CHAPTER 5

Effects of Crystal Size, Structure and Quenching on the Photoluminescence Emission Intensity, Lifetime and Quantum Yield of ZrO$_2$:Eu$^{3+}$ Nanocrystals
Chapter 5: Effects of Crystal Size, Structure and Quenching

5.1 Introduction

Zirconia (ZrO$_2$) is a material which has both fundamental and application-oriented importance. It is well known for low thermal conductivity, high melting point, high thermal and mechanical resistance, high refractive index, low phonon energy, high chemical and photochemical stability, etc [1-7]. Such properties make it find in various applications. It is used as refractory, catalyst, super hard materials, oxygen sensor, fuel cell, high corrosion resistance, diamond simulant, nucleic acid sensor, bone cement additives, etc [1-9]. Generally, it has three crystal structures viz. monoclinic, tetragonal and cubic [3,4]. Mention can be made that the properties of zirconia depend on crystal structure and the structure can be tailored by tuning crystal size [4,10]. In view of these facts, nanocrystals of ZrO$_2$ attracted researchers in the present realm of nanoscience and nanotechnology.

A plethora of reports are found on size dependent properties of doped zirconia nanocrystals. Among them one of the most reported areas is in the field of photoluminescence [10-12]. As a means of probing the crystal structure, researchers introduced luminescent dopant in the host ZrO$_2$ matrix and studied its properties through the dopant [10-12]. However, introduction of dopant in a host material result in size and structure alteration of the host crystal [3,10]. Consequently, properties of crystals which vary on crystal size and structure change as the concentration of the dopant changes. Apart from change in crystal size and structure, luminescence quenching is a common phenomenon in luminescence studies of doped nanocrystal which originates from doping. Recently, Karsten et al. reported effect of luminescence quenching on quantum yield of nanocrystals [13]. On the other hand, Smits et al. reported effect of crystal structure on decay lifetime of ZrO$_2$:Eu$^{3+}$ nanocrystals [12]. However, substantial amount of data on luminescence emission intensity, lifetime and quantum yield of ZrO$_2$:Eu$^{3+}$ nanocrystals are needed to validate the effect of size and its associated parameter viz. crystal structure and quenching on the luminescence properties of the nanocrystals. Furthermore, no detailed reports are found on the combined effect of crystal size, structure and quenching on the luminescent properties of a nanocrystal. Indeed, it is requisite to study the effects of crystal size, structure and quenching of a doped nanocrystal because they are interdependent and inherent from doping.

In this work, various crystal sizes and structures of ZrO$_2$ nanocrystals doped with different concentrations of Eu$^{3+}$ are synthesized through polyol, hydrothermal
Chapter 5: Effects of Crystal Size, Structure and Quenching Yield of ZrO$_2$:Eu$^{3+}$ Nanocrystals

and simple-precipitation techniques. X-ray diffraction (XRD), transmission electron microscopy (TEM) and selected area electron diffraction (SAED), Fourier transform infrared (FTIR) spectroscopy, energy dispersive analysis of x-ray (EDAX), photoluminescence (PL) emission, lifetime and quantum yield (QY) are studied exhaustively to observe the influences of crystal size, structure and quenching on this nanocrystal.

5.2 Experimental

Nanocrystals of ZrO$_2$:Eu$^{3+}$ are synthesized separately by three techniques viz. polyol, hydrothermal and simple-precipitation techniques as elaborated in the references [3,4,14]. The precursors obtained from polyol and simple-precipitation techniques are not crystalline. Therefore, the samples are annealed for 4 h at 500 and 800 °C respectively for crystallization. The selection of different annealing temperatures are to obtain different crystal sizes, structures, etc. at different annealing temperatures. In line with the above statements, samples synthesized by hydrothermal technique are not annealed as the precursors obtained are crystalline. XRD data of the samples are recorded in X’Pert PANalytical diffractometer at 40 kV and 30 mA. Wavelength of the x-ray used is 1.54060 Å (Cu K$_\alpha$). TEM images and SAED rings are recorded using JEM-2100 microscope (JEOL) (200 kV). FTIR spectra are recorded in MB102 spectrometer (BOMEN). Percentages of elements present in the sample are quantified by EDAX (AMETEK) attached to scanning electron microscope, SEM (Quanta 250). Photoluminescence (PL) emission and lifetimes are recorded on LS55 Luminescence Spectrometer (PerkinElmer).

