CHAPTER II

Fabrication principle and basic characterizations of nanoscale structures involving RE systems
Fabrication of nanoscale systems is a topic of intensive investigation in both basic and applied research. Size and shape controlled nanosystems can be obtained by following user friendly, yet standard fabrication techniques. There exist two general ways for synthesizing nanomaterials: the top-down approach and the bottom-up approach [1]. Nanomaterials have been generated by a number of physical and chemical methods, to name a few, laser ablation, arc-discharge and thermal evaporation etc. [2-4]. Chemical methods are proven to be more effective, as they provide better control over size tunability, doping and along with other functional capabilities. The chemical processing of nanomaterials has been reviewed by a number of groups and significant improvement over other methods was also realized in subsequent works [5, 6]. An appropriate growth mechanism is the key factor to yield quality nanomaterial products while introducing desired phase, shape and size for certain applications. However, from the application point of view the large scale production and stability of the nanomaterials are the key factors that decide the superiority of a synthesis method.

Particle size has an important role in any application. For instance, ultrasmall particles of Gd$_2$O$_3$ are highly desirable for its application as MRI contrast agent [7]. It has been shown that an average particle size ~14 nm could show an enhanced photocatalytic reduction of CO$_2$ when experimented with a series of pure TiO$_2$ anatase particles with crystallite diameters varying in the range of 4.5 and 29 nm [8]. On the other hand, unconventional nanoarchitecture of TiO$_2$ consisting of vertically-oriented, immobilized, highly-ordered and high-aspect ratio nanotubes have been grown using hydrothermal treatment [9, 10], template synthesis [11], and anodic oxidation [12]. This chapter focuses on the fabrication of undoped and RE ion doped Gd$_2$O$_3$ and TiO$_2$ nanostructured systems.
2.1 Fabrication principle and basic characterizations

Spherical nanoparticles of pure and doped Gd$_2$O$_3$ and TiO$_2$ are prepared through cost-effective physico-chemical routes. The structural analysis was carried out by a Miniflex X-ray diffractometer (XRD, Rigaku D/max-2000) employing Cu $K_{\alpha}$ line ($\lambda = 1.543$ Å). The visual information wrt morphological feature etc was revealed through transmission electron microscopy (TEM: JEOL JSM-100 CX and HRTEM: JEM-2100 and FEI, Tecnai S-twin) working at different accelerating voltages of electrons (80 kV for TEM and 60-200 kV for HRTEM). The elemental analysis was made through the Energy dispersive X-ray spectroscopy (EDS) attached to the SEM. The vibrational features were explored by Raman spectroscopy that employed micro-Raman spectrometer (Renishaw, UK) at room temperature. The hydrodynamic particle size and distribution of the particles were also calculated through dynamic light scattering (DLS nanoZS, Malvern Instruments) experiments. Moreover, magnetic measurement was carried out on a particular specimen using a MPMS SQUID VSM (Quantum Design, USA) working at room temperature.

2.1.1 Synthesis and characterization of undoped and RE ion doped Gd$_2$O$_3$ nanoparticles

The method of fabrication of undoped and RE ion doped Gd$_2$O$_3$ nanoparticles through physico-chemical routes involves the reaction among the reactants, where the bulk REO is first converted into its nitrate form. Subsequently, the reduction of the products to its hydroxide and final oxide form could be achieved in presence of a cationic surfactant CTAB (N-Cetyl-N,N,N-trimethylammonium bromide, C$_{19}$H$_{42}$BrN) (Appendix III). It is a quaternary ammonium cation and is widely used for providing buffer solution for DNA extraction and nano-material synthesis [13-15]. CTAB is one of the components of the topical antiseptic [16]. The molecular structure of the CTAB is shown in Fig. 2.1. The CTAB forms
micelles in aqueous solution due to its strong repulsion among its cationic head groups and attraction among the tails.

![CTAB structure](image)

Fig. 2.1 The structure of CTAB

Since RE oxides are very stable against temperature, pressure and mechanical stress, it is not wise to follow top-down approach (e.g. mechanical grinding) to synthesize nanosized RE oxide product from its bulk counterpart. In order to prepare nano-sized undoped Gd$_2$O$_3$ powders, a low-cost physico-chemical route is adopted as proposed by Chen et al. [17], but with some modification. In this method, bulk Gd$_2$O$_3$ is first converted into a nitrate compound followed by subsequent reduction to get hydroxide and oxide products. At first, 1 mmol of bulk Gd$_2$O$_3$ (99%, Otto) is added to 50mL of double-distilled (DD) water. Then, an appropriate amount of HNO$_3$ (69%GR, Merck) is mixed to this solution under vigorous stirring (~250 rpm) until a clear solution of Gd(NO$_3$)$_3$ is obtained. The solution is diluted to 100 mL in a volumetric conical flask by adding more distilled water and subsequently, 3.3 g of CTAB is added at 65 °C, thus resulting in a yellow coloured precursor. On cooling down to room temperature, 10 mL of a freshly prepared aqueous NaOH is transferred to the above mixer. As a result, a white precipitate of Gd(OH)$_3$ is formed which is then followed by continuous stirring for 30 min, and finally, subjected to high speed centrifugation (~5000 rpm). In order to obtain the finest quality precipitate, the as-received product is subjected to repeated washing with hot distilled water and centrifugation. The precipitate is first dried in air and then heated at 800°C for 1 h till an off-white powder of Gd$_2$O$_3$ is received.
In case of doping, a calculated amount of \( \text{Tb}_2\text{O}_7 \) (99%, Otto) for Tb doping and \( \text{Eu}_2\text{O}_3 \) (99%, Otto) for Eu doping is added along with the host \( \text{Gd}_2\text{O}_3 \) so as to fix dopant concentration at 1%, 2.5% and 5%. Rest of the steps are quite similar as for obtaining the undoped nanoscale product of \( \text{Gd}_2\text{O}_3 \). The respective samples are marked as Gd, EuT1, EuT2, and EuT3 and TbT1, TbT2 and TbT3 as for independent precursors of 0, 1, 2.5, and 5% of Eu and Tb. A relevant block diagram that witnesses all the necessary steps is shown in Fig. 2.2.

