This chapter puts forward the contribution of Co ions on the dielectric feature and magnetic properties on titania nanoparticles with stoichiometric formula Ti$_{1-x}$Co$_x$O$_2$ ($x = 0.00$, $0.03$, $0.05$ and $0.07$). The frequency dependent dielectric properties at room temperature have been investigated using LCR meter. Field and temperature dependent magnetic measurements have been done using VSM and SQUID magnetometers.
6.1 Introduction

There is a growing interest of nanostructure semiconductors due to their impact in different applications like catalytic, magnetic, optical, gas sensing, electrical, etc. [1]. One of the finest approaches to create novel materials for achieving rich functionality is to merge different physical properties into one. They offer a typical opportunity to fabricate new attractive devices with remarkable feature. In this direction, TiO$_2$ (titania) is one of the important semiconductors that has been studied exclusively. It has attracted the condensed matter community owing to its wide range of applications in optoelectronic devices, transparent conductors, gas sensors, variastors, photocatalytic devices, dye sensitized solar cells and an anode material for lithium-ion batteries etc [2-6]. Nano titania, a cost effective material of high dielectric constant [7, 8] and promising chemical stability [9], is expected to replace traditional capacitor dielectrics and dielectric resonators. Therefore, the interest is being focused also on high dielectric constant materials which is driven by the need to fabricate more reliable high capacitance DRAM cell and, hence, to achieve high density DRAMs. Generally, TiO$_2$ is known to exist in three types polymorphs: rutile, brookite and anatase. The majority of dielectric applications are affected by the presence of these crystalline polymorphs and morphologies [10]. For coarse-grained titania, rutile is the only stable phase, whereas other two are metastable and convert to rutile when heated [11]. However, for titania NPs, stabilities of anatase and rutile phases show opposite trend due to the competition between the surface and transformation energies [12]. Hence, anatase is more stable than the rutile phase when particle sizes are small [13].

In recent years, efforts are going on to dope transition metal (TM) in TiO$_2$ for diluted magnetic semiconductors (DMS) based spintronic applications [14-18]. The discovery of room temperature ferromagnetism (FM) in Co doped titania [19] has triggered an enormous experimental and theoretical efforts to understand the origin of magnetic properties in a class of semiconductors (TiO$_2$, ZnO, SnO$_2$ etc.) that shows correlation effects when doped with TM ions. A key component to exploiting titania based DMS is the realization of intrinsic FM with Curie temperature ($T_C$) at or above room temperature for device applications. The basic principle of developing these
ferromagnetic semiconductors is to potentially access their multifunctional properties for spin based electronic devices where both degrees of freedom (charge as well as spin) can be manipulated in a single material, without interrupting the semiconducting properties of the host [20, 21]. In this regard, controversy persists in the exact nature of the origin magnetism in these materials [22].

Many researchers have tried to investigate, analyze and understand the several behaviour of TiO₂ (pure and doped with different foreign elements) in bulk, nanoparticles as well as thin film. Only few reports can be found on structural refinement using Rietveld analysis and detail frequency dependent dielectric properties of Co doped TiO₂ NPs. This chapter is going to present systematic frequency dependent dielectric properties of Co doped titania NPs. In addition, magnetization measurements were carried out for all Co doped samples in order to bring deeper insight into the controversial origin of the ferromagnetism of such kind of DMS systems.

6.2 Experimental Details

6.2.1 Materials and Synthesis

Cobalt doped TiO₂ NPs with stoichiometric formula Ti₁₋ₓCoₓO₂ (x = 0.00, 0.03, 0.05, and 0.07) were prepared by acid modified sol-gel route. Details of materials and synthesis procedure are given in Chapter 2 (section 2.2.1).

6.2.2 Characterizations and Measurements

The crystallinity and phase of the Co doped samples were analyzed by XRD. The lattice parameters and other detailed structural information were obtained by using PowderX followed by the Rietveld refinement. FESEM, HRTEM and EDS investigated morphological and compositional details accordingly. Raman analysis was also carried out for further confirmation of single phase. All the above investigation were discussed in Chapter 5. The synthesized pure and Co doped TiO₂ NPs are in anatase type tetragonal structure having space group I₄/amd. In this chapter pure and all Co doped TiO₂ pallets of diameter 12.9 mm with thickness 1.2 mm were prepared and sintered at 450° C. The pallets were coated with silver paste on opposite faces to form parallel plate capacitor with the synthesized product as
dielectric medium. Frequency dependent dielectric properties were studied in the range frequency 75 kHz - 5 MHz using Agilent LCR meter (4285A). Field dependent magnetization of pure and Co doped samples was measured at room temperature using a vibrating sample magnetometer (VSM). Moreover, field dependent magnetization (M-H) at 300 K and temperature dependent magnetization (M-T) measurements were carried out with a superconducting quantum interference device (SQUID) magnetometer (MPMS SQUID VSM- 050, Quantum design, USA).