Photoluminescence quantum yield (QY) is calculated by using Integrating Sphere (IS) within the FSP920 Fluorescence Spectrometer (Edinburgh Instruments) by an absolute method. The IS consist of a 120 mm inside diameter spherical cavity, which is machined from BENFLEC block. The IS has two perpendicular ports, one with a lens to focus the excitation beam into the sample and a window to collect a portion of the light scattered off the sphere’s surface. For a typical QY calculation, emission scan (spectrum) of reference is recorded and, with the same parameters used in recording the reference sample, emission scan (spectrum) of the sample is recorded. Again, without changing the parameters used, the emission spectrum of the sample with the sample in place but the mirror set to cuvette (indirect measurement of a solid sample) is recorded. Indirect measurement of the sample emission ensure correct QY.
value whereby neglecting the re-excitation of the sample by scattered light [15]. Then from the three emission spectra quantum yield is calculated by using a wizard called “Quantum Yield Calculation”.

All data are recorded by using powder (solid) sample. And all the measurements are performed in room temperature.

5.3 Results and Discussion

5.3.1 Powder XRD

Figure 5.1(a), Figure 5.1(b) and Figure 5.1(c) show the XRD patterns of ZrO$_2$:Eu$^{3+}$ (2 to 10 mol\%) nanocrystals synthesized by polyol, hydrothermal and simple-precipitation techniques. PANalytical’s X’Pert HighScore Search Match Figure 5.1: XRD patterns of ZrO$_2$:Eu$^{3+}$ (2 to 10 mol\%) nanocrystals synthesized by (a) polyol, (b) hydrothermal and (c) simple-precipitation techniques [m, t and c indicate highest count of monoclinic, tetragonal and cubic phases respectively].
Analysis of the samples synthesized by polyol technique shows that the samples are all cubic in structure (ICDD Ref. Code: 00-049-1642). Same analysis of the samples synthesized by hydrothermal technique reveal that the samples containing 2 to 8 mol% Eu$^{3+}$ are found to have both monoclinic (ICDD Ref. Code: 01-086-1451) and tetragonal (ICDD Ref. Code: 01-079-1770) structures. The highest peak count (intensity) of the monoclinic structure decreases relative to that of tetragonal peak on increasing the Eu$^{3+}$ concentration. However, the sample containing 10 mol% of Eu$^{3+}$ is found to be cubic (ICDD Ref. Code: 00-049-1642). Further, the samples of ZrO$_2$:Eu$^{3+}$ (2 to 6 mol%) synthesized by simple-precipitation technique have both monoclinic (ICDD Ref. Code: 01-086-1451) and tetragonal (ICDD Ref. Code: 01-079-1770) structures. The percentage of tetragonal structure increases while the percentage of monoclinic structure decreases on increasing the Eu$^{3+}$ concentration up to 6 mol%. However, at 8 and 10 mol% of Eu$^{3+}$, the samples are found to be purely tetragonal in structure. The percentage of different phases present in the samples synthesized by the three techniques is tabulated in Table 5.1. The stabilization of structures from monoclinic to tetragonal and/or tetragonal to cubic are attributed due to substitution of Zr$^{4+}$ by Eu$^{3+}$. It can be noted that the appropriate place for Eu$^{3+}$ in the ZrO$_2$ is Zr$^{4+}$ site and the charge difference is compensated by an oxygen vacancy [16,17].

Table 5.1: Percentage of different structures present in the ZrO$_2$:Eu$^{3+}$ nanocrystals synthesized by the polyol, hydrothermal and simple-precipitation techniques.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Synthesis Technique</th>
<th>ZrO$_2$:Eu$^{3+}$ (mol%)</th>
<th>Crystal Structure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polyol</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Polyol</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Polyol</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Polyol</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>Simple-precipitation</td>
<td>2</td>
<td>42</td>
</tr>
<tr>
<td>6</td>
<td>Simple-precipitation</td>
<td>4</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>Simple-precipitation</td>
<td>6</td>
<td>14</td>
</tr>
<tr>
<td>8</td>
<td>Simple-precipitation</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>Simple-precipitation</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>Hydrothermal</td>
<td>2</td>
<td>43</td>
</tr>
<tr>
<td>11</td>
<td>Hydrothermal</td>
<td>4</td>
<td>37</td>
</tr>
<tr>
<td>12</td>
<td>Hydrothermal</td>
<td>6</td>
<td>25</td>
</tr>
<tr>
<td>13</td>
<td>Hydrothermal</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td>14</td>
<td>Hydrothermal</td>
<td>10</td>
<td>0</td>
</tr>
</tbody>
</table>
From XRD patterns, the peak \((hkl)\) corresponding to maximum intensity (count) is identified. Then the peak broadening at half the maximum intensity \((B)\) and centre of the peak \(x_c\) are determined by fitting the peak with Gaussian function:

\[
y = y_0 + \frac{A}{B} \left( \frac{\pi}{2} \right)^{1/2} \exp\left\{ -2 \frac{(x-x_c)}{B^2} \right\}
\]

where the parameters: \(y_0\) is the offset, \(A\) is the area of the peak. Figure 5.2 shows the Gaussian fit to the maximum XRD count (intensity) of the sample \(\text{ZrO}_2: \text{Eu}^{3+}\) \((2\ \text{mol}%)\) synthesized by hydrothermal technique. Subsequently, with the value of \(B\) and \(x_c\), average crystal sizes of the nanocrystals are calculated by using Scherrer formula, assuming the crystals to be spherical in shape.

\[
t' = \frac{(0.9\lambda)}{B \cos \theta}
\]

where 0.9 is shape factor, \(\lambda\) is the wavelength of x-ray used and \(\theta = x_c / 2\) is the Bragg angle \([3,4,18,19]\). The change in average crystal sizes, as a function of \(\text{Eu}^{3+}\) concentration, of the nanocrystals synthesized by the three techniques is shown in Table 5.2. This table also shows that the peak position \((2\theta)\) slightly shifts towards lower angle and the line broadening \((B)\) increases on increasing the concentration of \(\text{Eu}^{3+}\). These can be attributed to substitution of smaller ionic radius \(\text{Zr}^{4+}\) (87 pm) by larger \(\text{Eu}^{3+}\) (98 pm) \([4]\). Consequently, the crystal size decreases on increasing the \(\text{Eu}^{3+}\) concentration and it varies from 3.9 to 21.3 nm among the three synthesis techniques. The shifts in peak position \((2\theta)\) towards lower angle; the increase in the line broadening \((B)\); the decrease in crystal size \((t')\) on increasing the \(\text{Eu}^{3+}\) concentration are consistent with the Scherrer formula where \(t'\) is inversely proportional to \(B\) and \(\cos \theta\) \([19, 20]\).
Table 5.2: Shift in peak position (2θ), line broadening (B) and average crystal sizes (t’) as a function of Eu³⁺ concentration of the ZrO₂:Eu³⁺ nanocrystals synthesized by the three techniques.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Synthesis Technique</th>
<th>ZrO₂:Eu³⁺ (mol%)</th>
<th>Highest Peak (hkl)</th>
<th>x_c (2θ)</th>
<th>B</th>
<th>Crystal Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polyol</td>
<td>2</td>
<td>(111)</td>
<td>30.13</td>
<td>1.13</td>
<td>6.8</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>5</td>
<td>(111)</td>
<td>30.07</td>
<td>1.25</td>
<td>5.9</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>7</td>
<td>(111)</td>
<td>29.95</td>
<td>1.52</td>
<td>5.1</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>10</td>
<td>(111)</td>
<td>29.75</td>
<td>1.99</td>
<td>3.9</td>
</tr>
<tr>
<td>5</td>
<td>Hydrothermal</td>
<td>2</td>
<td>(101)</td>
<td>30.25</td>
<td>1.27</td>
<td>6.0</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>4</td>
<td>(101)</td>
<td>30.21</td>
<td>1.29</td>
<td>5.9</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>6</td>
<td>(101)</td>
<td>30.15</td>
<td>1.31</td>
<td>5.8</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>8</td>
<td>(101)</td>
<td>30.13</td>
<td>1.35</td>
<td>5.7</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>10</td>
<td>(111)</td>
<td>30.09</td>
<td>1.41</td>
<td>5.4</td>
</tr>
<tr>
<td>10</td>
<td>Simple-precipitation</td>
<td>2</td>
<td>(101)</td>
<td>30.24</td>
<td>0.36</td>
<td>21.3</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>4</td>
<td>(101)</td>
<td>30.22</td>
<td>0.41</td>
<td>19.7</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>6</td>
<td>(101)</td>
<td>30.21</td>
<td>0.43</td>
<td>18.7</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>8</td>
<td>(101)</td>
<td>30.19</td>
<td>0.49</td>
<td>17.8</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>10</td>
<td>(101)</td>
<td>30.17</td>
<td>0.56</td>
<td>17.0</td>
</tr>
</tbody>
</table>