![Fabrication procedure of undoped and doped \( \text{Gd}_2\text{O}_3 \) nanopowder from its bulk counterpart](image)

Fig. 2.2 Fabrication procedure of undoped and doped \( \text{Gd}_2\text{O}_3 \) nanopowder from its bulk counterpart

X-ray diffraction (XRD) is a powerful technique that is capable of revealing structural details on an atomic scale for both crystalline and non-crystalline (amorphous) systems. XRD method can be adequately applied to determine the crystal structures of metals and alloys, minerals, inorganic compounds, polymers and organic materials as well as to reveal information such as, crystallite size, lattice strain, surface and interface roughness, chemical composition, and crystal orientation etc.
Fig. 2.3 (a) shows a series of XRD pattern of the synthesized undoped, Tb$^{3+}$ (Tb$^{3+}$=1%, 2.5% and 5%) doped and Eu$^{3+}$ (Eu$^{3+}$=1%, 2.5% and 5%) doped nanopowders. All the diffraction peaks can be suitably indexed and correspond to the C-type cubic phase of Gd$_2$O$_3$ with the space group of \textit{Ia3}: the five prominent peaks are found to be located at Bragg angle ($2\theta$) of 28.52°, 33.10°, 34.67°, 43.54°, 57.45°. These peaks correspond to (222), (400), (134), (422) and (622) planes and with a preferred crystallographic orientation along (222) direction (JCPDS 36-1451) [18]. No diffraction peaks either due to byproducts or/and other phases were detected in the diffractrogram patterns. Essentially, this indicates the formation of phase pure cubic Gd$_2$O$_3$ nanoparticles with dopant ions occupying substitutional sites in the lattice. It is evident from the diffractrogram that there is a slight shifting in the $2\theta$ position with incorporation of a dopant, which could be due to the strain generation in the system. The lattice parameter ($a$) of the cubic lattice structure of Gd$_2$O$_3$ was calculated using the formula given by [19]

$$d_{hkl} = \frac{a}{\sqrt{(h^2 + k^2 + l^2)}}$$

(2.1)

where, $d$ is the interplaner distance and $(hkl)$ being the Miller indices. The calculated lattice parameters are highlighted in Table 1. In the XRD patterns, the presence of a number of diffraction planes owing to different crystal planes signifies polycrystalline nature of the nanoparticles. The polycrystalline solids are composed of a large number of crystallites (or small single crystals) of different sizes, orientations and the average crystallite size and the generated microstrain in the system can be determined by using the popular Willamson-Hall formula given by [20]

$$\beta_{hkl} \cos \theta = \frac{K\lambda}{D} + 4\varepsilon \sin \theta$$

(2.2)

Here, $\beta$ is full width at half maxima (FWHM), $D$ is the average crystalline size, $K$ is the shape factor (0.9), $\lambda$ is the wavelength of CuK$_\alpha$ radiation and $\varepsilon$ is the microstrain.
microstrain. The average crystallite size and microstrain values are presented in Table 2.1.

Table 2.1 Calculated lattice parameter, crystallite size and microstrain

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter, $a$ (Å)</th>
<th>Crystallite size, $D$ (nm)</th>
<th>Microstrain, $\varepsilon$ ($\times 10^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd</td>
<td>10.86 ± 0.13</td>
<td>4.5</td>
<td>-1.8</td>
</tr>
<tr>
<td>GdTb1</td>
<td>10.72 ± 0.34</td>
<td>3.8</td>
<td>-9</td>
</tr>
<tr>
<td>GdTb2</td>
<td>10.73 ± 0.42</td>
<td>3.2</td>
<td>-4.8</td>
</tr>
<tr>
<td>GdTb3</td>
<td>10.77 ± 0.59</td>
<td>3.7</td>
<td>-2.9</td>
</tr>
<tr>
<td>GdEu1</td>
<td>10.82 ± 0.43</td>
<td>4.8</td>
<td>-6.9</td>
</tr>
<tr>
<td>GdEu2</td>
<td>10.81 ± 0.28</td>
<td>4.2</td>
<td>-1.3</td>
</tr>
<tr>
<td>GdEu3</td>
<td>10.80 ± 0.61</td>
<td>4.0</td>
<td>-2.3</td>
</tr>
</tbody>
</table>

