Chapter 7

Synthesis, Characterization and Optical Properties of Europium, Dysprosium, Eribium-
Rare Earth Metal Oxide doped- Zirconia and Yttria Stabilized Zirconia
Synthesis, Characterization and Optical Properties of Europium, Dysprosium, Erbium Rare Earth Metal Oxide doped-Zirconia and Yttria Stabilized Zirconia

1. Introduction

Zirconia is a widely used multi-functional material. It is entirely a non-toxic material having superior properties such as optical transparency, chemical stability, high thermal expansion coefficient and low thermal conductivity [1]. Zirconia appears as an interesting material for optical applications. It is a good white pigment and a good opacifier due to its high refractive index (2.1-2.2) [2]. It has been used as a coating for titania white pigments to limit UV excitation of titania and thus limiting its photocatalytic activity in converting organic paint binders [3]. Zirconia has lower vibrational energy compared to silica matrix and thus results much higher efficiencies of luminescence in zirconia matrix, which makes its potential use as a host for telecommunication amplifier and cathode radiation tubes [4]. Zirconia is a direct band gap insulator with two direct band-to-band transitions at 5.2 and 5.79 eV (238 and 214 nm wavelength respectively) [5]. It is an active and typical photon absorber among wide band-gap metal oxides [6]. Due to its nature as an n-type semi-conductor, it has also been considered as a photocatalyst in photochemical heterogeneous reactions [7].

Zirconia exits in three polymorphs: monoclinic, tetragonal and cubic (as discussed in previous chapters). The crystalline phase significantly affects the optical properties of zirconia; monoclinic zirconia absorbs at lower energy in UV-vis region compared to cubic and tetragonal zirconia [3]. Furthermore, the method of synthesis of zirconia also influences its optical properties. For example, zirconia prepared by irradiation showed a sharp emission peak at 254 nm and a broad band emission at 608 nm under 412 nm
excitation [8], whereas zirconia prepared by a two-phase process showed a broad band emission at 365 nm under 250 nm UV excitation [9].

The structural modifications in zirconia to prepare stabilized zirconia also results into different optical properties. The type of dopant, its concentration and the specific synthetic procedure are the important factors that influence the optical properties. For example, cubic zirconia stabilized by Mg provides a blue green emission at ~510 nm for an excitation with 254 nm radiation [10]; whereas, a yellow-orange emission at ~590 nm is dominant in Ca stabilized zirconia having only minor contribution of the 510 nm emissions [11]. In recent years, research efforts have been focused on the fabrication of ceramic materials doped with rare earth (RE) oxides, due to the combination of optical properties of rare earth ions and the unique properties of ceramic materials [12]. Different rare-earth ions doped zirconia material may achieve different optical properties.

Considerable interest has emerged in studying the optical properties of doped semiconductor and has been explored as potential luminescent materials with application in optoelectronics [13]. These doped metal oxides may be used as nanoscopic optical storage elements or as probes in living systems [14]. The luminescent materials can be applied in electroluminescent flat panel display, color plasma panel display, fluorescent lamps, cathode ray tubes etc. [15-16]. The wide band gap oxide materials with short wavelength photoluminescence (PL) emission are used as compact disk (CD) read heads [17]. Since zirconia is a low energy matrix, which minimizes non-radiative quenching, optically active dopants have a higher probability for radiative transitions and thus are optical attractive material. The studies have been reported on various RE-doped zirconia
such as Zr-Eu [18], Zr-Tb [19], Zr-Sm [20], Zr-Er [21], Zr-Nd [22]; however, the optical properties of RE-doped stabilized zirconia are not well known.

In the present study, we have synthesized and characterized a series of pure and yittria stabilized zirconia (YSZ) doped with europium (Eu), dysprosium (Dy) and eribium (Er) rare earth metal oxides. The optical properties of undoped zirconia and YSZ have been studied by diffuse reflectance spectroscopy (DRS) and photoluminescence spectroscopy (PL) and compared with doped- ZrO₂ and doped-YSZ. The structural modifications in terms of crystalline phases and band gap energy have been calculated.

2. Experimental

2.1 Materials

Zirconium oxychloride (ZrOCl₂·8H₂O) was obtained from s.d.fine-chem. Ltd., India; yttrium nitrate hexahydrate, Europium acetate hydrate, dysprosium acetate hydrate and erbium nitrate pentahydrate (99.9% purity) were procured from Sigma-Aldrich, Germany and aqueous ammonia solution (25%) was purchased from Rankem, India. All the chemicals were used as such.

