Chapter 4

Dielectric Properties and Room Temperature Ferromagnetism in Cr Doped TiO$_2$ Nanoparticles

In this chapter, we have explored the effects of Cr doping on the thermal, dielectric and magnetic properties of TiO$_2$. The temperature and frequency dependent dielectric response of the prepared samples were studied using LCR meter. Magnetic properties as a function of field and temperature were investigated using SQUID magnetometer.
4.1 INTRODUCTION

Over the past few years, substitution of magnetic ions in semiconductors has received considerable attention owing to their mutual structure, electrical transport and magnetic properties suitable for diluted magnetic semiconductors (DMS). These properties have been exploited in various fields, especially for spintronic devices. This innovative field of spintronics requires spin ordered semiconductors or spin valves having multilayer structure [1–4]. In these materials spin of the magnetic moments and charge degree of freedom can be manipulated easily that may be used for high density data storage, information transfer at a very high speed, and also to boost the speed and storage capacity of nanoelectronic devices such as spin transistors and spin logic devices [5]. Moreover, the materials that can correlate the optical, electrical and magnetic properties for the development of optoelectronic devices must have high tunable character with the least hazardous effects for the environment. The challenging task in this regard is to achieve room temperature ferromagnetism (RTFM) in wide band gap semiconductors (E_g ~ 3.0 to 3.3 eV) like ZnO, TiO_2, SnO_2 etc. [6,7]. In this direction, several reports are available in literature to accomplish RTFM in undoped and transition metal (TM) doped semiconductors which predict that the oxygen vacancies or deficiencies of host element are the origin of ferromagnetism [8,9].

However, special attention has been devoted to the titania (TiO_2) nanostructures due to its unique physical and chemical properties, namely, higher refractive index and dielectric constant with good optical transmittance [10]. These valuable properties can be utilized for various applications like in LEDs, heat reflector, gas sensors, photo electrochemical cells and dye sensitized solar cells etc. [11–13]. In addition, pioneer work by Matsumoto et al.[4] reported the RTFM in Co doped TiO_2 samples in 2001, that initiated the revolution in the fields of DMS and spintronics. In this context, other TM ions (Co, Ni, Cr, Fe, Mn and V) doped TiO_2 systems have been studied, that have also given evidence of the ferromagnetism at room temperature or above [14]. Other wide bandgap semiconductors have also been tried to achieve these properties and Dietl et al.[15] predicted the RTFM in several Mn doped oxide based semiconductors like ZnO, SnO_2 and TiO_2. Among various reports on TM doped TiO_2, Cr doping is still a controversial topic in explaining the origin of ferromagnetism, as researchers have reported that Cr doped TiO_2 system does not exhibit ferromagnetism. However, Wang et al. [16] predicted that Cr ions
possess high magnetic moment (2.9μ_B/Cr) and p-d hopping interactions between Cr^{4+}
ions are responsible for the origin of ferromagnetism in the system [17]. Further, RTFM in Cr doped TiO_2 anodic nanotubes was observed by Liao et al. [18] and results were explained on the basis of the vital role of oxygen vacancies. Some of the reports predicted that the ferromagnetism in Cr doped TiO_2 may be due to the oxygen deficiencies, bound magnetic polaron (BMP) interactions, hole mediated interactions and other structural defects [19]. But still there is no established explanation of the RTFM in Cr incorporated TiO_2 nanoparticles (NPs). Beside this, it is a promising candidate for spintronic and other DMS based devices. Therefore, it is more exciting and convincing to investigate the electrical transport and magnetic properties of Cr doped TiO_2 nanoparticles, and also to establish possible root of the magnetism.

In this work, we report the synthesis of Ti_{1-x}Cr_{x}O_2 (x = 0, 0.02, 0.04, 0.06 and 0.08) nanoparticles through a simple sol-gel method as discussed in Chapter 3. The influence of Cr doping on the thermal, temperature dependent dielectric and magnetic properties has been studied in detail using various analytical tools viz. Perkin Elmer TGA Pyris, LCR meter, two probe resistivity and superconducting quantum interference device (SQUID) magnetometer. Moreover, temperature dependent dielectric properties and observation of room temperature ferromagnetism in all samples are the main outcomes of this study. In addition, various dielectric parameters at different temperatures as a function of frequency were estimated and explained in a systematic way.