Low and high resolution TEM images of the Gd, GdTb1 and GdEu1 are shown in Fig. 2.3 (b), (c) and (d) respectively. It can be observed that, the nanoscale systems are nearly spherical one and with a diameter of ~7 nm for the undoped case (Fig. 2.3(b)). The upper inset of Fig. 2.3 (b) apparently depicts distinct, equispaced lattice planes (shown by short parallel lines) having an interplanar spacing of ~0.31 nm. The magnitude of the interplanar spacing, between two successive (222) planes of the cubic Gd$_2$O$_3$ structure can also be estimated from the Bragg’s law ($2d_{hkl} \sin \theta = n\lambda$, considering 1st order diffraction) and is consistent to the above results. Moreover, Fig. 2.3(c) shows an isolated, spherical particle of size ~7 nm that corresponds to TbGd1, system. It depicts distinct, equispaced lattice planes (shown by short parallel lines) having an interplanar spacing of ~0.31 nm. A cluster of EuG1 nanoparticles can be found in Fig. 2.3 (d) and with an average particle size ~8 nm. The upper inset of Fig. 2.3(d) shows a representative lattice fringe pattern that corresponds to the most intense diffraction of (222) planes. The EDX pattern of the Gd specimen is characterized by intense signals arising from the Gd and O elements [Fig. 2.4(a)]. For TbGd1 and EuGd1 specimens apart from
the Gd, O related peaks, additional signals from the dopants (Tb and Eu) are clearly evident, shown in Fig. 2.4(c) and (d); respectively.

Fig. 2.3 (a) XRD pattern of undoped, Eu$^{3+}$ and Tb$^{3+}$ doped Gd$_2$O$_3$ nanopowder, (b) HRTEM micrographs of undoped Gd$_2$O$_3$ nanopowder, (c) HRTEM image of an isolated Tb$^{3+}$ doped Gd$_2$O$_3$, depicting an interplanar spacing of 0.31 nm and (d) HRTEM image of Eu$^{3+}$ doped Gd$_2$O$_3$ nanoparticles. The upper inset of (b) and (d) show distinct interplanar spacing of the isolated nanoparticles.

Fig. 2.4 EDX spectra of (a) undoped, (b) Tb$^{3+}$ doped and (c) Eu$^{3+}$ doped Gd$_2$O$_3$ nanopowder samples
Micro-Raman spectroscopy is a powerful non-destructive tool to investigate the phonon spectrum, electron phonon coupling, structural phase transitions, and anharmonic behavior of the optical modes/vibrational properties of the nanostructures under study (Appendix IV). The micro-Raman spectra of Gd, GdTb1, GdTb2, GdEu1 and GdEu2 were recorded at room temperature considering an excitation source of Ar$^+$ line of $\lambda = 514$ nm (Fig. 2.5). Since the phonon energy of the RE sesquioxides is very low [21], most of the previous reports have focused only on the spectral region lower than 1000 cm$^{-1}$ [22]. Here, the Raman spectra is assessed in the range between 100 and 600 cm$^{-1}$. As can be found, the strongest Raman signal is located at 356 cm$^{-1}$ for pure Gd sample and is assigned as ($A_g + F_g$) mode. The wavenumbers associated with the Raman bands of different samples are highlighted in Table 2.2.

According to group theory analysis, 22 Raman active modes at the zone centre brillioiun zone are possible for the cubic phase Gd$_2$O$_3$ and can be represented by [23]

$$\Gamma = 4A_g + 4E_g + 14F_g$$
In the present case we could detect only 8 Raman active modes. The upper inset of Fig. 2.5 shows the zoomed view of the prominent $E_g$ mode, where broadening of the spectra with RE inclusion is quite evident.

Table 2.2 Observed and reported Raman modes of the studied samples

<table>
<thead>
<tr>
<th></th>
<th>Observed Wavenumber (cm$^{-1}$)</th>
<th>Mode Assigned</th>
<th>Reported Wavenumber (cm$^{-1}$) [21]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>108</td>
<td>$A_g$</td>
<td>111</td>
</tr>
<tr>
<td>Eu doped Gd$_2$O$_3$</td>
<td>108</td>
<td>$A_g$</td>
<td>135</td>
</tr>
<tr>
<td>Tb doped Gd$_2$O$_3$</td>
<td>108</td>
<td>$A_g$</td>
<td>135</td>
</tr>
<tr>
<td>GdEu1</td>
<td>108</td>
<td>$A_g$</td>
<td>135</td>
</tr>
<tr>
<td>GdEu3</td>
<td>108</td>
<td>$A_g$</td>
<td>135</td>
</tr>
<tr>
<td>Tb doped Gd$_2$O$_3$</td>
<td>108</td>
<td>$A_g$</td>
<td>135</td>
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<tr>
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<td>315</td>
</tr>
<tr>
<td>GdTb3</td>
<td>307</td>
<td>$A_g$</td>
<td>315</td>
</tr>
<tr>
<td>Tb doped Gd$_2$O$_3$</td>
<td>307</td>
<td>$A_g$</td>
<td>315</td>
</tr>
<tr>
<td>Pristine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>352</td>
<td>$A_g$</td>
<td>360</td>
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<tr>
<td>Eu doped Gd$_2$O$_3$</td>
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<td>$A_g$</td>
<td>360</td>
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<tr>
<td>Tb doped Gd$_2$O$_3$</td>
<td>354</td>
<td>$E_g$</td>
<td>360</td>
</tr>
<tr>
<td>GdEu1</td>
<td>354</td>
<td>$E_g$</td>
<td>360</td>
</tr>
<tr>
<td>GdEu3</td>
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<td>360</td>
</tr>
<tr>
<td>Tb doped Gd$_2$O$_3$</td>
<td>354</td>
<td>$E_g$</td>
<td>360</td>
</tr>
<tr>
<td>GdTb1</td>
<td>485</td>
<td>$A_g$</td>
<td>479</td>
</tr>
<tr>
<td>GdTb3</td>
<td>485</td>
<td>$A_g$</td>
<td>479</td>
</tr>
<tr>
<td>Tb doped Gd$_2$O$_3$</td>
<td>485</td>
<td>$A_g$</td>
<td>479</td>
</tr>
<tr>
<td>Pristine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>562</td>
<td>$A_g$</td>
<td>568</td>
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<tr>
<td>Eu doped Gd$_2$O$_3$</td>
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<td>$A_g$</td>
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<tr>
<td>Tb doped Gd$_2$O$_3$</td>
<td>562</td>
<td>$A_g$</td>
<td>568</td>
</tr>
<tr>
<td>GdEu1</td>
<td>583</td>
<td>$A_g$</td>
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</tr>
<tr>
<td>GdEu3</td>
<td>583</td>
<td>$A_g$</td>
<td>583</td>
</tr>
<tr>
<td>Tb doped Gd$_2$O$_3$</td>
<td>583</td>
<td>$A_g$</td>
<td>583</td>
</tr>
</tbody>
</table>

