Chapter 6

Modification of local structure and the corresponding changes in optical and magnetic properties of Cr\(^{3+}\) doped TiO\(_2\) nanoparticles

This chapter starts with the doping effect of Cr on the lattice structure of TiO\(_2\). The location of chromium on the substitutional, interstitial position of titania may affect the coordination geometry of TiO\(_2\) and hence have influence on the physical properties of TiO\(_2\). We will precede our discussion on the doping effect of this ion on the absorption and photoluminescence property of TiO\(_2\). An equal importance will be given on the magnetic properties of this doped semiconductor. A density functional theory (DFT) based calculation reported that substitutional doping of chromium enhances magnetization while interstitial doping reduces the total magnetization [1]. Therefore, magnetic behavior of these samples will be thoroughly studied and will be delineated at the end of the chapter.

6.1 Local structure modification of TiO\(_2\) nanoparticles on doping of Cr\(^{3+}\)

The basic structural unit of TiO\(_2\) is TiO\(_6\)\(^2-\) octahedra with Ti\(^{4+}\) surrounded by six oxygen ions. In this structure Ti\(^{4+}\) has an octahedral coordination. Any disruption in the octahedra or changes in the number of oxygens may change the coordination from octahedral to tetrahedral or trigonal bipyramidal. When Cr\(^{3+}\) ions are incorporated into TiO\(_2\) the ion may go to the substitutional position or may be located in the interstitial position or may be loosely bound to the surface. In all these cases the lattice structure and thus the local coordination around Ti\(^{4+}\) may get affected. To investigate the doping effect on the local structure of TiO\(_2\) we first took XRD pattern of the nanoparticles. The XRD pattern of pure and chromium (1.5\(\leq\) Cr\(\leq\)4.5) doped TiO\(_2\) are shown in Figure 6.1(a). All the peaks are assignable to contributions from tetragonal anatase phase (JCPDS 78-2486). The average crystallite size is calculated using Scherrer’s formula \(d = \frac{0.9 \lambda}{(\beta \cos \theta)}\), where \(d\) is the crystallite size, \(\lambda\) is the wavelength of X-ray (0.154 nm), \(\beta\) is the full width at half maximum (FWHM) and \(\theta\)
is the angle of diffraction. The calculated crystallite sizes are 10 nm, 11 nm, 9 and 12 nm for 0.0 %, 1.5 %, 3.0 % and 4.5 % respectively. In the diffraction spectra we have not observed any impurity peaks related to oxide phases of chromium. However, some noticeable changes are observed in the peak position. The peak position of (101) crystallographic plane remains unaltered for Cr$^{3+} \leq 3.0 \%$ but got shifted to higher diffraction angle at 4.5 %. Compared to TiO$_2$, the (004) and (200) diffraction peaks of 1.5 % Cr doped TiO$_2$ shows shifting to lower 2θ angle which is quite expected since the ionic size of Cr$^{3+}$ is slightly larger (75.5 pm) than that of Ti$^{4+}$ (74.5 pm) and on substituting Ti$^{4+}$ lattice is expanded. However, this variation is not similar for 3.0 % and 4.5 % Cr$^{3+}$ doped TiO$_2$ samples. This means that extent of dopant incorporation on different facets is different. At 3.0 %, the peaks slowly diverge towards higher angle and at 4.5 % the peak gets shifted more towards the higher 2θ side. The lattice constant $a$ of each sample is calculated by Gaussian fitting of (200) peak. The respective values of $a$ are 0.3779 nm, 0.3781 nm, 0.3778 nm and 0.3774 nm for pure and for 1.5, 3.0 and 4.5 % Cr$^{3+}$ doped samples. The margin of error in each sample is ± 0.0003 nm. In the diffraction spectra analysis of cobalt and manganese doped TiO$_2$, we observed uniform variation of $d$-spacing (either increase or decrease) with dopant concentration. On the contrary, in Cr doped TiO$_2$ the changes in the magnitude of lattice parameter with Cr is not uniform.