4.2 EXPERIMENTAL DETAILS

Details of materials and synthesis procedure are discussed in Chapter 3 (section 3.2.1) and characterization techniques for the investigated properties are given below:

Thermogravimetric (TG) analysis on pre-calcinated samples was performed with Perkin Elmer TGA Pyris in the temperature range of 50 to 800 °C. The temperature dependent dielectric properties have been measured in the temperature range of 35 to 400 °C using LCR meter (Agilent 4284A) through parallel plate capacitor geometry in the frequency range of 75 kHz to 5 MHz. The dc resistivity measurements as a function of temperature were carried out using two probe method on a Keithley 6517B electrometer. Magnetic behaviour of the samples was observed through superconducting quantum interference device (SQUID) magnetometer.
4.3 RESULTS AND DISCUSSION

4.3.1 Thermal analysis

The TGA curves for undoped and Cr doped TiO$_2$ NPs in the temperature range of 60-800 °C are present in Fig. 4.1. These curves indicate three main regions of weight loss with rise in temperature. The maximum weight loss of 29% is observed in temperatures between 60 and 200 °C for TiO$_2$ due to adsorbed water loss on heating. In the temperature range of 200 to 300 °C, 7% weight loss is observed which may be due to the combustion of residual organic species. A weight loss of 6% is found to occur in the region from 300 to 450 °C that is related to the dehydroxylation of gel. Further increase in temperature above 500 °C resulted in thermally stable phase of TiO$_2$ NPs. Table 4.1 shows the weight loss of Ti$_{1-x}$Cr$_x$O$_2$ (0 ≤ x ≤ 0.08) nanoparticles that exhibits higher value of weight loss for TiO$_2$ as compared to doped samples. These results predict that the Cr doping enhances the thermal stability of TiO$_2$ NPs.

![Fig. 4.1. TGA curve of Ti$_{1-x}$Cr$_x$O$_2$ (x = 0, 0.02, 0.04, 0.06 and 0.08).](image-url)
Table 4.1 Weight loss (%) measured from TGA curves for undoped and Cr doped TiO$_2$ nanoparticles.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Temperature Range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60 -200</td>
</tr>
<tr>
<td>Undoped TiO$_2$</td>
<td>21%</td>
</tr>
<tr>
<td>Ti$<em>{0.98}$Cr$</em>{0.02}$O$_2$</td>
<td>17%</td>
</tr>
<tr>
<td>Ti$<em>{0.96}$Cr$</em>{0.04}$O$_2$</td>
<td>20%</td>
</tr>
<tr>
<td>Ti$<em>{0.94}$Cr$</em>{0.06}$O$_2$</td>
<td>19.7%</td>
</tr>
<tr>
<td>Ti$<em>{0.92}$Cr$</em>{0.08}$O$_2$</td>
<td>14.3%</td>
</tr>
</tbody>
</table>

4.3.2 Dielectric studies

In the presence of time varying electric field the dielectric constant is a complex entity as given by:

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

where $\varepsilon'$ and $\varepsilon''$ are the real and imaginary parts of dielectric constant that give the stored and dissipated energies respectively. The value of $\varepsilon'$ can be obtained using relation:

$$\varepsilon' = \frac{C_p t}{\varepsilon_0 A}$$

Here $C_p$ is the measured capacitance, $A$ stands for the area, $t$ represents thickness of the sample and $\varepsilon_0$ is the permittivity of free space. The imaginary part $\varepsilon''$ is calculated using the dielectric loss ($\tan\delta$) by employing the following relation:

