Photoluminescent properties of ZrO$_2$: Tm$^{3+}$, Tb$^{3+}$, Eu$^{3+}$ powders—A combined experimental and theoretical study

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Abstract

Rare-earth (RE) element-based materials for optical applications have received increasing attention owing to the emission properties of RE ions, which render these materials suitable for use in color displays, lasers, and solid-state lighting. In the present work, ZrO$_2$:RE (RE$^{3+} = $ Tm$^{3+}$, Tb$^{3+}$, and Eu$^{3+}$) powders were obtained via complex polymerization, and characterized by means of X-ray diffraction (XRD), Raman spectroscopy, UV–visible absorption spectroscopy, and photoluminescence measurements. The XRD patterns and Raman spectra revealed the tetragonal phase of ZrO$_2$ co-doped with up to 4 mol.% RE$^{3+}$ and stabilization of the cubic phase, for up to 8 mol.% RE$^{3+}$. In addition, the photoluminescence measurements revealed simultaneous emissions in the blue (477 nm), green (496.02 nm and 548.32 nm), and red-orange (597.16 nm and 617.54 nm) regions. These emissions result from the Tm$^{3+}$, Tb$^{3+}$, and Eu$^{3+}$ ions, respectively. Energy transfers, such as $^1$G$^4$ levels (Tm$^{3+}$) / $^5$D$^4$ (Tb$^{3+}$) and $^5$D$^4$ levels (Tb$^{3+}$) / $^5$D$^0$ (Eu$^{3+}$), occurred during the emission process. Calculations based on density functional theory (DFT) were performed, to complement the experimental data. The results revealed that structural order/disorder effects were generated in the cubic and tetragonal ZrO$_2$ phases in the ZrO$_2$:Eu$^{3+}$ powders, and changes in the electronic structure were manifested as a decrease in the band gap values. The chromaticity coordinates of all the samples were determined from the PL spectrum. The coordinates, $x = 0.34$ and $y = 0.34$, of the ZrO$_2$:8%RE sample corresponded to a point located in the white region of the CIE diagram and color correlated temperature (CCT) was found to be 5181 K. More importantly, the present results indicate that ZrO$_2$:RE powders constitute promising photoluminescent materials for use in new lighting devices.

1. Introduction

The synthesis and characterization of rare earth (RE)-doped nanomaterials have been extensively investigated. These materials have excellent properties [1,2], such as narrow emission bandwidths (<10 nm), long luminescence lifetime, high photostability, and low toxicity [3,4]. In recent years, these materials have received considerable attention owing to their use in several important applications, such as multiplexed imaging and sensing, bioassays, and multiplex biodetection [5–14]. The development of luminescent materials, which are more efficient than those currently available, is extremely challenging. Moreover, the use of a suitable host material for the RE ions is essential for achieving high efficiency [15].

Zirconium dioxide or zirconia (ZrO$_2$) and ZrO$_2$-based materials constitute an appropriate host for RE, owing to a unique combination of different properties. These include: high refractive index, large optical band gap, low optical loss, and high transparency in the visible and near-infrared regions, good chemical stability [16,17], and lower phonon frequency (~470 cm$^{-1}$) than other matrices such as Y$_2$O$_3$ (~597 cm$^{-1}$) and TiO$_2$ (~700 cm$^{-1}$) [18]. As such, the luminescence efficiency of active ions may be improved...
via incorporation into the ZrO$_2$ matrix [19].

RE ions can enhance the emission of photoluminescent mate-
rials, and the corresponding energy transfer (ET) process occurs be-
 tween an ion donor (D) and an ion acceptor (A). During the ET
process, the energy of D (which is in an excited electronic state) is
 transferred to A. Specific conditions must be fulfilled in order to
realize this mechanism. These include: (i) the emission band of D is
partially superimposed on the absorption band of A, and (ii) the
distance (R) between D and A must be sufficiently short, since the
energy transfer efficiency is proportional to 1/R$^6$, to enable inter-
action of the dipole–dipole emission bands of the material [20].
These unique properties have led to the widespread use of RE ions
in optical devices.