2.2 Synthesis of Eu-, Dy- and Er- Rare earth metal oxide doped-Zirconia and YSZ

Pure ZrO₂, Eu-, Dy- and Er- doped ZrO₂, YSZ and doped-YSZ samples have been prepared by precipitation method. Typically, 1 mol% of dopants precursors (Eu(CH₃COO)₃·H₂O = 0.1645g; Dy(CH₃COO)₃·H₂O = 0.1698g; Er(NO₃)₃·5H₂O = 0.2216g) were added to 0.5 M of ZrOCl₂·8H₂O (15.95g) in distilled water (100 ml). Similarly, 1 mol% of dopants were added to 8 mol% Yittria-ZrO₂ solution having Y(NO₃)₃·6H₂O (3.064g) and ZrOCl₂·8H₂O (13.53g) in distilled water (100 ml). The solution was hydrolyzed by drop-wise addition of aqueous ammonia under constant
stirring by magnetic stirrer until the pH became 10.5. After hydrolysis, the white precipitate was continuously stirred for 2 hour at ambient temperature. The precipitate were filtered and washed thoroughly (till the removal of acetate, chlorine and nitrate ions). The precipitates were dried in an oven at 110°C for 12h followed by calcination at 500°C for 4h.

2.3 Characterization

2.3.1) Structural Characterization

2.3.1.1) Powder X-ray Diffraction (PXRD)

The crystallinity and crystalline phase of zirconia in pure and doped samples after calcination at 500°C were determined with X-ray powder diffractometer (Philips X’pert, MPD system, Netherlands) using CuKα radiation (λ=1.5405 Å). The samples were scanned in a 2θ range of 0-80° at a scanning rate of 0.4°/s. The crystalline phases of zirconia were identified by PXRD database [23]. The percent composition of each phase was calculated from the intensity of the characteristic peak of each phase divided by total peak intensities [24]:

\[
\% \text{ monoclinic} = \left( \frac{\text{Intensity) monoclinic}}{\Sigma (\text{Intensity) monoclinic and tetragonal}} \right) \times 100
\]

\[
\% \text{ tetragonal} = \left( \frac{\text{Intensity) tetragonal}}{\Sigma (\text{Intensity) tetragonal and monoclinic}} \right) \times 100
\]

\[
\% \text{ cubic} = \left( \frac{\text{Intensity) cubic}}{\Sigma (\text{Intensity) cubic and monoclinic}} \right) \times 100
\]

Where, (Intensity) monoclinic = \( I_m(111) = 31.6°2θ \) and \( I_m (1'11) = 28.4°2θ; \) (Intensity) tetragonal = \( I_t (111) = 30.28°2θ \) and (Intensity) cubic = \( I_c (111) = 30.08 \°2θ \).
2.3.1.2) FT-IR Spectroscopy

FT-IR spectra of pure and doped samples, after calcination at 500°C, were recorded using a spectrophotometer (Perkin-Elmer Spectrum GX, USA) in the region of 400-4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) as KBr pellets having ~1 wt % of sample.

2.3.1.3) Thermal Analysis

Thermo gravimetric/differential thermal analysis (TG/DTG) of all prepared pure and doped samples, before calcination, was carried out by Mettler Toledo (TGA/SDTA 861e, Switzerland) using stare software. The samples were heated in a temperature range of 50-850 °C at the heating rate of 10 °C min\(^{-1}\) under a N\(_2\) atmosphere.

2.3.2) Textural Characterization

Specific surface area, pore volume, and pore size distributions of prepared pure and doped samples, after calcination at 500°C were determined from nitrogen adsorption-desorption isotherms at 77 K (ASAP 2010, Micromeritics, USA). Surface area and pore volume were calculated using BET equation and BJH method, respectively. The samples were degassed under vacuum (5x10\(^{-3}\) mmHg) at 120 °C for 4 h, prior to measurement, to evacuate the physisorbed moisture.

2.3.3) Morphological Characterization

The electron microscopic study was done with a scanning electron microscope (Leo seriesVP1430, Germany) equipped with Oxford Instruments EDX facility, having a silicon detector under a pressure of >1.34x10\(^{-2}\) Pa. The samples were coated with gold using a Polaron Sputter Coater.
2.3.4) Optical Characterization

2.3.4.1) Diffuse reflectance spectroscopy (DRS)

Diffuse reflectance spectroscopy (DRS) studies of as such and calcined samples were performed with a Shimadzu UV-Vis spectrophotometer (UV-2550) equipped with an integrating sphere. BaSO$_4$ was used as the reference material. The spectra were recorded at room temperature in the wavelength range of 200–800 nm with slit width 5 nm and slow scan speed. The spectra were recorded in % reflectance mode and were plotted in Kubelka-Munk function vs. wavelength.

$$F_{KM}(R) = \frac{(1-R)^2}{2R} = \frac{K}{S} = c,$$

Where, $F_{KM}$ = Kubelka-Munk function of diffuse reflectance R, $K$= absorption coefficient, $S$ = scattering coefficient, $c$ = concentration of the absorbing species.

The band-gap energies of pure and doped samples were calculated using following equation:

$$E_g (eV) = \frac{hc}{\lambda} = \frac{1240}{\lambda}$$

Where $E_g$ is the band-gap energy (eV), $h$ = Planck’s constant (6.626 x 10$^{-34}$ Joules sec), $c$ = speed of light (3.0 x 10$^8$ meter/sec), and $\lambda$ = wavelength (nm observed).