$$\varepsilon'' = \varepsilon' \tan\delta$$

The effect of temperature on the real part of dielectric constant ($\varepsilon'$) for undoped and Cr doped TiO$_2$ NPs is illustrated in Fig. 4.2 at various frequencies. Dielectric dispersion of the prepared samples decreases with the increase in frequency and becomes almost constant at higher frequencies. In nanostructures, the dielectric dispersion can be explained using the Maxwell and Wagner’s bilayer model. It interprets that the space charge polarization comes into account due to heterogeneous dielectric nature of the material. According to it, material composed of two layers, i.e.
well conducting grains divided via layer of poor conducting grain boundaries. It is known that the grain boundaries in the material are created because of the sintering process in which high temperature leads to the oxidation of crystallites or surface area gets reduced [20]. The conductivity of grain boundaries is relatively lower and hence at lower frequencies, grain boundaries play a significant role whereas the conductivity of grains is higher which is responsible for the lower value of the dielectric constant at higher frequencies. This is also explained by Koop’s theory which is based on the same principle as of Maxwell Wagner’s model [21]. However, behaviour of the dielectric constant was powered by the grain boundaries and their volume fraction [22]. It is observed from Fig. 4.2 that the dielectric constant enhances with the increase in temperature and attains maximum value, which can be explained by the Rezlescu model [23]. According to this model, polarization as a result of two varieties of charge carriers is temperature dependent and increase in dielectric constant attributed to rise in mobility of the molecules, resulted in excitation of charge carriers present at the defect sites in nanostructures. Although, relatively small value of the dielectric constant at lower temperatures is a consequence of charge carriers which are unable to align themselves with respect to the applied electric field direction and hence resulted in less polarization. On the other hand, at higher temperatures polarization enhances and it increases the dielectric dispersion because of increase in mobilities, hopping rate and thermal excitation of charge carriers that follow the external electric field easily. It is known that there are four types of dielectric polarizations viz. electronic, ionic, interfacial and dipolar [24].
Chapter 4: Dielectric Properties

Fig. 4.2. The variation of real part of dielectric constant ($\varepsilon'$) with temperature at selected frequencies for all samples.

Out of these, dipolar and interfacial polarizations govern the temperature dependent dielectric properties of materials. In the present case, doping of Cr ions creates oxygen deficiencies and crystal defects that lead to rise in interfacial polarization and decrease in the dipolar polarization at higher temperatures. Therefore, rapid increase in dielectric constant with temperature is observed in the system. However, low Cr doping in TiO$_2$ reduces $\varepsilon'$ due to the fact that the polarization depends on the particle size. Fig. 4.3 represents the variation of dielectric loss ($\tan\delta$) as a function of temperature at selective frequencies for undoped and Cr...
doped TiO$_2$ NPs. It follows almost the same trend as the dielectric constant ($\varepsilon'$) for all studied samples. The dielectric loss occurs because of energy loss by the sample when an electric field is applied, which is caused due to resonance created by the domain wall. Polarization changes the rotation motion and inhibits the domain wall at higher frequencies that decreases the value of the dielectric loss.

![Graphs showing variation of dielectric loss (tanδ) with temperature at selected frequencies for selected samples](image)

**Fig. 4.3.** The variation of dielectric loss (tanδ) with temperature at selected frequencies for all samples.

The defects and imperfections in the crystal make the loss significant when the polarization lags behind the applied field. In the studied samples, dielectric loss enhances with rise in temperature while its value decreases on Cr doping at higher
frequency. At higher temperatures, the dielectric loss increases (at lower frequencies) because of space charge polarization based on Shockley Read mechanism [25]. Space charge polarization takes place at the surface when defect or impurity ions capture (trap) the surface electrons at higher temperatures. Because of this Shockley-Read process, electron trapping increases with temperature and hence the loss tangent enhances as temperature increases. The ac conductivity of undoped and Cr doped TiO$_2$ NPs as a function of temperature at selected frequencies is shown in Fig. 4.4.

**Fig. 4.4.** The variation of ac conductivity with temperature at selected frequencies for all prepared NPs.

In these types of materials, electrical transport occurs when hopping of electrons takes place between ions of the elements present with more than one valence state that are distributed over the lattice sites randomly. Pollak et al. [26] show that
the electrical conductivity increases with the frequency due to hopping of electrons whereas it decreases with frequency in the conduction band. The total conductivity of a material can be represented as [27]:

$$\sigma_{total} = \sigma_0(T) + \sigma(\omega, T)$$

where $\sigma_0(T)$ stands for the dc conductivity which is frequency independent; while $\sigma(\omega, T)$ is the ac conductivity as a result of hopping processes. Ac conductivity is proportional to the dielectric relaxation due to immobile charge carriers that follow ac power law.

$$\sigma(\omega) = K\omega^n$$

Here $K$ and $n$ are the constants that depend on temperature and elemental composition. It is evident from Fig. 4.4 that the $\sigma_{ac}$ increases with the increase in frequency that can be described on the basis of transfer of charge carriers between localized states. This may be due to the driving force, generated through applied field (frequency) and helps to liberate the trapped charges [28]. These generated charges and electrons due to exchange interactions of different metal ions together participated in the conduction mechanism. Fig. 4.4 also exhibits strong temperature dependence of conductivity ascribed to the increase in drift mobility and hopping frequency of charge carriers. The increase in hopping of charge carriers between $\text{Cr}^{3+}\leftrightarrow\text{Cr}^{4+}$ in addition to free charges from different ion centers leads to the increase in conductivity of the nanoparticles. However, slight increase in ac conductivity is observed on Cr doping that can be understood on the basis of replacement of Ti with Cr ions and generate large density of charge carriers in the system.