6.3 Results and Discussion

6.3.1 Dielectric Properties

Dielectric properties depend on the nature of polarization of the material. They are sensitive to synthesis process, interfaces, grain scale, structural homogeneity, porosity, density, history of sintering, introduced strain, doping by ions and cations distribution. The following quantities explain the dielectric properties of materials.

6.3.1.1 Dielectric Constant

The response of materials in an alternating field is characterized by a complex dielectric constant ($\varepsilon^*$) defined by equation (2.8).

Dielectric measurements at room temperature were performed on pure and Co doped anatase TiO$_2$ NPs. Fig. 6.1 illustrates the variation of the real part of dielectric constant as a function of frequency of applied electric field between the frequency ranges of 75 kHz to 5 MHz for all the samples at room temperature. The dielectric constant decreases with increase in frequency and it is nearly constant in the higher frequency. All the samples have a strong frequency dispersion of permittivity in the low frequency, whereas nearly frequency independent behaviour has been observed in high frequency range. The decrease of $\varepsilon'$ with increase in frequency may be attributed to the electrical relaxation processes. It is seen that $\varepsilon'$ value decreases with the addition of cobalt in titania NPs.
The observed dispersion can be correlated qualitatively to interfacial polarization in accordance with the Maxwell-Wagner model [23] and Koop’s phenomenological theory [24]. This model expressed that the dielectric materials are composed of highly conducting grains separated by poorly conducting thin grain boundaries. The grain boundaries are formed during the sintering process. The grain boundaries are found to be more effective at lower frequency region, while grains are effective at higher frequencies. The nature of dielectric permittivity related to free dipoles oscillating in an alternating field depends on the relaxation time and frequency of applied field is as follows. At low frequency, dipoles can follow the applied field and are being got polarized. As the frequency increases dipoles begin to lag behind the frequency of a.c. field for the polarization and ε’ starts decreasing. At very high frequencies, dipoles can no longer follow the frequency of the field. This behaviour was observed for the pure and Co doped TiO$_2$ NPs. The investigation is also consistent, with the previous workers in this field. They have suggested that the
The dielectric constant will decrease as the size of the particle is reduced [25, 26]. The decreased crystallite size offers more grain boundaries. It means more restrictions to the flow of charge carriers to reach near the electrodes. One may expect a smaller value of the dielectric constant in such samples when NPs size decreases with increasing concentration of Co doping. Cobalt ions also could act as effective electron scavengers to trap the conduction-band electrons of titania NPs, hence, the polarization effect reduces and the permittivity decreases [26].

6.3.1.2 Dielectric Loss

The dielectric loss (tanδ) in the materials is a measure of lag in the polarization with respect to the alternating field applied. It is considered to be caused by domain wall resonance. The value of loss tangent of all the samples are large at lower frequencies, while the losses are found to be low at higher frequency since domain wall motion is inhibited. Equation (2.10) tells that tanδ is directly proportional to the imaginary part of dielectric constant, therefore, it exhibits similar dispersion behaviour. The behaviour of tanδ as a function of frequency at room temperature is shown in Fig. 6.2. The characteristic of dielectric loss can be correlated normally to the resistivity measurement. With the high resistivity, materials exhibit low dielectric losses and vice versa. A peak appearing at a characteristic frequency characterizes the dielectric loss spectra. Presence of the peak for both pure and Co doped TiO₂ suggest that relaxing dipoles are present in all the samples. The strength and frequency of relaxation depend on the characteristic property of dipolar relaxation. In Fig. 6.2, the peak for pure and 3 % Co doped titania can be seen. It gradually shift to the lower frequency with increase in Co doping concentration. For the rest of two samples, the peaks are not properly observed within the frame of Fig. 6.2 due to the frequency limitation of the LCR meter. The tangent loss peak for pure TiO₂ NPs was around 100 kHz and the peak intensity is increased on Co doping though it was not consistent. Increase in intensity of relaxation peak with Co doping is well explained by the Rezlescu model [27]. According to this model, the relaxation peak occurs due to the collective contribution of both p-type and n-type charge carriers [28].
Fig. 6.2 Variation of dielectric loss of Ti$_{1-x}$Co$_x$O$_2$ ($x = 0.00, 0.03, 0.05$ and $0.07$) NPs with frequency at room temperature.

