Structural properties and visible emission of Eu$^{3+}$-activated SiO$_2$–ZnO–TiO$_2$ powders prepared by a soft chemical process

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ABSTRACT

In this work, the structural and optical properties of the 60SiO$_2$–20ZnO–20TiO$_2$ system (in mol%) doped with 1 mol% of Eu$^{3+}$ were evaluated. Stable and transparent sols, homogeneous gels, and powders were prepared by a soft chemical process followed by annealing from 700 to 1100 °C. Visible emission was observed in the photoluminescence (PL) spectra from 570 to 700 nm owing to the Eu$^{3+}$ ions, with the most intense emission peaks at 614 and 590 nm related to the $^5$D$_0$ $\rightarrow$ $^7$F$_2$ and $^5$D$_0$ $\rightarrow$ $^7$F$_1$ transitions, corresponding to red (R) and orange (O) colors, respectively. The R/O intensity ratios between 3.16 and 3.73 were observed and correlated to the structural properties of the host. X-ray diffraction patterns indicated that the reduction of PL at 614 nm and changes in the R/O values were due to the crystallization process. In addition, the FTIR spectra showed a gradual decrease of the hydroxyl absorption bands around 3436 and 1640 cm$^{-1}$ and an increase of the bands related to Ti–O–Ti and Si–O–Si linkages, indicating polymerization and densification process of the host was achieved above 700 °C. Moreover, increasing the annealing temperature resulted in the formation of ZnTiO$_3$ and Zn$_2$TiO$_4$ crystalline phases, as well as rutile TiO$_2$. Finally, intensity parameters ($\Omega_2$), and quantum efficiency were calculated by applying Judd–Ofelt theory to Eu$^{3+}$ ions, which showed that the Eu$^{3+}$-doped samples can be used in displays and LEDs.

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1. Introduction

Lanthanide ion (Ln$^{3+}$)-doped inorganic luminescent materials have become an important topic of research in nanoscience and nanotechnology [1]. The optical properties of lanthanide ion-doped silicate systems are of great interest for fundamental studies and technological applications in optical devices, such as lasers, fiber amplifiers, and waveguides. Therefore, a detailed understanding of the local structure and bonding of dopant cations is important for optical device engineering [2].

The ZnO–TiO$_2$ binary system is commonly studied and can be obtained using different oxide combinations, synthesis processes, and thermal treatments, and can be doped with transition metal ions to obtain luminescent materials [3,4]. In this binary system, various crystalline phases are normally formed, such as Zn$_2$Ti$_3$O$_8$ (zinc metatitanate), and Zn$_3$Ti$_2$O$_4$ (zinc orthotitanate). As shown in chemical Equations (1) and (2), Zn$_2$Ti$_3$O$_8$ is metastable and forms at low temperatures ($<$820 °C), whereas between 820 and 950 °C, unstable ZnTiO$_3$ and TiO$_2$ (rutile TiO$_2$) are formed. However, the unstable ZnTiO$_3$ phase decomposes into stable Zn$_2$TiO$_4$ and TiO$_2$ phases around 950 °C. The stable Zn$_2$TiO$_4$ crystalline structure is highly energetically favorable and can be easily obtained by solid-state [5], which requires high temperatures to form the desired phases, and normally generates inhomogeneous and large particle sizes.

ZnTiO$_3$ and Zn$_2$TiO$_4$ have been doped with transition metals and their luminescent properties have been studied [3,4]. The crystal structure of these compounds can have two types of defects, and the dopant ions can be included in interstitial or substitutional sites. In particular, ZnTiO$_3$ shows photoluminescence at room
stoichiometry, caused by either excess metal (Zn1
2ZnTiO3
non-toxic sols to produce high quality thin
homogeneous thin
films of complex materials. On the other hand, if
a chemical method is used, it is interesting to use very stable and
non-toxic sols to produce high quality thin films by dip-coating or
spin-coating techniques.