![Figure 6.1](image.png)

**Figure 6.1** (a) XRD pattern of Cr doped TiO$_2$ nanoparticles. (b) Variation of lattice constant with changes in Cr concentration.

As shown in Figure 6.1(b), in comparison to TiO$_2$ (0.3779 nm ± 0.0003) the lattice constant value of the doped TiO$_2$ first increases at 1.5 % (0.3781 nm ± 0.0003) then decreases at 3.0 % (0.3778 nm ± 0.0003) and 4.5 % (0.3774 nm ± 0.0003). This behavior is not in agreement with Vegard’s law which states that the lattice constant
should vary linearly with dopant concentration and the breaking from linearity occurs when a phase transition takes place [2]. However, in the XRD results no such transitional phases (e.g. rutile) have been found after Cr\(^{3+}\) doping. This anomaly in our results can be ascribed to three different reasons which are represented schematically in Figure 6.2. Firstly, at 1.5 % Cr\(^{3+}\), when slightly large sized Cr\(^{3+}\) substitutes Ti\(^{4+}\) the lattice expands. Since dopant concentration is low the numbers of oxygen vacancies, formed due to breaking of Ti-O bonds, are not large enough to overcome the size effect induced by Cr\(^{3+}\) doping. Secondly, when the added impurity is slightly increased to 3.0 %, few more Ti\(^{4+}\) lattice sites will be substituted by Cr\(^{3+}\) with subsequent increase in the numbers of oxygen vacancies. Oxygen deficiency will diminish the numbers of Ti-O or Cr-O bond and will lead to the contraction of O-Ti-O or O-Cr-O bond angle. The ultimate result is the squeezing of the lattice and reduction in the values of lattice parameter. Thirdly, at 4.5 % of Cr\(^{3+}\), the numbers of oxygen vacancies are further increased. Since the dopant concentration is high, few Cr\(^{3+}\) ions occupy interstitial positions of TiO\(_2\). When Cr\(^{3+}\) ions are incorporated into the lattice of TiO\(_2\), only a few Ti\(^{4+}\) lattice sites will be occupied by Cr\(^{3+}\). Thermodynamically, there is a maximum solubility limit of dopants in TiO\(_2\) and on crossing this limit no more Cr\(^{3+}\) will be able to occupy the substitutional place and thus sit on the interstitial site [3]. These interstitial chromium ions will interact with lattice site chromium/oxygen ions and lead to unusual variation of Cr-O bond length and Cr-O-Cr bond angles.

![Figure 6.2 Lattice distortions of TiO\(_2\) nanoparticles caused by incorporation of Cr\(^{3+}\) ions.](image)

Therefore, location of the dopant ions may affect the local structure of TiO\(_2\) nanoparticles. Besides, a proper selection of dopant concentration and careful study of
the position of impurities is very much important to make efficient doped semiconductor nanoparticles.

6.2 Fano type antiresonance of Cr$^{3+}$ and related absorption spectra

We have understood that impurities may be present on the surface, on the substitutional and on the interstitial position. In all these locations the dopant interacts with the host lattice and changes the electronic structure of the host. UV-vis absorption spectroscopy may provide information on the changes in the electronic structure of TiO$_2$ on doping of Cr$^{3+}$ ions. To understand this, we took reflectance spectra of entire samples. Reflectance and the corresponding Kubelka-Munk (K-M) absorption plot of the samples are depicted in Figure 6.3(a,b) respectively. The maximum absorption peak of pure and doped TiO$_2$ appears at 340 nm. Apart from this peak, the absorption curves of the doped samples have two extra peaks related to $d$-$d$ electronic transition of Cr$^{3+}$ in octahedral ($O_h$) crystal field of TiO$_2$ [4-5]. These peaks appear at ~410 nm due to $^4A_2$(F) to $^4T_1$(F) transition and at 735 nm due to $^4A_2$(F) to $^2E$ electronic transition [4-6]. At 1.5 %, the vibronic transition is not strong enough to break the coordination symmetry around Cr$^{3+}$ and hence the absorption peaks in these regions are not intense.