Direct excitation of Eu$^{3+}$ ions is a relatively inefficient process,
owing to the forbidden nature of the 4f transitions. However, Eu-
doped inorganic materials may exhibit efficient luminescence
emissions upon ultraviolet excitation. These materials also exhibit a
large Stokes shift, sharp emission spectrum, and have a long life-
time, high chemical/photochemical stability, low toxicity, and
reduced photobleaching, owing to shielding of the 4f electrons [21].
As such, Quan et al. [22] obtained spherical ZrO$_2$:Eu$^{3+}$ particles by
using a spray drying process followed by a post annealing treat-
ment. Gedanken et al. [23] used a sonochemical method for the
europium-oxide doping of ZrO$_2$ nanoparticles. Furthermore, Tiwari
et al. [24] determined the effect of varying Eu$^{3+}$ concentration on
the photo- and thermoluminescence of ZrO$_2$ nanophosphors. Some
RE ion-doped ZrO$_2$ materials, such as ZrO$_2$:Eu [25], ZrO$_2$:Tb [26],
and ZrO$_2$:Tm [27], have interesting properties. Vidya et al. [28]
investigated the color-tunable photoluminescence photocatalytic
activities and phase transformation of a ZrO$_2$:Tb$^{3+}$ nanophosphor.
Mari et al. [29] determined the photoluminescence properties of
Tb$^{3+}$ in ZrO$_2$ zirconia host matrices (prepared via combustion
synthesis) at different calcination temperatures.

Shang et al. [30] examined the process of energy transfer be-
tween Tm$^{3+}$ and Ho$^{3+}$ excited by a UV nanocrystal-LaOF laser and
classified the interaction between the ions as a quadrupole–
quadrupole type of interaction. Joshi [31] examined the energy
transfer from Tb$^{3+}$ and Eu$^{3+}$ in zinc phosphate glasses and
concluded that these ions undergo mainly dipole-dipole in-
teractions. Moreover, the efficiency of this transfer was highest at
a concentration of 8.6 mol% Eu$^{3+}$. The emissions of Tm$^{3+}$, Eu$^{3+}$, and
Tb$^{3+}$ ions fall within the blue, red, and green regions, respectively,
of the visible spectrum [32–34]. Particles that have tunable emis-
sion colors are obtained from a combination of lanthanide ions in
a host material. The first-ever generation of white light from the
simultaneous emission of blue, green, and red, under UV excita-
tion, was obtained for borate-based glasses co-doped with Ce$^{3+}$, Tb$^{3+}$,
and Mn$^{2+}$ [35]. Furthermore, the spectra of Tm$^{3+}$, Tb$^{3+}$, and Sm$^{3+}$
co-doped silicate glass, which was excited in the near-UV region,
exhibited bands corresponding to blue, green, and orange-red
emissions [36].

This paper can be considered a prolongation of previously work
(CITA) in which the main focus is the investigation of the photo-
luminescent properties of the particles of ZrO$_2$ co-doped with
Tm$^{3+}$, Tb$^{3+}$, and Eu$^{3+}$, by using the polymerization method
[37–40]. The use of the complex polymerization method in the
research materials is widespread because it presents advantages
such as good homogeneous distribution of different metal ions
along the polymer formed, facilitating control stoichiometric. Other
positive aspects of the method are the low temperature synthesis,
obtaining nanometric particles and reproducibility. At this time, we
will examine the effect of the concentration of RE (mol%) in the
discussed property. In addition, first-principle calculations were
performed in order to explain the structural and electronic changes
induced by the doping of ZrO$_2$:Eu. The energy transfer processes
between Tm$^{3+}$ and Tb$^{3+}$ and between Tb$^{3+}$ and Eu$^{3+}$, were also
discussed. X-ray diffraction (XRD), Raman spectroscopy, UV–visible
reflexance spectroscopy, and photoluminescence (PL) measure-
ments were used to characterize the samples. Moreover, a chro-
maticity diagram was determined from emission spectra data, in
order to verify the efficiency of these materials during the emission
of white light.