The SiO2–ZnO–TiO2 ternary system choice was based on the
properties of crystalline phases and glasses mentioned above and its
technological applications. In this study, the synthesis of the
ternary system 60SiO2–20ZnO–20TiO2 (in mol%) doped with 1 mol % of Eu3+
was achieved using a mixed methodology (sol-gel process and Pechini method). This method is low cost, does not require
atmosphere control, and uses low annealing temperatures to obtain
powders. In addition, the structural properties and PL emission
spectra were determined as a function of heat-treatment to eval-
uate the use of these systems as phosphors in displays, and the Eu3+
quantum efficiency and Judd–Ofelt parameters were determined.
Here, we present only the results for the selected composition (60SiO2–20ZnO–20TiO2) as a function of heat-treatment, which shows the most interesting optical and structural features con-
cerning optical devices application.

2. Experimental procedures

Sols, gels, and powders of 60SiO2–20ZnO–20TiO2 (in mol%) doped with 1% mol of Eu3+ were prepared. A soft chemical process
combining sol-gel and polymeric precursor methodologies was
developed to obtain stable and transparent sols. The mixed meth-
odology was based on those used for SiO2–ZnO and SiO2–TiO2
binary systems in the literature [9,17].

The molar ratio between citric acid (CA), acting as a chelating
agent, and ethylene glycol (EC), acting as a polymerizing agent, was
3:2. The same molar ratio between metal citrates and EC was
proposed by Pechini [18] for polyesterification reactions. The molar ratio
between CA and the metal cations (MC) was 3:1. In accordance
with Neves et al. [19], this molar ratio allows the formation of stable
metallic citrate. The tetraethyl orthosilicate (TEOS) was used as
silica precursor. Thus, the molar ratio of CA:EG:TEOS:MC in solution
was 3:2:1:1. The synthesis of the sols was achieved using titanium
citrate formed by dissolving titanium(IV) isopropoxide (Ti(OC3H7)4)
Fluka, >97.0% purity) in a solution of CA (C5H7O8, Chemycalis, 95.0% pu-
urity) at 30 °C for 5 min. After homogenization of the solution,
europium nitrate pentahydrate (Eu(NO3)3·5H2O, Aldrich, 99.9% purity)
and zinc nitrate hexahydrate (Zn(NO3)2·6H2O, Vetec, 98.0% purity)
were added, and then TEOS (Si(OC2H5)4, Merck, >98.0% purity)
was added to form Zn–Eu–Ti–citrates. After further homo-
genization (10 min), EG (C2H5OH)3, Merck, >99.5% purity) was added
to the metal citrate solution. The gels were obtained by
drying the sols at 60 °C over 5 days. Then, the gels were subjected to
a heat treatment from 100 to 1100 °C at a heating rate of 5 °C/min
heating rate without a holding time to obtain powders for evalu-
ation of the crystallization process.

The optical transmittance and absorbance spectra of the sols
were measured using an UV/Vis/NIR spectrophotometer (Perki-
nElmer WB1050) from 350 to 750 nm using quartz cuvette as
sample holder and air as reference.

The sample weight losses over the temperature range of
30–950 °C were determined by thermogravimetric analysis (TG) in
a thermobalance (Shimadzu, model DTG-60H) under a continuous
flow of synthetic air (50 ml/min) with a heating rate of 10 °C/min,
using samples of about 23 mg.

Fourier-transform infrared (FTIR) spectra were recorded in
transmission mode on a PerkinElmer spectrometer (model Spec-
trum 400 FTIR) in the 400–4000 cm−1 range using the standard
KBr pellet technique. The spectra were obtained out with a reso-
lution of 4 cm−1 and a typical normalization procedure was applied.

Unpolarized Raman spectra were collected between 200 and
1200 cm−1 at room temperature with a micro-Raman spectrometer
(Horiba/Jobin Yvon, HR8000) using the backscattering geometry. The
powdered samples were excited using a He–Ne laser at 632.8 nm.

X-ray diffraction (XRD) patterns were collected with a Shimadzu
diffractometer (model XRD 6000) operating at 40 kV and 30 mA with Cu Kα radiation (λ = 1.54056 Å). The XRD data were obtained between 10° and 80° (2θ) using a scan rate of 2°/min and an increment of 0.02°.

High-resolution transmission electron microscopy (HR-TEM) images were acquired using a JEOL microscope (model JEM-2100) operating at 200 keV. The program used for the acquisition of planar distances was Gatan Digital Micrograph.