5.3.2 TEM and SAED

Figure 5.3(a), Figure 5.3(b) and Figure 5.3(c) show TEM images of samples synthesized by hydrothermal, simple-precipitation and polyol techniques. The images

Figure 5.3: TEM images of the ZrO₂:Eu³⁺ (2 mol%) nanocrystals synthesized by (a) hydrothermal, (b) polyol and (c) simple-precipitation techniques. Inset of each image shows their corresponding SAED rings.
show that the crystals are almost spherical in shape. Inset of each figure is their corresponding SAED rings. The rings show that the samples are crystalline. Other samples show similar trends in TEM images and SAED rings. Since the crystals sizes observed from TEM are not perfectly uniform and are limited in number, the crystals sizes calculated from the XRD data are noted for further study.

5.3.3 FT-IR

To supplement the crystalline phases observed from XRD data, FT-IR spectra of the samples are recorded. Figure 5.4 shows the FT-IR spectra of ZrO$_2$:Eu$^{3+}$ (2 mol%) synthesized by hydrothermal (H-2), polyol (P-2) and simple precipitation (S-2) techniques. Zirconia have low phonon energy [21]. Therefore, to observe its characteristic bands the spectra are shown within the fingerprint region, 300 to 800 cm$^{-1}$. The observed vibrational bands are at 354, 418, 448, 455, 502, 579 and 742 cm$^{-1}$. The bands at 354, 418, 502 and 742 cm$^{-1}$ correspond to monoclinic; 455 and 579 cm$^{-1}$ correspond to tetragonal and the broad band at 448 cm$^{-1}$ corresponds to cubic phase of ZrO$_2$ [17,22-27]. Similar characteristic vibrational bands of monoclinic, tetragonal or cubic phases are observed for other samples. Hence, the different phases of the samples, quantified by Search Match Analysis, are corroborated by FT-IR spectroscopy.

5.3.4 EDAX on SEM

Elemental compositions of the samples are recorded by EDAX on SEM. For a typical quantification of elements present in a sample, data from three different
regions of the sample are recorded. And average of which is taken as the elemental compositions of the sample. Figure 5.5 shows the EDAX spectrum of ZrO$_2$:Eu$^{3+}$ (2 mol%) nanocrystals synthesized by hydrothermal technique. The spectrum shows the presence of carbon (C), oxygen (O), zirconium (Zr) and europium (Eu) in the doped sample. Percentages of Zr and Eu present in the sample are observed to be 98 and 2 % respectively, within the error bar (0.05). This clearly indicates that the concentration of Eu introduced in the host zirconia is in agreement with the data from EDAX. Similar observations are found in other samples. It is to be noted that the presence of C, in the spectra, is due to carbon-coated tape used in recording the spectra.

![Figure 5.5: EDAX spectra of ZrO$_2$:Eu$^{3+}$ (2 mol%) nanocrystals synthesized by hydrothermal technique.](image)

### 5.3.5 Photoluminescence Emission

On monitoring the excitation wavelength at 394 nm corresponding to $^7$F$_0 \rightarrow ^5$L$_6$ transition of Eu$^{3+}$, emission spectra of the nanocrystals are recorded. Figure 5.6 shows magnetic ($^5$D$_0 \rightarrow ^7$F$_1$) and electric dipole ($^5$D$_0 \rightarrow ^7$F$_2$) transitions of Eu$^{3+}$ which result from the nanocrystals synthesized by the polyl technique. From the figure it is clearly observed that the intensity of the PL emission decrease on increasing the concentration of Eu$^{3+}$. This can be attributed to luminescence quenching [12,13]. At low concentration of Eu$^{3+}$ ions within the zirconia host, the ions are distributed randomly and the distances between Eu$^{3+}$ is large. Therefore, the probability of energy transfer between Eu$^{3+}$ ions is low. However, as the Eu$^{3+}$ concentration increases, the distance between the Eu$^{3+}$ ions are shortened and hence the probability of energy...
transfer between the Eu$^{3+}$ ions increase. Consequently, concentration quenching of luminescence occurs i.e., some amount of excitation energy is dissipated non-radiatively which result in decrease of luminescence intensity [12,13,28]. Besides the concentration quenching explained above; the decrease in emission intensity can also be explained due to decrease in crystal size or size quenching. It is clearly observed from Table 5.2 that the crystal sizes decrease on increasing the doping concentration. As a result, the surface areas of the nanocrystals increase on decreasing the crystal size. And therefore, increase in surface area of the nanocrystals can also lead to significant increase in non-radiative decay and hence decrease in the emission intensity [12,13,29]. Detailed analysis of radiative and non-radiative rate of transitions will be found subsequently.