The remainder of this paper is organized as follows: Section 2
describes the synthesis method, characterization techniques, and
computational details; Sections 3 and 4 present the results and
closeup, respectively.

## 2. Experimental section

### 2.1. Synthesis of ZrO$_2$:RE powders

The samples were prepared by using a complex polymerization
method. During the synthesis, the zirconium citrate was obtained
by dissolving zirconium nitrate (Vetec, 99%) in an aqueous citric
acid solution, under agitation, at a temperature of ~80 °C. Doping
was performed by adding cations of RE to the solution. A europium
solution and a thulium solution were prepared by dissolving Eu$_2$O$_3$
(Aldrich, 99.9%) and Tm$_2$O$_3$ (Aldrich, 99.9%), respectively, in nitric
acid. Each solution was then separately mixed with the zirconium
citrate solution. Terbium nitrate (Aldrich, 99.9%) was subsequently
added to the mixed solution. Furthermore, ethylene glycol was
added to the solution, under constant stirring, in order to promote
polymerization of the citrate, through the polyelectrolyte reac-
tion. The molar ratio between citric acid and ethylene glycol used
was set to 60/40 (mass ratio). After 4 h, water was completely
removed, thereby yielding a translucent resin. Various (1, 2, 4 and
8 mol % of RE) dopant concentrations were considered. This
percentage of RE is on the contribution of all dopants, such as:
ZrO$_2$: 1% RE, ZrO$_2$:2%RE, ZrO$_2$:4%RE and ZrO$_2$: 8%RE correspond respectively to
Zr$_{0.95}$O$_2$: 0.0033 Tb$_{0.0033}$ Tm$_{0.0034}$ Eu$_{0.0049}$, Zr$_{0.99}$O$_2$: 0.0066 Tb$_{0.0066}$ Tm
$_{0.0068}$ Eu$_{0.0068}$, Zr$_{0.96}$O$_2$: 0.0133 Tb$_{0.0133}$ Tm$_{0.0134}$ Eu$_{0.0134}$ and Zr$_{0.92}$O$_2$: 0.0266
Tb$_{0.0266}$ Tm$_{0.0268}$ Eu$_{0.0268}$. The polymeric resin was heat-treated at 350 °C
(10 °C/min) for 4 h, leading to partial decomposition of the poly-
meric gel; this resulted in the formation of an expanded resin,
which consisted of partially pyrolyzed material. The resulting
powders were annealed at 600 °C for 2 h at a heating rate of 10 °C
min.

### 2.2. Characterization of ZrO$_2$:RE (RE = Tm$^{3+}$, Tb$^{3+}$, and Eu$^{3+}$) powders

The as-synthesized powders were examined by XRD (Shimadzu
diffactometer model XR D–7000), using Cu–K$_\alpha$ radiation. In addi-
tion, Raman spectrometry (Horiba Jobin-Yvon Raman Labram) was
performed at room temperature; an Olympus BX41 TM microscope
equipped with a 514 nm–wavelength laser, was used as the excita-
tion source. UV–vis reflexance spectra (Cary model 5G) and PL
spectra (Thermal Jarrel-AsheMonospec 27 monochromator and
Hamatsu R446 photomultiplier) of the ZrO$_2$:RE particles were also
obtained. A 350.7 nm-wavelength laser with krypton ions (Coher-
ent Innova) and an output of ~13.3 mW, was used as the excitation
source during the PL measurements; these measurements were all
performed at room temperature. To characterize white light
resulting from the aforementioned mixing, we calculated the
cromaticity 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 [41,42] using the following relationships:
where parameters $X$, $Y$ and $Z$ are the following spectral integrals:

\[
X = \int xP(\lambda) d\lambda \quad Y = \int yP(\lambda) d\lambda \quad Z = \int zP(\lambda) d\lambda
\]

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 and $x$, $y$ and $z$ are functions of spectral summarizing. Integrals (2) were calculated through the spectral interval of $350–800$ nm. The CCT value was estimated by using McCamy empirical formula [43]. The quality of white light is calculated using McCamy empirical formula in terms of CCT values, which is expressed as:

\[
\text{CCT} = -449n^3 + 3525n^2 - 6823n + 5520.33
\]

where $n = (x - xe) / (ye - ye)$ is the inverse slope line, $xe = 0.332$ and $ye = 0.186$.