PL excitation and emission spectra of the powders were measured using a Horiba/Jobin Yvon spectrophotometer (Fluorolog-3 model FL3-221) with fixed slits for 1.0 nm-resolution, a 450 W Xe arc lamp was used as excitation source, and detection was carried out using a Hamamatsu photomultiplier tube. The excitation spectra of samples from 350 nm to 595 nm were collected monitoring emissions at 614 nm, and the emissions spectra between 500 and 750 nm were collected under excitation at 394 nm, in front face mode. Eu³⁺ 5D0 decay times were obtained with a pulsed Xe arc lamp (3 µs bandwidth). The PL emission was corrected for the spectral response of the monochromators and the detector using the typical correction spectrum provided by the manufacturer. All measurements for the samples were carried out at room temperature.

3. Results and discussions

3.1. Thermal and structural properties

In Fig. 1(a) shows digital photos of the sol as prepared, the dried gel at room temperature, and dried gels and powders heat-treated between 100 °C and 1100 °C. The sol is well transparent between 400 and 750 nm (>71% at 400 nm) with low absorbance (<0.15 at 400 nm), as we can see from transmittance and absorbance spectra in Fig. 1(b). The high absorbance from 350 nm to 400 nm is due to metal-ligand charge-transfer bands and absorptions of organic species. Note that, white color powders could be obtained after heat-treatments from 700 °C to 1100 °C.

Fig. 2 illustrate the TG/DTG curve for the dried gel of 60SiO₂ – 20ZnO – 20TiO₂ gels dried at 60 °C. The second weight loss stage occurs in the temperature range between 160 and 500 °C (Fig. 2) and can be attributed to the elimination of organic matter and carboxyl groups bonded to ions, corresponding to a weight loss of approximately 70%. In the FTIR spectra (Fig. 3), for powders annealed between 200 and 500 °C, a complete disappearance of the bands at 1736 cm⁻¹ related to the C=O stretching mode of free CA, suggesting that some of the CA is eliminated in this temperature range [20].

Above 700 °C, a gradual decrease of the hydroxyl absorption on the powder surface. The FTIR spectra obtained in the temperature range of 100–200 °C shows a decrease in the intensity of the band at 1736 cm⁻¹ related to the C=O stretching mode of free CA, suggesting that some of the CA is eliminated in this temperature range [20].

Fig. 1. (a) Digital photos of the sol as prepared, the dried gel at room temperature, and the materials (dried gels and powders) heat-treated between 100 °C and 1100 °C. (b) Transmittance and absorbance spectra of the sol.
bands around 3436 cm\(^{-1}\) is observed in the FTIR spectra (Fig. 3), and another pattern is detected in the 800–400 cm\(^{-1}\) region corresponding to the absorption bands of Zn–O (450 and 610 cm\(^{-1}\)), Ti–O (462 and 526 cm\(^{-1}\)), Ti–O of TiO\(_6\) (580 cm\(^{-1}\)), and Si–O–Ti (900–1000 cm\(^{-1}\)). At the same temperature, the Raman spectra (Fig. 4) show peaks at 410, 740, and 950 cm\(^{-1}\), suggesting the formation of the ZnTiO\(_3\) structure [22,23], which is confirmed by the XRD patterns presented below. After annealing at 800 °C, the sample showed FTIR absorption bands at 460, 610, 660, and 780 cm\(^{-1}\), which are related to M–O stretching (where M = metal), which is characteristic of spinel-type structures. These observations are in agreement with the XRD diffraction patterns and Raman spectra reported by Chaves et al. [3].

Finally, a decrease in the intensity associated with Si–O–Ti (900–1000 cm\(^{-1}\)) and an increase in the absorption of new linkages, such as Si–O–Si (800 and 1200–1200 cm\(^{-1}\)) and Ti–O–Ti (500–600 cm\(^{-1}\)) are observed in the FTIR spectra (Fig. 3). The Raman spectra for powders heat-treated above 900 °C (Fig. 4) show a structural change, is associated with the beginning of the crystallization of the Zn\(_2\)TiO\(_4\) phase and segregation of TiO\(_2\) as the rutile phase. Such crystallization leads to titanium oxide segregation, as reported by Gunji et al. [24], and will be well discussed below with the XRD results.