According to the Heisenberg uncertainty principle, the particle size and phonon position hold the following relationship [24],

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$  \hspace{1cm} (2.3)

where, $\Delta x$ is the particle size, $\Delta p$ is the phonon momentum distribution, and $\hbar$ is the reduced Planck’s constant. As the particle size decreases, the phonon is increasingly confined within the particle, and the spread of phonon momentum tend to increase. This situation leads to the peak broadening of the scattered phonons according to the law of conservation of momentum [24]. Another factor governing this shift may be that when the size is decreased the momentum conservation is relaxed and in this case, the Raman active modes are not limited at the center of the Brillouin zone.
Note that, in the case of nanoscale systems, particularly in semiconductor systems, the Raman frequency undergoes a red shift with the particle size reduction [25, 26]. The red shift in the Raman spectra may arise from the cohesive bond weakening of the lower coordinated atoms near the surface region of the nanograin [26]. In the present study also red shift has been observed for Raman peaks. Another factor responsible for this shift may be the short-range interactions between a phonon and photon, which typically describe the covalent bonding and thus can be correlated to bond energy and bond length [27].

For a pure crystal, the phonon contribution comes from the center of the Brillouin zone, at \( q=0 \) [28]. However, for small nanocrystallites, the phonon contribution emerges from the entire Brillouin zone [29, 30]. Moreover, the breaking of the phonon selection rule directly influences the Raman line shape, position, etc. [30]. A positive dispersion from the center leads to the asymmetric broadening, blue shift and reduction of intensity [28]. Intensity of the 1\(^\text{st}\) order Raman scattering of nanocrystals of diameter, ‘\( d \)’ is given by

\[
I(w, d) = \int_{BZ} \frac{|c(q, d)|^2}{[\omega - \omega(q)]^2 + \left(\frac{\Gamma_0}{2}\right)^2} d^3q
\]

where, \( c(q,d) \) is the Fourier transformation of the confinement function, \( \omega(q) \) is the phonon dispersion frequency, and \( \Gamma_0 \) is the natural line width [28]. The size of the nanocrystals and presence of defects have a profound effect on the Raman peak position, line width, etc. in order to study the effect of size, defects, and dopant on the position and width of the Raman peak, the \( E_g \) Raman peak is taken into account. As can be seen from Fig. 2.5, the intensity of the \( E_g \) Raman peak tends to decrease with increasing dopant concentration.
The Raman shifting due to the phonon confinement effect can be described by the confinement model. The size dependent Raman shift can be represented by [31]:

$$\Delta \omega = \omega(d) - \omega_0 = -A \left( \frac{a}{d_{clus}} \right)^{\gamma}$$  \hspace{1cm} (2.5)

Here, $\omega(d)$ is the frequency of the phonon in a nanocrystal of size $d$, $\omega_0$ is the frequency of the bulk Gd$_2$O$_3$, $\Delta \omega$ is the Raman frequency shift, $a$ is the lattice parameter of Gd$_2$O$_3$, $d_{clus}$ is the nanocluster size, and $A$ and Grüneisen parameter ($\gamma$) are the parameters related to nanocrystal geometry. The parameter $A$ has a value of 52.3 cm$^{-1}$ in the Richter model [31], and the value of $\gamma$ is 1.543 [32]. The calculated nanocrystal size from the above mentioned formula is presented in Table 2.3. This value resembles closely the average crystallite size as obtained through XRD (Table 1.1).