2.3. Computational details

First-principle calculations, based on the density functional theory (DFT), were performed by using the Vienna $ab$ initio simulation package (VASP). The Kohn-Sham equations were solved by using the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional [44], and the electron-ion interaction was described via the projector-augmented-wave pseudo potentials. Moreover, the functional [44], and the electron-ion interaction was described via the projector-augmented-wave pseudo potentials. Moreover, the functional theory (DFT), were performed by using the Vienna plane-wave expansion was truncated at a cut-off energy of $520$ eV, and the Brillouin zones were sampled by using Monkhorst-Pack special k-point grids. Cubic and tetragonal phases of ZrO$_2$, both undoped and doped at $12\%$ of Eu substituted for Zr, were considered. In addition, a $12\%$ of Tb and Tm substitutions were tested. The valence electron density is defined by $12 (4s^24p^65s^24d^{10})$ electrons for Zr atoms, $6 (2s^22p^6)$ electrons for O atoms and $17 (5s^25p^66s^24f^7)$ electrons for Eu atoms. For Tb and Tm atoms, three f-like electrons are treated as core states and 9 electrons are used as valence states for both.

A supercell with 48 atoms was used for both systems, $2 \times 2 \times 1$ and $2 \times 2 \times 2$ for cubic and tetragonal phases, respectively. In the case of $12\%$ doping, two Zr$^{4+}$ were substituted by two Eu$^{3+}$ and oxygen vacancy (both near and far from Eu atoms) was included, to maintain the electroneutrality of the cell. In order to obtain a small amount of Eu doping, extremely large supercells must be used, thereby resulting in a high computational cost. The cell parameters and positions of all atoms were allowed to relax, and the conjugated gradient energy minimization method was used to obtain relaxed systems. This was achieved by setting a threshold value (i.e., 0.01 eV Å$^{-1}$) for the forces experienced by each atom. To ensure geometrical and energetic convergence of the cubic and tetragonal ZrO$_2$ structures, a $3 \times 3 \times 1$ Monkhorst-Pack special k-point grid was used.

3. Results and discussion

3.1. XRD characterization

XRD patterns of pure ZrO$_2$ and co-doped ZrO$_2$:xRE ($x = 1$, 2, and 4$\%$) powders are shown in Fig. 1(a)–(d). Diffraction peaks are located at approximate angles of: $30.07^\circ$, $35.02^\circ$, $50.28^\circ$, $59.87^\circ$, $62.60^\circ$, and $73.66^\circ$ corresponding to the (101), (110), (112), (201), (203), and (202) planes, respectively, of the ZrO$_2$ tetragonal phase [ICSD 81-1546]. Fig. 1(e) shows the pattern corresponding to ZrO$_2$:8$\%$RE. In this case, peaks occur at $–29.79^\circ$, $34.57^\circ$, $50.02^\circ$, $59.56^\circ$, $62.27^\circ$, and $73.35^\circ$, corresponding to the (111), (200), (220), (311), (222), and (400) planes, respectively, of the cubic phase of ZrO$_2$ [ICSD 81-1551]. This phase is stabilized with increasing amount of bi- or trivalent cations introduced into the ZrO$_2$ structure [45,46]. In addition, the replacement of Zr$^{4+}$ cations by RE$^{3+}$ results in the formation of oxygen vacancies. This leads, in turn, to a change in the lattice parameters of the unit cell (c/a → 1) and consequently, arrangement of the ions in a cubic structure [46]. The ionic radius of oxygen is large, it becomes difficult to maintain the four O$^{2-}$ ions around an ion Zr$^{4+}$ with a fluorite structure (cubic), due to large repulsion between the ions O$^{2-}$. With the introduction of dopant RE$^{3+}$ replacing Zr$^{4+}$, there is the appearance of oxygen vacancies in order to offset the charges and as result the force of repulsion between the O$^{2-}$ decreases, giving conditions to accommodate the ions in the cubic structure.