Similarly, emission spectra of the nanocrystals synthesized by hydrothermal and simple-precipitation techniques are recorded on monitoring the excitation wavelength at 394 nm. Figure 5.7 shows emission intensity (at 591 nm) as a function of Eu$^{3+}$ concentration for the nanocrystals synthesized by the three techniques. The figure shows that emission intensities of the samples synthesized by polyol and hydrothermal techniques decrease on increasing Eu$^{3+}$ concentration. Interestingly, emission intensities of the nanocrystals synthesized by simple-precipitation technique increase on increasing the doping concentration. The observed trends in the emission intensities of the nanocrystals suggest that the intensity is governed not only by the quenching processes described above i.e., concentration and crystal size quenching. If
Chapter 5: Effects of Crystal Size, Structure and Quenching

Yield of ZrO$_2$:Eu$^{3+}$ Nanocrystals

Synthesis, Characterization and Photoluminescence of ZrO$_2$:Eu$^{3+}$ Nanocrystals
Ph.D. Thesis: Sanoujam Dhiren Meetei

the quenching processes solely governed the luminescence intensities, the emission intensities of the samples synthesized by simple-precipitation technique could have been decrease because of luminescence quenching due to concentration and crystal size. However, this is contrary to what is observed in Figure 5.7. Therefore, there must be a parameter which governs the emission intensity besides the concentration and size quenching processes. Fortunately, apart from decrease in crystal sizes, it was observed from analysis of the XRD data that crystal structures of the nanocrystals synthesized by simple-precipitation technique changes from low symmetric monoclinic to higher symmetric tetragonal structure on increasing the Eu$^{3+}$ concentration. Similar symmetry shift was also observed from the nanocrystals synthesized by hydrothermal technique. Consequently, the observed patterns in the emission intensities of the nanocrystals synthesized by simple-precipitation technique may be related to difference in crystal structures of the nanocrystals. Necessarily, to confirm and extend the results of XRD, symmetries of the nanocrystals are studied with the dopant Eu$^{3+}$ as a probe. The symmetries of the crystals are determined from the emission spectra by using the following equation:

$$A_s = \frac{E}{M} \quad (5.3)$$

where $A_s$ is a quantity called asymmetry ratio; $E$ and $M$ are areas under the electric and magnetic dipole transitions of Eu$^{3+}$ respectively [18]. A representative graph for determination of asymmetry ratio is shown in Figure 5.8.

![Figure 5.7: Maximum emission intensity (at 591 nm) as a function of Eu$^{3+}$ concentration for ZrO$_2$:Eu$^{3+}$ nanocrystals synthesized by the three techniques (P = Polyol, H = Hydrothermal and S = Simple-precipitation techniques)]
The values of $A_s$ are given in Table 5.3. It is clearly observed from the table that asymmetry decreases (symmetry increases) on increasing the doping concentration for all the synthesis techniques. Therefore, the increase in emission intensities, of the nanocrystals synthesized by simple-precipitation technique, is attributed to domination of effect due to higher symmetric crystal structure over the effects due to concentration and size quenching processes. Moreover, the increase in emission intensities at 10 mol% from 8 mol% (both tetragonal structures) could have been decrease if the concentration and crystal size quenching processes dominate over the crystal structure effects. This can be visualized from the observed trends of 

![Graph showing emission spectrum with areas under magnetic (M) and electric dipole (E) transitions of Eu$^{3+}$ for determination of asymmetric ratio from ZrO$_2$:Eu$^{3+}$ (2 mol %) nanocrystals synthesized by polyol technique.](image)

