CHAPTER 3
Polyol Synthesis and Characterization of Cubic ZrO$_2$:Eu$^{3+}$
Nanocrystals
3.1 Introduction

Recently nanomaterials and nanocrystals have attracted considerable scientific interest due to their improved properties resulting from grain size refinement in nanometer scale. Different novel properties of materials are revealed at nano regime; their properties can be tuned by their sizes, shapes, etc [1-5]. In these point of views, nanocrystalline zirconia (ZrO$_2$) and ZrO$_2$:Eu$^{3+}$ are synthesized and studied for various applications [6-11]. Zirconia is a technologically important material due to its high melting point, high thermal and mechanical resistance, high thermal expansion coefficient, low thermal conductivity, high thermochemical resistance, high corrosion resistance, high dielectric constant, photothermal stability, etc [8-11]. High chemical and photochemical stability with high refractive index and low phonon energy makes it an optimized luminescent host [8,10,11]. Therefore, it has extensive applications in photonics and other industries.

Zirconia have three crystalline phases, that is, monoclinic (below 1170°C), tetragonal (1170 to 2370 °C) and cubic (above 2370 °C) [8,9]. Among these, cubic phase is the most desirable phase for technical applications [12]. In order to manufacture zirconia components, it is necessary to lock the material wholly or partially into the cubic phase [13]. In fact, the crystal lattice tends to transform into a structure with higher symmetry as the crystal size decreases [14-19]. As a result, it is an important task to synthesize the crystal size as small as possible. The synthesis of small crystal size is achieved by polyol technique and it is reported in this work.

The tetragonal and cubic phases have similar x-ray diffraction (XRD) patterns and therefore assignment of the two phases solely from the XRD can be misleading [12,14-17]. The problem is more pronounced when the peaks are broadening due to small sizes of the crystals [17]. With these views, characterization of cubic phase, especially nanocrystalline, zirconia is a challenging task. Moreover, since the properties of zirconia depend on the crystal structures [6], proper identification of phases are needed for application in various fields and the problems which may arise due to miss identification. Therefore, transmission electron microscopy (TEM), selected area electron diffraction (SAED), Fourier transform infra-red (FT-IR) and photoluminescence (PL) studies are also reported to substantiate the results from the XRD study. In view of the fact that, electron diffraction is very sensitive to changes in the crystal structure that cannot be detectable through XRD; TEM and SAED studies.
are performed to distinguish the tetragonal and cubic zirconia [18]. FT-IR spectroscopy has been widely used in the characterization of different morphologies of ZrO₂ and related materials. It is reported that FT-IR spectra may be more sensitive than XRD in the characterization of the phases of ZrO₂ [20]. Therefore, the samples are further characterized by FT-IR. A considerable amount of works has been done on the PL characterization of monoclinic and tetragonal ZrO₂:Eu³⁺ [12,17,21]. However, PL characterization of cumbersome cubic zirconia is limited and need further studies. Here, the PL characterization of cubic zirconia is reported.

3.2 Experimental

3.2.1 Polyol Synthesis

Undoped ZrO₂ and Eu³⁺ (2, 5, 7 and 10 mol%) doped ZrO₂ nanocrystals are synthesized by polyol technique. Ethylene glycol (EG) and polyethylene glycol (PEG) are used as reaction medium and capping agent. For synthesis of ZrO₂:Eu³⁺ (2%), ZrOSO₄ (2 g) is introduced in deionized water (10 ml). Then it is allowed to dissolve by warming (50 °C). Then, Eu₂O₃ (70.68 mg) is introduced and make it dissolve in the solution. After that, the solution is treated with another solution of PEG (10 g), EG (50 ml) and urea (10 g). Subsequently, the solution is allowed to warm (50 °C). The whole solution is then heated at 120 °C, temperature at which precipitate formation took place (30 min). The precipitate is collected as gel by centrifugation (12000 rpm). The gel so obtained is annealed (4 hours) at constant temperature (500 °C) in ambient atmosphere. Similar procedures are performed for synthesis of other samples.

3.2.2 Characterization

XRD data are recorded in PANalytical diffractometer at 40 kV and 30 mA. The wavelength used is that of Cu Kα (1.54060 Å). TEM images and SAED rings are recorded using JEM-2000FX microscope (JEOL) at 160 kV. FT-IR spectra are recorded in MB 102 spectrometer (BOMEN). PL emission and excitation spectra are obtained from LS55 Luminescence Spectrometer (PerkinElmer). All the data are recorded at room temperature.