The size of the crystallites in the sample was estimated from the Scherrer equation [47,48] and the full-width half-maximum (FWHM) of an observed peak. The average crystallite size (D) of ZrO$_2$:RE powders was determined from the strongest peaks corresponding to the (101) tetragonal phase and (111) cubic phase. The lattice parameter (a, c), unit-cell volume (V), and crystallite size of the ZrO$_2$:RE samples are listed in Table 1.

3.2. Raman characterization

ZrO$_2$ polymorphism may lead to inaccurate results when the crystalline phases of ZrO$_2$ are identified only via XRD. Das et al. [45] attributed inaccuracies in XRD identification of tetragonal and cubic phases, to the low angular resolution (0.03$\%$) of the equipment used; this resolution resulted in an overlap of the peaks
corresponding to these phases. Compared to XRD, Raman spectroscopy can more accurately distinguish among the crystalline phases of ZrO₂ [49]. The band positions, intensities, and shapes can be determined from the Raman spectra. In fact, as shown in Fig. 2 and Table 2, each structure exhibits certain characteristics that correspond to specific locations in the spectra.

The bands that occur at 142, 257, 314, 461, 609, and 627 cm⁻¹ in the spectra shown in Fig. 2(a), (b), and (c) are attributed to the vibration modes of tetragonal ZrO₂ [49][51]. The spectrum (d) of the cubic phase of ZrO₂ (fluorite) is characterized by a broad band that occurs at ~605 cm⁻¹ [49]. The active modes in the Raman spectra (corresponding to each crystal) and the c/a ratio of the lattice parameters of tetragonal zirconia, are shown in Table 2. Theoretical calculations of the Raman-active modes of pure tetragonal ZrO₂ yield values of 149.4, 294.2, 301.5, 453.6, 611.5, and 650.9 cm⁻¹ for the Eg, A₁g, B₁g, Eg, B₁g, and Eg modes, respectively. In the case of pure cubic ZrO₂, a unique mode, which has T₂g symmetry, occurs at a wavenumber of 600.7 cm⁻¹. These values concur with previously obtained experimental data.

3.3. UV-visible spectroscopy analysis

The band gap energies of the ZrO₂:RE nanoparticles were estimated from the respective diffuse-reflectance spectra, by plotting the square of the Kubelka–Munk function (i.e., F(R)²) as a function of the energy (in eV). The values were determined by extrapolating the linear part of the curve to F(R)² = 0, as shown in Fig. 3. The ratio between the molar absorption coefficient (k) and scattering coefficient (s) is estimated from reflectance data using the Kubelka–Munk relation [52] in equation (4):

\[ F(R) = \frac{k}{s} = \frac{(1 - R)^2}{2R} \] (4)

where R is the percentage of reflected light. The incident photon energy (hv) and the optical band gap energy (E_g) are related to the transformed Kubelka–Munk function, \[ F(R) hv^p = A (hv - E_g) \], where E_g is the band gap energy, A is a constant depending on the transition probability and p is the power index that is related to the optical absorption process. p equals to 1/2 or 2 for an indirect or a direct allowed transition, respectively.

The E_g values are shown in Fig. 3. Intermediate levels of energy in the band gap region result from the structural defects in ZrO₂ [53]. For example, oxygen vacancies, the type of structural defect that occurs in the present case, are generated in order to compensate for the Zr⁴⁺ ions replaced by RE³⁺ ions. E_g values of 5.21, 5.09, 5.06, 4.97, and 4.92 eV are obtained for the undoped, 1, 2, 4, and 8 mol.% RE-doped materials, respectively.