The p-type charge transfer in the studied sample is due to the hopping of electrons between Ti$^{4+}$ / Ti$^{3+}$ (Ti$^{4+} + e^{-} \leftrightarrow$ Ti$^{3+}$) ions whereas n-type charge transfer between Co$^{2+}$ / Co$^{3+}$ (Co$^{2+} \leftrightarrow e^{-} +$ Co$^{3+}$). The resultant polarization of both types of charge carriers gives peaking behaviour.

6.3.1.3 A.C. Conductivity

The electrical conductivity of a dielectric material has contribution of two terms of equation (2.12). It was first reported by Jonscher [28, 29] for wide variety of materials (e.g. glasses, polymers, amorphous semiconductors, etc.). The d.c. conductivity, $\sigma(0, T)$ is due to the band conduction or frequency independent part. It is related to the drifting of charge carriers and follows the Arrhenius relation. The second term $\sigma(\omega, T)$, temperature as well as frequency dependent function, is related to the dielectric relaxation caused by the localized electric charge carriers. In wide range of frequency, it obeys the empirical power law and takes the form given in
equation (4.1). Jonscher led to denote these behaviour as “universal dielectric response” (UDR) [28, 29]. According to this model, localized charge carriers hopping between spatially fluctuating lattice potentials produce the conductivity as well as they give rise to the dipolar effects. If it is true, log$f$ versus log ($\varepsilon'$) plots should show a linear behaviour. This is indeed the case at higher frequencies for all the samples (Fig. 6.3). It means that UDR phenomenon is responsible for dielectric response of these samples at higher frequency region. However, the linear behaviour of Fig. 6.3 supported the possibility of the presence of other contribution (electrode, Maxwell - Wagner, or grain boundary effects) to the dielectric response. With the proliferation of Co concentration, linear behaviour is improved.

![Graph](image.png)

*Fig. 6.3 Plot of log $f$ versus log ($\varepsilon'$) for Ti$_{1-x}$Co$_x$O$_2$ (x = 0.00, 0.03, 0.05 and 0.07) NPs at room temperature.*
The a.c. conductivity ($\sigma_{ac}$) from the dielectric data may be computed using the equation (2.13). From equations (2.10) and (2.13), the measurement of $\sigma_{ac}$ generally shows frequency dispersion, i.e. the dependence of $\sigma_{ac}$ on $\omega$.

Fig. 6.4 shows the variation of a.c. conductivity with frequency for pure and Co doped titania NPs at room temperature.

![Graph showing variation of a.c. conductivity with frequency for pure and Co doped titania NPs at room temperature.](image)

**Fig. 6.4** Variation of a.c. conductivity of Ti$_{1-x}$Co$_x$O$_2$ ($x = 0.00, 0.03, 0.05$ and $0.07$) NPs with frequency at room temperature.

Initially, a.c. conductivity increases slowly with increase in frequency but at higher frequency, conductivity shows a steep increase, which is characteristic feature of disordered materials. In addition, initially a.c. conductivity decreases upon increasing Co concentration up to 5 mol %. As the particle size decreases, the surface to volume ratio increases. The large surface scattering corresponds to the decrease in electronic conductivity. The internal lattice strain may also arise because of increasing dopant level and can break the local electrical neutrality to produce an electrical polarization of the crystal. This leads to a long-range electric field, which in turn
disturb the electron motion, indicating that the doped electrons do not enhance the conductivity in Co doped titina NPs. However, the conductivity increases for 7% Co doped samples. It may have happened due to the fact that the increase in dopant concentration increases the hopping process of charge between Co$^{2+}$ and Co$^{3+}$ ions which dominates over these charge carriers blocking effect.

### 6.3.2 Magnetic Properties

#### 6.3.2.1 Field Dependent Magnetization by VSM

The magnetic properties of the Co doped TiO$_2$ NPs were investigated using VSM. Fig. 6.5 represents the field dependent specific magnetization M-H curves of pure and Co doped TiO$_2$ NPs measured at room temperature. Literature reports that the pure titania NPs shows the diamagnetic (DM) properties at the temperature higher than 20 K [1, 30].