2.3.4.2) Photoluminescence study

Photoluminescence emission spectra were recorded at room temperature with a Horiba Jobinyvon Spectrophotometer (Fluorolog) equipped with a 400 W xenon lamp as the excitation source. The emission spectra of calcined samples were recorded in UV-Vis region (up to 800 nm) at different excitation wavelength according to diffuse reflectance peaks.
3. Results and Discussions

3.1) Structural Properties

3.1.1) Powder X-ray Diffraction (PXRD)

PXRD patterns of pure and doped ZrO\(_2\) were observed to be amorphous in nature before calcination (Fig 1a). However, after calcination at 500°C, pure ZrO\(_2\) and Eu, Dy, Er-doped ZrO\(_2\) showed the presence of tetragonal and monoclinic phase of zirconia (Fig 1b). Pure ZrO\(_2\) showed predominantly monoclinic phase (80\%) along with tetragonal phase (20\%) of ZrO\(_2\) (Table 1). Eu, Dy, Er-doped ZrO\(_2\) showed decrease in monoclinic phase with an increase in tetragonal phase of ZrO\(_2\) from 20\% to 30-41\% (Table 1).

![PXRD patterns of pure ZrO\(_2\), YSZ and Eu, Dy, Er-doped ZrO\(_2\) and YSZ before calcination.](image)

![PXRD patterns of pure ZrO\(_2\) and Eu, Dy, Er-doped ZrO\(_2\) after calcination of 500°C.](image)

**Fig 1.** PXRD patterns of (a) pure ZrO\(_2\), YSZ and Eu, Dy, Er-doped ZrO\(_2\) and YSZ before calcination (b) pure ZrO\(_2\) and Eu, Dy, Er-doped ZrO\(_2\) after calcination of 500°C
Table 1. Crystalline phases\(^a\) (% of pure and doped-ZrO\(_2\), YSZ and doped-YSZ after calcination at 500°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystalline phase (%)</th>
<th>Sample</th>
<th>Crystalline phase (%)</th>
</tr>
</thead>
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<tr>
<td>Z</td>
<td>20 (T) +80 (M)</td>
<td>YSZ</td>
<td>100 (C)</td>
</tr>
<tr>
<td>Eu-Z</td>
<td>41 (T) +59 (M)</td>
<td>Eu-YSZ</td>
<td>100 (C)</td>
</tr>
<tr>
<td>Dy-Z</td>
<td>30 (T) + 70 (M)</td>
<td>Dy-YSZ</td>
<td>100 (C)</td>
</tr>
<tr>
<td>Er-Z</td>
<td>37(T) +64 (M)</td>
<td>Er-YSZ</td>
<td>100 (C)</td>
</tr>
</tbody>
</table>

\(^a\) C=Cubic, T=Tetragonal, M=Monoclinic

YSZ samples resulted into pure cubic zirconia and further doping with Eu, Dy, Er rare earth metal oxides also showed the presence of pure cubic phase of zirconia (Fig 2). These all phases were confirmed by PXRD database [23].

Fig 2. PXRD patterns of YSZ and Eu, Dy, Er-doped YSZ after calcination of 500°C
3.1.2 FT-IR Spectroscopic Studies

The FT-IR spectra of ZrO$_2$ and Eu, Dy, Er-doped ZrO$_2$ (Fig 3a) showed peaks in the region of 400-900 cm$^{-1}$ due to stretching frequency of Zr–O–Zr, Zr–O–RE vibrations. Pure and Eu, Dy, Er-doped ZrO$_2$ showed peaks at 738 and 418-498 cm$^{-1}$ corresponding to monoclinic and tetragonal ZrO$_2$ respectively. Doped YSZ samples (Fig 3b) showed only one prominent peak at around 414-450 cm$^{-1}$ corresponding to cubic ZrO$_2$ indicating the formation of single cubic phase in the system. The samples also exhibited peaks at 3400 cm$^{-1}$ (not shown in the figure) and 1624 cm$^{-1}$ attributed to the presence of stretching and bending vibration of absorbed water molecules in the samples, respectively. In addition, a weak, broad peak at 1339-1382 cm$^{-1}$ is ascribed to the presence of carbon impurities, which may be present in small amount due to the calcination in static air at 500°C.

**Fig 3.** FT-IR spectra of (a) ZrO$_2$ and Eu, Dy, Er-doped ZrO$_2$ (b) YSZ and Eu, Dy, Er-doped Y-ZrO$_2$ after calcination of 500°C
3.1.3) Thermo gravimetric analysis

The thermal analysis of pure ZrO$_2$ showed 13.7 wt% loss; YSZ, doped- ZrO$_2$ and doped-YSZ samples showed weight loss in the range of 15-23 wt%. Differential thermal analysis (DTA) of all samples showed one peak at ~100°C, which is attributed to the removal of physisorbed water in the samples; the peak at ~200°C and >200°C are due to dehydroxylation and crystallization of ZrO$_2$ and doped ZrO$_2$, respectively.