The XRD patterns of the powders annealed from 700 to 1100 °C are presented in Fig. 5. At 700 °C, the powder is completely amorphous, whereas the XRD pattern of the powder heat-treated at 800 °C shows peaks characteristic of zinc metatitanate (ZnTiO\(_3\), JCPDS card N° 39-0190) [25]. In contrast, the diffraction patterns of the powders heat-treated from 900 to 1100 °C show a slight shift of the main peaks at 35.4° the rutile structure (JCPDS card N° 25-1164) [26]. The XRD pattern for the powders heat-treated at 1100 °C reveals a low intensity peak corresponding to an additional phase, the TiO\(_2\) rutile structure (JCPDS card N° 88-1175) [27]. The segregation of this oxide occurs concomitantly with the formation of zinc titanate (Zn\(_2\)TiO\(_4\)). The Raman spectra (Fig. 4) confirms the presence of the TiO\(_2\) rutile phase in the powder heat-treated at 900 °C or higher.

Both zinc titanate phases have numerous similarities in their crystallographic cards; however, the phases obtained are consistent with those reported in the literature for the ZnO–TiO\(_2\) binary system [28,29]. In this system, the Zn\(_2\)TiO\(_4\) phase decomposes to ZnTiO\(_3\) and TiO\(_2\) rutile phases at temperatures below 820 °C, but at temperatures higher than 950 °C, the ZnTiO\(_3\) phase transforms into Zn\(_2\)TiO\(_4\) and TiO\(_2\) rutile phases. The main peak of the TiO\(_2\) rutile phase had a very low intensity, and was not easily observed in the diffractograms collected at 2.0°/min (inset, Fig. 5), the main diffraction peak of the TiO\(_2\) rutile phase at 27.6° was clearly observed, confirming the assignment of the phases in the Raman spectra in Fig. 4. The powders had crystallite sizes of 9.0 and 19.0 nm at 900 and 1100 °C, respectively.

TEM images show that the sample does not have crystalline structures at 700 °C. The material remained amorphous up to a temperature of 800 °C, where crystallization began and spherical nanoparticles with an average size of 5.4 ± 0.1 nm were observed (Fig. 5(a)). At a temperature of 900 °C, spherical nanoparticles were
observed to be dispersed in an amorphous medium (Fig. 6(b)), with an interatomic distance of \(2.54 \pm 0.05\) Å, which corresponds to the (311) plane of ZnTiO\(_3\) [24]. Planar distances of \(3.14 \pm 0.04\) Å (Fig. 6(c)) and \(3.39 \pm 0.05\) Å (Fig. 6(d)) were measured for the powders heat treated at 1000 and 1100 °C, which are similar to that expected for the (220) plane of the Zn\(_2\)TiO\(_4\) phase and the (110) plane of the TiO\(_2\) rutile phase, respectively [25,26]. These images corroborate the data obtained by XRD. Fig. 6(e) shows a statistical histogram of the narrow size distribution of the nanoparticles in Fig. 6(a).

The zinc titanate compounds obtained here are consistent with those observed by Chang et al. [5]. However, in our work, the crystallization of Zn\(_2\)Ti\(_3\)O\(_8\), as proposed by Yang and Swisher [30] and Kim et al. [31], was not observed, probably due to modification of the phase formation kinetics by the used chemical process.

Many reports on the synthesis of binary ZnO–TiO\(_2\) indicate that different compounds can be formed simultaneously [4,32]. Hou et al. [22] used the sol-gel process to prepare compounds with a 1:1 mol ratio of ZnO and TiO\(_2\), and obtained a mixture of crystalline phases from 800 to 1000 °C, as elucidated by XRD. However, in these systems, crystalline compounds were already observed around 500 °C, whereas the silica present in our ternary system increases the crystallization temperature. Gunji et al. [24] reported that silica retarded titanium oxide segregation in a SiO\(_2\)–TiO\(_2\) binary system. On the other hand, Aubert et al. [33] reported the formation of ZnTiO crystallites with an unidentified ratio at temperatures higher than 600 °C, showing that Eu\(^{3+}\) doped thin films showed high red emission when annealed at 800 °C. The various zinc titanate structures have been evaluated by researchers. In 1960, Dulin and Rase [34] proposed a phase diagram for the ZnO–TiO\(_2\) binary system, and recently, Yang and Swisher [30] and Kim et al. [31] have included new structures in the phase diagram, specifically Zn\(_2\)Ti\(_3\)O\(_8\). Our FTIR, Raman, and XRD results showed that despite the presence of SiO\(_2\) led to phase crystallization as indicated in the phase diagram proposed by Kim et al. [31].
3.2. Eu$^{3+}$ ion excitation and emission