When Cr$^{3+}$ substitutes Ti$^{4+}$ in anatase TiO$_2$, it comes under the influence of six oxygen ligands. Since doping is predicted to distort local structure of TiO$_2$, it can be said that Cr$^{3+}$ is now in pseudo octahedral coordination. Since the field strength of O$^{2-}$ lies at the same level as that of oxalate [4], entire $d$-$d$ electronic transitions of Cr$^{3+}$ are analyzed considering the corresponding transitions in [Cr(ox)$_3$]$^{3-}$ as a reference. In
Figure 6.3(c), we observed a small absorption dip at 735 nm in the spectral range from 600–900 nm. This dip arises due to spin forbidden transition from ground state \( ^4A_2 \) to excited \( ^2E \) level \([6-7]\). This spin forbidden transition is due to Fano type antiresonance between quasicontinuum \( ^4T_2 \) (t\( _{2g}^3 \)e\( _g \)) and sharp discrete \( ^2E \) (t\( _{2g}^3 \)) doublet level of Cr\(^{3+}\) via spin–orbit interactions \([7]\). Figure 6.4 pictorially represents these spin forbidden transitions with the help of Tanabe-Sugano diagram \([5]\). The mixing of these doublet and quartet states by spin–orbit coupling relaxes the spin–forbidden transition making a suitable path for the electron to transit to the doublet states. Although Fano type antiresonance is mostly found for Cr\(^{3+}\) in octahedral coordination, reports are there where this resonance is observed in tetrahedral system, e.g. in Co\(^{2+}\) doped ZnO \([8]\).

![Tanabe-Sugano diagram](image)

**Figure 6.4** Tanabe-Sugano diagram (after Ref. \([5]\)) representing spin allowed and spin-forbidden \(d-d\) transition of Cr\(^{3+}\) in the framework of TiO\(_2\).

For band gap calculation \([F(R)h\nu]^{1/2}\) is plotted against \(h\nu\) and the linear part of the curve was extrapolated to \([F(R)h\nu]^{1/2}=0\). As it is seen in Figure 6.5(a), pure TiO\(_2\) nanoparticles (3.24 eV) have a band gap that is larger than that of bulk TiO\(_2\). The line diagram in Figure 6.5(b) shows that band gap decreases slowly upto 1.5 % Cr\(^{3+}\) and then the decrease is fast when the concentration is 3.0 %. The band gap decreases very slowly at 4.5 % and has a magnitude nearly similar to that of 3.0 %.

There may be three possible reasons for the reduction in the band gap. On doping Cr\(^{3+}\) form \(d\)-states in between valence and conduction band. Since the \(d\)-states are splitted into various ground and excited states, these states may act as active trap
centers of photoexcited electrons. In this case most of the photoexcited electrons will jump from the valence band to the upper d-states instead of jumping to the conduction band. Therefore, the absorption edge of pure TiO$_2$ is affected and the effective band gap becomes less than that of pure TiO$_2$. There is another possibility that the ground and excited d-states of Cr$^{3+}$ interact with the valence band O 2p and conduction band Ti 3d states and thus undergo sp-d hybridization [11-12]. Due to the sp-d interaction the valence band maximum moves upward and conduction band minimum moves downward. Therefore, presence of intermediate Cr$^{3+}$ d-states and interaction of these states with the CB of TiO$_2$ lead to the lowering of the band gap.