![Fig 4 a. TG and DTG profile of pure and doped-ZrO$_2$](image)
Fig 4 b. TG and DTG profile of pure and doped-YSZ

3.2) Textural Properties

N₂ isotherms of pure ZrO₂ and Eu-, Dy- and Er-doped ZrO₂ after calcination at 500 °C (Fig 5a) showed type IV isotherm, typical of mesoporous material having H₂ hysteresis [25]. A broad pore size distribution was observed in all the samples (Fig 5b).
YSZ and doped-YSZ samples also showed type IV isotherm having H2 hysteresis (Fig 6a), however with narrow pore size distribution (Fig 6b).

**Figure 5.** (a) N$_2$ adsorption-desorption isotherm and (b) pore size distribution of pure and Eu-, Dy- and Er-doped ZrO$_2$ samples after calcination at 500 °C

**Figure 6.** (a) N$_2$ adsorption-desorption isotherm and (b) pore size distribution of pure and Dy- and Er-doped YSZ samples after calcination at 500 °C
3.3) Microscopic study

The surface morphology of Eu, Dy, E-doped ZrO$_2$ and Eu, Dy, Er-doped YSZ showed agglomerated mass of different shapes like spherical, disordered shape (Figure 7).

Figure 7: SEM images of doped-ZrO$_2$ and doped-YSZ
3.4 Optical properties

3.4.1) Diffuse reflectance study (DRS)

3.4.1.1) Pure ZrO$_2$ and doped-ZrO$_2$

DRS is an useful tool to identify the zirconia phases in the UV-Vis range. Fig.8 shows the DRS spectra of pure ZrO$_2$ before and after calcination at 500 °C in UV-Vis range of 400-800 nm. The figure displayed the absorption bands at higher energies in the UV region, which are attributed to charge transfer (CT) transition from the valence band to conduction band of zirconia. As the configuration of Zr$^{4+}$ ions is d$^0$ ([Kr]$^{36}$4d$^0$5s$^0$), absorption characteristics of d-d transitions in the visible region (>400 nm) were not observed. The charge transfer transitions correspond to the excitation of electrons from the valence band of O (mainly having 2p character) to the conduction band of Zr (mainly having 4d character) [3, 26].

**Table 2.** Electronic configuration of host and dopant elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic number</th>
<th>Electronic configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconium</td>
<td>40</td>
<td>1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$3d$^{10}$4s$^2$4p$^6$4d$^2$5s$^2$ (or) [Kr]$^{36}$5s$^2$4d$^2$</td>
</tr>
<tr>
<td>Yttrium</td>
<td>39</td>
<td>1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$3d$^{10}$4s$^2$4p$^6$4d$^1$5s$^2$ (or) [Kr]$^{36}$5s$^2$4d$^1$</td>
</tr>
<tr>
<td>Europium</td>
<td>63</td>
<td>1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$3d$^{10}$4s$^2$4p$^6$4d$^{10}$5s$^2$5p$^6$4f$^6$6s$^2$ (or) [Xe]$^{54}$4f$^6$6s$^2$</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>66</td>
<td>1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$3d$^{10}$4s$^2$4p$^6$4d$^{10}$5s$^2$5p$^6$4f$^{10}$6s$^2$ (or) [Xe]$^{54}$4f$^{10}$6s$^2$</td>
</tr>
<tr>
<td>Erbium</td>
<td>68</td>
<td>1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$3d$^{10}$4s$^2$4p$^6$4d$^{10}$5s$^2$5p$^6$4f$^{12}$6s$^2$ (or) [Xe]$^{54}$4f$^{12}$6s$^2$</td>
</tr>
</tbody>
</table>

The DRS spectra (Fig 8) of amorphous zirconia (before calcination) showed a band edge at 207 nm (5.99 eV band gap or photon energy) which after calcination at 500 °C showed a well defined absorption band at 232 nm (5.34 eV), however with much
lower absorption intensity. The band gap energy of amorphous zirconia (5.99 eV) was significantly decreased in crystalline zirconia (5.34 eV) having predominantly monoclinic (80%) crystalline phase, which indicated the change in the electronic properties in well defined crystalline nature as compared to amorphous nature of zirconia. The band gap of zirconia also varies with its crystalline phase. To confirm this, we have also done DRS of pure tetragonal (100%) (after calcination at 350°C), which showed a band at 209 nm (5.93 eV) (Fig 8, Table 3). The results were in agreement with the reported absorption for zirconia [3, 26]. This variation in absorption is attributed to eight-coordinate tetravalent Zr species in tetragonal phase absorbing at higher energy and seven-coordinate Zr species in monoclinic phase, which absorbs at lower energy due to decrease in electrostatic repulsion between O\(^2\) anions and d orbitals of Zr\(^{4+}\) when one oxygen atom is removed from the surrounding environment [3].

