plots reveal the formation of highly ordered polaron magnetic moments, a characteristic of DMS material. However, our results revealed a strong correlation with simultaneous doping of Cr/Co ions in TiO$_2$. 
References

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Ph.D. Thesis


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