![Figure 6.5 Determination of band gap of (a) pure and Cr$^{3+}$ doped TiO$_2$ nanoparticles at $[F(R)hv]^{1/2} = 0$. (b) Variation of band gap with Cr$^{3+}$ concentration.](image)

### 6.3 $^2\text{E} \rightarrow ^4\text{A}$ Fano type emission of Cr$^{3+}$ and the related defect emission peaks

Figure 6.6(a) shows the photoluminescence spectra of pure and doped TiO$_2$ nanoparticles excited at 340 nm. The asymmetry in PL emission peaks confirms that the observed luminescence is a superposition of different types of defect related emissions. In TiO$_2$ the visible emissions are attributed to the presence of defect levels (mostly oxygen vacancies) [13-15]. The UV emission peak appears at 379 nm. The intensity of this as well as of other peaks are diminished in doped TiO$_2$ as compared to pure TiO$_2$, indicating formation of large numbers of non radiative centers on doping. The UV peak is assigned to band to band transition in TiO$_2$ [16]. In contrast to the single excitonic emission of bulk TiO$_2$, nanoparticles of TiO$_2$ display different emission peaks and these emissions are due to the presence of shallow and deep trap centers, associated with oxygen vacancies and Ti$^{3+}$ [17]. As compared to pure TiO$_2$
nanoparticles, the numbers of oxygen vacancies and Ti\(^{3+}\) both increases in Cr\(^{3+}\) doped TiO\(_2\). The emission peaks at 423 nm, 462 nm, 487 nm and 531 nm are common for both pure and doped TiO\(_2\). The emission peak at 423 nm appears due to self trapped excitons localized on TiO\(_6\) octahedra [18]. The peaks at 460 nm and 531 nm are due to oxygen vacancy with two trapped electrons (F centre) and one trapped electron (F\(^+\) centre) respectively [19].

![Figure 6.6](image)

**Figure 6.6** Photoluminescence spectra of (a) pure and Cr\(^{3+}\) doped TiO\(_2\) nanoparticles at \(\lambda_{ex} = 320\) nm. Cr\(^{3+}\) doped TiO\(_2\) exhibit emission peak corresponding to emission peak of Cr\(^{3+}\). (b) PL spectra at \(\lambda_{ex} = 480\) nm. Cr\(^{3+}\) exhibit Fano emission peak at 688 nm.

Formation of defect states such as Ti\(^{3+}\), V\(_0\) (neutral oxygen vacancy), F/F\(^+\) may be described with the following steps [9].

\[
\begin{align*}
O^{2-} & \rightarrow O + V_0 + 2e^- \\
V_0 + 2e^- & \rightarrow F \\
V_0 + e^- & \rightarrow F^+ \\
-O^{2-} & \rightarrow - \{ \equiv V_A = F^{++} \} \\
Ti^{i+} + e^- & \rightarrow Ti^{3+}
\end{align*}
\]

The 487 nm emission peak appears as a charge transfer band due to electronic transition from Ti\(^{3+}\) to oxygen anion in a TiO\(_6^{8-}\) complex associated with oxygen vacancies [20]. The emission peak at 446 nm is possibly due to \(^4T_1 \rightarrow ^4A_2\) transition of Cr\(^{3+}\). The peak at 575 nm is due to the defect states lying deep in the band gap of TiO\(_2\). Figure 6.6 (b) depicts the PL spectrum at an excitation wavelength of 480 nm. Cr\(^{3+}\) doped TiO\(_2\) samples exhibit a broad peak at around 688 nm which is absent in
the pure sample. In many of the Cr\textsuperscript{3+} doped materials [6,21-23], a sharp emission line appears in this region which is assigned to \(^2\text{E} \rightarrow ^4\text{A}_2\) electronic transition in the strong ligand field with octahedral symmetry. In our samples, instead of a sharp emission line we observed a broad emission spectrum (inset of figure 6.6 (b)). The appearance of the emission band in between 600–700 nm is due to the overlapping of closely lying \(^4\text{T}_2 \rightarrow ^4\text{A}_2\) and \(^2\text{E} \rightarrow ^4\text{A}_2\) emission bands [22]. It has been reported that this kind of broad emission occurs when Cr\textsuperscript{3+} is under weak crystal field and also when the crystal symmetry is broken from octahedral [22-23]. Since in our case, the usual octahedral coordination around Ti\textsuperscript{4+} is somehow distorted on doping, we got a broad emission line comprising \(^4\text{T}_2 \rightarrow ^4\text{A}_2\) and \(^2\text{E} \rightarrow ^4\text{A}_2\) emission. Presence of this broad emission peak supports the existence of Fano peak in the absorption spectra of the doped TiO\textsubscript{2} nanoparticles.