The natural logarithm of ac conductivity as a function of the inverse of temperature for undoped and Cr doped TiO$_2$ NPs is depicted in Fig. 4.5. The behaviour of the data follows the relation $\sigma_{ac} = \sigma_0 \exp(-E_a/kT)$ for all the samples, here $\sigma_0$ is a constant having dimension of conductivity, $E_a$ is the activation energy and $k$ is the Boltzmann constant. It is observed that the conductivity rises with the increase in temperature (Fig. 4.5) that predicts semiconducting behaviour of the samples. Using these graphs, specific conductivity ($\sigma_a$) and activation energy ($E_a$) at elevated temperatures are calculated and tabulated in Table 4.2. Activation energy is found to decrease systematically with the increase in frequency and large value of activation energy at higher temperatures implies the presence of polarons that take part in the conduction mechanism [29].
Fig. 4.5. The variation of ac conductivity with inverse of absolute temperature at selected frequencies for all prepared NPs.
Table 4.2 Activation energies ($E_a$) and specific conductivities ($\sigma_a$) for Ti$_{1-x}$Cr$_x$O$_2$ (0 ≤ $x$ ≤ 0.08) NPs at different frequencies.

<table>
<thead>
<tr>
<th>Frequency (MHz)</th>
<th>$x=0$</th>
<th>$x=0.02$</th>
<th>$x=0.04$</th>
<th>$x=0.06$</th>
<th>$x=0.08$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$ (eV)</td>
<td>ln$\sigma_a$</td>
<td>$E_a$ (eV)</td>
<td>ln$\sigma_a$</td>
<td>$E_a$ (eV)</td>
</tr>
<tr>
<td>0.075</td>
<td>0.10</td>
<td>6.653</td>
<td>0.192</td>
<td>4.355</td>
<td>0.004</td>
</tr>
<tr>
<td>0.580</td>
<td>0.089</td>
<td>6.802</td>
<td>0.136</td>
<td>4.349</td>
<td>0.036</td>
</tr>
<tr>
<td>1.0</td>
<td>0.064</td>
<td>5.704</td>
<td>0.089</td>
<td>4.769</td>
<td>0.037</td>
</tr>
<tr>
<td>2.5</td>
<td>0.051</td>
<td>5.512</td>
<td>0.126</td>
<td>3.885</td>
<td>0.042</td>
</tr>
<tr>
<td>3.0</td>
<td>0.051</td>
<td>5.201</td>
<td>0.156</td>
<td>3.0195</td>
<td>0.037</td>
</tr>
<tr>
<td>5.0</td>
<td>0.043</td>
<td>5.019</td>
<td>0.097</td>
<td>3.885</td>
<td>0.047</td>
</tr>
</tbody>
</table>

4.3.3 Resistivity measurements

The temperature dependent dc resistivity of the Ti$_{1-x}$Cr$_x$O$_2$ (0 ≤ $x$ ≤ 0.08) samples is measured by two probe set up in the temperature range of 35 to 130 °C and shown in Fig. 4.6. It is observed that the resistivity decreases exponentially with the increase in temperature for pristine, 2% and 4% Cr doped samples which predict semiconducting nature of the samples. When temperature of the semiconducting material increases the trapped electron gains suitable amount of energy to become free from the valence state. However, it leads to the effective rise in density of charge carriers i.e electron and holes in the conduction and valence band respectively thereby increasing their drift mobility which in turn decreases their resistivity [30]. The variation in resistivity clearly shows a decrease in its value with the Cr doping in TiO$_2$ matrix from □ 46 to 2.93 MΩ·m, attributed to the splitting of $d$ state of the transition metal i.e. $e_g$ and $t_{2g}$ under the effect of crystal field in TiO$_2$ [31]. Since the donor level is shifted close to the conduction band with the substitution of dopant ions, therefore small increase in temperature leads to transition of electron from the donor level to conduction band that enhances the electrical conductivity. Whereas 6% and 8 % Cr doped samples exhibit different behavior than that of the pristine, 2% and 4% samples. These samples indicate metal to insulator transition (MIT) with transition temperatures ($T_{MI}$) at 332 and 321 K respectively. It means resistivity increases with the rise in temperature to $T_{MI}$ and then decreases for further increase in temperature. The metallic behavior at low temperatures can be explained on the basis of localization of charge carriers in small region that too surrounded with grain boundaries. At $T_{MI}$, the
value of resistivity is found to increase for higher doping, while $T_{MI}$ shifts towards the lower temperature. The increase in resistivity is attributed to the introduction of Cr ions at the grain boundary that obstructs the magnetic spin alignment near the grain boundary region of the TiO$_2$ and therefore increases the tunneling barrier height between the neighboring magnetic grains which results in shifting of $T_{MI}$ towards lower temperature [21]. This reveals that the potential barrier scattering plays a pivotal role in electrical conduction.