**Table 5.3:** Values of asymmetry ratio ($E/M$) for ZrO$_2$:Eu$^{3+}$ nanocrystals synthesized by the three techniques.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Synthesis Technique</th>
<th>ZrO$_2$:Eu$^{3+}$ (mol%)</th>
<th>Asymmetry Ratio ($E/M$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polyol</td>
<td>2</td>
<td>1.428</td>
</tr>
<tr>
<td>2</td>
<td>Polyol</td>
<td>5</td>
<td>1.372</td>
</tr>
<tr>
<td>3</td>
<td>Polyol</td>
<td>7</td>
<td>1.202</td>
</tr>
<tr>
<td>4</td>
<td>Polyol</td>
<td>10</td>
<td>1.130</td>
</tr>
<tr>
<td>5</td>
<td>Simple-precipitation</td>
<td>2</td>
<td>1.073</td>
</tr>
<tr>
<td>6</td>
<td>Simple-precipitation</td>
<td>4</td>
<td>1.048</td>
</tr>
<tr>
<td>7</td>
<td>Simple-precipitation</td>
<td>6</td>
<td>1.008</td>
</tr>
<tr>
<td>8</td>
<td>Simple-precipitation</td>
<td>8</td>
<td>0.832</td>
</tr>
<tr>
<td>9</td>
<td>Simple-precipitation</td>
<td>10</td>
<td>0.723</td>
</tr>
<tr>
<td>10</td>
<td>Hydrothermal</td>
<td>2</td>
<td>1.290</td>
</tr>
<tr>
<td>11</td>
<td>Hydrothermal</td>
<td>4</td>
<td>1.262</td>
</tr>
<tr>
<td>12</td>
<td>Hydrothermal</td>
<td>6</td>
<td>1.261</td>
</tr>
<tr>
<td>13</td>
<td>Hydrothermal</td>
<td>8</td>
<td>1.233</td>
</tr>
<tr>
<td>14</td>
<td>Hydrothermal</td>
<td>10</td>
<td>1.155</td>
</tr>
</tbody>
</table>
Chapter 5: Effects of Crystal Size, Structure and Quenching Yield of ZrO$_2$:Eu$^{3+}$ Nanocrystals

emission intensities of the samples (all cubic structures) synthesized by polyol technique. The samples synthesized by polyol technique are all cubic in phase and emission intensities decrease as the doping increases. Similar report on decrease in decay lifetime, as dopant concentration increases, of cubic structure is found [11]. Therefore, it can be inferred from the observed trends of emission intensities that luminescence quenching dominates over the effect of crystal structure at small crystal size (3.9 to 6.8 nm) while the effect of crystal structure dominate over the quenching at larger crystal size (17.0 to 21.3 nm). Consequently, it can be concluded that crystal size plays an important role on the PL emission intensity. Since PL emission, lifetime and quantum yield are the manifestation of a luminescent material, similar size effect is expected from lifetime and quantum yield of the nanocrystals. Thus, to substantiate the observed trends of the emission intensities; lifetime and quantum yields of the nanocrystals are also studied and reported subsequently.

![Decay curves resulting from $^5D_0$ of Eu$^{3+}$ from the ZrO$_2$:Eu$^{3+}$ (2 mol%) nanocrystals synthesized by polyol technique ($\lambda_{ex} = 394$ nm and $\lambda_{em} = 591$ nm).](image)

**Figure 5.9**: Decay curves resulting from $^5D_0$ of Eu$^{3+}$ from the ZrO$_2$:Eu$^{3+}$ (2 mol%) nanocrystals synthesized by polyol technique ($\lambda_{ex} = 394$ nm and $\lambda_{em} = 591$ nm).

### 5.3.6 Photoluminescence Lifetime

Lifetime of the ZrO$_2$:Eu$^{3+}$ nanocrystals are recorded on monitoring the excitation and emission wavelengths at 394 and 591 nm respectively. The 394 nm corresponds to $^7F_0 \rightarrow ^5L_6$ transition of Eu$^{3+}$ while, 591 nm corresponds to magnetic dipole transition, $^5D_0 \rightarrow ^7F_1$, of Eu$^{3+}$.

**Figure 5.9** shows the decay curve resulting from $^5D_0$ of Eu$^{3+}$ from the ZrO$_2$:Eu$^{3+}$ (2 mol %) nanocrystals synthesized by polyol technique. From the figure it
is clearly observed that bi-exponential decay fits more than mono-exponential decay.

