CHAPTER III

Luminescent response and D-F transition in nanoscale rare earth oxides and RE ion doped nanoscale systems
Luminescence, the emission of light from a solid state object after being excited by a light source (UV, visible, infrared), electron bombardment, X-rays, or some other means of excitation has a long standing fascination since ancient times. The family of luminescent materials includes a wide range of inorganic materials, composites and hybrid systems which are capable of emitting light under suitable excitation. On the other hand, the organic light emitting systems are relatively new but have great relevance in flexible electronic elements/components.

3.1 Optical absorption and emission processes

The light matter interaction gives an idea on how excitation and de-excitation process can be understood. The atoms, ions or molecules have well defined energy levels which are usually associated with the electronic energy levels of the system. In any material, the difference in energy between molecular bonding, non-bonding and anti-bonding orbitals corresponds to the ultraviolet (UV) region (100-350 nm), visible (Vis) region (350-700 nm) of the electro-magnetic spectrum. So, the absorption of Vis and UV radiation is observed in corresponding material as a result of promotion of electrons from the lower energy state to the higher energy states.

All the semiconductor and RE oxide materials absorb UV or visible light. The absorption properties of the material can be studied by UV-Visible absorption spectroscopy. In case of semiconductor system, the origin of the absorption spectra is due to the transition of electrons from the valence band to the conduction band which is separated by an energy gap (called band gap). It is the nature of energy gap parameter which determines working of light emitting device in particular emission spectrum. There are two types of band gap, direct (crystal momentum, \( k \) vectors are same) and indirect band gap (\( k \) vectors are different) which are schematically shown in Fig. 3.1 [1]. Optical absorption is strongly affected by the nature of band gap a material would possess. The
absorption of photons by the semiconductor and RE oxides occurs in the near UV region. Fig. 3.2 shows a pictorial view of the transition associated with the optical absorption process in nanostructures [2]. Semiconductor nanostructures, shows a bandgap enhancement owing to quantum confinement effect [3]. The control and measurement of band gap is an important aspect in semiconductor nano-material industries.

![Schematic representation of (a) direct (b) indirect band-gap](image)

Fig. 3.1 Schematic representation of (a) direct (b) indirect band-gap

![Schematic view of optical absorption process in semiconductor nanostructures](image)

Fig. 3.2 Schematic view of optical absorption process in semiconductor nanostructures
Both absorption and luminescence provide complementary information about carrier relaxation process. Photoluminescence emission occurs when a system is excited to a higher energy state by the absorption of photons, and then, the system spontaneously relax back to ground state configuration by releasing photons of lower energy. The excited electrons release excess energy in order to stabilize, or to acquire equilibrium position, either by way of radiative emission of photons (fluorescence, phosphorescence) or via nonradiative emission pathways (vibrational relaxation, intersystem crossing, internal/external conversion). Photoluminescence process in a semiconductor system is shown schematically in Fig. 3.3. As a principle mechanism, photoluminescence involves coherent radiative events as a result of indirect recombination of electron-hole pairs (excitons), and is popularly termed as band edge emission [4]. Apart from band edge emission other emission patterns can also be realized. The native defects of the crystals generally possess electronic states within the band gap which act as trap centers (sites for trapping of electrons or holes) or, recombination centers which are also capable of influencing overall emission process. Depending on the nature of these defects, they are classified as donor, acceptor or neutral defects. Such defects of the crystal can attract the excitons via Coulomb interaction and form bound excitons. The nonradiative transitions mediated by recombination of free holes with the trapped electron, can be responsible for handling the excess energy being given to the lattice. This involves three process, Auger effect, surface recombination and phonon emission [5].

The tunable luminescence of QDs results from the quantum confinement of electrons and holes [6]. Unconfined conduction electrons in a bulk semiconductor experience the apparently endless periodic electric potential of the crystal lattice. When electrons in the conduction band recombine radiatively with the holes in the valence band and essentially return to their ground state, photons are emitted with energies near or just below the band gap energy ($E_g$). In contrast to bulk,
nanomaterials possess a large number of native defects owing to high surface to volume ratio. Accordingly, the defect related emission is a dominant process, in most of the nanostructured materials, where band edge emission is quenched [7, 8].

