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White photoluminescence emission from ZrO$_2$ co-doped with Eu$^{3+}$, Tb$^{3+}$ and Tm$^{3+}$

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Abstract

The search for high efficiency, reliable, low power consumption and environmental friendly materials for white light-emitting diodes has become a proficient field. Single-phase doped materials have been made to solve some of these challenges. Particles with color-tunable emission can be obtained by a combination of some lanthanide ions in the host material. The luminescence properties and crystalline structure of ZrO$_2$ particles co-doped with rare earth ions (RE$^{3+}$ = Tb$^{3+}$, Eu$^{3+}$ and Tm$^{3+}$) calcined at different temperatures were studied. We aimed to investigate the emission spectrum of the particles in the red, green, and blue regions under UV excitation. The x and y coordination chromaticity - (x = 0.34, y = 0.34) and (x = 0.31, y = 0.34) - presented values close to those of the white color (x = y = 0.33). In conclusion, the ZrO$_2$: RE$^{3+}$ powers were successfully obtained by the complex polymerization method and are promising candidates for white light-emitting applications.

Keywords: Complex polymerization method; ZrO$_2$:RE$^{3+}$; Luminescence; CIE.

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1. Introduction

The incorporation of luminescent materials into host lattices, including transition metals and lanthanide ions, and their utilization has been reported by Blasse and Grabmaier [1]. Feldman and co-authors [2] have described numerous matrices with characteristic color emission and ending with the first use of the rare earth phosphors in the 1970s, including tricolor devices (RGB) containing lanthanide ions for application in white light emission based on f–f transition. Lanthanide doped particles have been recognized as a new promising class of fluorescent materials due to the unique luminescence properties, narrow line-width emission bands, high quantum yields and photostability [3]. Particles with color-tunable emission can be obtained by a combination of some lanthanide ions in the host material. Such a color-tunable phosphorus can find potential applications in display and security printing areas [4].

Thulium, terbium, and europium are lanthanide ions that emit blue, green, and red color, respectively [5-12]. Many hosts can serve as promising matrices to accommodate these ions, yielding materials with efficient emission for application in tricolor white light-emitting devices [13-18]. Other lanthanides have also been used [19-25], but they have been incorporated separately or the excitation appears in a different wavelength.

Zirconia particles doped with different rare earths ions have been recognized to have potential in the area of photonic applications [26-28]. The low-phonon energy of ZrO$_2$ opens up the possibility of more efficient luminescence from the activator ions incorporated in it [29]. This is due to the fact that the lower the phonon energy of the host, the higher the probability of radiative transitions of RE$^{3+}$. The energy phonon and symmetries of the normal modes of vibration of the ZrO$_2$ are determined as a function of crystalline structure [30, 31]. According to Negita [32], in his study lattice vibrations and cubic to tetragonal phase transition in ZrO$_2$, shows through of analyzes of phonon modes in ZrO$_2$ that there is a condensation of the phonon $X_2^-$ associated with the cubic phase to tetragonal transition in ZrO$_2$.

Zirconium dioxide is an excellent material for optical application due to its hardness, optical transparency and high refractive index. Zirconia coatings due to its
chemical and photochemical stability, high refractive index and low phonon energy seem to be an ideal material for preparation of active wave guides [33]. The wide band gap of ZrO$_2$ enables RE emission in the visible range, as low phonon energies of the matrix suggest a high yield luminescence (multiphonon relaxation). The luminescence spectrum of lanthanides in the trivalent state caused by ionization of 6s$^2$ and 5d electrons and intracenter transitions of 4f electrons shielded by outer 5s and 5p electrons consists of a set of fairly narrow spectral lines from the UV to the IR range [34, 35].

Thus, rare earth ion doped ZrO$_2$ can be a good choice as phosphor materials for white light-emitting UV-LEDs. Recently, the luminescence properties of Eu$^{3+}$/Dy$^{3+}$/Tm$^{3+}$ activated ZrO$_2$ nanocrystals have been reported [36-38]. These rare earth ion doped ZrO$_2$ nanophosphors have been reported to give multicolor emissions.