In addition, the calculated values of the cell parameters concur with the experimentally determined results (a = 5.127 Å for the cubic phase, and a = 3.630 Å and c = 5.264 Å for the tetragonal phase). The results of the theoretical calculations indicate that, in both the cubic and tetragonal structures, 12% of Eu produces a local distortion that is both centered on the dopant, and located near the oxygen vacancy (Vo). The geometry of doped ZrO₂ with Eu³⁺

### Table 1

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<th>Parameters</th>
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<td>5.19164</td>
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### Table 2

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Fig. 2. Raman spectrum of ZrO₂:xRE, (a) x = 1%, (b) x = 2%, (c) x = 4%, and (d) x = 8%.

Fig. 3. UV-visible absorption spectra for particles: undoped ZrO₂ and ZrO₂:x% RE (x = 1, 2, 4, and 8% mol).
showing the coordination polyhedra of the cubic and tetragonal phases is shown in Fig. 4.

The vacancy corresponding to an O atom missing from the structure was examined by taking into account the proximity of the Eu atoms. For both phases, large distances between the oxygen vacancy and the Eu atoms, constitute more favorable arrangements than other configurations. Consequently, some Zr atoms are seven-coordinated in the case of the cubic phase and are also neighbored by an Eu atom in the case of the tetragonal phase (see Table 3).

The difference between the formation energies of the cubic and tetragonal phases ($\Delta E_{\text{C-T}}$) of ZrO$_2$ and Zr$_{0.88}$Eu$_{0.12}$O$_{1.94}$ are 0.84 eV and $-0.34$ eV, respectively. These results indicate that the incorporation of Eu into the ZrO$_2$ structure increases the already higher stability of the cubic phase, relative to that of the tetragonal phase. This explains the preferential Eu doping of the cubic phase of the films.

We used a supercell model in which the cubic and tetragonal phases are each assigned 48 atoms, to determine the effect of Eu incorporation into the ZrO$_2$ lattice. The total and projected density of states (DOS) of the atoms and orbitals inside the gap. Moreover, the effect of Tb and Tm incorporation into the ZrO$_2$ lattice has been also explored, and the total and projected density of states on atoms for doped Tb and Tm, in cubic and respective undoped cubic and undoped tetragonal phases.

The top of the VB and the bottom of the conduction band (CB) are composed mainly of O 2p levels and Zr 4d levels, respectively. Furthermore, $E_g$ values of 3.21 eV and 3.83 eV were calculated for the respective undoped cubic and undoped tetragonal phases. These values are both lower than their experimentally determined counterparts. However, compared to the former (3.21 eV), the latter (3.83 eV) is closer to $E_g$ of the pure ZrO$_2$ (5.21 eV), investigated in this work. A comparison of the electronic structures shown in Figs. 5(b) and 6(b) reveals that Eu doping leads to a systematic decrease in $E_g$ and an increase in the density of electronic states around $E_g$. Moreover, the effect of Tb and Tm incorporation into the ZrO$_2$ lattice has been also explored, and the total and projected density of states on atoms for doped Tb and Tm, in cubic and tetragonal phases, are shown in Fig. S1 of Supplementary Information. Therefore, the theoretical calculations indicate that these states occur in the forbidden zone of energy, owing to the presence of Eu, Tb and Tm transition metals and O vacancies in the ZrO$_2$ lattice.

3.4. PL studies

The optical properties of Eu dopants in various host materials, have been characterized [54–62]. Owing to the hypersensitivity of the $^5D_0 \rightarrow ^7F_2$ transition, Eu ions can be used to monitor morphological changes in the host material, which are induced by external stimuli [63–66].

Fig. 7 shows the PL spectra of both the undoped and co-doped ZrO$_2$. The band in the emission spectrum of undoped ZrO$_2$ ranges from 376 nm to 648 nm with a peak centered at 460 nm, as shown in Fig. 7. This is attributed to the $(O^{2-}) p \rightarrow d (Zr^{4+})$-type transition [53], which results from a sequence of non-radiative relaxations of localized electrons in the CB; this is followed by band recombination within the band gap, and subsequent decrease in energy of the electrons when they move to the VB [67]. Factors such as the particle size and morphology, crystallinity, and the method of synthesis [68,69] may influence the photoluminescent properties of the zirconia.