![Diagram of optical emission process in semiconductor nanostructures](image)

Fig. 3.3 Schematic view of optical emission process in semiconductor nanostructures

In contrast to semiconductor quantum dots, the emission wavelength of the RE oxide nanomaterials is independent of the particle size, as the exciton Bohr radius in such materials is very small, and thus the nanoparticle size in the latter material is not critical for the spectral properties [9,10]. Moreover, when the RE ions are incorporated into a nanosize medium (in the form of dopant), modification occurs due to the modification of surface defects and their sensitivity to the new environment. Imperfect shielding of $4f^n$ electrons also result in RE system being drawn inside of the $5s^25p^6$ closed shell of the Xenon shell. The $4f^n$ electrons interact weakly with the external environment, as a result small crystalline Stark splitting of the $4f$ levels takes place [11]. As a result, absorption and emission band appears sharp and narrow.
3.2 Light emission characteristics of undoped and doped Gd$_2$O$_3$ and TiO$_2$ nanoscale structures

The optical properties of the synthesized nanostructures were explored through optical absorption spectra (OAS) and photoluminescence (PL) spectra. The absorption spectra were recorded using a computer interfaced UV-Visible spectrophotometer (Shimadzu Corporation, Japan). The room temperature PL spectra of the samples were characterized by using a PerkinElmer LS 55 spectrophotometer, having Xe line as the excitation source. In this case, the data were collected by a computer controlled standard monochromator based photodetection system.

3.2.1 Gd$_2$O$_3$ nanoscale system

The UV-visible absorption spectra of the undoped Gd$_2$O$_3$ nanopowder is presented in Fig. 3.4. Note that Gd$^{3+}$ has [Xe] 4$f^7$ electronic configuration, having a half-filled shell and $^8S_{7/2}$ level as the ground state. The energy absorption process in Gd ion is mediated via transition of 4$f$ electrons to the 5$d$ level and then reorganization of the 4$f$ electrons into various multiplets [11]. The seven electrons in the 4$f$ orbitals of Gd have as many as 3432 multiplets while considering the ground state as $^8S_{7/2}$ [11]. Among these multiplets, the low lying multiplet above the ground state is represented by $^6P_{7/2}$.

Essentially, two absorption peaks are observed in the spectrum. The absorption peak positioned at $\sim$ 274 nm (upper inset of Fig. 3.4) is typical for Gd$_2$O$_3$ nanoparticles and is attributed to $^8S_{7/2} \rightarrow ^6I_{7/2}$ transitions [11]. The broad peak positioned at $\sim$ 390 nm is ascribed to the recombination of delocalized electrons close to the conduction band with a single charged state of surface oxygen vacancy as per Wang’s proposition [12].
Luminescence response of $d$-$f$ transition in nanoscale rare earth oxides and RE ion doped nanotitania

Chapter III

Fig. 3.4 UV Visible absorption spectra of the Gd$_2$O$_3$ nanoparticles

Fig. 3.5 (a) Room temperature PL spectra ($\lambda_{ex} = 300$ nm) of Gd$_2$O$_3$ nanoparticles with multiple Gaussian fitting, (b) Schematic of PL response, (2) band-to-band recombination, (3) recombination due to native defects. The solid arrows represent radiative recombination, while dotted arrow signifies non-radiative transition. Here, ‘1’ represents excitation.

The radiative transitions in material system can be assessed through the PL spectra. The room temperature PL spectra of the Gd$_2$O$_3$ nanopowder excited at a wavelength of 300 nm is shown in Fig. 3.5. Here, the asymmetrically broadened PL spectrum indicates that the overall pattern is superimposition of multi peaks.
In order to make out a clear picture of the PL peaks, multiple peak fitting (Gaussian) is introduced. In this procedure, the position and width of the peaks under consideration are adjusted in such a way that the empirical curve formed by the superposition of these fitted peaks matched quite well with the experimentally obtained curve. Accordingly four peaks positioned at ~405 nm, 430, 455 and 490 nm are revealed. The deep UV blue band and located at ~405 nm is attributed to the recombination of a delocalized electron close to the conduction band with a single charged state of surface oxygen vacancy in accordance with Wang’s proposition [12]. The blue emissions with maxima at ~430, 455 and 490 nm are attributed to the radiative responses mediated via surface defects of both Schottky and Frenkel types [13-15].