![Graph showing temperature dependence of resistivity](image)

**Fig. 4.6.** Temperature dependence dc resistivity measurements for Ti$_{1-x}$Cr$_x$O$_2$ ($x = 0, 0.02, 0.04, 0.06$ and $0.08$) NPs.

Temperature dependent resistivity in case of semiconductors follows Arrhenius relation and activation energy ($E_a$) can be obtained by the following expression

$$\rho(T) = \rho_0 \exp\left(\frac{E_a}{KT}\right)$$

where $E_a$ is the activation energy required for the hopping of charge carriers and estimated from the slope of $\ln\rho$ versus $1000/T$ for all the samples shown in Fig. 4.7. The value of activation energy gradually decreases from 627 to 484 meV on the increase in Cr doping. It indicates that the conduction in this type of systems is due to tunnelling of thermally assisted charge carriers across the grain boundaries and transition from a donor level to the conduction band. In the temperatures between 300 and 400 K, the lower value of activation energy is observed that suggest hopping and tunnelling of localized charge carriers that manage the electrical transport in the system [21].

100
4.3.4 Magnetic properties

In order to explore the magnetic nature of the synthesised nanoparticles of Ti$_{1-x}$Cr$_x$O$_2$ ($0 \leq x \leq 0.08$), magnetization measurements as a function of applied magnetic field were carried out using a superconducting quantum interference device (SQUID) magnetometer. Fig. 4.8 exhibits field dependent magnetization ($M-H$) curves at room temperature that revealed quite weak ferromagnetic behaviour of the NPs and magnetizations do not saturate even at higher field because of the paramagnetic (PM) contribution to the data. Fig. 4.9 exhibits field dependent magnetization ($M-H$) curves at room temperature after subtracting the paramagnetic contribution from the data. These $M-H$ curves illustrate the occurrence of ferromagnetic nature of all prepared samples with higher values of saturation magnetisation ($M_s$). It can be easily noticed that the ferromagnetic behaviour of the samples interestingly increases upto 4% Cr doping and then reduces with further increase in doping level. These results signify that the ferromagnetism in doped samples is not due to the extrinsic origin, hence not because of CrO$_2$ or other phases of chromium. Table 4.3 displayed the saturation magnetisation ($M_s$), remanent magnetisation ($M_r$) and coercive field ($H_c$) for all the samples. Despite of many years of research on induced ferromagnetism in oxide based diluted magnetic semiconductors, a proper explanation for the origin of