The phonon lifetime, $\tau$ is also calculated considering peak broadening aspect of the $E_g$ peak, for each sample. The energy-time uncertainty relation for the determination of phonon lifetime is:

$$\Delta E / \hbar = \frac{1}{\tau} = 2 \Pi c \Gamma$$  \hspace{1cm} (2.6)

where $\Delta E$ is the uncertainty in the energy of phonon mode, $\hbar$ is the reduced plank constant, $\Gamma$ is the FWHM of the Raman peak, and $\tau$ is the phonon lifetime [33]. The values of phonon life time are presented in Table 2.3. As a general trend, $\tau$ value likely to drop with doping. The phonon lifetime can be influenced by the defects, as the concentration of the defects increases; the confined phonons may undergo inelastic scattering process, with crystal defects limiting the phonon lifetime.
Superconducting quantum interference device (SQUID) is a very sensitive magnetometer used to monitor very small changes in magnetic flux and to reveal the magnetic polarization response to a field of the sample. The working principle of a SQUID is based on the superconducting loops containing Josephson junctions. Fig. 2.6 depicts the response of magnetization vs. magnetic field ($M-H$), measured at room temperature (300 K). The magnetization feature was recorded when the applied field was varied in the range $-6$ to $6$ T. The samples are nearly paramagnetic since no clear hysteresis and steep slope are observed without exhibition of any saturation magnetization trend. On zooming in the magnetic response near the zero field (origin), we find that the doped Gd$_2$O$_3$ system is nearly superparamagnetic as compared to the undoped one (inset Fig. 2.6). Essentially, paramagnetic nature of Gd$^{3+}$ centres is due to the presence of half-filled $f$ orbitals with seven unpaired electrons in the interlocked shell [34]. It may be noted that, the paramagnetic characteristics of a system is caused by a number of magnetic dipole moments summing up to zero in the absence of an applied field. But the net moment becomes nonzero when the system is subjected to a field. However, superparamagnetism arises when the thermal energy is strong enough to orient individual moments randomly. As far as superparamagnetism is concerned, in the past, numerous studies have been devoted mostly to iron oxide based nanostructures [35]. Herein, we anticipate that, the paramagnetism in Gd$_2$O$_3$ nanoparticles has arisen owing to the non-interacting localized nature of
the magnetic moments. The magnetic properties of the Gd$^{3+}$ ions originate from seven unpaired inner $4f$ electrons, which are closely bound to the nucleus and effectively shielded by the outer closed shell electrons ($5s^25p^6$) from the crystal field [36]. Among various paramagnetic RE ions, Gd$^{3+}$ ions possess a high magnetic moment due to isotropic electronic ground state ($^8S_{7/2}$).

Fig.2.6 Room temperature $M\sim H$ plots of Gd1 and GdTb1 nanopowder. The inset shows an enlarged view of the plot near zero-field.

In the high field region, the $M (H)$ can acquire a resulting feature due to linear (paramagnetic) and nonlinear (ferromagnetic) responses. As the field increases the nonlinear contribution gets reduced but the linear contribution is not altered. Therefore, it is assumed that at a large enough field it is only the linear response which sustains. The extrapolation to zero field, infact, gives an estimate of the nonlinear saturation moment of the (ferromagnetic) term. Remarkably, the magnitude of $M$ was found to experience a non-zero value in the absence of the field ($H=0$) as for Gd sample, unlike for GdTb1 specimen. This suggests that, the investigated sample (Gd) cannot represent an idealistic superparamagnetic system and it has contribution both from paramagnetic as well as ferromagnetic parts. As for undoped sample, the coercive field ($H_c$) and remanence ($M_r$) were
found to be $0.0076$ T and $0.0123$ emu/g, respectively. It indicates that, the magnetic moments can be reversed even by changing the direction of a small applied field. It is worth mentioning here that, the coercivity prevents the nanoparticles from being superparamagnetic, especially in case of pure Gd$_2$O$_3$. Nevertheless, for Tb doped Gd$_2$O$_3$ sample, only a linear contribution is prevalent that indicate paramagnetic character of the system.

2.1.2 Synthesis and characterization of pure and RE ion doped nanotitania

Sol-gel routes are quite useful in the sense that, they are capable of synthesizing high surface area nanotitania along with adequate doping for a given stoichiometry. The un-doped, TiO$_2$ nanoparticles are fabricated by hydrolyzing titanium isopropoxide (TTIP, Aldrich, 99.9% pure, St. Louis, MO) in an alcoholic medium and followed by a rapid condensation process [37]. In a typical reaction, 3 mL of TTIP is first transferred to a conical flask containing 15 mL of propanol and then, the sol was subjected to stirring (~250 rpm) for 30 min. After a while, a hydrolyzer solution of 1 mL of HCl in 5 mL of H$_2$O is added to it followed by stirring at a moderate temperature (~75 °C), for 3 h. The precursor solution is then kept in the dark overnight for homogenous growth of nanoscale colloids. The gel formed was separated through filtration and high speed centrifugation. Finally, the as-received gel is dried at room temperature and subsequently, annealed at different temperatures (200-600 °C) to yield fine powders of TiO$_2$.

In order to study the impact of RE ion doping on the performance of photocatalytic activity along with the $D$-$F$ transition of RE ions, Eu and Tb are considered as dopants. For doping purpose, a suitable amount of europium acetate (EuAc, 99.9% pure, CDH) and terbium acetate (TbAc, 99.9% pure, CDH) were added in the hydrolysis step. In this case, the as-received gel is annealed at 300 °C. In the titania host, the doping level of Eu and Tb is varied as 1, 2.5, and 5%. The respective samples are marked as, Gd, EuT1, EuT2, and EuT3 and TbT1,
TbT2 and TbT3 that were derived from independent precursors of 0, 1, 2.5, and 5% of Eu and Tb.