**6.4 Room temperature ferromagnetism exhibited by Cr\textsuperscript{3+} doped TiO\textsubscript{2} nanoparticles**

From the lattice distortion of TiO\textsubscript{2} caused by the incorporation of Cr\textsuperscript{3+} and from the characteristic absorption and emission peaks of Cr\textsuperscript{3+} we can say that most of the Cr\textsuperscript{3+} ions are on the substitutional position. However, fractions of Cr3+ ions may occupy interstitial position when the dopant concentration is higher. To clarify the doping effect of Cr\textsuperscript{3+} on the magnetic properties of TiO\textsubscript{2}, we carried out room temperature magnetic field dependent magnetization (M-H) measurement of all Cr\textsuperscript{3+} doped TiO\textsubscript{2} nanoparticles. Figure 6.7 shows the M-H curves of the doped samples. As it is seen in the figure, pure TiO\textsubscript{2} nanoparticles are diamagnetic in nature. However, incorporation of chromium imparts ferromagnetism in the otherwise nonmagnetic TiO\textsubscript{2}. There are many reports on ferromagnetism in pure TiO\textsubscript{2} oxide films without any magnetic impurities. Most of these papers have attributed the magnetism to the presence of oxygen vacancies on the surface, interface of the films [24-26]. The absence of magnetism, in our TiO\textsubscript{2} nanoparticles, indicates unavailability of considerable numbers of oxygen vacancies required to stimulate ferromagnetism. In contrast, incorporation of Cr\textsuperscript{3+} generates considerable numbers of oxygen vacancies and these oxygen vacancies undergo strong exchange interaction with neighboring Cr\textsuperscript{3+} ions and induce ferromagnetism. The saturation magnetization (\(M_s\)) of 1.5 %, 3.0 % and 4.5 % Cr doped TiO\textsubscript{2} are 0.0045 emu/g, 0.0082 emu/g and 0.007 emu/g.
respectively. Since chromium is antiferromagnetic, the observed magnetism is not due to the presence of metallic chromium clusters. Of all the oxides of chromium, only CrO$_2$ is ferromagnetic with bulk magnetic moment of 134 emu/g and Curie temperature of 386 K [27-28]. Cr$_2$O$_3$ is antiferromagnetic with Neel temperature of 308 K [28]. The ferromagnetic nature of CrO$_2$ puts a question mark on the intrinsic nature of ferromagnetism in this doped TiO$_2$. The best way to clarify the intrinsic magnetism is to consider the saturation magnetization of the doped samples and the variation of $M_s$ with Cr loading. First, if the ferromagnetism is due to CrO$_2$, the magnetization should be increasing with increase in chromium concentration. Second, if CrO$_2$ is present in large fraction, XRD and Raman should be able to detect these phases.

![Figure 6.7 Room temperature M-H curves of (a) pure and doped TiO$_2$ with (b) 1.5 % (c) 3.0 % and (d) 4.5 % chromium loading.](image)