In this paper, we used photoluminescence spectroscopy to investigate the white light emission of ZrO$_2$ particles co-doped with rare earth ions (RE$^{3+}$ = Tb$^{3+}$, Eu$^{3+}$ and Tm$^{3+}$). The samples were prepared by the complex polymerization method (CPM) [39-41] and characterized by XRD and diffuse reflectance spectroscopy.

1. Experimental

2.1. Synthesis of ZrO$_2$:RE particles

The samples were prepared by a Complex Polymerization Method (CPM) [42, 43]. In the process of synthesis, zirconium citrate was obtained by dissolution of zirconium nitrate (Vetec, 99%) in an aqueous citric acid solution under agitation at an approximate temperature of 80°C. After the complete dissolution of zirconium nitrate, the cations of RE were added for doping. A europium solution and a thulium solution were prepared through the dissolution of Eu$_2$O$_3$ (Aldrich, 99.9%) and Tm$_2$O$_3$ (Aldrich, 99.9%), respectively, in nitric acid. Then, the solutions were mixed with the zirconium citrate solution. Terbium nitrate was added (Aldrich, 99.9%). In order to promote the polymerization of citrate through the polyesterification reaction, ethylene glycol was added, and the solution was stirred constantly. The molar ratio between citric acid and ethylene glycol was set to 60/40 (mass ratio). After 4 h, the removal of water and the formation of translucent resin was observed. The dopant concentration was maintained at 8 mol% RE, this content is the contribution of all RE, corresponding to ZrO$_2$: 2.66% Tm 2.66% Tb 2.68% Eu. The polymeric resin was heat treated at 350ºC (10ºC/min) for 4 h, leading to the partial decomposition of the polymeric gel and the formation of an
expanded resin composed of partially pyrolyzed material. The particles were annealed at 600, 800 and 1000ºC for 2 h at a heating rate of 10ºC/min.

2.2 Characterization of ZrO$_2$:RE particles

The phases present in the ceramic powder were investigated by X-ray diffraction (XRD) using a Shimadzu diffractometer, model XRD-7000, with CuK$_\alpha$ radiation. Raman spectrometry required use of Horiba Jobin-Yvon Raman Labram equipment at room temperature as the source of excitation by means of an Olympus BX41 TM microscope with a laser at a wavelength of 514 nm, in the 100-700 nm. The UV-vis reflectance spectra of the ZrO$_2$: 8%RE particles were measured using Cary equipment, model 5G, in the 200-800 nm range. Photoluminescence spectra were obtained using a Thermal Jarrell-Ash Monospec 27 monochromator and Hamamatsu R446 photomultiplier. The excitation source used on the samples was a laser at a wavelength of 350.7 nm with krypton ions (Coherent Innova) with an output of approximately 13.3 mW; all measurements were performed at room temperature. To characterize white light resulted from the described mixing, we calculated the chromaticity coordinates using the spectrum represented in Fig. 3. The chromaticity coordinates of red (the $x$ coordinate), green (the $y$ coordinate) and blue (the $z$ coordinate) were determined according to the system of the International Commission on Illumination given in 1968 [44, 45] using the following relationships:

$$
\begin{align*}
    x &= \frac{(X)}{(X+Y+Z)} \\
    y &= \frac{(Y)}{(X+Y+Z)} \\
    z &= \frac{(Z)}{(X+Y+Z)} \\
\end{align*}
$$

(1)

where parameters $X$, $Y$ and $Z$ are the following spectral integrals:

$$
\begin{align*}
    X &= \int xP(\lambda)d\lambda \\
    Y &= \int yP(\lambda)d\lambda \\
    Z &= \int zP(\lambda)d\lambda \\
\end{align*}
$$

(2)

Here $P(\lambda)$ is luminescence spectrum of the samples, that provide, for each within the visible range , the emitted intensity. The function $P(\lambda)$ is determined empirically, the
values of $\lambda$ for components $x$, $y$ and $z$ are 599, 555 and 446 nm, respectively [46] and $x$, $y$ and $z$ are functions of spectral summarizing. Integrals (2) were calculated through the spectral interval of 350-800 nm.