Fig. 2.7 (a) XRD patterns of (a) un-doped TiO$_2$ nanopowders synthesized by annealing at different temperatures of 200 °C (T1), 300 °C (T2), 400 °C (T3), 500 °C (T4), and 600 °C (T5); and (b) XRD pattern of undoped (T2), Eu doped (EuT1, EuT2 and EuT3) and Tb doped (TbT1, TbT2 and TbT3) TiO$_2$ nanopowder sintered at 300 °C.

Fig. 2.7 (a) depicts a series of XRD patterns of the un-doped nanopowder samples synthesized at different annealing temperatures of 200, 300, 400, 500 and 600°C and are labeled as T1, T2, T3, T4 and T5; respectively. As can be noticed for
samples T1 to T4, the diffraction peaks (101), (004), (200) and (105) correspond primarily to the tetragonal anatase phase of TiO$_2$ ($a=b=3.785$ Å, $c=9.514$ Å; space group: $D_{4h}^{19}$) [38]. Nevertheless, the T5 sample has exhibited a mixed phase of tetragonal anatase, rutile ($a=b=4.593$ Å, $c=2.959$ Å; space group: $D_{4h}^{14}$) and orthorhombic brookite ($a=5.143$ Å, $b=5.456$ Å, $c=9.182$ Å; space group: $D_{15}^{2h}$) ones [39]. As for T5 case, in addition to the (101) diffraction peak corresponding to the anatase phase, there existed three prominent peaks emanating from (121) and (131) planes of brookite and (220) of rutile phases which are in consistency with an earlier work (JCPDS 36-1451) [40]. Thus significant phase transformation was realized at a comparatively higher annealing temperature (600 °C) with the intense diffraction signal located at $2\theta\sim31.38^\circ$ that representing (121) crystal plane of the brookite phase.

It was revealed earlier that, the activation energy of nucleation has a size dependency along with other physical parameters [41]. Essentially, anatase phase is thermodynamically stable for crystallite sizes smaller than ~11 nm. Whereas, a stable brookite phase is evident for an average size in the range of 11-35 nm [41]. In the present case, the average crystallite size, as estimated using popular Williamson-Hall method were 5, 5.6, 6, 9 and 23 nm for T1, T2, T3, T4 and T5 samples; respectively. The phase transformation (for T5 sample) is also accompanied by an increment in the crystallite size which is in agreement with the other works [42, 43]. The phase contents of the nano-TiO$_2$ samples were calculated from the integrated intensities using the following model formula [44]:

\[
W_b = \frac{K_b A_b}{K_a A_a + A_r + K_b A_b} \quad 2.7(a)
\]

\[
W_a = \frac{K_a A_a}{K_a A_a + A_r + K_b A_b} \quad 2.7(b)
\]

\[
W_b = \frac{A_r}{K_a A_a + A_r + K_b A_b} \quad 2.7(c)
\]
where, $W_a$ and $W_b$ represent the respective weight fractions of the anatase and brookite phases, and $A_b$ as the integrated intensity of the brookite peak. Optimized correction coefficients $K_a$ and $K_b$ are introduced as per reference [45] which give values of 0.886 and 2.721. The respective wt% of different phases of T5 sample was calculated to be 73.68, 14.89 and 11.43% as for brookite, rutile and anatase phases. The diffractograms of the un-doped (T2) and Eu-doped and Tb-doped (EuT1, EuT2 and EuT3, and TbT1, TbT2 and TbT3) nano-titania samples annealed at 300 °C and synthesized from independent precursors (1, 2.5 and 5% of Eu and Tb) have revealed the existence of mostly anatase phase (Fig. 2.7(b)). Previously, a dominant anatase phase was also observed in case of Ag-doped TiO$_2$ particles obtained from a rapid quenching technique [45]. Since the anatase phase is superior over other phases of TiO$_2$ in terms of photocatalytic response, we took interest in obtaining and characterizing anatase phase [46]. As the diffraction peak positions remained intact for the un-doped and doped samples, it is possible that the dopant (Eu$^{3+}$ and Tb$^{3+}$) has undergone substitutional doping into the titania host lattice. Moreover, the intensity of diffraction peaks gets suppressed with adequate increase in dopant concentration thus signifying loss of crystallinity due to lattice distortion [24]. The average crystallite size was calculated to be 5.6, 5, 4, 3.4, 3, 4.8, 4.7 and 2.8 nm for T2, EuT1, EuT2, EuT3, TbT1, TbT2 and TbT3; respectively. An apparent suppression of the diffraction signal with increase in dopant content would indicate an increment of micro-strain in the lattice.