![Fig 8. DRS spectra of pure ZrO\(_2\) before (Z-a) and after calcination at 350 (Z-350) and 500°C (Z-500)](image-url)
The Eu, Dy and Er-doped zirconia samples showed the absorption bands in the region of 220 to 234 nm, showing the presence of both tetragonal and monoclinic zirconia (Fig 9). The small absorption bands extended in the range of 250-330 nm were observed due to surface defects centers produced by these dopants as substitution of tetravalent Zr$^{4+}$ ion by trivalent Eu$^{3+}$, Dy$^{3+}$ and Er$^{3+}$ ions creates anion vacancy require for charge neutrality [27-28]. The intensity of absorption was similar in the case of uncalkined and calcined Eu-doped and Dy-doped ZrO$_2$ samples, whereas, calcined Er-Z-500 showed much higher absorption intensity compared to uncalkined Er-Z. These results of DRS indicated that Er$^{3+}$ ions has been doped in zirconia lattice by substituting Zr$^{4+}$ ions due to its size (Er$^{3+}$ = 0.88 Å) in the similar range of Zr$^{4+}$ (Zr$^{4+}$ = 0.84 Å). This is also confirmed by the absorption bands in the range of 319 to 653 nm, which are attributed to Er$^{3+}$ transitions [29]; whereas Eu$^{3+}$ and Dy$^{3+}$ ions have been doped only in the interfacial spaces of zirconia lattice due to their larger size (Eu$^{3+}$ = 0.95 Å, Dy$^{3+}$ = 0.91 Å).

Furthermore, higher heat treatment (>500-1000°C) is reported [18] to promote the dopant ions to substitute Zr$^{4+}$ ion in the lattice and substitution increases at higher temperature, however, in the present study we focused on effect of various dopants at similar (500°C) calcination temperature. Among all three RE-metal oxides, Er-Z-500 sample showed highest absorption intensity at 229 nm (5.41 eV).

Furthermore, as doping with Eu, Dy and Er rare earth metal oxides resulted into the increase in tetragonal crystalline phase of zirconia, the band gap of Eu, Dy and Er-doped ZrO$_2$ increased from 5.34 eV to 5.61-5.71 eV due to increase in tetragonal composition from 20% to 30-41% as compared to pure ZrO$_2$ (Table 3). The variation in band gap was observed as the samples have varied composition of tetragonal and
monoclinic crystalline phase and two absorption bands/shoulder were observed in crystalline samples corresponding to both tetragonal and monoclinic phase.

**Fig 9.** DRS spectra of Eu, Dy, Er-doped ZrO$_2$ before (Z-a) and after calcination at 500°C (Z-500)
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These results showed that tetragonal ZrO$_2$ (30-40\%) absorbs at lower wavelength (217-221 nm) and therefore higher photon energy (5.61-5.71 eV) as compared to monoclinic ZrO$_2$ (80\%), which absorbs at higher wavelength (232 nm) and thus lower photon energy (5.34 eV). These results are in agreement to the reported ones [3], where pure tetragonal and monoclinic ZrO$_2$ are reported to absorb in the range of 200-210 nm and 240 nm (~5.9 and ~5.2 eV photon energy, respectively).

**Table 3:** Absorption band (nm), band gap (eV) and crystalline phase (%) of pure ZrO$_2$ and doped- ZrO$_2$ before and after calcination at 500°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption band (nm)</th>
<th>Band gap (eV)</th>
<th>Crystalline phase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-a</td>
<td>207</td>
<td>5.99</td>
<td>amorphous</td>
</tr>
<tr>
<td>Z-350</td>
<td>209</td>
<td>5.93</td>
<td>100 (T)</td>
</tr>
<tr>
<td>Z-500</td>
<td>232</td>
<td>5.34</td>
<td>20 (T) +80 (M)</td>
</tr>
<tr>
<td>Eu-Z-a</td>
<td>225</td>
<td>5.51</td>
<td>amorphous</td>
</tr>
<tr>
<td>Eu-Z-500</td>
<td>217, 233</td>
<td>5.71, 5.32</td>
<td>41 (T) +59 (M)</td>
</tr>
<tr>
<td>Dy-a</td>
<td>221</td>
<td>5.61</td>
<td>amorphous</td>
</tr>
<tr>
<td>Dy-Z-500</td>
<td>221, 234</td>
<td>5.61, 5.29</td>
<td>30 (T) + 70 (M)</td>
</tr>
<tr>
<td>Er-Z-a</td>
<td>229</td>
<td>5.41</td>
<td>amorphous</td>
</tr>
<tr>
<td>Er-Z-500</td>
<td>220, 233</td>
<td>5.63, 5.32</td>
<td>37(T) +64 (M)</td>
</tr>
</tbody>
</table>

a = before calcination, T=Tetragonal, M= Monoclinic

**3.4.1.2) YSZ and doped-YSZ**

Before calcination, YSZ showed absorption band at 229 nm (5.41eV), which shifted to 234 nm (5.3 eV) after calcination at 500°C (Fig 10). The small bands extended
in the range of 250-300 nm were observed attributing to the surface defects and oxygen vacancies. The calculated band gap (5.3 eV) was found in agreement with the reported (5.0-5.5 eV) [30].