3.2.2 Tb$^{3+}$ doped Gd$_2$O$_3$ nanoparticles

Fig. 3.6, shows a set of optical absorption spectra of the Tb$^{3+}$ doped Gd$_2$O$_3$ nanopowder which depict a broad absorption feature over a wide wavelength range. However, all the samples were characterized by three characteristic peak maxima located at ~254, ~340 nm and ~380 nm. Possibly, a weak peak at 254 nm is due to the one of the transition corresponding to $^8S_7/2 \rightarrow ^6I_{j/2}$ multiplets where $j = 9, 12, 13, 15, \text{ and } 17$ [16]. The peak at ~350 nm is ascribed to the $^6P_{7/2} \rightarrow ^8S_{7/2}$ of Gd(III) [17]. The nature of the ~380 nm is detailed in the previous section #3.2.1, and is similar to the undoped case.

Fig. 3.6 UV-Visible absorption spectra of the Tb$^{3+}$ doped Gd$_2$O$_3$ nanoparticles
The normalized PL emission spectra of Tb$^{3+}$ doped Gd$_2$O$_3$ nanopowders ($\lambda_{ex}=330$ nm) are depicted in Fig. 3.7. Typically, three main emission peaks are found ∼450 nm, 490 nm and 544 nm, but with varying intensity responses. The description of the 450 nm is given in section #3.2.1. Whereas, peaks positioned at ∼490 nm and 544 nm corresponded to $^5D_4 \rightarrow ^7F_6$ and $^5D_4 \rightarrow ^7F_5$ related transitions of Tb$^{3+}$ ion, respectively [18]. In this system, the PL peak at ∼490 nm corresponds to Tb$^{3+}$ related transition ($^5D_4 \rightarrow ^7F_6$) as well self trapped excitons (STE) related peak in Gd$_2$O$_3$ system. Although Tb$^{3+}$ ions are responsible for intense green emission (544 nm), the intensity of 490 nm peak is quite comparable to the intensity of peak at 544 nm peak. This could be due to the superposition of the above mentioned peaks. However, the transitional events are found to be stronger for a higher level of Tb$^{3+}$ doping.

![Normalized intensity vs Wavelength](image)

Fig. 3.7 Room temperature photoluminescence spectra of Tb$^{3+}$ doped Gd$_2$O$_3$ nanoparticles ($\lambda_{ex} = 330$ nm). Dotted line indicates different emission peak positions.

PL excitation spectroscopy is a useful method to investigate the electronic structure of the materials with low absorption features. The wavelength of the excitation light is monitored, for a fixed emission wavelength of the material being studied. The PL excitation spectrum corresponding to an emission
wavelength of ~544 nm is shown in Fig. 3.8. The excitation peak at ~254 nm corresponds to the inter ionic energy transfer due to good matching of the excited states (4f levels) of Gd\(^{3+}\) and Tb\(^{3+}\) ions [16]. The two ions form a coupled system where energy absorbed by the Gd\(^{3+}\) ions were transferred to the Tb\(^{3+}\) via a non-radiative relaxation pathway and then, released as Tb\(^{3+}\) fluorescence [18]. The energy transfer does not occur until Gd\(^{3+}\) and Tb\(^{3+}\) related energy levels reside very close.

Below these peaks, a broad band is appeared, which is associated with the inter-configurational transitions (e.g., \(4f^n \rightarrow 4f^{n\rightarrow n-1}5d^l\)) of Tb\(^{3+}\) in the Gd\(_2\)O\(_3\) host. Furthermore, the peak at ~285 nm and those between ~345 and ~400 nm are believed to have originated from the 4f intra configuration of the Tb\(^{3+}\) ions as predicted in earlier works [19].

Fig. 3.8 Room temperature photoluminescence excitation (PLE) spectra of Tb\(^{3+}\) doped Gd\(_2\)O\(_3\) nanopowder (\(\lambda_{em} = 544\) nm). The arrows indicate different absorption peaks.
3.2.3 Eu\textsuperscript{3+} doped Gd\textsubscript{2}O\textsubscript{3} nanoparticles

Fig. 3.9 shows a set of optical absorption spectra of the Eu\textsuperscript{3+} doped Gd\textsubscript{2}O\textsubscript{3} nanoparticles. As described above, all the samples were characterized by three characteristic peak maxima located at \( \sim 274 \), \( \sim 340 \) nm and \( \sim 380 \) nm.