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**Fig. 4.7.** Variation of ln($\rho$) versus 1000/T for Ti$_{1-x}$Cr$_x$O$_2$ ($x = 0, 0.02, 0.04, 0.06$ and $0.08$) NPs.
ferromagnetism (FM) is still lacking. This presents discrepancy in the results attributed to the generation and random diffusion of defects, that depend on the synthesis of the nanostructures or on the growth conditions [32]. In earlier reports on induced FM in undoped TiO$_2$, it is observed that the oxygen vacancies play a significant role. Moreover, doping of various ions in TiO$_2$ creates defects occurring due to deficiency of oxygen atom and the presence of extra electrons. The interaction of these electrons with neighbouring Ti$^{4+}$ ions creates oxygen vacancies with different types of color centers and Ti$^{3+}$ species [33]. Pandey et al. [34] reported that the oxygen deficiency produces doping of electron in TiO$_2$ lattice however it does not give substantial magnetism. However, exchange interactions are required for the induced ferromagnetism because of interstitial Ti$^{3+}$, Ti$^{3+}$ cations or isolated F$^-$ which is paramagnetic species. Therefore, distribution of oxygen vacancies and the formation of particular charge configuration and their interaction with Ti 3$d$ neighbouring electron is required for induced ferromagnetism. The mechanism behind the ferromagnetic nature of the transition metal doped TiO$_2$ is complicated and several mechanisms were proposed to explain it like double and superexchange interactions [35]. Carrier mediated Rudeman-Kittel-Kasuya-Yashida (RKKY) like interaction and interaction of coupling of bound magnetic polarons (BMP) which arises due to localized electrons formed by oxygen vacancies defects and surrounding transition metal cations are two theories that explained the ferromagnetic nature in this system. RKKY theory is applicable for a metallic system with large number of delocalized electrons whereas BMP theory is applicable to semiconductors or insulators with localized electrons [5,18,36]. However, Cr$^{3+}$ ions in the system show 3$d^5$ high spin state that induces long range ferromagnetic exchange interactions with the vacancies created due to oxygen deficiencies in semiconductors. We have observed comparatively lower value of the magnetic moment in 6% and 8% than that of 4% Cr doped TiO$_2$ samples, which strongly support the fact that the carrier mediated theory is not appropriate to explain the origin of magnetism in Cr doped TiO$_2$ NPs. Moreover, 4% Cr doped sample shows significant increase in magnetization as compared to undoped TiO$_2$ which may be ascribed to ionic charge imbalance between Cr$^{3+}$ and Ti$^{4+}$ or generation of oxygen vacancies due to Cr$^{3+}$ doping in Ti$^{4+}$, hence resulting enhanced ferromagnetic nature of the sample. However, reduction in magnetization value for higher doping of Cr$^{3+}$ ions can be explained on the basis that Cr$^{3+}$ would have existed at the interstitial site in 6% and 8% Cr doped TiO$_2$ host.
lattice. Further, the decrease of magnetization in absence of the oxygen vacancies may be due to the superexchange interactions between $\text{Cr}^{3+}$–$\text{Cr}^{3+}$ or $\text{Cr}^{3+}$–O–$\text{Cr}^{3+}$ associated with antiparallel spins alignment [37].

**Fig. 4.8.** Magnetic field dependent $M$-$H$ hysteresis loops at room temperature of all prepared samples.

**Fig. 4.9.** Magnetic field dependent hysteresis loops of ferromagnetic component of the samples at room temperature.

The temperature dependent magnetization ($M$-$T$) in an applied field of 500 Oe is shown in Fig. 4.10 for 0%, 4% and 8% Cr doped TiO$_2$ samples. These measurements were performed in cooling mode from room temperature to 5 K in the absence of magnetic field and then 500 Oe field is applied while heating it to 300 K.
which gives ZFC curve. The sample is again cooled down to 5 K with the application of field, then heated to 300 K and magnetization is measured which gives FC curve. These curves illustrate ferromagnetic nature with small signatures of paramagnetism in the samples, follows Curie-Weiss law at lower temperatures and observed temperature independent behaviour of magnetization at higher temperatures [33]. At lower temperatures, paramagnetic contributions are detected on Cr doping that are correlated with non-interacting Cr$^{3+}$ ions contribution and confirms the essence of mass susceptibility ($\chi_m$) at room temperature on Cr doping. However, further analysis of magnetism at lower temperatures using Curie Weiss law [$\chi = C/(T-\theta)$] indicates the existence of weak antiferromagnetic coupling. The sharp increase in magnetisation at lower temperatures attributes to the expansion in polaron size and percolation of more polarons occurs, however this produces ordering of polaron magnetic moments.

![Fig. 4.10. Temperature dependent magnetization (applied magnetic field at 500 Oe) (a) FC and ZFC curves of undoped TiO$_2$ (b) FC and ZFC curves of 4% Cr doped and (c) FC and ZFC curves of 8% Cr doped TiO$_2$ NPs.](image)

M-T curve for undoped TiO$_2$ (Fig. 4.10(a)) shows the bifurcation in ZFC and FC plots, which represents thermo magnetic irreversible temperature ($T_{irr}$) that depends on the magnetic field, coercivity and magneto-crystalline anisotropy [38]. It predicts the presence of magnetic phase or ferromagnetic clusters with no evidence of
magnetic blocking in the NPs. Fig. 4.10(b-c) shows M-T plots under ZFC and FC conditions for 4% and 8% Cr doped TiO$_2$ NPs that reveal that the magnetization decreases with the rise in temperature. It also reveals that there is no magnetic blocking phenomenon like peak in both ZFC and FC curves. This suggests the absence of any magnetic impurity and secondary phase in the prepared samples as also ruled out by the EDS, Raman and XPS results [39].