![M-H hysteresis curve of Ti$_{1-x}$Co$_x$O$_2$ (x = 0.00 0.03, 0.05 and 0.07) NPs at room temperature measured with VSM.](image)

**Fig. 6.5** M-H hysteresis curve of Ti$_{1-x}$Co$_x$O$_2$ (x = 0.00 0.03, 0.05 and 0.07) NPs at room temperature measured with VSM.
The magnetization behaviour of the pure TiO$_2$ NPs sample, as shown in Fig. 6.5, is slightly different from that of the other reports [1, 30]. Fig. 6.5 shows nonlinear M-H behaviour at low field for the pure titania sample. It can be seen in this figure that there is a small hysteresis at low fields and the weak ferromagnetic (FM) signal is detected only in the low field range while being dominated by DM order in the high field range. On the other hand, the in plane hysteresis loop of Co doped TiO$_2$ NPs, as shown in Fig. 6.5, represents distinct evidence of the FM nature at room temperature, although the response is weak. In the high field region M-H curve of the Co doped samples from the VSM data do not show any saturation.

### 6.3.2.2 Field and Temperature Dependent Magnetization by SQUID

To verify the presence of the magnetic phase and the kind of magnetic order, magnetization (M) versus magnetic field (H) behaviour was also investigated using SQUID magnetometer.

![M-H variation of Ti$_{1-x}$Co$_x$O$_2$ (x = 0.00, 0.03, 0.05 and 0.07) NPs as observed with SQUID magnetometer at 300 K. Inset shows the enlarged view at low field.](image)

**Fig. 6.6** M-H variation of Ti$_{1-x}$Co$_x$O$_2$ (x = 0.00, 0.03, 0.05 and 0.07) NPs as observed with SQUID magnetometer at 300 K. Inset shows the enlarged view at low field.
The M-H variations of the Co doped TiO$_2$ NPs (at 300 K) have been depicted in Fig. 6.6 and they show ferromagnetic behaviour. In the high field region M-H does not also show any saturation, which suggests some paramagnetic (PM) contribution to the M-H data. The appearance of PM contribution in a ferromagnetic (FM) hysteresis loop is well known and is usually subtracted out to obtain the FM part [31, 32]. After subtracting the PM contribution from the experimental M-H plot, saturation of magnetization can be observed in the high field region as shown in Fig. 6.7. The extracted coercivity ($H_C$), remanant magnetization ($M_R$) and ferromagnetic saturation magnetization ($M_S$) are summarized in Table 6.1.

**Fig. 6.7** M-H variation of Ti$_{1-x}$Co$_x$O$_2$ ($x = 0.03, 0.05$ and $0.07$) NPs at 300 K after subtracting PM contribution along with experimental undoped TiO$_2$ NPs. Bottom-right inset is the enlarged view. Top-left inset of the figure shows the expanded low field region of the experimental M-H variation of pure TiO$_2$ NPs.
Table 6.1 Magnetic parameters estimated from M-H measurements of Co doped anatase TiO$_2$ NPs.

<table>
<thead>
<tr>
<th>Co conc.</th>
<th>$H_C$ (Oe)</th>
<th>$M_R$ (emu/g)</th>
<th>$M_S$ (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>36.05</td>
<td>$2.70 \times 10^{-4}$</td>
<td>$0.51 \times 10^{-2}$</td>
</tr>
<tr>
<td>5</td>
<td>48.15</td>
<td>$3.89 \times 10^{-4}$</td>
<td>$0.59 \times 10^{-2}$</td>
</tr>
<tr>
<td>7</td>
<td>69.57</td>
<td>$13.84 \times 10^{-4}$</td>
<td>$1.01 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

M-H measurement for undoped TiO$_2$ sample has also been performed using SQUID at 300 K and is presented along with the experimental plot (Fig. 6.6), and also after subtraction of PM contribution (Fig. 6.7). The magnetization behaviour of the synthesized pure TiO$_2$ NPs, as shown in Fig. 6.7, is slightly different from that of the other report [30]. Top-left inset of Fig. 6.7 shows nonlinear M-H behaviour at low field for the undoped titania sample. It can be seen from this figure that there is a small hysteresis at low fields and the weak ferromagnetic (FM) signal is detected only in the low field range while it is dominated by DM order in the high field range. There are many reports on ferromagnetism in undoped TiO$_2$ thin films without any magnetic impurities [22, 33-35]. Most of them accused to the presence of oxygen vacancies on the surface or interface of the films for this unexpected FM ordering. The weak FM ordering at low field in the synthesized pure sample may be mediated by the oxygen vacancy or defect associated with NPs. However, the noteworthy point is that the observed ferromagnetism is quite weak in pure TiO$_2$ NPs. It indicates unavailability of considerable number of oxygen vacancies to impart ferromagnetism and to overcome diamagnetism properly. On the other hand, incorporation of cobalt into titania host matrix generates considerable number of oxygen vacancies nearby Co ions and the in plane hysteresis loop of doped samples (Fig. 6.7) represents distinct evidence of the FM ordering at room temperature although response is weak.