Both un-doped and doped TiO$_2$ nanoscale specimens were also viewed under the electron microscope (HRTEM) for which the micrographs are presented in Fig. 2.8. As revealed from the micrograph, the un-doped system comprises of apparently spherical particles of size $\sim$7 nm (Fig. 2.8(a)). The system was believed to be highly crystalline in nature owing to the existence of distinct lattice fringes
and having an interplanar spacing of ~3.52 Å (Fig. 2.8(a)). The estimated value corresponds to the spacing between the consecutive (101) crystal planes of the tetragonal anatase phase of the TiO$_2$ system which is also substantiated from calculation at one of the major diffraction peaks of the XRD pattern. The HRTEM image of EuT2 specimen, shown in Fig. 2.8(b), depicts a number of crystalline particles having a well resolved crystal planes. A dotted red circle basically signifies a ~7 nm sized particle with an interplanar spacing of ~3.52 Å. A number of nanoscale defects were also evident from a closer look of the micrograph. Several vacancies, missing planes as well as edge-dislocations can be found which are denoted by open-red arrows. Although different defects could have their own origin but the chief reason is the difference in ionic radii of Ti$^{3+}$ and Eu$^{3+}$ (ionic radii: Ti$^{4+}$=64 pm and Eu$^{3+}$ = 94 pm). Note, a particle may comprise of several crystallites and that, the crystallite and particle sizes are generally not same in polycrystalline systems. This is the reason why a difference in the average size predicted through XRD and TEM analysis is observed. The selected area electron diffraction (SAED) pattern of EuT2 sample is shown in Fig. 2.8(c). Though the diffraction rings are distinguishable they are not sharp owing to the introduction of appreciable amount of polycrystallinity. The rings were indexed as (101), (004), (200) and (105) and are concomitant with the XRD patterns (Fig. 2.8(b)) [20]. A cluster of TbT2 nanoparticles can be seen in the separate HRTEM micrograph, where individual nanoparticles are represented by red circles (Fig. 2.8 (d)). The inset shows an isolated nanoparticle with approximate size ~7 nm, along with distinct lattice spacing corresponding to (222) diffraction planes. The corresponding SAED pattern is depicted in Fig. 2.8 (e). The compositional analysis was performed by energy dispersive x-ray (EDX) studies. The EDX pattern of T2 specimen is characterized by strong X-ray signals arising from Ti and O elements (Fig.2.9 (a)). In contrast, as for EuT1 and TbT1 specimens, in
addition to Ti, O, an appreciable signal from Eu and Tb were also clearly observable (Fig. 2.9 (b),(c)).

![HRTEM images and SAED patterns](image1)

**Fig. 2.8(a)** HRTEM image of an isolated pure TiO$_2$ nanoparticle, **(b)** HRTEM image, **(c)** SAED pattern of EuT$_2$, **(d)** HRTEM image and **(e)** SAED pattern of TbT$_2$ specimen

![EDX spectra](image2)

**Fig. 2.9** EDX spectra of **(a)** undoped, **(b)** Tb doped and **(c)** Eu doped TiO$_2$ nanopowder specimen

### 2.1.3 Growth of undoped and Ag$^+$ nanotitania and their basic characterization

Undoped TiO$_2$ nanopowders were synthesized from bulk TiO$_2$ by a solid-state mixing cum rapid quenching method. Solid-state quenching method is advantageous over other conventional physicochemical methods like solution
growth, chemical reduction, coprecipitation etc. which may produce a mixed phase of TiO$_2$ nanoparticle system. In the solid-state quenching technique, bulk TiO$_2$ (Loba Chemie, 99.5% pure) is considered as the starting material and was used without further purification. First, the bulk TiO$_2$ powder is subjected to unidirectional grinding with the help of a mortar and pestle for 2 h. The product is then sintered in a muffle furnace (~1173 K) for 4 h. Next, the sample is taken out of the furnace and subjected to repeated solid state grinding for 2 h. This sample is labeled ‘$R$.’ In the second case, after the sintering step, the product was quenched down to ice-cold (~273 K) temperature followed by solid-state grinding process, for 2 h. The as-received product, in this case is labeled $l$. In the final case, after the sintering step, the product is quenched at the liquid nitrogen temperature (77 K) which was then followed by the unidirectional grinding for 2 h. As the particles obtained in this case (quenching at LN$_2$ temperature) are relatively smaller in size, the process was repeated several times upto sixth cycle and the respective samples are labeled accordingly as, $C_1$ to $C_6$; for respective cycles. The block diagram of the above mentioned steps are shown in Fig. 2.10.

Fig. 2.10 Block diagram of the solid state cum rapid quenching method for synthesis of titania
Fabrication principle and basic characterizations of nanoscale structures involving RE systems

Similar procedure is also adopted for the Ag-doped nanotitania upto the third cycle of LN2 quenching. The Ag-doped samples are prepared considering 1% M ratio of AgNO₃ (Loba Chemie) being added to TiO₂ in the initial step. Aq. AgNO₃ is added dropwise to the bulk powder TiO₂ prior to grinding and quenching with LN2 and consequently, repeated for 3 cycles. All the above samples are denoted as A1, A2 and A3.

Ag doped nanotitania is also prepared through a sol-gel route. In this case all the steps are kept same as described in section #2.1.2. Here, Ag-doped nanotitania films were casted by dip-coating as well as by spin-coating methods. The as-received sol was drawn on 1x1 cm² laboratory glass slides followed by natural drying and heat treatment at 200°C.