3. Results and Discussion

The XRD patterns of ZrO$_2$: 8%RE samples calcined at different temperatures are shown in Fig. 1(a). Diffraction peaks are located at approximately 29.94º, 34.75º, 49.87º, 59.43º, 62.45º and 73.66º, which correspond to the (111), (200), (220), (311), (222), and (400) planes, respectively, of cubic ZrO$_2$ phase [ICSD 81-1551]. According to the literature [47, 48], stabilization of the cubic phase of ZrO$_2$ is achieved by increasing the amount of bi- or trivalent cations introduced into the ZrO$_2$ structure. The replacement of cations of Zr$^{4+}$ by RE$^{3+}$ promotes the appearance of oxygen vacancies (Vo). The oxygen vacancies are responsible for weakening the repulsive force between neighboring O$^{2-}$ and results in a change in the lattice parameters of the unit cell ($c/a \rightarrow 1$), which causes the ions to be arranged in a cubic structure [47].

The identification of the crystalline phase of ZrO$_2$ by only XRD is inaccurate due to the polymorphism of ZrO$_2$. This difficulty is reported by Das et al [48] which in his work confirms an inaccuracy in identifying the tetragonal and cubic phases by XRD due to low angular resolution of the equipment used (0.03º), assuming an overlap of peaks of the two phases of ZrO$_2$. Raman spectroscopy can distinguish modifications of the crystalline structure of ZrO$_2$ with higher efficiency [49]. The analysis is based on the different vibrations that each crystalline structure of ZrO$_2$ has. The Raman spectra of oxide ceramics typically contain a large amount of information that is extracted from the band positions, their intensities, and their shapes.

The Raman spectrum of the sample treated at different temperatures is shown in Fig. 1(b). The spectrum shows a single band centered at between 600 cm$^{-1}$. This band is associated to the T$_{2g}$ characteristic vibration of the cubic phase of ZrO$_2$ [49]. Kontoyannis and Orkoula [49], in his study of the quantitative determination of the phases of ZrO$_2$, show quite clearly the distinct behavior in Raman spectra between the tetragonal and cubic phases. To tetragonal phase are assigned six active raman modes ($A_{1g} + 2B_{1g} + 3E_{g}$), for the cubic phase have only one mode (T$_{2g}$). **The results for the raman confirm the response obtained by XRD: stabilization of cubic phase** [50].
Fig. 1: (a) Diffraction pattern of ZrO$_2$: RE samples, (b) Raman spectrum of ZrO$_2$: RE samples, calcined at different temperatures: (I) 600°C, (II) 800°C and (III) 1000°C.

Crystallite size of the samples was estimated by the Scherrer equation and the full-width half-maximum (FWHM) of an observed peak. The strongest peaks for the cubic phase (111) were used to calculate the average crystallite size (D) of the ZrO$_2$:RE particles. Table 1 gives the lattice parameters (a), unit cell volume (V), and crystallite size for the ZrO$_2$: 8%RE samples.

Table 1 - Value of structural parameters of ZrO$_2$:RE particles

A significant reduction in the FWHM value with increasing temperature is observed from Table 1. This behavior indicates that there was an increase in crystallinity with temperature effect. Samples presented small crystallite size ranging from 13.2 to 17.9 nm. Crystallite size of the samples was estimated by the Scherrer equation and the full-width half-maximum (FWHM) of an observed peak. The strongest peaks for the cubic phase (111) were used to calculate the average crystallite size (D) of the ZrO$_2$: RE particles. Table 1 gives the lattice parameters (a), unit cell volume (V), and crystallite size for the ZrO$_2$: 8%RE samples.

The band gap energies of the ZrO$_2$: 8%RE nanoparticles were estimated from their diffuse reflectance spectroscopy by plotting the square of the Kubelka–Munk function F(R)$^2$ vs. energy in electron volts and extrapolating the linear part of the curve to F(R)$^2 = 0$, as shown in Fig. 2. The ratio between the molar absorption coefficient (k) and scattering coefficient (s) is estimated from reflectance data using the Kubelka–Munk relation [51] in equation 3:
where $R$ is the percentage of reflected light. The incident photon energy ($h\nu$) and the optical band gap energy ($E_g$) are related to the transformed Kubelka–Munk function, 

$$F(R) = \frac{k}{s} = \frac{(1 - R)^2}{2R}$$

The calculated values of band gap $E_{gap}$ were listed in Fig. 2. The spectra behavior shows that the $E_{gap}$ is dependent of heat treatment temperature. This result indicates that the exponential optical absorption edge and optical band gap are controlled by the degree of structural defects into the lattice. Thus, the increase of optical band gap value with the heat treatment temperature promotes a reduction of the intermediary energy levels, as consequence of the structural organization in the lattice [52].