Fig. 7(a) shows the excitation spectra from 60SiO$_2$–20ZnO–20TiO$_2$ (mol%) powders doped with 1 mol% of Eu$^{3+}$ heat-treated (H.T.) from 700 °C to 1100 °C. The narrow bands around 362, 382, 394, 413, 464, 533, and 579 nm are attributed to the f-f transitions of the Eu$^{3+}$ 4f$^6$ configuration. These peaks are assigned to the transitions $^7$F$_0$ → $^5$D$_4$ (362 nm), $^7$F$_0$ → $^5$D$_{2,4}$ (382 nm), $^7$F$_0$ → $^5$D$_6$ (394 nm), $^7$F$_0$ → $^5$D$_3$ (414 nm), $^7$F$_0$ → $^5$D$_2$ (464 nm), $^7$F$_0$ → $^5$D$_1$ (533 nm), and $^7$F$_0$ → $^5$D$_0$ (579 nm). For powders H.T. between 700 °C and 900 °C the strongest peak is located at 394 nm, but those ones H.T. at 1000 °C and 1100 °C the strongest peak is centered at 464 nm. In fact, increasing the temperature of heat-treatment, the intensity peak at 464 nm in comparison with that at 394 nm increases, indicating that the Eu$^{3+}$ surroundings have been changed. Another feature is observed for $^7$F$_0$ → $^5$D$_0$ transition, which is not only at 579 nm, but also another narrow and centered at 587 nm for H.T. at 1100 °C; and a broadening is observed for powders H.T. from 700 °C to 1000 °C, probably mainly due to two different microenvironments for Eu$^{3+}$ ions. It is reasonable suppose that the ZnTiO$_3$ and Zn$_2$TiO$_4$ lattices distorts to have enough space for extra oxygen accommodation and this extra oxygen in the lattices could be responsible for another Eu$^{3+}$ transition $^7$F$_0$ → $^5$D$_9$ (at 587 nm). Only 394 nm excitation was chosen to achieve emission spectra due to its dominant intensity in most samples.

Fig. 7(b) shows the emission spectra of Eu$^{3+}$ excited at 394 nm for 60SiO$_2$–20ZnO–20TiO$_2$ as a function of annealing temperature (from 700 to 1100 °C). The observed emissions are due to $^5$D$_0$ → $^7$F$_0$ (578 nm), $^5$D$_2$ → $^7$F$_1$ (591 nm), $^5$D$_0$ → $^7$F$_2$ (614 nm), $^5$D$_0$ → $^7$F$_3$ (652 nm), and $^5$D$_2$ → $^7$F$_4$ (701 nm) transitions, and the dominant emission occurs for the electric dipole allowed transition around 614 nm.

Yaiphaba et al. [1] mention that the splitting levels depend on the (i) intensity of the excitation source; (ii) excitation/emission slit widths; and (iii) crystallinity. At high annealing temperatures (at 900 °C and at 1000 °C), the energy levels do not split, as expected due to the high sample crystallinity, and similarity regarding the distribution of Eu$^{3+}$ ions, which are located in similar regions or sites. On the other hand, although the annealing temperature can result in organization around active ions, defects around the ions can decrease the PL emission. In addition, Eu$^{3+}$ ion segregation can occur to form Eu–O–Eu clusters, which leads to energy transfer between adjacent Eu$^{3+}$ ions, and defects can quench the PL emission [35]. Stark splitting is well observed only for sample H.T. at 1100 °C, related to Eu$^{3+}$ ions located in crystalline sites, also a broad band centered at 440 nm was noted in this sample, probably from defects in the host.

