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Photoluminescent ZrO$_2$:Tb$^{3+}$ thin films synthesized by USP technique using a metal-organic precursor

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Abstract

Photoluminescent ZrO$_2$ and ZrO$_2$:Tb$^{3+}$ thin films were synthesized from metal-organic precursor, zirconium acetylacetonate [Zr(C$_5$H$_7$O$_2$)$_4$], using Ultrasonic Spray Pyrolysis method. These thin films were deposited on Corning glass substrates at several deposition temperatures. ZrO$_2$ and ZrO$_2$:Tb$^{3+}$ (X a/o) films were characterized by x-ray diffraction to identify the crystalline structure; results showed tetragonal phase of zirconia; with a crystalline size of approximately 4 nm according to Scherrer’s formula. Also, SEM micrographs revealed that surface morphology of these films is very flat. Chemical composition microanalysis showed presence of oxygen and zirconium as major species. Analysis by Infrared spectroscopy demonstrates that 900 and 760 nm bands correspond to presence of ZrO$_2$. In addition, these films showed optical transmittances from 75 to 98 % in the visible range. Photoluminescent features varied as a function of excitation wavelength; when excited at $\lambda_{ex} = 286$ nm strong green emission is observed, which is associated to electronic transitions $^5D_4 \rightarrow ^7F_n$ (n = 6, 5, 4, 3) corresponding to Tb$^{3+}$ ions. Excitation with $\lambda_{ex} = 336$ nm exhibits spectra with simultaneous emissions from host lattice and Tb$^{3+}$ ions; here, observed color was blue-green.

1. Introduction

Chemical Vapor Deposition (CVD) includes a set of material synthesis techniques. One of these techniques is Ultrasonic Spray Pyrolysis (USP) which was introduced in the 1960’s by Chamberlin and Skarman for manufacturing solar cells [1]. In this technique an aerosol is generated (by ultrasound) from a precursor liquid solution. This aerosol is directed towards a hot substrate where pyrolysis is carried out to produce a solid film [2]. This synthesis process is applied to develop high-performance luminescent devices [3–7], such as solid-state lighting, new generation television screens, high-powered laser mirrors, as well as in manufacture of portable energy devices and interference filters [5, 8, 9]. Among other parameters, properties of thin films depend on nature of precursor solution, so it is necessary to take into account the characteristics of reagent precursors and their effects on quality of deposited films [10–13]. Furthermore, USP technique represents a viable alternative compared to other deposition techniques, due to its simplicity of operation, low cost, relatively simple equipment, and because it is possible to deposit thin films from metal-organic and inorganic reagents [2, 14, 15]. It has been possible to obtain various metallic oxides with this technique, including zirconium oxide (ZrO$_2$) [16], which has been extensively researched for its multiple inherent properties, such as its high refractive index (~2.17), biocompatibility, high mechanical resistance, thermal and corrosion properties as well as its chemical
and photochemical stability. Bandgap of this oxide is 5.22 eV (indirect band) and 5.87 eV (direct band), these properties make it a suitable material for optical applications [3, 8, 17]. ZrO₂ in thin film form is a versatile material and plays an important role in industrial development. One advantage of this material is that its properties can be modified according to immediate industrial applications [18]. These thin films have applications in antireflective coatings, transparent electrodes, solar cells, gas sensors, varistors, surface acoustics waves devices, and photoluminescent devices. Besides, different deposition conditions produce thin films with dense, packaged, and soft structures for optical applications or very porous films for use in sensors, catalysis and electrocatalysis [19]. Additionally, ZrO₂ has a polymorphic crystalline structure (monoclinic, tetragonal and cubic) with vacancies and interstitial spaces, which allows donor elements to be admitted as active impurities, whether divalent or trivalent, which is the reason it is considered as an optimal host lattice to generate luminescence [3, 4, 20, 21]. These active donor elements, mainly rare earth ions, become crystal structure stabilizers and luminescent activators, favoring light emission in visible range of electromagnetic spectrum. For example, Terbium ion (Tb³⁺) produces a green emission when exposed to UV light and can, therefore, be used in aforementioned applications as a primary color [22–24]. It is important to highlight that in other works synthesis of ZrO₂ has been obtained through different techniques, using metalorganic precursor zirconium acetylacetonate Zr(C₅H₇O₂)₄ among other precursor elements [25–27]. Also, incorporation of rare earth ions, such as Tb³⁺ ions, was facilitated because they are known as a good green light emitter for technological applications that make it essential in composition of optically active devices [28, 29]. There are numerous investigations in the literature that study the properties of ZrO₂: Tb (nanocrystals and films). These materials have been synthesized with various techniques and oriented to several applications. Some of them have been macroporous for drugs release and photonic devices [30]; others for mammary cancer imaging in mice [31]. Transparent ceramics applicable in luminescent thermometry have also been reported [32]. Luminescent and transparent films in visible range have been deposited by Sol-Gel technique [33, 34]. Films with good luminescent properties have been deposited by Spray Pyrolysis from inorganic reagents (metal chlorides) [35, 36]; but its transmittance (in the visible region) and surface roughness are not suitable for applications such as multilayer devices. Preliminary results on ZrO₂: Tb films have recently been exhibited; these films were deposited from metalorganic reagents (acetylacetonates) [37].