Table 2 shows a comparative between $E_{gap}$ values of ZrO$_2$: 8%RE prepared by CPM with those reported in the literature for the doped ZrO$_2$ particles prepared by different methods [53-56].

**Fig. 2: UV-Vis absorption spectroscopy of ZrO$_2$:RE particles thermally treated at 600°C, 800°C and 1000°C.**

**INSERT TABLE 2**

Table 2 - Comparative results between optical band gap values of ZrO$_2$:8%RE obtained in this work with those reported in the literature for doped ZrO$_2$ obtained by different methods.

In this table, it was verified that the $E_{gap}$ of ZrO$_2$ can be influenced by the formation methods. Also, there has been a change in the gap energy values is a function of the type and amount of dopant introduced in the ZrO$_2$ lattice.
According to band theory, the energy of a forbidden band is dependent on material structure since the changing of atom positions lead to changing of the integral of exchange interaction. This is the reason for forbidden band energy dependence on the ZrO$_2$ crystal structure (monoclinic, tetragonal and cubic). The experimentally estimated forbidden gap for monoclinic phase is $4.2 - 5.83$ eV, for tetragonal $4.2 - 5.78$ and for cubic $4.6 - 6.1$ eV [57, 58]. The theoretically calculated forbidden gap for monoclinic phase is $4.46$ eV, for tetragonal phase is $4.28$ eV and for cubic phase is $4.93$ eV [57, 58].

The emission spectra of the ZrO$_2$:8%RE excited at 350.7 nm (Fig. 3a) presented the peaks ascribed to the lanthanides ions Tm$^{3+}$, Tb$^{3+}$ and Eu$^{3+}$. The peak detected at 466 nm (blue region) corresponds to the Tm$^{3+}$ $^1G_4\rightarrow^3H_6$ transition [59]; it had a different relative intensity in each spectrum. The peaks at 495 and 550 nm (green region) refer Tb$^{3+}$ $^5D_4\rightarrow^7F_6$ and $^5D_4\rightarrow^7F_5$ transitions [60], respectively. The ones relative to the Eu$^{3+}$ $^5D_0\rightarrow^7F_j$ (1, 2, 3 and 4) transitions [61] appeared at 596, 619, 656 and 706 nm (region red), respectively. Table 3 lists the transitions we observed in Fig. 3.

Owing to the different charge for the cations, oxygen vacancies were formed to balance the charge difference. The defect reaction equation can be described in the following Eq. (4):

$$\begin{align*}
(1 - x)\text{ZrO}_2 + 1/2x\text{RE}_2\text{O}_3 & \rightarrow x\text{RE}_{Zr}^{x} + 1/2xV'_o^n + (1 - x)\text{Zr}_{Zr}^{x} + (2 - 1/2x)O'_o^n
\end{align*}$$

(4)

where $\text{RE}_{Zr}^{x}$ means RE$^{3+}$ occupying the normally occupied by a Zr$^{4+}$ due to replacement by RE$^{3+}$. $V'_o^n$ is the O$^{2-}$ vacancy. $\text{Zr}_{Zr}^{x}$ represents the rest zirconium in the lattice of ZrO$_2$ and $O'_o^n$ is the oxygen in the lattice of ZrO$_2$. At low concentrations of RE, there is little $V'_o^n$ in ZrO$_2$, and the symmetry of the host structure is not seriously influenced. The larger the concentration of RE in the host, higher the number of oxygen vacancies is able to create a new surrounding in the host. The new surrounding disturbs the symmetry of the host.

INSERT Fig. 3
Fig. 3: (a) PL emission of ZrO$_2$:RE to temperature at 600, 800 and 1000ºC; (b) CIE diagram of ZrO$_2$:RE, A: 600ºC, B: 800ºC, C: 1000ºC. Inset shows emission light white of the sample A.

Table 3 - Assignments of the rare earth ions transitions and the respective wavelength.