The characteristics of the PL spectra shown in Fig. 7(b) and the crystallographic process are directly related to changes in the R/O values (Table 1). The R/O value is the relation between the emission intensities at 614 and 590 nm due to the (i) intensity of the excitation source; (ii) excitation/emission slit widths; and (iii) crystallinity. At high annealing temperatures (at 900 °C and at 1000 °C), the energy levels do not split, as expected due to the high sample crystallinity, and similarity regarding the distribution of Eu$^{3+}$ ions, which are located in similar regions or sites. On the other hand, although the annealing temperature can result in organization around active ions, defects around the ions can decrease the PL emission. In addition, Eu$^{3+}$ ion segregation can occur to form Eu–O–Eu clusters, which leads to energy transfer between adjacent Eu$^{3+}$ ions, and defects can quench the PL emission [35]. Stark splitting is well observed only for sample H.T. at 1100 °C, related to Eu$^{3+}$ ions located in crystalline sites, also a broad band centered at 440 nm was noted in this sample, probably from defects in the host.

Fig. 8 shows the emission decay profiles of the samples annealed between 700 and 1100 °C. The $^5$D$_0$ decay time was obtained from the profiles with an excitation wavelength of 394 nm and an emission wavelength of 614 nm. As shown in Fig. 8, non single-exponential decays were observed for all of the samples. In this case, the average lifetime can be calculated by Refs. [11,37]:

$$\tau_{avg} = \frac{t_f}{\int_0^{t_f} \frac{I(t)}{I_0} dt.} \tag{3}$$

where $\tau_{avg}$ is the average lifetime, $I(t)$ is the PL intensity at time $t$, $I_0$ is the initial PL intensity at 0 ms, and $t_f$ is the time at which the PL emission becomes zero (~10 ms). The average lifetimes ($\tau_{avg}$) for the samples annealed between 700 and 1100 °C varied from 1.95 to 1.11 ms, as listed in Table 1.

As the decay profiles were not single-exponential curves, all five curves in Fig. 8 could be fitted to the sum of two exponential functions [38]:

<table>
<thead>
<tr>
<th>Heat-treatment (°C)</th>
<th>R/O ratio</th>
<th>Average lifetime ($\tau_{avg}$) (±0.05 ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>3.55</td>
<td>1.99</td>
</tr>
<tr>
<td>800</td>
<td>3.70</td>
<td>1.82</td>
</tr>
<tr>
<td>900</td>
<td>3.73</td>
<td>1.59</td>
</tr>
<tr>
<td>1000</td>
<td>3.27</td>
<td>1.24</td>
</tr>
<tr>
<td>1100</td>
<td>3.16</td>
<td>1.11</td>
</tr>
</tbody>
</table>
This result can be correlated with the differences in the symmetry incorporated in Zn sites of the ZnTiO₃ phase, likely because the ionic radius of Eu³⁺ ions is larger than that of Ti⁴⁺.

Increasing the temperature from 700 °C to 1100 °C causes an increase of the crystalline content and its features are corroborated by XRD patterns presented in Fig. 5, or by the emission spectrum. As this transition does not depend on the local ligand field experienced by Eu³⁺ ions, it can be used as a reference for the entire spectrum [43,44]. The A₀₁ spontaneous decay rate for the S₀D₀ → T₁F₁ transition is A₀₁ = A₀₁,n, where A₀₁ = 14.65 s⁻¹ in vacuum and n is the refractive index of the host material. Then, the intensity of the S₀D₀ → T₁F₀,F₅,F₆ transitions in terms of the area of the emission curves (S₀J) is:

\[ S₀J = h c Α₀₁ N(S₀D₀), \]

where N(S₀D₀) is the S₀D₀ level population that emits. The total radiative decay rate can be written as:

\[ Α₅ = \sum_{J=0}^{6} A₀J \frac{h c Α₀₁}{S₀₁} \sum_{J=0}^{6} \frac{S₀J}{h c Α₀J} \]

The branching ratio for the S₀D₀ → T₁F₀,F₅,F₆ transitions must be neglected owing to its low relative intensity, and the radiative contribution can be calculated using only the S₀D₀ → T₁F₄,F₅,F₆ transitions [44].