In this work, use of a metalorganic agent Zr(C₅H₇O₂)₄ is proposed in such a way that transparent (in visible range of electromagnetic spectrum) thin films can be obtained; additionally, this type of precursor generates films with non-rough and very flat surfaces. These two characteristics are essential in films that are incorporated into multilayer electroluminescent devices such as MISIM (Metal-Insulator-Semiconductor-Insulator-Metal) type. Therefore, this research focused on synthesizing ZrO₂(Tb³⁺) thin films with good luminescent properties and with the features mentioned above.

2. Experimental development

This research was developed employing USP technique for ZrO₂ and ZrO₂(Tb³⁺) thin films deposition; using Corning 7059 glass substrates with dimensions of 1 × 1 cm. Samples underwent a cleaning process with water, industrial soap, and ultrasonic bath, and were then subsequently immersed in an isopropyl alcohol bath (C₃H₇OH). The precursor agent, Zr(C₅H₇O₂)₄ with 3, 5 and 7 M (Molarities) was used, which was dissolved in a mixture of methyl alcohol (CH₃OH) and dimethylformamide [HCON(CH₃)₂] in a 4:1 ratio, with constant agitation until reaching total dissolution. Regarding precursor mass, Tb³⁺ dopant ions were incorporated as TbCl₃·6H₂O, ranging from 1 a/o (atomic percent) to 15 a/o with 2 a/o increments. USP system mainly has a nebulizer with an ultrasonic frequency of 0.8 MHz. Precursor solution was then transformed into an aerosol and transported (using dry air as carrier gas with flow set at 10 liters/minute) towards a heating system where substrates were suspended on a bath liquid tin. Deposition substrate temperatures were: 300 °C–550 °C with increments of 50 °C. It is important to mention that film deposition was not observed at 600 °C, since at this temperature the aerosol evaporates almost completely without reaching the substrate. Deposition procedure starts placing clean substrates on heating system for 1 min before deposition. Aerosol is directed and applied onto surface of hot substrate for 25 min, providing thermal treatment to the substrate for 1 min at the end of process, to obtain thin films with good adhesion with substrate. Crystallographic analysis (XRD) was carried out by a Rigaku diffractometer Grazing Incidence x-ray (GIXRD) with radiation Kα Cu = 1.540 56 Å. Surface morphology was analyzed by means of a scanning electron microscopy (SEM), Leica Cambridge Electron Microscope Stereoscan 440, operating at 18 kV voltage. Chemical composition microanalysis was carried out with a Dispersive Energy Spectroscopy (EDS) detector, connected to same microscope. For infrared analysis, an FT-IR Spectrometer Spectrum 100 Perkin Elmer was used; while for optical transmittance, an Ocean Optics DH-200–BAL USB4000–XR1–ES spectrometer was employed. Photoluminescence (PL) measurements were recorded using a Jobin-Yvon Spectrofluorimeter. All characterizations were performed at room temperature.
3. Analysis of results