The fitted bi-exponential equation is of the form:

$$ I = \{I_1 \exp(-t/\tau_1) / I_2 \exp(-t/\tau_2)\} + I_0 $$

(5.4)

where $I_1$ and $I_2$ are intensities at two different values of time ($t$) i.e., $\tau_1$ and $\tau_2$; and $I_0$ is the offset. The validity of bi-exponential decay suggests that the PL decay is associated with two different probabilities of decay. From the fitting, the values of $\tau_1$ and $\tau_2$ are found to be 0.66 and 2.67 ms corresponding to $I_1$ and $I_2$ values of 34 and 66% respectively. Slow component (2.67 ms) results from the Eu$^{3+}$ in the inner core of the crystals and the fast component (0.66 ms) results from the surface Eu$^{3+}$ [11]. Similar observations are also obtained for the nanocrystals synthesized by hydrothermal and simple-precipitation techniques.

![Figure 5.10](image.png)

Figure 5.10: Lifetimes as a function of Eu$^{3+}$ concentration for the nanocrystals synthesized by the three synthesis techniques (P = Polyol, H = Hydrothermal and S = Simple-precipitation techniques)

Average lifetime, $<t>$ of ZrO$_2$:Eu$^{3+}$ (2 mol %) nanocrystals synthesized by polyol technique is calculated by using the equation [3,18,30]:

$$ <t> = (I_1\tau_1^2 + I_2\tau_2^2) / (I_1\tau_1 + I_2\tau_2). $$

(5.5)

The calculated $<t>$ is found to be 2.44 ms. Similarly, the lifetimes of the other nanocrystals are also calculated. Figure 5.10 shows the lifetimes as a function of Eu$^{3+}$ concentration for the nanocrystals synthesized by the three synthesis techniques. As expected from the notion of emission intensities, the lifetimes of the nanocrystals synthesized by polyol technique decrease on increasing Eu$^{3+}$ concentration in the same trend as the emission intensities change. As explained in the decrease of emission intensities (above), the decrease in lifetime can be attributed to combined
effect of crystal structure, concentration and size quenching of the nanocrystals where the quenching processes dominate over the effect due to crystal structure.

The Figure 5.10 also shows that the lifetimes of the nanocrystals synthesized by hydrothermal technique decrease as the Eu$^{3+}$ concentration increases. However, the lifetimes of the nanocrystals synthesized by simple-precipitation technique increases on increasing the Eu$^{3+}$ concentration. The increase in lifetimes as similar to emission intensities can be attributed to increase in symmetries of the crystals [3,10,12]. The trends observed from the Figure 5.10 are similar to that is observed from Figure 5.7. Therefore, the observed trends of the decay lifetimes support the expectation that luminescence quenching dominates over effect of crystal structure at small crystal size while the effect of crystal structure dominates over quenching processes at larger crystal size.

5.3.7 Photoluminescence Quantum Yield

Luminescence quantum yield is perhaps the most important parameter of a luminescent material [30,31]. It is the percentage of photon emitted by a sample when a given number of photons are absorbed by the sample. It can be represented by the following equation:

$$\eta_1 = \frac{\varepsilon}{\alpha} = \frac{\int L_{\text{direct}}}{(\int E_{\text{without}} - \int E_{\text{direct}})}$$  \hspace{1cm} (5.6)

where $\eta_1$ is the quantum yield; $\varepsilon$ is the photon emitted by the sample; $\alpha$ is the photon absorbed by the sample; $L_{\text{direct}}$ is the luminescence emission spectrum of the sample, collected using the IS; $E_{\text{direct}}$ is the spectrum of the light used to excite the sample, collected using the IS and $E_{\text{without}}$ is the spectrum of the light used for excitation with only the reference in the sphere, collected using the IS [18]. However, for more accurate measurement of the quantum yield re-excitation of the sample by excitation light reflected within the IS is removed by an indirect method of measurement given below:

$$\eta_2 = \frac{(E_{\text{indirect}}L_{\text{direct}} - E_{\text{direct}} L_{\text{indirect}})}{(E_{\text{indirect}}E_{\text{without}} - E_{\text{direct}} E_{\text{without}})}$$  \hspace{1cm} (5.7)

where $E_{\text{indirect}}$ is the emission spectrum of the excitation light recorded with the sample in place but the mirror set to cuvette (for solid sample) and $L_{\text{indirect}}$ is the emission spectrum of the sample with the sample in place but the mirror set to cuvette (for a solid sample) [15]. Other parameters are same as detailed for equation (5.6).