If we consider the fraction of CrO$_2$ is ranging from 0.01-1.0 %, then the observed magnetization should be at least 0.0134-1.34 emu/g (considering bulk $M_s = 134$ emu/g). But, in our curves we have neither observed steady rise in magnetization nor very high magnetization. This infers that the magnetism is not due to the presence of ferromagnetic impurity phases. Therefore, we can suggest that the magnetism is
intrinsic in nature. The saturation magnetizations of our samples are very low. This is probably because of the weak coupling of Cr\(^{3+}\) with the host lattice. Although there are different theories to explain ferromagnetism in doped system, we will consider Ruderman-Kittel-Kasuya-Yosida (RKKY) and F-center mediated bound magnetic polaron or BMP theory to understand the mechanism of the observed ferromagnetism [29-31]. RKKY theory is mostly applicable in case of metallic system with large number of delocalized free electrons while BMP theory is applicable in case of semiconducting or insulating system with localized electrons [29]. From PL spectra, it is inferred that the visible emission peaks are mostly associated with electrons bound to oxygen vacancies (or F centers). As Cr\(^{3+}\) concentration increases, the numbers of these oxygen vacancies increases with the simultaneous increase in the numbers of F centers. Since the electrons are localized in the oxygen vacancy centers, nearby Cr\(^{3+}\), F-center mediated BMP model will be more applicable in our system rather than RKKY model. BMP is formed when the electron spin of an F center interacts with that of the spins of the neighboring Cr\(^{3+}\) within the diameter of the hydrogen like orbit of the F center [30-31]. Two or more BMPs overlap with each other leading to the long range ferromagnetic ordering in the lattice of doped TiO\(_2\). As compared to 1.5 \%, the numbers of F centers and Cr\(^{3+}\) both increases at chromium loading of 3.0 \%. Therefore, large number of F centers and Cr\(^{3+}\) interacts with each other increasing the size of the BMPs and hence the magnetization. The magnetization, however, decreases at 4.5 \%. When TiO\(_2\) is doped with Cr\(^{3+}\), entire Cr\(^{3+}\) ions may not be associated with an oxygen vacancy to form BMP. Some of the Cr\(^{3+}\) ions may bind with oxygen ions forming Cr\(^{3+}\)-O\(^{2-}\)-Cr\(^{3+}\) bonds. Similarly, some Cr\(^{3+}\) ions may not be associated with an oxygen vacancy or even with an oxygen ion, and may be associated with another Cr\(^{3+}\) ion and gets paired up. Since Cr\(^{3+}\) concentration is very high at 4.5 \%, the decrease of magnetization may be due to Cr\(^{3+}\)-O-Cr\(^{3+}\) super exchange interaction or due to the Cr\(^{3+}\)-Cr\(^{3+}\) interaction [32]. These interactions lead to antiparallel alignment of the spins and therefore enhance the antiferromagnetic interaction, resulting in the effective reduction in magnetization.

6.5 Conclusion
1. In summary it can be concluded that doping of chromium has effect on the local structure of TiO\(_2\). The anomalous changes in lattice parameter with Cr\(^{3+}\) clearly
indicate that the structural distortion is affected not only by substitutional doping but also by interstitial Cr$^{3+}$ and oxygen vacancies. We observed Fano type absorption and emission peak at 735 nm and 688 nm respectively. This Fano peak appears due to spin forbidden $^4T_2 \ (t_{2g}^3 e_g^1)$ to $^2E \ (t_{2g}^3)$ $d$-$d$ transition. The direct consequence of modification of local structure of TiO$_2$ from octahedral to low symmetry can be evidenced from the broad Fano emission line at 688 nm which on the contrary is expected to have a sharp line in system where octahedral symmetry is preserved.

2. We have observed very nice magnetization curves in Cr doped TiO$_2$ nanoparticles. All the doped samples exhibit ferromagnetic ordering and the magnetism is intrinsic in nature. F center mediated exchange interaction between nearest Cr$^{3+}$ with $d^3$ configuration leads to this ferromagnetic ordering at room temperature. If the Cr$^{3+}$ ions are isolated and form coupled pairs, without any oxygen vacancies, antiferromagnetic interaction takes place and reduces the magnetization. This is observed at the highest dopant concentration where magnetization decreases.

References


[7] Voda, M., et al. Fano antiresonances in the optical-absorption spectra of Cr$^{3+}$-doped La$_3$Ga$_{5.5}$Nb$_{0.5}$O$_{14}$ and La$_3$Ga$_{5.5}$Ta$_{0.5}$O$_{14}$ crystals, Phys. Rev. B 49 (6), 3755, 1994.