In a previous analysis [37], it was observed that films with best characteristics were those deposited at 450 °C, with 5 M (molarity) and doped with 5 a/o of Tb$^{3+}$ ions, when excited with $\lambda_{ex} = 336$ nm. In the present research, best results are obtained in samples deposited at 450 °C, with molarity $= 5$ M, doping concentration $= 7$ a/o and excited with $\lambda_{ex} = 286$ nm.

Figure 1 exhibits x-ray diffraction patterns for films deposited considering different deposition parameters. This characterization was performed on three samples deposited at 450 °C, considering: a) ZrO$_2$: Tb$^{3+}$($5$ a/o, $5$ M), b) ZrO$_2$: Tb$^{3+}$($7$ a/o, $7$ M), and c) undoped ZrO$_2$, $5$ M. Tetragonal crystalline structure for ZrO$_2$ appears in all cases in according to standard PDF-96-153-9832.

![Figure 1: Diffractograms of films deposited at 450 °C: (a) ZrO$_2$: Tb$^{3+}$ ($5$ a/o, $5$ M), (b) ZrO$_2$: Tb$^{3+}$ ($7$ a/o, $7$ M), (c) undoped ZrO$_2$, $5$ M. Tetragonal crystalline structure for ZrO$_2$ appears in all cases in according to standard PDF-96-153-9832.](image1)

Figure 2 shows diffractogram used to estimate, by Scherrer formula (equation (1)) [23], crystallites size using crystallographic plane (101) because it is most intense. The value obtained for average crystallite size was approximately 4 nm.

![Figure 2: Diffractogram of ZrO$_2$: Tb$^{3+}$ ($7$ a/o, $5$ M) thin films deposited at 450 °C, for to estimate the average crystal size, by using Scherrer formula. The estimated value for this sample was 4 nm.](image2)
where \( D \) is crystallites average size, \( K = 0.9 \), \( \lambda = 1.5406 \) Å, \( B \) is width in maximum half (FWHM) of peak and \( \theta \) is Bragg’s angle.

Figure 3 displays SEM micrographs for (a) ZrO\(_2\) and (b) ZrO\(_2\):Tb\(^{3+}\) (7 a/o) thin films deposited at 450 °C; molarity was 5 M. Very flat surfaces are observed.

Table 1. Chemical composition microanalysis, by EDS, of ZrO\(_2\) and ZrO\(_2\):Tb\(^{3+}\) (7 a/o, 5 M) thin films.

| Element | ZAF Weight (%) | Atom (%) | Compound (%) |
|---------|----------------|----------|--------------|
|         | ZrO\(_2\) | ZrO\(_2\):Tb\(^{3+}\) | ZrO\(_2\) | ZrO\(_2\):Tb\(^{3+}\) | ZrO\(_2\) | ZrO\(_2\):Tb\(^{3+}\) |
| O       | 1.355 | 1.290 | 33.13 | 30.68 | 73.85 | 72.82 | 33.13 | 30.68 |
| Zr      | 1.188 | 1.176 | 66.87 | 59.83 | 26.15 | 24.91 | 66.87 | 59.83 |
| Tb      | 1.490 |       | 9.49  |       | 2.27  |       | 9.49  |       |
| Total   | 100   | 100   | 100   | 100   | 100   | 100   |

\[
D = \frac{k\lambda}{B^* \cos \theta_{B/2}}
\]  

where \( D \) is crystallites average size, \( K = 0.9 \), \( \lambda = 1.5406 \) Å, \( B \) is width in maximum half (FWHM) of peak and \( \theta \) is Bragg’s angle.