3.3 Results and Discussion

3.3.1 Powder XRD

Figure 3.1 shows the XRD patterns of undoped ZrO₂ and doped ZrO₂:Eu³⁺ (2, 5, 7 and 10%) nanocrystals. Due to nanocrystalline nature of the samples, the patterns
show a significant peak broadening. From X’pert HighScore’s Search Match Analysis, undoped ZrO$_2$, shows the presence of both tetragonal $P4_2/nmc$ (137) (ICDD Ref. Code: 01-079-1770) and $P2_1/c$ (14) monoclinic (ICDD Ref. Code: 01-083-0944) phases. The percentage of monoclinic to tetragonal phase quantified from the X’pert HighScore is 43/57. However, the patterns of Eu$^{3+}$ doped samples show $Fm3m$ (225) cubic phase (ICDD Ref. Code: 00-049-1642). It is reported that most of the XRD peaks of the tetragonal and cubic phase of zirconia are overlapped and it is very difficult to distinguish between the two from XRD patterns [12,14-17]. Meanwhile, reports have been found that the crystal lattice tends to transform into a structure with higher symmetry, cubic phase, as the crystal size decreases [15,19]. Therefore, to determine the crystal sizes, Scherrer formula: $t' = (0.9 \lambda)/(B \cos \theta)$ is employed; where $0.9$ is shape factor, $\lambda$ is the x-ray wavelength, $B$ is peak broadening at half the maximum intensity in radians, and $\theta$ is the Bragg angle. As expected, the crystal sizes are found to decrease with increase in Eu$^{3+}$ concentration, Table 3.1. This can also be visualized from the intensities of XRD patterns shown in Figure 3.2. That is, the intensity decreases indicating that the crystal size decreases. Therefore, the proposition that the crystal structures of doped samples are cubic but not tetragonal is likely. This will further be substantiated from TEM, FT-IR and PL studies.

Unit cell parameters of the samples are calculated from the XRD data. Unit cell volume and lattice parameter are found to increase with increase in Eu$^{3+}$. 

![Figure 3.1: XRD patterns of undoped ZrO$_2$ and doped ZrO$_2$:Eu$^{3+}$ (2, 5, 7 and 10 mol %) nanocrystals.](image-url)
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Table 3.1: Crystal sizes and unit cell parameters of the samples.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Sample (mol%)</th>
<th>Crystal Size (nm)</th>
<th>Unit Cell Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$a$ (Å)</td>
</tr>
<tr>
<td>1</td>
<td>ZrO$_2$</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>ZrO$_2$:Eu$^{3+}$ (2)</td>
<td>7</td>
<td>5.13</td>
</tr>
<tr>
<td>3</td>
<td>ZrO$_2$:Eu$^{3+}$ (5)</td>
<td>6</td>
<td>5.16</td>
</tr>
<tr>
<td>4</td>
<td>ZrO$_2$:Eu$^{3+}$ (7)</td>
<td>5</td>
<td>5.17</td>
</tr>
<tr>
<td>5</td>
<td>ZrO$_2$:Eu$^{3+}$ (10)</td>
<td>4</td>
<td>5.19</td>
</tr>
</tbody>
</table>

Moreover, with increase in doping concentration, the shift in diffraction peaks positions towards the lower diffraction angle is observed (Figure 3.2). These are attributed to the substitution of smaller Zr$^{4+}$ (ionic radius = 87 pm) by Eu$^{3+}$ (ionic radius = 98 pm) [14]. It establishes that Eu$^{3+}$ is properly doped in ZrO$_2$.

Figure 3.2: XRD patterns of the samples showing shift in peak intensity and peak position with increase in Eu$^{3+}$ concentration.