The PL spectra of ZrO$_2$:RE (RE = Tm$^{3+}$, Tb$^{3+}$, and Eu$^{3+}$) powders exhibit characteristics of each dopant-ion emission. For example, in the case of excitation at 350 nm, the emission peak at 477 nm is attributed to Tm$^{3+}$, which is associated with the $^4I_{11/2} \rightarrow ^4I_{5/2}$ transition [70,71]. The $^2D_4 \rightarrow ^7F_6$ and $^2D_4 \rightarrow ^7F_5$ transitions occur at wavelengths of 496.02 nm and 548.32 nm, respectively, and are associated with the emission of Tb$^{3+}$ [72,73]. In addition, the Eu$^{3+}$, $^5D_0 \rightarrow ^7F_6$, and $^5D_0 \rightarrow ^7F_7$ transitions occur at respective wavelengths of 597.16 nm and 617.54 nm [74,75]. The interference of the host has a more significant effect on the photoluminescent behavior of ZrO$_2$:RE than on the behavior of ZrO$_2$. This effect is manifested as the occurrence of a broad band at wavelengths ranging from 380 nm to 480 nm, and results from the structural defects in ZrO$_2$. The order-disorder effects in the coordination of some Zr and doped atoms, verified by theoretical calculations, can result in the production of new levels between the valence and the conduction bands, which favor the PL emission properties. As Fig. 7(c) shows, the emission intensity of the Eu$^{3+}$ ions increases with increasing...
concentration of Eu$^{3+}$, reaches a maximum at 4 mol.% RE, and decreases thereafter (owing to the quenching effect) [76]. The critical quenching concentration of Eu$^{3+}$ is defined as the concentration at which the emission intensity begins to decrease. Similarly, the critical distance, corresponding to the critical quenching concentration, is defined as the average distance between the nearest Eu$^{3+}$ ions, at which energy transfer processes occur.

### Table 3
Distances in Å for the coordination polyhedra for doped ZrO$_2$ with Eu$^{3+}$ for the cubic and tetragonal phases.

<table>
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3.5. Energy transfer in ZrO$_2$:RE ($RE = \text{Tm}^{3+}, \text{ Tb}^{3+}, \text{ and Eu}^{3+}$) powders

A schematic energy level diagram illustrating Tm$^{3+}$, Tb$^{3+}$, and Eu$^{3+}$ absorption, non-radiative relaxation, and processes leading to blue, green, and red emissions is shown in Fig. 8. The energy level $^5D_4$ of Tb$^{3+}$ is very close to the energy level of Tm$^{3+}$ $^1G_4$ as seen in the energy diagram (Fig. 8). This setting energy levels contributes to efficient energy transfer process (ET1) between Tm$^{3+}$ ions and Tb$^{3+}$ [77]. The $^1G_4$ level of Tm$^{3+}$ is completely filled by the charge carriers (electrons) from the excitation process ($\lambda = 350$ nm). The increased concentration of Tm$^{3+}$ promotes the increase of the intensity of the transition $^1G_4 \rightarrow ^3H_6$, this increased intensity of Tm$^{3+}$ also acts as a source for transporting energy for the sublevel $^5D_4$ of Tb$^{3+}$, this effect is realized by increasing the intensity of transition $^5D_4 \rightarrow ^7F_5$ (550 nm) Tb$^{3+}$, shown in Fig. 7.

The Energy transfer (ET2) between Tb$^{3+}$ and Eu$^{3+}$ has been extensively studied, in order to understand the photoluminescent behavior [78]. In fact, the luminescence intensities of various rare-earth ions can be enhanced or quenched by the energy transfer.