Figure 3 displays SEM micrographs for (a) ZrO\(_2\) and (b) ZrO\(_2\):Tb\(^{3+}\) (7 a/o) thin films, both deposited at 450 °C; molarity was 5 M. These micrographs show a surface morphology very uniform, compacted and flat. A few semi-spherical particles scattered on the surface are also observed. It can be noted that both samples (doped and undoped) display very similar characteristics. This planarity is very important when these films are integrated into a multilayer device.

On the other hand, chemical analysis by EDS (table 1) shows presence of Zr and O\(_2\) as main species, with an approximate atomic stoichiometric ratio of 1:2 corresponding to ZrO\(_2\) stoichiometric formula. These measurements correspond to samples ZrO\(_2\) and ZrO\(_2\):Tb\(^{3+}\) (7 a/o) with solution molarity 5 M. Apparently there is evidence that deposited film does not contain residual contaminants from organic precursor solution. Although this may be due to detection limits of this technique, which is more qualitative than quantitative.

The Infrared analysis for ZrO\(_2\) and ZrO\(_2\):Tb\(^{3+}\) (7 a/o) films deposited at 450 °C was carried out by IR spectrometry (figure 4). This was to ensure that synthesis of ZrO\(_2\) carried out through a metal-organic precursor Zr(C\(_5\)H\(_7\)O\(_2\))\(_4\) at 5 M did not contain presence of residual contaminating compounds, such as (CO, CO\(_2\), OH, CH\(_4\), among others). It can be observed that only one change in intensity is displayed in a region corresponding to ZrO\(_2\), comprised of bands at 900 nm and 760 nm [38–40]. Same samples were used to obtain optical transmittance, figure 5. Optical transmittances between 78%–98% for ZrO\(_2\) and 75%–95% for ZrO\(_2\):Tb\(^{3+}\) (Tb\(^{3+}\) 7 a/o) were found. From these results and employing Swanepeol method [41] the thicknesses of some deposited films were obtained. Considering two consecutive points of maximum transmittance (TM) as well as two points of minimum transmittance (Tm) with ‘s’ as substrate refraction index.
From resulting values of equations (2)–(4), thickness obtained was 571 nm.

\[
N = \frac{2s}{T_m T_i} + \frac{s^2 + 1}{2} \quad (2)
\]

\[
n = \sqrt{N + \sqrt{N^2 - s^2}} \quad (3)
\]

\[
d = \frac{\lambda_1 \ast \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \quad (4)
\]

Figure 6 shows excitation spectra for ZrO₂ and ZrO₂:Tb³⁺ (7a/o) thin films (deposited at 450 °C and with solution molarity = 5 M), monitoring emission at 545 nm associated with Tb³⁺ ion and 460 nm associated with intrinsic emission of undoped ZrO₂. These spectra are made up of asymmetric broad bands with some shoulders and with maxima centered at 286 nm and 336 nm, respectively. These excitation wavelengths are used to obtain the PL emission spectra of the ZrO₂ and ZrO₂:Tb³⁺ samples reported in this research work. Figure 7 displays the PL emission spectra for ZrO₂:Tb³⁺ (7a/o) films, deposited at 450 °C, with solution molarity = 5 M, excited with \(\lambda_{ex} = 286\) nm and \(\lambda_{ex} = 336\) nm. In both cases, typical bands of electronic transitions of Tb³⁺ ions are observed. In addition, when the excitation is \(\lambda_{ex} = 336\) nm, a prominent broad band centered about 461 nm is seen, which is associated with host lattice and which is generated by structural defects such as oxygen deficiencies.