It is observed in Fig. 3 that increasing crystallinity favored obtaining a better answer of photoluminescence. Emissions of Eu$^{3+}$ $^5D_0 \rightarrow ^7F_j$ ($j = 1, 2$) can be caused by the direct activation of photon or through energy transfer of Tb$^{3+}$ [donor (Tb$^{3+}$) → receptor (Eu$^{3+}$)]. It is known that the photoluminescence is dependent on the degree of order-disorder of the material; so this property follows the structural evolution of the material.

The spectrum presents a broad band between 378 nm and 572 nm, associated with the interference of the host. Generally, the photoluminescent is related to defects and/or impurities found on the lattice [62-65]. The structural defects of ZrO$_2$ in most are related to O$^2-$ and Zr$^{4+}$ vacancies. The formation of these defects can be described through the equations (5), (6) e (7) [66]:

$$ZrO_2 + hv \rightarrow Zr^{4+} + O_2 + 4e^-$$  \hspace{1cm} (5)

$$Zr^{4+} + e^- \rightarrow Zr^{3+}$$  \hspace{1cm} (6)

$$2O_o \rightarrow 2V_o^{2+} + O_2 + 4e^-$$  \hspace{1cm} (7)

Zr$^{4+}$ ions may generate Zr$^{3+}$ centers by capturing electrons. The $O_o$ represents an oxygen atom in a regular position in the lattice, $V_o$ indicates an oxygen vacancy. The oxygen vacancy always leads to formation of energy levels within the band gap. When ZrO$_2$ is excited by a photon, the electrons are trapped by $V_o$ and centers are created (F) [67]. Then recombination centers (F) with the holes (h$^+$) creates the transmitter excited states. From these states originate transitions which decay to a state with lower energy level. Wang et al [68] analyzed the effect on temperature treatment between 600ºC e 1550ºC on ZrO$_2$ photoluminescence behavior. It was observed a gradual growth of the PL intensity until the temperature of 1100ºC and surprisingly, from 1200ºC was verified...
a very rapid growth of the PL intensity. According to authors, at high temperature the
diffusion of various species present in the material is favored, as the case of the oxygen
vacancy. The quantity of oxygen vacancies tend to gradually increase with increasing
treatment temperature and, therefore, the emissions due to recombination centers also
grow. For the sample treated at 1000ºC, the ZrO$_2$ matrix shows a significant
contribution in the blue region, favored by increasing the treatment temperature. It is
observed that on this last case, the energy transfer between ZrO$_2$ $\rightarrow$ RE$^{3+}$ [36] was not
effective, which clarifies the decrease in emissions intensity of Tb$^{3+}$ (548.32 nm) and
Eu$^{3+}$ (617.54 nm).

The white emission can be verified by determining the coordinates x and y. The
CIE chromatic coordinates can be calculated by integration of the X, Y, and Z values
[69]. Fig. 3b illustrates the CIE chromaticity diagram. The standard white light presents
x = 0.33 and y =0.33 [70]. Table 4 lists the chromaticity coordinates for ZrO$_2$: 8%RE
excited at 350.7 nm. The contributions from certain emission regions define the color of
the matrix. The samples treated at 600ºC and 800ºC represented by letters A and B,
respectively, show white emission as illustrated in Fig. 3b. It is observed in the inset in
Fig. 3, white light-emission for sample calcined at 600ºC under Uv excitation. The
sample treated at 1000ºC, identified by letter C, presented violet color.

It has been recognized that the luminescence intensities of various rare earth ions
can be enhanced or quenched by the energy transfer from other codoped rare earth ions.
The energy transfer (ET) between Tb$^{3+}$ and Eu$^{3+}$ in nanopowder has been widely
studied to understand its photoluminescent behavior [71, 72].

A schematic energy level diagram involving Tm$^{3+}$, Tb$^{3+}$, and Eu$^{3+}$ absorption;
nonradiative relaxation; and processes leading to the blue, green, and red emission is
given in Figure 4.

Fig. 4: The energy transfer mechanism scheme between the ions Tm$^{3+}$/Tb$^{3+}$/Eu$^{3+}$.