**Table 4.3** Room temperature coercivity ($H_c$), remanent magnetization ($M_r$) and saturation magnetization ($M_s$) for Ti$_{1-x}$Cr$_x$O$_2$ ($0 \leq x \leq 0.08$) samples.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>$H_c$ (Oe)</th>
<th>$M_r$ (emu/g) x $10^{-4}$</th>
<th>$M_s$ (emu/g) x $10^{-4}$</th>
<th>$E_a$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped TiO$_2$</td>
<td>190.19</td>
<td>5.62</td>
<td>24</td>
<td>627</td>
</tr>
<tr>
<td>Ti$<em>{0.98}$Cr$</em>{0.02}$O$_2$</td>
<td>142.92</td>
<td>3.35</td>
<td>20</td>
<td>315</td>
</tr>
<tr>
<td>Ti$<em>{0.96}$Cr$</em>{0.04}$O$_2$</td>
<td>456.46</td>
<td>32.0</td>
<td>100</td>
<td>517</td>
</tr>
<tr>
<td>Ti$<em>{0.94}$Cr$</em>{0.06}$O$_2$</td>
<td>45.32</td>
<td>0.09</td>
<td>0.95</td>
<td>505</td>
</tr>
<tr>
<td>Ti$<em>{0.92}$Cr$</em>{0.08}$O$_2$</td>
<td>68.74</td>
<td>0.8</td>
<td>9.61</td>
<td>484</td>
</tr>
</tbody>
</table>

**4.4 Conclusions**

In summary, we have successfully synthesized undoped and Cr (2%, 4%, 6% and 8%).doped TiO$_2$ nanoparticles via acid modified sol-gel method. Thermogravimetric analysis shows the formation of thermally stable crystalline form of undoped and Cr doped TiO$_2$ NPs. The dielectric properties were studied as a function of temperature and frequency (75kHz $\leq \nu \leq$ 5MHz) by employing complex impedance spectroscopy. The TiO$_2$ NPs has high dielectric constant at lower frequencies and slightly decreases for higher frequencies. The incorporation of Cr ions in TiO$_2$ significantly increases the dielectric constant and ac conductivity having the advantage in device fabrication like nano sized dielectric material. Dielectric loss is decreasing with frequency and increases with the temperature which can be explained by Shockley Read mechanism. Moreover, temperature dependent dielectric parameters exhibit characteristic features associated with hopping of electrons among the ions, whereas thermal activation and drift mobility of the charge carriers are responsible for the enhancement in ac conductivity with the rise in temperature. Temperature dependent two probe resistivity measurements established semiconducting nature of the pristine, 2% and
4% samples, while metal-insulator transition observed in 6% and 8% Cr doped TiO$_2$ that suggests thermally activated Arrhenius mechanism is responsible for the conduction process in high-temperature region. The present magnetic investigations predict the room temperature ferromagnetic (FM) nature of the NPs attributed to the doping effect and oxygen deficiency. This further proves that the oxygen vacancy related defects, distribution of dopant concentration and their exchange interactions in TiO$_2$ nanoparticles play an important role in the origin of ferromagnetism. With the increase in Cr$^{3+}$ concentration, the oxygen vacancies increase which in turn enhances RTFM explained on the basis of BMP theory. However, decrease in FM on further doping may be ascribed to the antiferromagnetic (AFM) coupling in the absence of oxygen vacancies because of superexchange coupling in Cr$^{3+}$ neighbouring ions. This AFM coupling with superexchange interaction reduces the magnetic moment with the incorporation of Cr in TiO$_2$ hence weak ferromagnetism is observed.
References

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Chapter 5

Influence of (Cr/Co) co-doping on the microstructural, optical and photocatalytic properties of microwave assisted sol-gel derived TiO$_2$ nanoparticles

This chapter deals with the detailed description of codoped titania nanoparticles with stoichiometric formula Ti$_{1-x}$Cr$_{x/2}$Co$_{x/2}$O$_2$ (x= 0, 0.04 and 0.06) synthesized via microwave assisted sol-gel route. Influence of Cr/Co co-doping on various physical properties like microstructural, optical, and photocatalytic activity was explored using various analytical techniques viz. XRD, FTIR, Raman, XPS, TEM and UV-visible absorption spectroscopy.