Excitation of these samples with \(\lambda_{ex} = 336\) nm generates an PL emission spectrum much more intense than the previous one and band centered at 461 nm looks much smaller. The color of samples excited with \(\lambda_{ex} = 336\) nm is slightly intense blue-green and those samples excited with \(\lambda_{ex} = 286\) nm appears green with a
high emission intensity. In the latter case, evidently excitation of Tb$^{3+}$ ions is much more effective than when excitation is with $\lambda_{ex} = 336$ nm. The strong emission from Tb$^{3+}$ ions represented mainly by band at 545 nm is close to optimal standards required for some applications [42, 43]. PL emission spectrum obtained by exciting with $\lambda_{ex} = 286$ nm displays four main bands located at 489, 545, 589 and 621 nm, which correspond to electronic transitions $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_3$, respectively of Tb$^{3+}$ ions.

Figure 8 shows the CIE chromatic diagrams [44] for ZrO$_2$:Tb$^{3+}$ (7 a/o) films, deposited at 450 °C, solution molarity = 5 M, excited with $\lambda_{ex} = 336$ nm and $\lambda_{ex} = 286$ nm. In both cases, typical bands of electronic transitions of Tb$^{3+}$ are observed. As already explained in description of figure 7, when these films are excited by $\lambda_{ex} = 336$ nm, observed color is blue-green which is a combination of light emitted by host lattice (ZrO$_2$) and Tb$^{3+}$ ions. In this case, chromatic coordinates were $x = 0.1968$ and $y = 0.3789$. Simultaneous PL emission of the host lattice and the doping ions is remarkable. PL properties of ZrO$_2$ without doping have been studied by other researchers [45, 46]; from these studies it has been concluded that PL emission of ZrO$_2$ is related to structural defects such as oxygen vacancies [47], which occur during growth of films [48]. If samples are excited by $\lambda_{ex} = 286$ nm, PL emissions from doping ions (Tb$^{3+}$) are preferably observed. In this case, chromatic coordinates were $x = 0.2390$, $y = 0.6593$ typical of an intense green color.

In figure 9 it is possible to observe PL emission spectra of ZrO$_2$:Tb$^{3+}$ (7 a/o) films, deposited at 450 °C, exciting with $\lambda_{ex} = 336$ nm and varying some values of solution molarity (3 M, 5 M, 7 M). These spectra show...
typical bands of Tb$^{3+}$ ions in addition to characteristic broad band (461 nm) generated by the defects of host lattice. It is evident that maximum PL emission intensity is reached when solution molarity is 5 M. If molarity is low (3 M), probably at deposition temperature used (450 °C) a good part of precursor aerosol is evaporated and does not reach to touch substrate, which could produce a thinner film as compared to those deposited with higher solution molarities. Naturally, thinner films show a lower PL emission intensity. When solution molarity is high (7 M) it is possible that decrease in emission intensity is due to phenomenon of concentration quenching; since high concentration of precursor material prevents an adequate distribution of Tb$^{3+}$ ions, giving rise to regions rich in Tb$^{3+}$ ions, a condition that favors energy transfers between Tb$^{3+}$ ions themselves, giving rise to aforementioned concentration quenching phenomenon.

A similar study to that shown in figure 9 was carried out; in this case, films were excited with $\lambda_{ex} = 286$ nm. Results were equivalent to previous ones; except that broad band centered at 461 nm, attributed to host lattice, decreased markedly. Again, films deposited with a solution molarity of 5 M showed highest PL emission intensity; also, these spectra have a higher total intensity. This is because $\lambda_{ex} = 286$ nm excites to Tb$^{3+}$ ions more efficiently. The results are displayed in figure 10.
Figure 11 shows PL emission spectra for ZrO$_2$:Tb$^{3+}$ (7 a/o) films, as a function of deposition temperature; here $\lambda_{ex}=286$ nm, excitation with $\lambda_{ex}=286$ nm and deposited at 450 °C, as a function of the solution molarity (3 M, 5 M, 7 M).