A graph for calculation of quantum yield showing sample, reference and sample (indirect) emission spectra of ZrO$_2$: Eu$^{3+}$ (2 mol%) synthesized by polyol
Chapter 5: Effects of Crystal Size, Structure and Quenching... Yield of ZrO$_2$:Eu$^{3+}$ Nanocrystals

technique is shown in Figure 5.11. Then from these three emission spectra, quantum yields of the nanocrystals are calculated by using equation (5.7) with the help of the wizard “Quantum Yield Calculation”. The quantum yield values of the samples synthesized by three techniques are shown as a function of Eu$^{3+}$ concentration in Figure 5.12. The quantum yield up to 27.72% at 2 mol% of Eu$^{3+}$ can be obtained. To the best knowledge of the authors, no previous reports are found for quantum yield of 27.72% from ZrO$_2$: Eu$^{3+}$ nanocrystals of 7 nm. Furthermore, from Figure 5.7, Figure 5.10 and Figure 5.12, it is clearly observed that the trends of the quantum yields are similar to that of the emission intensities and lifetimes. That is, at small crystal sizes (3.9 to 6.8 nm) the emission intensities, lifetimes and quantum yields decreases while at larger crystal sizes (17.0 to 21.3 nm) the three quantities increase as the Eu$^{3+}$ concentration increases.

![Figure 5.11: Emission spectra for calculation of quantum yield from ZrO$_2$: Eu$^{3+}$ (2 mol%) synthesized by polyol technique.](image)

**5.3.8 Radiative and Non-radiative Transitions**

The luminescence intensity, lifetime and quantum yield depend on radiative ($\Gamma$) and non-radiative rate ($k_{nr}$) of transitions. To quantify the radiative and non-radiative rate of transitions on the observed nature of luminescence, $\Gamma$ and $k_{nr}$ are calculated by using the following two equations [30]:

---

*Synthesis, Characterization and Photoluminescence of ZrO$_2$:Eu$^{3+}$ Nanocrystals*

Ph.D. Thesis: Sanoujam Dhiren Meetei
<t> = 1 / (Γ + k_{nr}) \quad \text{and} \quad \eta = Γ / (Γ + k_{nr}). \quad (5.8, 5.9)

Here, all possible non-radiative decay processes are grouped to a single rate constant \( k_{nr} \). Calculated values of the radiative and non-radiative rate of transitions are tabulated in Table 5.4. The table clearly shows that non-radiative rate of transition increase for the nanocrystals synthesized by polyol and hydrothermal techniques while it decreases for the nanocrystals synthesized by simple-precipitation technique. The increase in the non-radiative rate of transition for the nanocrystals synthesized by polyol and hydrothermal techniques validate the decrease in emission intensity, lifetime and quantum yield of these nanocrystals. On the other hand, increase in radiative rate of transition obtained from larger nanocrystals synthesized by simple-precipitation technique validates the increase in emission intensity, lifetime and quantum yield of these nanocrystals. This table confirms that, on increasing the Eu\(^{3+}\) concentration, non-radiative rate increases at small crystal size and radiative rate increases at larger crystal size. Therefore, it can be established that luminescence quenching dominates over the effect of crystal structure at small crystal size while the effect of crystal structure dominate over luminescence quenching at larger crystal size. Hence, crystal size, structure and quenching are interrelated and their studies are of fundamental importance to doped nanocrystal.
5.4 Conclusions

The present works clearly revealed that crystal size plays an important role in luminescence quenching and crystal structure of ZrO$_2$: Eu$^{3+}$ nanocrystals. On increasing Eu$^{3+}$ concentration, photoluminescence emission intensity, lifetime and quantum yield of nanocrystals increase at large crystal size while decrease at smaller crystal sizes. It suggests that the effect of crystal structure dominate over quenching at large crystal size while quenching dominates over the effect of crystal structure at smaller crystal size. Hence, crystal size, structure and quenching are interrelated and their studies are fundamental to luminescence properties of doped nanocrystals. Further, quantum yield of 27.72% can be obtained from 7 nm ZrO$_2$: Eu$^{3+}$ (2 mol%) nanocrystals. Varied values of lifetime (0.48 to 2.62 ms) and quantum yield (3.45 to 27.72%) of the ZrO$_2$:Eu$^{3+}$ nanocrystals ensure fabrication of devices from this material for varied applications.
Chapter 5: Effects of Crystal Size, Structure and Quenching on the Yield of ZrO$_2$:Eu$^{3+}$ Nanocrystals

References


[3] Chapter 2

[4] Chapter 3