The understanding of the origin of ferromagnetism in oxide based DMS materials is incomplete and the exact origin is not known. It may be an extrinsic effect due to direct interaction between the local moments in magnetic impurity clusters or indeed an intrinsic property caused by exchange coupling between the spin of the carriers and the local magnetic moments. Phase analysis strikes out the possibility of
Co clustering or any Co oxide phase as there is no trace of any secondary phase other than the anatase TiO$_2$ up to the detection limit of phase analysis: XRD, HRTEM and Raman (Chapter 5).

In order to further elucidate and to achieve a deeper insight into the origin of the FM ordering (although weak) of Co doped NPs samples, temperature dependent magnetization measurements (M-T) have been performed at low applied field, H = 200 Oe. Fig. 6.8 shows zero field cooling (M$_{ZFC}$) and field cooling (M$_{FC}$) plots for the NPs in the temperature range from 5 - 300 K with different Co concentrations.

![Diagram](image)

**Fig. 6.8** M-T curves recorded at a constant applied field of 200 Oe for Ti$_{1-x}$Co$_x$O$_2$ ($x = 0.03, 0.05$ and $0.07$) NPs.
It is seen that the samples with \( x = 0.03 \) [Fig. 6.8 (a)], 0.05 [Fig. 6.8(b)] and 0.07 [Fig. 6.8 (c)] exhibit M-T (FC–ZFC) curves with similar trends and they do not show any additional features usually associated with superparamagnetism (SPM) or spin-glass (SG) like systems [36]. The observed minute separation between ZFC and FC curves of these Co doped NPs can only be ascribed to a weak FM ordering present in the system. Furthermore, there is no trace of any characteristic peak or hump in the ZFC curve, signifying absence of ferromagnetic [37] or antiferromagnetic [35] contamination in the doped samples. Therefore, the observed weak FM ordering in the synthesized Co doped TiO\(_2\) NPs seems to be intrinsic here.

For the quantitative evaluation of the intrinsic magnetic coupling between the Co ions of Ti\(_{1-x}\)Co\(_x\)O\(_2\) (\( x = 0.03, 0.05 \) and 0.07) NPs, M-T measurements of all the doped samples have also been performed under ZFC condition at a field strength of 4000 Oe. The field is higher than the maximum field at which hysteresis loop is observed in M-H curves (Figs. 6.6 and 6.7) and at which difference between \( M_{\text{FC}} - M_{\text{ZFC}} \) expected to be zero [38]. The behaviour of inverse of the magnetic susceptibility \((1/\chi)\) (estimated from \( M_{\text{ZFC}} \) data performed at 4000 Oe) against temperature has been shown in Fig. 6.9 for doped TiO\(_2\) NPs. The inverse susceptibility versus temperature \((1/\chi - T)\) curves exhibit typical antiferromagnetic (AFM) behaviour but they deviate from linearity at lower temperature region. To analyze such type of \((1/\chi - T)\) variations, one can make a linear fit of the high temperature inverse susceptibility data, which follows Curie-Weiss law, but impossible to fit \(1/\chi\) at lower temperature, as \(1/\chi\) against T deviates from linearity in this region. So, a phenomenological approach has been adopted as discussed by Banerjee et al. [39]. According to this phenomenology, the system consists of two sets of Co ion spins. One set contains the Co ions having no nearby Co ions i.e. paramagnetic and \(\chi\) follows Curie behaviour \((M/H = \chi = C(x)/T)\). The other set contains at least one Co nearest neighbor interacting via mean field like interactions and \(\chi\) can be expressed by Curie-Weiss function, given by equation (4.2) [40]. Now magnetic susceptibility, \(\chi\) can be written as [39]:

\[
\frac{M}{H} = \chi = C(x)[f/T + (1-f)/(T + 0(x))] \quad (6.1)
\]
where, \( x \) is the molar concentration of Co atoms and \( f \) is the fraction of Co atoms with no other Co in the nearest neighbor positions. Curie constant \( C(x) \) and the Curie-Weiss temperature \( \theta(x) \) are expressed as