Figure 4 shows that no resonant energy transfer process from the $^5$D$_4$ state of
Tb$^{3+}$ to $^5$D$_0$ of Eu$^{3+}$ can occur. The most probable mechanisms responsible for the direct
transfer of excitation are:
\[ ^5D_4(Tb) + ^7F_0(Eu) + \Delta E(1) \rightarrow ^7F_4(Tb) + ^5D_0(Eu) \] (8)

\[ ^5D_4(Tb) + ^7F_1(Eu) \rightarrow ^7F_4(Tb) + ^5D_0(Eu) + \Delta E(2) \] (9)

where the energy mismatches \( \Delta E(1) \) and \( \Delta E(2) \) can be bridged respectively by the absorption or the emission of the phonons or by the involvement of energy levels of other ions in a many-body process. Further information about the mechanism responsible for the transfer can be obtained from the analysis of the kinetics of the luminescence as a function of the fractional concentration \( x \) and of the temperature.

First, electrons in Tb\(^{3+}\) ions are excited from the ground state (4f\(^8\)) to the excited state (4f\(^7\)5d) by 350.7-nm UV light. Subsequently, these electrons relax to the lowest excited state, \( ^5D_4 \), through multiphonon relaxation and then either return to the ground state to produce the Tb\(^{3+}\) emissions (\( ^5D_4 \rightarrow ^7F_{6,5,4} \)) or transfer their excitation energy from the \( ^5D_4 \) (Tb\(^{3+}\)) level to the higher excited energy levels of Eu\(^{3+}\) (4f\(^6\)) through cross relaxation, in which they relax to the \( ^5D_0 \) (Eu\(^{3+}\)) level, where red-orange emission (\( ^5D_0 \rightarrow ^7F_{0,1,2} \)) occurs. Because the \( ^5D_4 \rightarrow ^7F_{6,5,4,3} \) emissions of Tb\(^{3+}\) effectively overlap with the \( ^7F_{0,1} \rightarrow ^5D_{0,1,2} \) absorptions of Eu\(^{3+}\), the energy transfer from Tb\(^{3+}\) to Eu\(^{3+}\) is very efficient in general.

3. Conclusion

ZrO\(_2\) 8%RE particles were successfully obtained by the complex polymerization method. Through XRD analysis, the phase identified in ZrO\(_2\): 8%RE was the cubic phase. The photoluminescence emission spectra show transitions of the type \( ^1G_4 \rightarrow ^3H_6 \) (466 nm) from Tm\(^{3+}\), \( ^5D_4 \rightarrow ^7F_{5,6} \) (495 nm and 550 nm) from Tb\(^{3+}\), and \( ^5D_0 \rightarrow ^7F_{1,2} \) (597, 619, 656 and 706 nm) from Eu\(^{3+}\). Energy transfer was observed between levels \( ^5D_4 \) (Tb\(^{3+}\)) → \( ^5D_1 \) (Eu \(^{3+}\)). The CIE coordinates calculated for particles treated at 600 °C and 800 °C showed values of \( (x = 0.34, y = 0.34) \) and \( (x = 0.31, y = 0.34) \), respectively; according to the CIE diagram, the values represent a points in the white region. The ZrO\(_2\):RE materials presented here are promising photoluminescent materials for applications in new white light-emitting devices.
References


[52] M. D. Gonçalves, L. S. Cavalcante, J. C. Sczancoski, J.W.M. Espinosa, P.S. Pizani, E. Longo, I.L.V. Rosa, (Sr,Tm)ZrO_{3} powders prepared by the polymeric


Table captions:

Table 1 - Value of structural parameters of ZrO$_2$:RE particles

Table 2 - Comparative results between optical band gap values of ZrO$_2$: 8%RE obtained in this work with those reported in the literature for doped ZrO$_2$ obtained by different methods

Table 3 - Assignments of the rare earth ions transitions and the respective wavelength.

Table 4 - CIE coordinates of ZrO$_2$: 8%RE; A: 600°C, B: 800°C, C: 1000°C
Fig. 1: (a) Diffraction pattern of ZrO$_2$: RE samples, (b) Raman spectrum of ZrO$_2$: RE samples, calcined at different temperatures: (I) 600°C, (II) 800°C and (III) 1000°C.