Fig. 5. Total and projected density of states on atoms and orbitals for the pure (a) and doped cubic phase (b).

from other co-doped rare-earth ions [79–81]. ET2 between Tb$^{3+}$ and Eu$^{3+}$ may occur in hosts, such as tungstates, zeolite-Y, ytttria, porous silicon, borate, hydrate, and molybdates [82–85]. The probability of this transfer is proportional to $R^{-6}$ ($R$: average distance between Tb$^{3+}$ and Eu$^{3+}$), and hence the efficiency of the ET2 process increases gradually with increasing Eu$^{3+}$-doping concentration. Furthermore, $R$ decreases with increasing Eu$^{3+}$ concentration and therefore, the energy transfer efficiency of Tb$^{3+}$ → Eu$^{3+}$ increases. Owing to the quenching effect, this behavior is not unique to the ZrO$_2$:8% RE, as shown in Fig. 7(c).

An analysis of the results depicted in Fig. 8 renders that electrons on Tb$^{3+}$ ions are promoted from the ground state (4f$^8$) to the excited state (4f$^7$5d), by 350.7-nm UV light. These electrons then relax to the lowest excited state $^5$D$_4$, by means of a multi-phonon
relaxation process. The electrons may return to the ground state, thereby resulting in Tb$^{3+}$ emissions ($^5D_4 \rightarrow ^7F_{0,5,4}$). Alternatively, their excitation energy may be transferred from the $^5D_4$ ($Tb^{3+}$) level to the higher excited energy levels of $Eu^{3+}$ ($4f^6$) through cross relaxation; these levels then relax to the $^5D_0$ ($Eu^{3+}$) level, thereby resulting in red-orange emissions ($^5D_0$/$^7F_{6,5}$). The emissions are characterized by the colors emitted from each sample. This characteristic is defined by chromaticity coordinates $x$ and $y$.

Table 4 lists the CIE coordinate values and CCT values for samples in this study. The white light emission obtained, resulting from the simultaneous blue, green, and red emission of the $Tm^{3+}$, $Tb^{3+}$, and $Eu^{3+}$ ions. It is observed in Fig. 7, for the sample $ZrO_2$: 8% RE, the photoluminescent behavior of $ZrO_2$ host was very significant. The presence of oxygen vacancies ($V_O$) in the matrix is responsible for the emergence of broad-band emission at around 450 nm [86]. 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) [87]. 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. The band of blue emission from the $ZrO_2$ contributes along with the specific emission of rare earth on white emission as shown in Fig. 8. A single-composition white-emitting phosphor is therefore obtained. In fact, this white emission occurs independent of the excitation, depends on the doping concentration of the rare-earth ions, and is obtained by blending the aforementioned simultaneous emissions. The emissions are characterized by the colors emitted from each sample. This characteristic is defined by CIE chromaticity coordinates $x$ and $y$.

4. Conclusions

$ZrO_2$:RE powders were successfully obtained via complex polymerization. The phase (i.e., tetragonal) comprising the $ZrO_2$:RE (x = 1, 2, and 4 mol%) samples was identified via XRD analysis, whereas the cubic phase, stabilized in $ZrO_2$:8%RE, was identified via Raman spectroscopy. The structural and electronic effects, resulting from Eu in both the cubic and tetragonal $ZrO_2$:Eu$^{3+}$ phases, were explained by calculating (using DFT) the relevant energies. The photoluminescence emission spectra reveal transitions of the type: $^1G_4 \rightarrow ^3H_6$ (477 nm), $^3D_4 \rightarrow ^7F_{4,5,6}$ (496.02 nm and 548.32 nm), and $^3D_0 \rightarrow ^7F_{1,2}$ (597.16 nm and 617.54 nm) from $Tm^{3+}$, $Tb^{3+}$, and $Eu^{3+}$, respectively. An inter-level energy transfer, $^5D_4$ ($Tb^{3+}$) $\rightarrow ^7F_1$ (Eu$^{3+}$), also occurred. In addition, according to the CIE diagram, the CIE coordinates (x: 0.34 and y: 0.34) calculated for $ZrO_2$: 8%RE, correspond to a point that lies in the white region. The results of this work suggest that these materials have significant potential for use in the field of light-emitting diodes.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jallcom.2016.11.341.

References