\[
C(x) = xC_0 = x(g\mu_B)^2S(S + 1)n/3k_B
\]

\[
\theta(x) = x\theta_0 = 2xS(S + 1)zJ/3k_B
\]

where \( n \) is the number of Co atoms/cm\(^3\); \( g = 2.0; \mu_B = 9.27 \times 10^{-21} \) erg/Oe; \( k_B = 1.38 \times 10^{-16} \) ergs/K; \( S \) represents the value of the spin for the Co\(^{2+}\) in TiO\(_2\); \( J/k_B \) is the effective exchange integral between nearest neighbor Co\(^{2+}\) ions, and \( z \) is the number of nearest neighbor cations (= 4 for anatase structure). The values of \( C(x) \), \( \theta(x) \), \( f \), \( J/k_B \) and \( S(S+1) \) are presented in Table 6.2. \( J/k_B \) has been estimated from equation (6.3). It is found that equation (6.1) gives an excellent fit to the susceptibility \((1/\chi)\) over the entire temperature range and shown in Fig. 6.9.

\begin{table}[h]
\centering
\caption{Parameters estimated from M-T measurements (at 4000 Oe) of Co doped anatase TiO\(_2\) NPs.}
\begin{tabular}{cccccc}
\hline
Co conc. & C(x) & f & \theta(x) (K) & \( J/k_B \) (K) & \( S(S+1) \) \\
\cmol \% & & & & & \\
\hline
3 & 0.0014 & 0.33 & 162.36 & 186.12 & 7.27 \\
5 & 0.0020 & 0.39 & 218.65 & 170.82 & 6.40 \\
7 & 0.0064 & 0.12 & 532.83 & 129.10 & 14.74 \\
\hline
\end{tabular}
\end{table}

The large negative values of Curie-Weiss temperature confirm the presence of strong AFM coupling in Ti\(_{1-x}\)Co\(_x\)O\(_2\) \((x = 0.03, 0.05 \) and 0.07) samples which is gradually increasing with Co concentration. Actually, in competition between two spontaneous interactions i.e. FM and AFM exchange, stronger FM interaction dominates and that is, an on average, reflected in M–H measurement. Therefore, magnetization is found to be weak.
Fig. 6.9 Inverse of magnetic susceptibility with temperature (1/χ vs T) plot (experimental and fitted) of Ti$_{1-x}$Co$_x$O$_2$ ($x = 0.03, 0.05$ and $0.07$) NPs estimated from $M_{ZFC}$ data performed at a field 4000 Oe.

6.4 Conclusions

In summary, pure anatase cobalt doped TiO$_2$ NPs of basic composition Ti$_{1-x}$Co$_x$O$_2$ ($x = 0.00, 0.03, 0.05$ and $0.07$) were successfully synthesized by simple acid modified sol-gel method. The titina NPs has high dielectric constant and display a gradual dielectric relaxation in the high frequency region. The incorporation of Co ions significantly reduces the dielectric constant as well as a.c. conductivity. Co ions can act as effective electron scavengers to trap the conduction-band electrons of
titania NPs, hence, the polarization effect reduces and the dielectric constant decreases. Although, the conductivity increases for 7 mol % Co doped NPs. It may have happened because the hopping process of charge between Co\(^{2+}\) and Co\(^{3+}\) is increased due to further increase in dopant concentration, which dominates over charge carriers blocking effect and, hence, conductivity is increased. The loss tangent peak appearing at a characteristic frequency suggests the presence of relaxing dipoles in all the synthesized Co doped samples. It increases with Co doping and is gradually shifted towards lower frequency region. It can be explained that the weak ferromagnetism in the samples may be caused by exchange interactions between Co ions in the titania host lattice, where the intrinsic defects of oxygen vacancies associated with NPs played an important role in promoting long-range FM order in Co doped anatase titania NPs. In the high field region, M-H curves do not show saturation for Co doped TiO\(_2\) NPs due to the presence of PM contribution. After subtraction the PM component, the doped samples show ferromagnetic hysteresis loop with saturation magnetization of the order of 10\(^{-2}\) emu/g, which increases as the doping Co content increases. Moreover, M-T result allows ruling out the premise of a strict correlation between Co clustering/Co composite and the ferromagnetism reported for the Co doped anatase oxide NPs. The presence of strong AFM coupling has been estimated. This AFM coupling reduces the magnetic moment of the doped TiO\(_2\) NPs and weak ferromagnetism is the outcome of synthesized Co doped TiO\(_2\) NPs samples.
References


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