Fig. 2.11(a) and (b) depict the respective XRD patterns of the undoped and Ag-doped TiO₂ nanopowders synthesized via a solid-state cum quenching method. For both the types of samples, the diffraction peaks corresponding to (101), (103), (004), (112), (200), (105), (211), (118), (116) crystallographic planes are revealed thereby representing anatase phase of the TiO₂ system [38]. XRD patterns of the synthesized Ag doped titania nanopowder via sol-gel methods are shown in Fig. 2.11(c). The XRD pattern shows the anatase phase of TiO₂ with peaks corresponding to (101), (004), (200) and (105) planes, in consistency with other the reports [38]. In case of Ag-doping, no impurity related peaks are observed, thereby ensuring homogeneous Ag doping into titania lattice.
Nanoscale titania systems as obtained via solid-state grinding and rapid quenching (through room, ice-cold and LN2 temperatures) display adequate improvement in the full widths of the characteristic diffraction peaks. This clearly indicates subsequent particle size reduction induced by solid state quenching (at 

Fig. 2.11 (a) XRD pattern of (B) bulk TiO$_2$ powder, (R) synthesized sample at room temperature, (I) at ice bath, (C1) 1st cycle, (C2) 2nd cycle, (C3) 3rd cycle, (C4) 4th cycle and (C5) 5th cycle of LN2 quenching. (b) XRD pattern of Ag-doped TiO$_2$ nanosystem prepared via solid state cum rapid quenching method: (A1) 1st cycle, (A2) 2nd cycle and (A3) 3rd cycle of LN2 quenching.
LN2 temperature) repeated for several cycles. On repeating up to a number of (six) cycles of quenching, the average crystallite size is found to vary from ~36.6 to 22.2 nm (as estimated from the W-H formula) [20]. The particle size reduction with repeating LN2 cycles is also evident from TEM images shown in Fig. 2.11(i), (ii) and (iii) for C1, C3 and C6 samples; respectively. The particles are found to be nearly spherical in shape and with the respective dimension as ~ 150 nm, ~125 nm and ~45 nm. The HRTEM image of the A3 sample, shown in Fig. 2.12 (iv) shows that the particle size is ~100 nm. The inset of Fig. 2.12 (iv) depicts a set of crystal lattice fringe pattern that correspond to (101) planes of TiO$_2$, which is believed to be the preferred orientation plane of the crystallites as evident from the intense diffraction peaks in XRD patterns.

Fig. 2.12 TEM micrographs of (i) C1, (ii) C3 and (iii) C6 samples of TiO$_2$ prepared via repeated solid state quenching. (iv) HRTEM image of Ag-doped TiO$_2$ (A3 sample) exhibiting a number of nanoparticles with clear facets. The inset shows clear lattice fringe pattern corresponding to (101) plane.
2.2 Ferrofluid preparation using novel materials

In order to carry out magneto-optic study and rheological aspects, some new FFs were prepared using nanoparticles of undoped and 1% Tb doped Gd$_2$O$_3$. Most of the reports are based on preparation of conventional type of FFs containing iron oxide nanoparticles [47]. For making a FF system, surfactant-coated particles are required to be dispersed in a carrier fluid. Here, while preparing FFs, the AR-grade ethanol (Appendix III) is chosen as the carrier fluid knowing that CTAB is chemically inert in ethanol. The CTAB coated nanoparticles (0.5 g) were dispersed in 40 mL carrier fluid (concentration of nanoparticles to ethanol is kept as 12.5 g L$^{-1}$) and then subjected to stirring (~200 rpm) for ~8 h so that the particles are distributed homogeneously without aggregation.

Dynamic Light Scattering (DLS) study is a versatile nondestructive technique for determining the average secondary particle size as well as the size distribution of the nanoparticles undergoing Brownian motion in colloidal suspensions. In general, it gives us an idea of the hydrodynamic diameter of the nanoparticles. The DLS spectra of the undoped and Tb$^{3+}$ Gd$_2$O$_3$ nanoparticles, as-prepared for the ethanol based FFs, are shown in Fig. 2.13 (a) and (b); respectively. Both the curves show a narrow distribution of particles. In order to find the average particle size, each of the spectra is subjected to curve fitting using Gaussian distribution. The fitted data reveals that the respective particle size can be ~ 7.8 nm and 7 nm for the undoped and Tb doped Gd$_2$O$_3$ nanoparticle based FFs. Note that, the predicted values are somewhat larger than the values obtained from TEM analyses. This is because the DLS study which relies on scattering events depends largely on the hydrodynamic diameter of the particles. The respective full width at half maxima (FWHM) are found 4.4 and 2.59 nm for undoped and Tb doped systems. Apparently, a marginal improvement in the size distribution is realized for Tb doped Gd$_2$O$_3$ nanoparticle based FF.
2.3 Concluding remarks

A variety of nanoparticles have been fabricated considering two oxide systems: pure and RE doped form of Gd$_2$O$_3$ and TiO$_2$. The nanosized pure and doped Gd$_2$O$_3$ are prepared via a user friendly physico-chemical method. On the other hand, TiO$_2$ and Ag-doped nanoparticles were synthesized via; sol-gel and solid state cum quenching routes. In case of RE ion doping, only sol-gel method was employed. Different microscopic and spectroscopic characterization methods ensure the production of quality Gd$_2$O$_3$ and TiO$_2$ nanoparticles. Finally, several ferrofluids were made by dispersing a desired concentration of surfactant coated Gd$_2$O$_3$ nanoparticles in ethanol medium.

References


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