![Fig 10. DRS spectra of YSZ before and after calcination at 500°C](image)

The doped-YSZ samples showed one additional absorption band in the range of 219-227 nm due to charge transfer band of dopants (Fig 11). The intensity of calcined doped-YSZ samples showed higher absorption intensity compared to uncalcined doped-YSZ samples, which indicated the substitution of these dopants in YSZ lattice. The smaller size of dopants (Eu³⁺ = 0.95 Å, Dy³⁺ = 0.91 Å, Er³⁺ = 0.88 Å) may resulted into easy substitution in YSZ due to the larger size of size of Y³⁺ (1.09 Å). Er-doped YSZ showed absorption bands in the range of 400-654 nm due to Er³⁺ transitions (Fig 11) as was also observed in Er-doped ZrO₂ (Fig 9). Pure YSZ having pure cubic phase has the band gap of 5.3 eV, whereas doped-YSZ samples showed the band gap of 5.14-5.21 ev (236-241 nm) and 5.46-5.66 eV (219-227 nm) (Table 4).
Fig 11. DRS spectra of Eu, Dy, Er-doped YSZ before and after calcination at 500°C
**Table 4.** Absorption band (nm), band gap (eV) and crystalline phase (%) of pure YSZ and doped- YSZ before and after calcination at 500°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption band (nm)</th>
<th>Band gap (eV)</th>
<th>Crystalline phase (%)</th>
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</thead>
<tbody>
<tr>
<td>YSZ-a</td>
<td>229</td>
<td>5.41</td>
<td>-</td>
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<tr>
<td>YSZ-500</td>
<td>234</td>
<td>5.30</td>
<td>C</td>
</tr>
<tr>
<td>Eu-YSZ-a</td>
<td>226, 239</td>
<td>5.48, 5.19</td>
<td>-</td>
</tr>
<tr>
<td>Eu-YSZ-500</td>
<td>227, 239</td>
<td>5.46, 5.19</td>
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<td>Er-YSZ-a</td>
<td>225, 238</td>
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<tr>
<td>Er-YSZ-500</td>
<td>224, 238</td>
<td>5.53, 5.21</td>
<td>C</td>
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3.4.2) Photoluminescence (PL) study

3.4.2.1) Pure ZrO₂

The pure and doped crystalline samples have been studied for photoluminescence study by exciting the sample at varied wave lengths as per the absorption band observed in DRS. The pure zirconia sample was excited at three different wavelengths in the UV range of 230-380 nm. The PL spectra (Fig 12) of pure zirconia excited at 232 nm wavelength (5.34 eV, band gap energy of the sample) showed a broad band ranging from 330 to 420 nm and centered at 370 and 406 nm. The sample excited at higher wavelength of 280 nm (4.41 eV) also showed a broad emission band in the same region, however centered at 350 nm which tailed and centered at 382 nm. The sample excited at higher
wavelength of 380 nm (3.26 eV) showed one broad emission band centered at 422 nm (2.9eV) along with two small bands at 657 (1.89eV) and 683 nm (1.81 eV).

Fig 12. PL spectra of pure ZrO$_2$ calcined at 500 °C at different excitation wavelengths.

As Zr$^{4+}$ is non-luminous, so the observed luminescence from pure zirconia, having no extrinsic activators, should be related to lattice or surface defects or impurities in the material, which acts as intrinsic activators and contribute to emission of UV radiation [26,31]. The principle intrinsic defects in powdered zirconia are oxygen vacancies, V$_o$, the formation of which can be described as below [26]:
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\[ \text{ZrO}_2 \rightarrow \text{ZrO}_{2-n} + n/2 \text{O}_2 \]  \hspace{1cm} (1)

\[ \text{O}_o \rightarrow 1/2 \text{O}_2 + \text{V}_o \]  \hspace{1cm} (2)

\[ \text{V}_o \rightarrow \text{V}_o^\prime + e^- \]  \hspace{1cm} (3)

\[ \text{V}_o \rightarrow \text{V}_o^\prime\prime + 2e^- \]  \hspace{1cm} (4)

Where \( \text{O}_o \) is an oxygen atom in regular lattice site, \( e^- \) is an electron in conduction band, \( \text{V}_o \) represents a neutral oxygen vacancy, \( \text{V}_o^\prime \) is singly and \( \text{V}_o^\prime\prime \) is doubly ionized oxygen vacancy. The UV transitions in pure \( \text{ZrO}_2 \) are attributed to singly and/or doubly ionized oxygen vacancy and the emissions results from radiative recombination of a photo-generated hole with an electron occupying the oxygen vacancy [26]. Also, the observed PL emission peak of \( \text{ZrO}_2 \) at 350-382 nm by excitation at 232 (5.34 eV) is in good agreement with that of \( \text{ZrO}_2 \) nanoparticles [32] at 387 nm and \( \text{ZrO}_2 \) nanowires [26] at 388 nm by excitation in the range of 230-240 nm.