The emission quantum efficiency (q) is defined by the experimental and radiative lifetime ratio:

\[ q = \frac{\tauₐ}{\tau_Rad} \]

The site symmetry and luminescence behavior of Eu³⁺ ions in the matrix was carried out by calculating the Judd–Ofelt parameters Ω₃, Ω₄, and Ω₅. In the Judd–Ofelt theory, the intensity parameters Ω₃ are given by:

\[ Ω₃ = \frac{3h}{64π^2c^2n^2} \frac{9}{4} \frac{1}{\left( <S₀D₀|U^{(i)}|T₁F₄,F₅,F₆> \right)} A₀J \]

The values for the reduced matrix elements are 0.0032 for λ = J = 2 and 0.0023 for λ = J = 4. Table 3 lists the determined A₀₁, A₀₂, A₀₄, A₀₅, τ_Rad, q(%), Ω₂, and Ω₄ values. For comparison, the
emission quantum efficiency was calculated using the $\tau_{\text{avg}}$ values. In this calculation, we used the refractive index ($n$) previously determined for thin films with the same composition and heat-treatment. The dependence of the radiative lifetime on the heat-treatment originates from the radiation field polarization of the medium and the photon density change in an optically dense medium. In fact, the refractive index varies due to the formation of crystalline phases [45]. The oscillator strength of the electric dipole transition for Eu$^{3+}$ should increase from 700 to 1000 °C, and due to this, the $5^D_0$ radiative lifetime of Eu$^{3+}$ decreases or the radiative transition rates are higher, as seen in Table 3. In this way, the quantum efficiency ($q$) of the $5^D_0 \rightarrow 5^F_2$ transition is higher for samples heated at 700 °C (55%), but slightly reduced by increasing the heat-treatment to 900 °C (51%), taking into account $\tau_{\text{avg}}$. Taking into account the two experimental lifetimes obtained at 900 °C by fitting the decay curve to a bi-exponential function, $q$ values of 56% and 23% are obtained for $\tau_1$ and $\tau_2$, respectively. This result indicates that a high portion of Eu$^{3+}$ ions is located in a protected site that is not well coupled to hydroxyl groups or defects. The polarization and asymmetry behavior of rare-earth ligands are determined by the $Q_2$ parameter, whereas $Q_4$ depends on long-range effects [46]. The higher $Q_2$ value for Eu$^{3+}$ ions in samples heated at 900 °C indicates a highly asymmetric nature, which is corroborated by the R/O ratio of 3.73, which is probably related to the formation of a single ZnTiO$_3$ phase. The low $Q_4$ value implies that $5^D_0 \rightarrow 5^F_2$ transition efficiency increases, and this transition accounts for the majority of Eu$^{3+}$ emission, resulting in this material having almost pure red emission.

4. Conclusions

Homogeneous and transparent solutions of 60SiO$_2$–20ZrO$_2$–20TiO$_2$ doped with 1 mol% of Eu$^{3+}$ were prepared by a mixed methodology consisting of a sol-gel process and a polymeric precursor method. The structural evolution of the gels and powders were evaluated, with effective removal of organic compounds at annealing temperatures between 600 and 700 °C, and the residual hydroxyl groups removed at higher annealing temperatures, especially 1100 °C. The crystalline phases obtained depending on the annealing temperature, with zinc tinate (Zn$_2$TiO$_4$) as the major phase as high temperatures. However, at 800 °C only ZnTiO$_3$ is formed. At 900 °C, the largest R/O ratio was obtained as a consequence of the low symmetry around Eu$^{3+}$ ions in the crystallized ZnTiO$_3$ phase. Moreover, this sample had good quantum efficiency (55% and 23% for $\tau_1$ and $\tau_2$ or 51% for $\tau_{\text{avg}}$). Eu$^{3+}$ ions in the 60SiO$_2$–20ZnO–20TiO$_2$ host system have a high $Q_2$ value, revealing their highly asymmetric nature, which depends on the annealing temperature and the crystalline phases. Finally, interesting structural characteristics and optical emission were obtained for Eu$^{3+}$-doped samples with potential application in displays as nanostructured red emitters.

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