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Fig. 4: The energy transfer mechanism scheme between the ions Tm$^{3+}$/Tb$^{3+}$/Eu$^{3+}$. 
Table 1 - Value of structural parameters of ZrO$_2$:RE particles

<table>
<thead>
<tr>
<th>Treatment temperature</th>
<th>Crystal Sistem</th>
<th>Space group</th>
<th>2θ (º)</th>
<th>FWHM (rad)</th>
<th>Lattice parameter: a (Å)</th>
<th>Unit cell volume (Å$^3$)</th>
<th>Crystallite size (nm)</th>
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<tr>
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<td>Cubic</td>
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<td>29.9</td>
<td>0.82</td>
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<td>13.5</td>
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<tr>
<td>T: 1000°C</td>
<td>Cubic</td>
<td>Fm-3m</td>
<td>29.9</td>
<td>0.3149</td>
<td>5.1579</td>
<td>137.2</td>
<td>17.9</td>
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</table>
Table 2 - Comparative results between optical band gap values of ZrO$_2$: 8\%RE obtained in this work with those reported in the literature for doped ZrO$_2$ obtained by different methods

<table>
<thead>
<tr>
<th>Material</th>
<th>Method employed</th>
<th>Temperature (°C)</th>
<th>Concentration of dopant (mol %)</th>
<th>Optical band gap (eV)</th>
<th>Ref. []</th>
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<tr>
<td>ZrO$_2$:Ce</td>
<td>Microwave irradiation</td>
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<td>ZrO$_2$:Au (films)</td>
<td>Sol–gel dip coating</td>
<td>500</td>
<td>4, 8, 10, 12</td>
<td>5.71, 5.70, 5.64, 5.40</td>
<td>[54]</td>
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<tr>
<td>ZrO$_2$: Eu</td>
<td>Combustion</td>
<td>400</td>
<td>1, 3, 5, 7, 9, 11</td>
<td>4.70, 4.60, 4.50, 4.40, 4.30, 4.20</td>
<td>[55]</td>
</tr>
<tr>
<td>ZrO$_2$: Mg (films)</td>
<td>Sol-Gel</td>
<td>500</td>
<td>4, 8, 12, 16, 20</td>
<td>5.69, 5.59, 5.44, 5.14, 4.42</td>
<td>[56]</td>
</tr>
<tr>
<td>ZrO$_2$:RE</td>
<td>CPM</td>
<td>600, 800, 1000</td>
<td>8</td>
<td>5.05, 5.14, 5.16</td>
<td>This work</td>
</tr>
</tbody>
</table>
Table 3 - Assignments of the rare earth ions transitions and the respective wavelength.

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Transitions</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$^1G_4 \rightarrow ^3H_6$ (Tm$^{3+}$)</td>
<td>466</td>
</tr>
<tr>
<td>2</td>
<td>$^5D_4 \rightarrow ^7F_6$ (Tb$^{3+}$)</td>
<td>495</td>
</tr>
<tr>
<td>3</td>
<td>$^5D_4 \rightarrow ^7F_6$ (Tb$^{3+}$)</td>
<td>550</td>
</tr>
<tr>
<td>4</td>
<td>$^5D_0 \rightarrow ^7F_1$ (Eu$^{3+}$)</td>
<td>596</td>
</tr>
<tr>
<td>5</td>
<td>$^5D_0 \rightarrow ^7F_2$ (Eu$^{3+}$)</td>
<td>619</td>
</tr>
<tr>
<td>6</td>
<td>$^5D_0 \rightarrow ^7F_3$ (Eu$^{3+}$)</td>
<td>656</td>
</tr>
<tr>
<td>7</td>
<td>$^5D_0 \rightarrow ^7F_4$ (Eu$^{3+}$)</td>
<td>706</td>
</tr>
</tbody>
</table>
Table 4 - CIE coordinates of ZrO$_2$: 8%RE; A: 600°C, B: 800°C, C: 1000°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>x</th>
<th>y</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.34</td>
<td>0.34</td>
</tr>
<tr>
<td>B</td>
<td>0.31</td>
<td>0.34</td>
</tr>
<tr>
<td>C</td>
<td>0.28</td>
<td>0.24</td>
</tr>
</tbody>
</table>