![Absorbance vs Wavelength](image)

Fig. 3.9 UV-Visible absorption spectra of the Eu\textsuperscript{3+} doped Gd\textsubscript{2}O\textsubscript{3} nanoparticles

The room temperature PL spectra of the Eu\textsuperscript{3+} doped Gd\textsubscript{2}O\textsubscript{3} nanopowder, excited at a wavelength of 400 nm, is depicted in Fig. 3.10 (a). Each of the spectra corresponds to an asymmetrically broadened feature, which may be due to the superposition of a number of peaks of diverse origins. The Gaussian fitted spectrum of GdEu3 is presented in Fig. 3.10 (b). Here, every spectrum is characterized by five important peaks, which are located at \( \sim 579 \), 591, 619, 660 and 699 nm and corresponded to \( ^5D_0 \rightarrow ^7F_0 \), \( ^5D_0 \rightarrow ^7F_1 \), \( ^5D_0 \rightarrow ^7F_2 \), \( ^5D_0 \rightarrow ^7F_3 \) and \( ^5D_0 \rightarrow ^7F_4 \) transitions of Eu\textsuperscript{3+} [20]. Note that, the overall-intensity of the PL emission increases with the increase in Eu content of the host.

The most striking feature was the enhancement of electrically driven \( ^5D_0 \rightarrow ^7F_2 \) transition, which is sensitive to the surrounding environment of the Eu\textsuperscript{3+} ions, while magnetically allowed \( ^5D_0 \rightarrow ^7F_1 \) transition is affected only weakly [21]. All the possible radiative transitional events are highlighted in the scheme of Fig.
3.10(c). Fig. 3.10(d) shows the PL excitation spectra of the Eu\(^{3+}\) doped Gd\(_2\)O\(_3\) nanopowder (at an emission wavelength of 619 nm as it gives most intense emission). The peaks near 400 nm, 425 nm, 455 and 490 nm can be assigned to the higher energy level (f-f) transitions of Eu\(^{3+}\) [22].

![Fig. 3.10](image_url)

Fig. 3.10 (a) Room temperature PL spectra of EuGd1, EuGd2 and EuGd3 samples excited at 405 nm, (b) Gaussian fitted PL spectra of EuGd3, (c) schematic of radiative transition of Eu\(^{3+}\) ions in Gd\(_2\)O\(_3\) matrix, and (d) PLE spectra of EuGd3 at an emission wavelength of 619 nm.

### 3.2.4 Judd–Ofelt parameter calculation

In the cubic structure, the emission mainly originates from the C2 site, because this site has a statistically higher occupancy level and has no center of inversion,
and as a result the splitting of the spectra is not observed [23]. In such sites, Eu\(^{3+}\) is in seventh fold coordination [23]. The coordination of two Eu\(^{3+}\) ions can be described by six oxygen at the apexes of a trigonal prism with a seventh oxygen atom along a normal to the face. The third Eu\(^{3+}\) ion is in the middle of the distorted octahedron and with the seventh oxygen at a long distance [23, 24]. The Eu\(^{3+}\) ions are used in spectroscopy to determine the environment around Eu\(^{3+}\) ions in the host, since its electric dipole transition is hypersensitive to its local symmetry.

The emission spectra of Eu\(^{3+}\) doped Gd\(_2\)O\(_3\) samples are used for the calculation of Judd-Ofelt parameter of Eu\(^{3+}\) ion. According to Judd-Ofelt theory, the electric dipole transition intensity should be more than the magnetic dipole transition in such an asymmetric environment. The \(^{5}D_0 \rightarrow \(^{7}F_0\) transition is forbidden according to Judd-Ofelt theory [25, 26]. However, its occurrence could be realized in our case (Fig. 3.9(b)). This may be due to either parity mixing (e.g. \(d-f\)) or \(j-j\) mixing at the excited state (\(^{5}D_{j=0,1,3}\)) or the ground state (\(^{7}F_{j=0,1,2,3,4}\)) due to thermal population. The parity mixing (e.g. \(d-f\)) is ruled out because of the high energy gap between them. The \(j-j\) mixing at the excited state (\(^{5}D_{j=0,1,3}\)) is not feasible because of the significant energy gap. There is a probability of \(j-j\) mixing of at the ground state (\(^{7}F_{j=0,1,2,3,3}\)) due to thermal population [27]. The \(^{5}D_0 \rightarrow \(^{7}F_{1,3}\) magnetic dipole transitions are almost independent of local crystal field strength. The mixing of the higher \(j = 4, 6\) with \(j = 0\) is lower because of their emission intensities are weak as compared to \(j = 2\). The most probable event is from mixing of \(j = 2\) with \(j = 0\) at the ground state of \(^{7}F_j\), which gives rise to a significant transition probability (and hence intensity) of the \(^{5}D_0 \rightarrow \(^{7}F_0\) transitions through the second order term of the local crystal field [27]. Also, the Judd-Ofelt theory states that, the transitions between the initial and final states in europium crystals (electronic configuration \(4f^6\)) are parity forbidden. For the transitions between \(J\) and \(J'\) energy levels, the
following conditions are assumed in order to simplify the calculation: (1) $4f^n$ coordinate energy levels are regarded as the linear combination of the Russell-Saunders correlated levels (interspaced states); (2) the particles are equally populated on the sublevels of the initial $J$ levels; (3) the energy levels of the particles in the $4f^n$ configuration are higher than the original energy state level $J$; and (4) simplified local field [28]. For calculation the Einstein’s coefficient of spontaneous emission is quoted as [28, 29]