3.3.2 TEM and SAED

The TEM image of ZrO$_2$:Eu$^{3+}$ (2 mol%) and its corresponding SAED rings are shown in Figure 3.3(a) and Figure 3.3(b) respectively. It is observed from the TEM image that crystals are distributed uniformly. Crystallinity of the sample is confirmed from the SAED rings. From the diffraction rings of SAED, interplaner spacings, $d_{hkl}$ are calculated by using camera equation: $d_{hkl} = (L\lambda')/R$, where $L$ = camera length, 100 cm; $\lambda'$ = wavelength of electron, 0.0306 Å and $R$ = radius of diffraction rings. The calculated $d_{hkl}$ values of the four main diffraction rings are 2.96, 2.56, 1.81 and 1.54 Å.
Å. These \( d_{hkl} \) values agree well, respectively, with that of (111), (200), (220) and (311) corresponding to ICDD’s Ref. Code: 00-049-1642, which is cubic.

### 3.3.3 FT-IR

The FT-IR spectra of the samples are shown in Figure 3.4(a). All samples exhibit bands at 3420 and 1655 cm\(^{-1}\) assigned to the bending vibration and stretching vibration of the O-H bond in absorbed and coordinated water, showing that there is residual structural OH. Below 1000 cm\(^{-1}\), there is a sharp fall in transmittance spectra. To observe characteristic vibration bands due to ZrO\(_2\) and to identify either the phase is tetragonal or cubic or both; FT-IR spectra of ZrO\(_2\) and ZrO\(_2\):Eu\(^{3+}\) (2 mol\%) nanocrystals are shown within 300 to 900 cm\(^{-1}\), Figure 3.4(b). The spectrum of ZrO\(_2\), where both monoclinic and tetragonal phase co-exist, shows bands at 354, 455, 498, 575, and 741 cm\(^{-1}\). The bands at 354, 498 and 741 cm\(^{-1}\) correspond to the monoclinic phase and that at 455 and 575 cm\(^{-1}\) are related to tetragonal phase of zirconia [20-25]. However, the sample ZrO\(_2\):Eu\(^{3+}\) (2 mol\%), where existence of cubic phase or tetragonal phase is uncertain, shows no bands due to tetragonal phase. Rather a broad band at 449 cm\(^{-1}\) and a shoulder at 617 cm\(^{-1}\) are observed. This is consistent with the conclusion that for cubic zirconia only one fundamental mode is active in IR [23]. Similar observations are obtained from other doped samples. It confirms the proposition that the doped samples are cubic but not tetragonal.

Figure 3.3: (a) TEM image of ZrO\(_2\):Eu\(^{3+}\) (2 mol\%) nanocrystals and (b) its SAED rings showing (hkl).
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**3.3.4 Photoluminescence Excitation**

Figure 3.5 shows the excitation spectra of ZrO$_2$:Eu$^{3+}$ (2, 5, 7 and 10 mol%) nanocrystals. The spectra are recorded on monitoring emission wavelength at 613 nm. The peak within 231-307 nm is due to charge transfer state (CTS) of Eu$^{3+}$. It
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originates from interaction between Eu$^{3+}$ and O$^{2-}$ [12]. It is clearly observed from the figure that peak position and intensity changes with change in Eu$^{3+}$ concentration. The peak position and intensity of ZrO$_2$: Eu$^{1+}$ (2 mol%) and ZrO$_2$: Eu$^{3+}$ (5 mol%) are almost same. However, the peak position of ZrO$_2$: Eu$^{2+}$ (7 mol%) and ZrO$_2$: Eu$^{3+}$ (10 mol %) shift toward lower and higher wavelength, respectively. On the other hand, the peak intensity increases with increase in Eu$^{3+}$ concentration. These variations in CTS peak position and intensity are summarized in Table 3.2. It is reported that Eu-O bond distance is a factor that strongly determine the CTS position in the case of cubic phase [26]. Therefore, the variation in peak position and intensity can be attributed to variation in bond length of Eu-O [12,26]. With increase in bond length the peak shifts towards higher wavelength while the peak intensity decreases [12,26].

Table 3.2: Peak intensities and positions of CTS, electric (E) and magnetic (M) dipole transitions of Eu$^{3+}$ in the cubic ZrO$_2$:Eu$^{3+}$ nanocrystals.