Figure 12 exhibits behavior of emission intensity for band centered at 545 nm (belonging to Tb$^{3+}$ ions) of PL emission spectra as a function of deposition temperature (300 °C–550 °C), excited by $\lambda_{ex}=286$ nm. Samples deposited at 450 °C show optimum PL emission intensity. In this case, samples considered were those of figure 11. On the other hand, figure 13 exhibits PL emission spectra for ZrO$_2$:Tb$^{3+}$ films, as a function of doping concentration; these films were deposited at 450 °C, excited by $\lambda_{ex}=286$ nm, where solution molarity was 5 M. PL emission spectra display typical bands of Tb$^{3+}$ ions. Also, it is observed that as doping concentration increases, the broad band associated with host lattice tends to decrease. It is clearly observed, in this figure, that spectra increase in intensity up to a doping concentration of 7 a/o; for higher values PL emission intensity decreases.

Figure 11 shows PL emission spectra for ZrO$_2$:Tb$^{3+}$ (7 a/o) films (solution molarity was 5 M), as a function of deposition temperature; here $\lambda_{ex}=286$ nm. Emission spectra show typical bands of Tb$^{3+}$ ions. In this figure, it can be seen that films deposited at 450 °C exhibit highest PL emission intensity. It is evident that samples deposited at 500 °C and 550 °C display a notable decrease in their PL emission intensity. A possible explanation for this phenomenon is that at high deposition temperatures precursor aerosol does not reach substrate completely, which leads to films with lower thickness. Consequently, PL emissions from thinner films show a lower emission intensity. It is also likely that at high deposition temperatures the Tb$^{3+}$ precursor evaporates more easily leading to films with a lower amount of these ions, which causes a decrease in PL emission intensity.

Figure 12 exhibits behavior of emission intensity for band centered at 545 nm (belonging to Tb$^{3+}$ ions) of PL emission spectra as a function of deposition temperature (300 °C–550 °C), excited by $\lambda_{ex}=286$ nm. Samples deposited at 450 °C show optimum PL emission intensity. In this case, samples considered were those of figure 11. On the other hand, figure 13 exhibits PL emission spectra for ZrO$_2$:Tb$^{3+}$ films, as a function of doping concentration; these films were deposited at 450 °C, excited by $\lambda_{ex}=286$ nm, where solution molarity was 5 M. PL emission spectra display typical bands of Tb$^{3+}$ ions. Also, it is observed that as doping concentration increases, the broad band associated with host lattice tends to decrease. It is clearly observed, in this figure, that spectra increase in intensity up to a doping concentration of 7 a/o; for higher values PL emission intensity decreases.
decreases notably. This can be attributed to concentration quenching phenomenon. As Tb$^{3+}$ ions are incorporated into lattice host, PL emission intensity increases, but when a certain number of dopant ions is exceeded, they are located at distances (critical radius) such that excitation energy transfers between them; finally this energy is lost in a crystal lattice defect. That is, this energy is dissipated as phonons (ceded to crystalline lattice) and not as photon emission, which causes the PL emission intensity to decrease.

Figure 12. Trend of PL emission intensity for the band centered at 545 nm, as a function of deposition temperature in ZrO$_2$:Tb$^{3+}$ (7 a/o) films excited with $\lambda_{ex} = 286$ nm, molarity = 5 M. Optimal PL emission intensity is observed for samples deposited at 450 °C.

![Figure 12](image)

Figure 13. Emission spectra of ZrO$_2$:Tb$^{3+}$ films excited with $\lambda_{ex} = 286$ nm, molarity = 5 M, deposited at 450 °C, as a function of the doping concentration (1–15 a/o). The optimal PL emission intensity is achieved for 7 a/o.