The emission band observed at 422 nm under excitation at 380 nm was reported due to presence of carbon impurities in the sample [31,33] (as also shown in FT-IR spectra) and the small bands at 657 and 683 nm due to presence of oxygen vacancies [33-34]. The results indicated that the luminescence properties are significantly influenced by the structural properties of the material and thus luminescence studies can provide useful information about the electronic excitation and defects in pure and doped zirconia [33].

3.4.2.2) YSZ

The YSZ sample was also excited at three different wavelengths in the UV range of 236-317 nm. The PL spectra (Fig 13) of YSZ sample excited at 236 nm wavelength (5.25 eV) showed two emission bands centered at 348 and 419 nm. The YSZ sample excited at 256 nm wavelength (4.84 eV) showed three emission bands centered at 343,
373 and 451 nm and YSZ sample excited at 317 nm wavelength (3.9 eV) showed one intense emission band centered at 551 nm. The PL emission bands appear at shorter wavelength excitation are ascribed to near band-edge transitions and the bands appear at higher wavelength excitation are due to surface defects and oxygen vacancies [26]. Nakajima and Mori [35] also found PL bands at 450 and 570 nm under 240 and 280 nm excitation, wherein previous band was attributed to bulk defect states of oxygen vacancies and the later to defect states of oxygen vacancies that exist at the grain boundaries, at the surface or at both, in YSZ samples.

**Fig 13.** PL spectra of YSZ-500 at different excitation wavelengths.
Thus, in pure ZrO$_2$ and YSZ, the presence of surface and inner oxygen vacancies are mainly responsible for the formation of new energy levels and thus resulting into PL spectra. The formation of oxygen vacancies may be resulted from intrinsic oxygen (equation 1) as well as from dopants causing non-stoichiometric oxygen vacancies (equation 2):

$$O_o = 1/2O_2 + 2e^- + V_o^{\ldots} \quad \text{-------- (1)}$$

$$\text{Zr}^{4+} \rightarrow \text{Y}^{3+}_{\text{Zr}} + 1/2V_o^{\ldots} \quad \text{-------- (2)}$$

Where $O_o$ is an oxygen atom in regular site, $e^-$ is an electron in conduction band, $V_o^{\ldots}$ is doubly positive ionized oxygen vacancy, $Y_{\text{Zr}}^{\ldots}$ is singly negative ionized substitution site when a Zr (IV) is substituted by Y(III) [36].

3.4.2.3) **Doped- ZrO$_2$ and doped-YSZ**

The PL spectra of Eu-YSZ under excitation at 279 nm showed luminescence bands in two areas (Fig14). The bands from 400-500 nm are associated with YSZ host emission and 570-650 nm are due to the f-f transitions within 4t$^6$ of Eu$^{3+}$ ions [18,37]. The PL band at 577, 591, 606 and 628 nm were attributed to $^5D_0^{-7}F_j$, where $j = 0, 1, 2,$ and 3 respectively [38]. The transition $^5D_0^{-7}F_2$ at 606 nm was found to be almost similar to the transition $^5D_0^{-7}F_1$ at 591 nm. The ratio of intensity of 606 to 591 nm can be considered as an indicative of the asymmetry of the coordination of Eu$^{3+}$ ions [39]. The relative intensity depends strongly on the local symmetry of Eu$^{3+}$ ions and lower symmetry around Eu$^{3+}$ ions results into a higher ratio of both transitions [40]. The almost similar intensity of both transitions in the present study, suggested that the environment around Eu$^{3+}$ in cubic-YSZ is symmetrical [39]. The emissions of Eu$^{3+}$ were observed to be relatively weak as compared to YSZ host emissions due to the heating of material at
500°C. Heat treatment at higher temperature ( >500 -1000°C) promotes Eu$^{3+}$ ions to substitute Zr$^{4+}$ sites easily resulting into stronger emission lines for energy transfer from host to Eu$^{3+}$ [18,37]. Quan et al. [37] observed the characteristic emission lines for Eu$^{3+}$ after heating the material at higher temperature ( >500-900°C).

Fig 14. PL spectra of Eu-YSZ-500 under excitation at 279 nm wavelength

Fig 15. PL spectra of Eu-Z-500 under excitation at 279 and 236 nm wavelengths
PL spectra of Eu-Z-500 under excitation at 279 nm (Fig 15) showed one broad peak at 441 nm due to zirconia host and five bands due to $^5D_0$-$^7F_j$ transitions of Eu$^{3+}$, where $j = 0, 1, 2, 3$ and $4$ respectively. The ratio of intensity of 616 to 597 nm was higher, in contrast to PL spectra of Eu-YSZ-500, which indicated the lower symmetry around Eu$^{3+}$ ions. As Eu-Z-500 have mixture of both monoclinic and tetragonal phase (59% M+41% T), it has lower symmetry than cubic (100%) Eu-YSZ-500. Eu-Z-500 excited at 236 nm also showed almost similar PL spectra. Gedanken et al. [12] also studied Eu doped in pure ZrO$_2$ and YSZ and found weak luminescence for pure ZrO$_2$ and intense spectra for YSZ. The reason was explained due to the better miscibility of Eu$^{3+}$ in YSZ, whereas Eu$^{3+}$ does not dissolve very well in ZrO$_2$ and form large clusters, which hinders the energy transfer between host and Eu$^{3+}$ ions. However, in the present study we observed almost similar PL spectra of both Eu-YSZ-500 and Eu-Z-500 samples which indicated better miscibility of Eu$^{3+}$ in our ZrO$_2$ samples as compared to reported ones [12].