$$A_{0-\lambda} = \frac{4e^2\omega^3}{3hc^3}\chi \sum_{\lambda} \Omega_{\lambda} \left( U_{\lambda} || F_{\lambda} \right)^2$$  \hspace{1cm} (3.1)

Where $e$ is the electron’s charge, $c$ is velocity of light, $\hbar$ is the reduced Planck’s constant, $\omega$ is the transition centroid, $|| U_{\lambda} ||^2$ are the reduced matrix elements of the unit tensor operators, $\chi = n_\lambda (n_\lambda + 2)/9$ is the Lorentz local field correction, in which $n_\lambda$ is determined from the single term Sellmeier equation [30]

$$\frac{1}{n_\lambda^2 - 1} = \frac{-A}{\lambda^2} + B$$  \hspace{1cm} (3.2)

Here, $A=62 \times 10^{-16}$ m$^2$, $B= 0.3163$. The symbol $\Omega_{\lambda}$ ($\lambda = 2, 4, \text{and} 6$) denotes the spectral intensity parameter, determined by the coordinate characteristics of the host material. $A_{0-\lambda}$ could also be obtained from the relationship given by [30]:

$$A_{0-\lambda} = A_{0-1} \frac{S_{0-\lambda} \sigma_{\lambda}}{S_{0-1} \sigma_1}$$  \hspace{1cm} (3.3)

The $S_{0-\lambda}$ is the area under the spectral line of the radiative transition of $^5D_0 \rightarrow ^7F_{\lambda}$ transition in the emission curve (Fig. 3.10 (b)). The $\sigma_\lambda$ is the energy barycenter of different transition and $A_{0-1}$ is the Einstein’s coefficient of magnetic dipole transitions of $^5D_0 \rightarrow ^7F_1$. The $S_{0-\lambda}$ and $\sigma_\lambda$ can be measured in the fluorescent spectra of Eu ion doped systems. From equation (2) and (4), we can calculate the intensity parameter $\Omega_{\lambda}$. The intensity parameters $\Omega_{\lambda}$ ($\lambda = 2, 4, 6$) can be calculated using equation
Luminescence response of \(d-f\) transition in nanoscale rare earth oxides and RE ion doped nanotitania

Chapter III

Here, \(I_{0J}\) and \(I_{01}\) are integral intensities of different transition [30]. The calculated values of \(\Omega_\lambda\) are presented in Table 3.1. The values of \(\Omega_2\) and \(\Omega_4\) correspond to the apparent variation of the crystal the field environment. Through the selection rules of Eu\(^{3+}\) ions, the transition from \(J = 0 \rightarrow J'\) (even) is considered to be electric dipole allowed. The \(5D_0 \rightarrow 7F_6\) transition (850 nm) is, however, beyond the visible region. The \(J-O\) parameter, \(\Omega_6\) can not be determined experimentally from the visible spectra, however it has been estimated by other researcher as \(\Omega_6 = 5 \times 10^{-21}\) cm\(^2\) [31].