![Figure 13](image)

decreases notably. This can be attributed to concentration quenching phenomenon. As Tb$^{3+}$ ions are incorporated into lattice host, PL emission intensity increases, but when a certain number of dopant ions is exceeded, they are located at distances (critical radius) such that excitation energy transfers between them; finally this energy is lost in a crystal lattice defect. That is, this energy is dissipated as phonons (ceded to crystalline lattice) and not as photon emission, which causes the PL emission intensity to decrease.

Figure 14 presents behavior of PL emission intensity for band centered at 545 nm (belonging to Tb$^{3+}$ ions) of PL emission spectra versus Tb$^{3+}$ ions concentration; in this case, films were deposited at 450 °C with solution molarity = 5 M. Optimal PL emission intensity is observed for samples deposited at 450 °C.

In figure 15 some photographs of ZrO$_2$:Tb$^{3+}$ (7 a/o) films (deposited at 450 °C, solution molarity = 5 M) are exhibited. In figure 15(a) an unexcited sample is observed, in this case, it can be seen that these films have high transparency in the visible. Figure 15(b) shows the same sample excited with a UV lamp with $\lambda_{ex} = 302$ nm. Here, the light emission and transparency are observed. Figure 15(c) displays thicker sample also excited with a UV lamp with $\lambda_{ex} = 302$ nm. Finally, figure 15(d) exhibits a sample excited by an electron beam.
The electron accelerating voltage was 3 kV, and this image is included here only to show the high emission intensity of these films (excited by accelerated electrons) even with small thicknesses. Currently, a cathodoluminescence study is being carried out on these samples, which will be sent to publication later.
4. Conclusions

Photoluminescent ZrO$_2$ and ZrO$_2$:Tb$^{3+}$ thin films were synthesized from metal-organic precursor Zr(C$_5$H$_7$O$_2$)$_4$ (5 M) using the USP technique. Results of XRD presented only tetragonal structural phase for ZrO$_2$ and ZrO$_2$:Tb$^{3+}$ (Tb$^{3+}$ 7 a/o), with a crystallite size of approximately 4 nm, according to Scherrer formula. SEM micrographs exhibited a very smooth surface morphology, while EDS composition microanalysis showed that there was a presence of oxygen and zirconium as major species. Analysis by IR showed bands at 900 nm and 760 nm which correspond to ZrO$_2$ with absence of carbon and chlorine compound impurities. Furthermore, these thin films display optical transmittances between 75%–98% as they are highly transparent in visible range. Regarding deposition parameters, it was determined that PL emission of these thin films depends on the Tb$^{3+}$ ion concentration (a concentration quenching was observed for Tb$^{3+}$ concentrations greater than 7 a/o), also on substrate temperature (best was 450 °C) and on molarity of precursor solution (best results are obtained for a molarity of 5 M). In addition, PL emission intensity depends on excitation wavelength; when samples were excited with $\lambda_{ex} = 286$ nm, it was observed a strong green emission associated to electronic transitions $^5$D$_4 \rightarrow ^7$F$_{5/2}$, $^5$D$_4 \rightarrow ^7$F$_{7/2}$, $^5$D$_4 \rightarrow ^7$F$_{3/2}$, located at 489, 545 (main band and maximum intensity), 589 and 621 nm, respectively, corresponding to the Tb$^{3+}$ dopant ions; for this case, chromatic coordinates were (0.2390, 0.6593). Once these films were excited with $\lambda_{ex} = 336$ nm, PL emission of host lattice ZrO$_2$ was favored (simultaneously with Tb$^{3+}$ ions), in this case, color observed was blue-green, as perceived in chromatic diagram of figure 8; here, chromatic coordinates were (0.1968, 0.3789). Considering that these films have excellent characteristics such as: high PL emission intensity, very smooth surface morphology and high transparency in visible region of electromagnetic spectrum, they would be ideal to be incorporated into electroluminescent multilayer structures of MISIM (Metal Insulator Semiconductor Insulator Metal) type for manufacture of visual displays.

Acknowledgments

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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