The PL spectra of Dy-YSZ sample (Fig 16) showed four emission bands; the two bands at 378 and 417 nm correspond to YSZ host matrix. The other bands at 468 and 544 nm belongs to Dy$^{3+}$ transitions; 468 nm for $^4F_{9/2}$-$^6H_{15/2}$ and 544 nm for $^4F_{9/2}$-$^6H_{13/2}$ transitions [41]. The emission bands for Dy$^{3+}$ ions were in agreement with the reported literature (480-485 nm and 575-580 nm respectively) [41,42]. The $^4F_{9/2}$-$^6H_{13/2}$ transition of Dy$^{3+}$ ions at 544 nm belongs to hypersensitive transition and is strongly influenced by outside surrounding. When Dy$^{3+}$ ion is located at a low symmetry local site, this emission transition is often prominent [43]. Fig 16 clearly showed that this band (544
nm) was not prominent in the present study, which confirmed the higher symmetry of Dy$^{3+}$ ions in cubic YSZ matrix.

The PL spectra of Dy-Z sample (Fig 16) showed two broad emission bands; one ranging from 400 to 450 nm and centered at ~421-432 nm belongs to ZrO$_2$ host matrix and another broad peak at 467 nm for $^4F_{9/2} - ^6H_{15/2}$ Dy$^{3+}$ transitions.

![PL spectra of Dy-YSZ-500 and Dy-Z-500 sample under excitation at 218 and 270 nm wavelengths](image)

**Fig 16.** PL spectra of Dy-YSZ-500 and Dy-Z-500 sample under excitation at 218 and 270 nm wavelengths

The PL spectra of Er-YSZ-500 sample (Fig 17a), under excitation at 379 nm, showed a broad emission band ranging from 400-500 nm and centered at 417, 439 and 467nm corresponding to YSZ host matrix. The sample when excited at 488 nm (Fig 17b) showed the three groups of Er$^{3+}$ transitions; the band at 520 nm belongs to $^2H_{11/2} - ^4I_{15/2}$ and 536-547 nm belongs to $^4S_{3/2} - ^4I_{15/2}$ transitions; the bands of second group at 567-572 nm belongs to $^4F_{9/2} - ^4I_{15/2}$ transitions; and the bands of third group at 608 nm belongs to $^2H_{11/2} - ^4I_{13/2}$ and bands at 621-635 nm belongs to $^4S_{3/2} - ^4I_{13/2}$ transitions [44]. The PL spectra of ER-Z-500 also showed Er$^{3+}$ transitions similar to Er-YSZ samples (Fig 18).
Fig 17. PL spectra of Er-YSZ-500 under excitation at 379 and 488 nm wavelength

Fig 18. PL spectra of Er-Z-500 under excitation at 488 nm wavelength

4. Conclusions

The present study showed that the optical properties of ZrO$_2$ are significantly influenced by its crystalline phases and the dopants; the size of dopants and the heating temperature is also important for the substitution of the dopants into the host lattice. Monoclinic zirconia was observed to have absorption at higher wavelength compared to
tetragonal zirconia. The addition of Eu, Dy and Er RE dopants increased the tetragonal percentage of ZrO₂. In YSZ single cubic phase was observed in pure as well as doped YSZ samples.

The above results showed that YSZ is more favorable host to Eu³⁺, Dy³⁺ and Er³⁺ ions resulting into intense emission of dopants as compared to pure ZrO₂. This is explained by the fact that incorporation of Y³⁺ ions into ZrO₂ host matrix gives rise to substantial number of oxygen vacancies, which might act as a sensitizer for the effective energy transfer from the host to activators [44]. The larger size of size of Y³⁺ (1.09 Å) is also helpful to substitute the dopants of smaller size (Eu³⁺ = 0.95 Å, Dy³⁺ = 0.91 Å, Er³⁺ = 0.88 Å). On the other hand, smaller size of Zr⁴⁺ (0.84 Å) than these dopants has the restriction on easy substitution within the Zr host lattice. The better miscibility of these dopants in YSZ matrix hinders the creation of large clusters [45] and avoids the concentration quenching process. Furthermore, at the lower calcination temperature of 500 °C, only a minor fraction of these dopants might have introduced in Zr substitution, most of the dopants may introduce only in the interfacial spaces of zirconia lattice resulting into the formation of clusters, which hinders the energy transfer between the host and dopants and thus resulting into weak emissions [12,41].

DRS and PL spectra were found to be very sensitive tools to observe any structural informations such as crystalline phase, presence of surface defects, oxygen vacancies and carbon impurities etc. RE doped ZrO₂ and YSZ can be used as new environmentally friendly luminescent materials.
5. References

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