Table 3.1: Calculated Judd–Ofelt intensity parameters \(\Omega_\lambda\) (\(\lambda = 2, 4\))

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>(\sigma_{02} (\times10^{-4}))</th>
<th>(\sigma_{04} (\times10^{-4}))</th>
<th>(\Omega_2 (10^{-20} \text{ cm}^2))</th>
<th>(\Omega_4 (10^{-20} \text{ cm}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>GdEu1</td>
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<td>14.19</td>
<td>13.5</td>
<td>43</td>
</tr>
<tr>
<td>GdEu2</td>
<td>16.14</td>
<td>14.08</td>
<td>2.32</td>
<td>1.87</td>
</tr>
<tr>
<td>GdEu3</td>
<td>16.15</td>
<td>14.12</td>
<td>1.62</td>
<td>1.32</td>
</tr>
</tbody>
</table>

3.3 Radiative emission and \(D-F\) transitions in RE ion doped nanotitania

TiO\(_2\) has been doped with a range of RE ions with the exception of promethium due to its unstable and radioactive nature. Eu\(^{3+}\) and Tb\(^{3+}\) are well known luminescent material in the rare earth family. To be specific, doping with rare earth (RE) ions has a unique advantage owing to half-filled/incomplete \(4f\) and empty \(5d\) orbital electrons for which the ions are capable of maintaining neutral-atom like behavior without much interference with the surrounding host (shielding effect), unlike transition metal ions that have partially filled \(3d\) orbitals [32]. As a consequence, the excited RE ions would experience comparatively long
lifetime ($\tau_e$) owing to the parity forbidden intra $4f$ transition (e.g., for Tb$^{3+}$, $\tau_e \sim 0.01-1$ ms) [32]. This is the reason why RE ions (Tb, Eu, Dy, Ce etc.) are believed to be promising dopants when modified carrier transport properties are desired in nanoscale TiO$_2$. In the past, numerous studies have been conducted with an intention to vary carrier transport properties of titania doped with RE ions [33, 34].

3.3.1 Tb$^{3+}$ doped nanotitania system

Influence of Tb$^{3+}$ doping on light absorption features of nano-titania powder is assessed through UV-Vis optical absorption spectra, shown in Fig. 3.11 (a). There exist, a broad absorption edge in the visible region, for all the samples (T2, TbT1, TbT2, and TbT3) under study. As for the un-doped sample T2, a sharp absorption edge is found to be located at $\sim 380$ nm. The extent of broadening in the optical spectra tends to improve with increasing Tb$^{3+}$ concentration. The variation in the optical band edge could occur due to the incorporation of localized impurity states owing to adequate Tb$^{3+}$ doping. The schematic of band gap reduction and band edge distortion owing to incorporation of the Tb$^{3+}$ is depicted in Fig. 3.11 (b).

![Fig.3.11](image)

Fig.3.11 (a) UV-Vis absorption spectra of undoped and Tb$^{3+}$ doped TiO$_2$ nanopowder samples, (b) the schematic of band gap reduction and band edge distortion owing to incorporation of Tb$^{3+}$ ions.
The characteristic radiative emission, as a result of light-matter interaction, can be visualized from the PL spectra (considering excitation wavelength, $\lambda_{ex}=300$ nm). The emission response was revealed in the emission range of 350 - 550 nm (Fig. 3.12). Each of the PL spectra is believed to be as a result of superimposition of six emission lines and accounts for radiative recombination of carriers via energy levels of diverse origin. The strong UV emission peak located at ~390 nm is due to the phonon assisted indirect transitions from the edge ($X$) to the zone center of the Brillouin zone, i.e., $X_{1b}$ to $C_3$ [35]. As predicted earlier, the emission band at ~430 nm is assigned to the intrinsic self-trap excitons (STE) localized on TiO$_6$ octahedra [22]. The emission peaks, positioned at ~460 and ~530 nm correspond to two-trap electrons ($F$ center) and single-trap electron ($F^+$ center); respectively [21]. Whereas, the ~485 nm peak is ascribed to the charge transfer from Ti$^{4+}$ to the oxygen ions in the TiO$_6$ octahedron associated with the oxygen vacancies. Accompanied by $^5D_3 \rightarrow ^7F_5$, $^5D_3 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_6$ transitions, the characteristic emission lines of Tb$^{3+}$ ions, were located at ~418 nm, 431 nm, and 491 nm; respectively. Noting that the defect related emission of TiO$_2$ and several Tb related transitions may occur via close energy states, it was not possible to isolate individual contributions. Accordingly, no emission response in the green ($^5D_4 \rightarrow ^7F_5$) and yellow ($^5D_4 \rightarrow ^7F_4$) regions could be witnessed. An adequate mismatch of the energy levels of the $^5D_4$ state of Tb$^{3+}$ ions with that of the defect state of titania may have quenched away the above mentioned peaks [36].
3.3.2 Eu³⁺ doped nanotitania system