<table>
<thead>
<tr>
<th>ZrO$_2$:Eu$^{3+}$ (mol%)</th>
<th>CTS</th>
<th>$^5$D$_0$→$^7$F$_2$ (E)</th>
<th>$^5$D$_0$→$^7$F$_1$ (M)</th>
<th>E/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.05</td>
<td>267</td>
<td>1.20</td>
<td>612</td>
</tr>
<tr>
<td>5</td>
<td>1.05</td>
<td>269</td>
<td>1.17</td>
<td>609</td>
</tr>
<tr>
<td>7</td>
<td>1.17</td>
<td>258</td>
<td>1.44</td>
<td>607</td>
</tr>
<tr>
<td>10</td>
<td>1.60</td>
<td>272</td>
<td>1.73</td>
<td>615</td>
</tr>
</tbody>
</table>

3.3.5 Photoluminescence Emission

The PL emission spectra of ZrO$_2$: Eu$^{3+}$ nanocrystals are shown in Figure 3.6. The spectra are recorded on monitoring excitation wavelength at 267 nm. It is observed from this figure that the samples show two peaks due to Eu$^{3+}$ between 580 and 640 nm. The first peak originated from magnetic dipole transition (M), $^5$D$_0$→$^7$F$_1$, while the other is originated from structurally sensitive electric dipole transition (E), $^5$D$_0$→$^7$F$_2$ of Eu$^{3+}$. The position of the first peak varies from 590 to 593 nm while that of the second peak varies from 607 to 615 nm. The variation of the peak position is more prominent for the later peak. It is to be noted that $^5$D$_0$→$^7$F$_2$ transition is highly sensitive to structural change and environment effects; and the difference of $^5$D$_0$→$^7$F$_2$ emission peaks in relative positions is due to the difference of the effects of the crystal field perturbation on the individual f-f transitions [12]. On the other hand, the emission peaks intensities are almost same for ZrO$_2$: Eu$^{3+}$ (2 mol%) and ZrO$_2$: Eu$^{3+}$ (5 mol%). However, higher Eu$^{3+}$ concentration doped samples show increase in peak...
intensity. The variations in the emission peak intensity and position is similar to that of CTS, discussed above. That is, the shift of CTS peak position towards higher wavelength corresponds to the shift of emission peaks toward the higher wavelength. And the increase in peak intensity of CTS corresponds to the increase in emission peak intensity. These correlations can be clearly observed from the Figure 3.5, Figure 3.6 and Table 3.2. Consequently, it is expected that the variation of Eu$^{3+}$ emission peak positions and intensity might also related with the Eu-O bond length as in the case of CTS peak. But no previous reports are found for the same.

Asymmetry ratio, intensity ratio of the structurally sensitive electric dipole transition, $^5D_0 \rightarrow ^7F_2$ and magnetic dipole transition, $^5D_0 \rightarrow ^7F_1$ ($E/M$) strongly depends on the local symmetry of the Eu$^{3+}$ [12,15]. And a higher symmetry of the crystal field around Eu$^{3+}$ will results in a lower $E/M$ value [12]. To understand the symmetry of the sample, $E/M$ is calculated and tabulated in Table 3.1. The highest value of $E/M$ obtained is 1.26. This value is less than that of reported tetragonal phase. The reported $E/M$ value is 1.46 for tetragonal [15]. Therefore, the symmetry of Eu$^{3+}$ site in the present analyzing sample is higher than tetragonal phase. The phase which has higher symmetry than tetragonal is cubic phase. Therefore, the notion of $E/M$ supports the doped samples to be cubic in phase.

Figure 3.6: PL emission spectra of Eu$^{3+}$ in ZrO$_2$:Eu$^{3+}$ nanocrystals.
3.4 Conclusions

By polyol technique, ZrO$_2$ and cubic ZrO$_2$:Eu$^{3+}$ nanocrystals are synthesized at significantly lower temperature than that of the temperature reported in literature. The sizes of the crystals are within the range 4-12 nm. Both monoclinic and tetragonal phases are present in undoped ZrO$_2$ nanocrystals. And only cubic phase is present in doped ZrO$_2$:Eu$^{3+}$ nanocrystals. The characterizations of cubic phase are done effectively by XRD, TEM, FT-IR and PL studies. They are consistent with each other. From the PL studies, Eu$^{3+}$ emission peak position and intensity variations are found to be consistent with that of the CTS. Hence, it is expected in cubic zirconia that the variation of Eu$^{3+}$ emission peak positions and intensity might also related with the Eu-O bond length. This nano-sized cubic phase ZrO$_2$:Eu$^{3+}$ may find important application in fabricating devices.
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References