Fig. 3.13 (a) shows the UV-visible absorption spectra of T1-T5 titania nanopowder samples. As can be noticed from the spectra, the absorption edge of the samples prepared at a higher annealing temperature is broadened and extends up to the visible region. The feature is more prominent in case of T5 sample which comprised of mixed phase, with proportionately large amount of brookite phase and small amount of anatase and rutile contents [37].

Fig. 3.13 UV-Vis absorption spectra of (a) undoped (T1 to T5) and (b) Eu-doped TiO₂ (EuT1, EuT2 and EuT3) samples. The inset shows the zoomed view of the absorption in the range of 380-475 nm.

The absorption spectra of Eu³⁺ doped TiO₂ samples with different Eu³⁺ concentrations are presented in Fig. 3.13(b). There exist, a broad absorption edge in the visible region, for all the cases (EuT1, EuT2 and EuT3). For the un-doped sample, the sharp absorption edge was found to be located at ~380 nm. The extent of broadening in the spectra increases with increasing Eu³⁺ concentration due to incorporation of localized impurities. The optical band gap, as predicted from the Tauc’s plot shows a decreasing trend with the respective values of 3.2, 3.16, 3.06, 2.93 eV for T2, EuT1, EuT2 and EuT3 samples [38]. Apart from the band edge
absorption, two distinct absorption peaks can be noticed (for doped samples, EuT1, EuT2 and EuT3 shown in inset of the Fig. 3.13 (b)) which corresponded to $^7F_0 \rightarrow ^5L_6$ and $^7F_0 \rightarrow ^5D_2$ transitions and positioned at ~394 and 464 nm; respectively [20]. However, such transitions are absent in the un-doped case (T2).

Fig. 3.14 (a) illustrates the room temperature PL spectra of the un-doped and Eu$^{3+}$ doped TiO$_2$ systems excited at a wavelength of 300 nm. The normalized Gaussian fitted curves are presented in Fig. 3.14 (b-e). Essentially, five peaks could be revealed which are located at ~392, 430, 460, 490 and 540 nm. As a general trend, all the spectra exhibited strong UV emission peak (~392 nm) due to the phonon assisted indirect transition from the edge ($X$) to the zone center of the Brillouin zone, i.e., $X_{1b}$ to $\Gamma_3$. As predicted earlier, the emission band at ~430 nm is assigned to the intrinsic self-trap excitons (STE) localized on the TiO$_6$ octahedra [39]. The peaks at ~460 and 540 nm are due to colour centres associated with the oxygen vacancy of two-trap electron (F center) and single-trap electron (F$^+$ center); respectively [40].

The peak positioned at ~490 nm is ascribed to the charge transfer from Ti$^{4+}$ to oxygen ions in TiO$_6$ the octahedron associated with oxygen vacancies [41]. The variation of the intensity ratio of the band edge emission to the STE and oxygen defect-related emissions is highlighted in Fig. 3.14(f). For a sufficiently large Eu$^{3+}$ concentration, the number of ionized oxygen defects tend to increase owing to introduction of charge imbalance created by Ti$^{4+}$ (64 pm) and Eu$^{3+}$ (93 pm) ions. Consequently, an enhanced local charge imbalance would influence the radiative emission events without affecting phase transformation and crystallite dimension. However, the RE-doping related higher order transitions (and hence, emission) originated via luminescent centers of Eu$^{3+}$ ions was found to be merely absent.
Fig. 3.14 (a) Room temperature PL spectra ($\lambda_{ex}$=300 nm) of the undoped and Eu-doped TiO$_2$ nanopowders; (b-e) respective Gaussian fitted curves for T2, EuT1, EuT2 and EuT3 samples. The intensity ratio of NBE to STE and defect emission peaks vs. Eu-content are shown in (f).
Fig. 3.15(a), illustrates the room temperature PL spectra of the un-doped (upper inset of Fig. 3.15(a)) and Eu\(^{3+}\) doped nanotitania systems excited at a wavelength of \(~405\) nm. A different excitation wavelength is used since Eu shows a broad absorption feature at \(~405\) nm in the PLE spectra. Each of the spectra is characterized by four important peaks of Eu\(^{3+}\) which are located at \(~579, 591, 615\) and \(~699\) nm and are attributed to \(5D_0 \rightarrow 7F_0\), \(5D_0 \rightarrow 7F_1\), \(5D_0 \rightarrow 7F_2\) and \(5D_0 \rightarrow 7F_4\) transitions [38]. Note that, the overall-intensity of the PL emission increases with the increase in Eu content of the host. The most striking feature is the enhancement of electrically allowed \(5D_0 \rightarrow 7F_2\) transition which is sensitive to the surrounding environment of the Eu\(^{3+}\) ions, while magnetically allowed \(5D_0 \rightarrow 7F_1\) transition is affected only weakly [21]. To uncover superimposed peaks, the PL spectrum of EuT1 specimen was subjected to normalized Gaussian fitting, as shown in Fig. 3.15 (b). In reality, the relative intensity ratio \((\delta)\) of \(5D_0 \rightarrow 7F_2\) to \(5D_0 \rightarrow 7F_1\) transitions would describe the breaking of centro-symmetry and degree of disorderness around the Eu\(^{3+}\) ions [36]. The \(\delta\) value follows an increasing trend with increase in Eu\(^{3+}\) level and with representative values as \(~1.32, 2.44\) and \(~2.56\) for EuT1, EuT2 and EuT3; respectively (Fig. 3.15 (c)). In other words, the electrically driven transitions \((5D_0 \rightarrow 7F_2)\) are more favorable than spin-exchange mediated magnetically allowed ones \((5D_0 \rightarrow 7F_1)\). The \(\delta\) value has a saturation trend at a higher Eu\(^{3+}\) doping concentration. The substitutional doping which leads to a local charge imbalance and facilitating thereby electrically driven transition, is not an indefinite process. As the \(\delta\) value of both the EuT2 and EuT3 sample is greater than \(~2\), this type of phosphor is highly desirable in LED applications and can be comparable with other reported oxide phosphors [42].
Luminescence response of $d$-$f$ transition in nanoscale rare earth oxides and RE ion doped nanotitania

Chapter III

Fig. 3.15 (a) Room temperature PL spectra ($\lambda_{ex}$=405 nm) of Eu-doped TiO$_2$ nanopowders, (b) Gaussian fitted spectra of EuT1, (c) the intensity ratio of $^5D_0\rightarrow^7F_2$ and $^5D_0\rightarrow^7F_1$ transitions with Eu-doping level and (d) Scheme highlighting the $D$-$F$ transitions of Eu$^{3+}$ ion in nanotitania alongwith defect mediated emissions. Inset of (a) represents PL spectra of undoped TiO$_2$ excited at same wavelength

Furthermore, nanotitania are characterized through the PLE spectra, emission wavelength is fixed at 619 nm as Eu$^{3+}$ shows most intense emission bands in this wavelength (Fig. 3.16). The PLE spectrum consists of several sharp lines with maxima at 380, 432, 465, and 530 nm, which correspond to the direct excitation of the $f$ electrons. Because the spectrum has been recorded at room temperature, the transition from the $^7F_1$ state is observed to be located at $\sim$32.7 meV above the $^7F_0$ ground state [43].
Luminescence response of $d$-$f$ transition in nanoscale rare earth oxides and RE ion doped nanotitania

Chapter III

Fig. 3.16 PLE spectra of EuT1 and EuT2 sample at an emission wavelength of 619 nm

3.4 Concluding remarks

The optical properties of pure and doped Gd$_2$O$_3$ and TiO$_2$ nanostructures have been explored by analyzing UV-Visible absorption and photoluminescence spectra. The quantum confinement effect has been witnessed in the respective absorption spectra. The PL spectra of the Gd$_2$O$_3$ nanopowders were characterized by $D$-$F$ transition along with various native defect mediated emissions. The Eu$^{3+}$ and Tb$^{3+}$ doped Gd$_2$O$_3$ nanostructures have showed the characteristic red and green emission due to intra-4f transitions respectively. The emission responses accompanied by Eu$^{3+}$ and Tb$^{3+}$ are found to be dependent on the doping concentration and no quenching has been witnessed upto a marginal concentration 5%. In case of TiO$_2$ nanostructures, various defect related peaks were observed with an occasional presence of the characteristic band edge emission.
References


