Synthesis and photoluminescent properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ thin films prepared from F127-containing solution

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Dense and transparent $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ films were prepared by the sol-gel process and dip-coating technique from an yttrium 2–4 pentanedionate, europium nitrate and a methanol solution modified with F127 pluronic acid, by incorporation of acetic acid as pH modifier and acetylacetone as sol stabilizer. It was evaluated the effect of the F127/Y molar relationship (0, 0.1, 0.2, 1.0, 1.2 and 5.0) on the structure and photoluminescent properties of the derived thin films. After 3 dipping-cycles, XRD results showed that the F127-modified films began to crystallize at 600°C into the cubic structure, and from 800°C, was found that the presence of F127 changes the preferential orientation from a (100) orientation, for the non-modified sample, to a (111) orientation, for the modified ones. M-lines spectroscopy characterization showed that the maximum thickness of the films modified and annealed at 900°C was 1937 nm ($\rho = 4.87 \text{ g cm}^{-3}$, $\eta = 1.887$), compared with the 881 nm ($\rho = 4.94 \text{ g cm}^{-3}$, $\eta = 1.907$) for a non-modified sample. Differential thermal analysis (DTA) and infrared spectroscopy (FTIR) were carried out to evaluate the chemical and structural evolution of the xerogel formed during the annealing process. AFM micrographs showed smooth crack-free surface ($R_a = 9.2 \text{ nm}$) on a F127/Y = 0.2 sample. Finally, the films presented a typical Eu^{3+} reddish emission at 611 nm ($D_0 \rightarrow {}^7F_2$), which was analyzed as function of the F127 pluronic content and the annealing temperature.

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1. Introduction

Eu-doped Y_2O_3 luminescent material has been widely studied due to its exceptional properties, like superior chemical stability, wide transparency range (0.2–8 μm), high refractive index (1.92484, $\lambda = 633 \text{ nm}$), and high quenching efficiency^{(1)–(3)} which makes it a potential candidate for several applications in luminescent devices, such as CCD cameras, electroluminescent displays (ELDs), field emission displays (FEDs) or plasma displays (PDs).^{(4)–(6)} For several applications, the best option is to obtain the phosphor as a film rather than compacted powder, since films presents several advantages like: better adhesion, reduced outgassing, smaller grain size, improved uniformity over substrate faces,⁽⁷⁾ and transparency, which is important for a good image contrast and resolution,⁽⁸⁾ difficult to achieve by conventional methods of powder processing.⁽⁹⁾ Therefore, these devices require preparing films directly on a glass or an organic substrate.⁽¹⁰⁾ Several methods have been used to prepare $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ films such as: magnetron sputtering,^{(11),(12)} vacuum nano-imprint,⁽¹³⁾ microwave electron cyclotron resonance plasma,⁽¹⁴⁾ sputtering,⁽¹⁵⁾ excimer-laser-assisted metal organic deposition,⁽¹⁶⁾ chemical bath deposition,⁽¹⁷⁾ CVD,^{(18),(19)} electrodeposition^{(20),(21)} or pulsed laser

deposition.^{(22),(23)} However, these techniques usually require expensive and complicated equipment setup.⁽²⁴⁾ An alternative is the sol-gel and the dip-coating method, which have attracted attention because it is particularly efficient in to produce high optical quality oxide films on different substrates.⁽²⁵⁾ However, since the maximum thickness achievable via a single deposition is often below 0.1 μm ,⁽²⁶⁾ and since it has been accepted that it is important to obtain thickness of at least 1 μm in order to fulfill an optical quality for luminescent devices,⁽²⁷⁾ one of the biggest challenges is to obtain, by means of this technique, thick films without cracks that appears as consequence of stress product of the heating-cooling cycles induced by the cycles of dipping. An alternative is the incorporation of a polymer into the sol formation, which could reduce the stress during the annealing procedure, and increment the viscosity of the sol, increasing the film thickness and reducing crack formation, as has been demonstrated by using polyvinylpyrrolidone (PVP),⁽²⁸⁾ which has been employed in luminescent systems such as $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$,⁽²⁹⁾ $\text{BaTiO}_3:\text{Eu}^{3+}$ ⁽³⁰⁾ or $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$.⁽³¹⁾ The most recently alternative is to add Pluronic F127 acid,^{(32),(33)} a $\text{PEO}_{106}\text{PPO}_{70}\text{PEO}_{106}$ (PEO = polyethylene oxide, PPO = polypropylene oxide) tri-block copolymer with an average molecular weight of 13600 g mol^{-1} . The present work reports the structural, morphological, optogeometrical and optical properties of transparent and crack-free $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ thin films prepared from a F127 containing sol

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dipped on SiO_2 glass, as function of the F127/Y molar relationship and annealing temperature.

2. Experimental

The starting sol for the deposition of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ modified with F127 films, was prepared by dissolving yttrium (III)-2,4-pentadionate, $\text{Y}(\text{CH}_3\text{COCHCO}-\text{CH}_3)_3$ (Alfa Aesar, 99.96%) and europium nitrate $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Alfa Aesar, 99.5%) in 20 mL of methanol (Fermont) under vigorous stirring at 60°C to obtain a sol with an yttrium concentration of 0.19 M, and a 2.5 at. % Eu^{3+} content. The pH solution was adjusted by incorporating acetic acid, CH_3COOH (Fermont, 98%), and 2-4-pentanedione $\text{CH}_3\text{COCH}_2\text{COCH}_3$ (Alfa Aesar, 99%) was added as organic chelating compound (0.82 M). The obtained solution was stirred 24 h. Later, F127 was slowly incorporated into the sol under vigorous stirring at 70°C , with F127/Y molar ratio of 0.0, 0.1, 0.2, 1.0, 1.2 and 5.0 (F127 monomer atomic weight = 102 g mol^{-1}). Finally, it was stirred for 1 h to obtain a completely dissolution of the F127. To obtain the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ luminescent films, silica glass substrates (refractive index = 1.417, Corning) were dipped into the F127 modified sol after being filtered through $0.2 \mu\text{m}$, and pulled up at a constant rate of 8 cm min^{-1} . After each dipping, the films were heat treated in the following cycle: first, dried for 10 min at 100°C in a conventional oven; after that, heat treated at 300°C for 10 min. The dipping cycle was repeated 5 times. Finally, the thin film layers were annealed at the fixed temperature 500, 600, 700, 800 and 900°C for 30 min to obtain the desired cubic structure. As observed, most of the films were completely transparent, except for the F127/Y = 5.0 sample (Fig. 1).

The xerogel product, obtained drying the remnant sol for 24 h at 100°C , was used on the thermogravimetric (TGA) and differential thermal analyses (DTA) using a SDT Q600 TA instrument; the studies were performed in air with a heating rate of $10^\circ\text{C min}^{-1}$. To analyze the chemical behavior during the annealing process, IR spectra of the samples were obtained using the KBr pelleting technique for the range of $4000\text{--}400 \text{ cm}^{-1}$ using Fourier transform infrared spectroscopy (FTIR 2000, Perkin Elmer). X-ray diffractions patterns (XRD) were obtained with a Bruker D8 Advance diffractometer using $\text{Cu K}\alpha$ radiation ($1.5418 \text{ \AA}$), with an operating voltage of 40 kV and a current of 30 mA. After each annealing temperature, the optogeometrical properties (thickness and refractive index,) as well as density and porosity, were investigated by m-lines spectroscopy, which uses a prism coupling method to launch a laser light into the optical layer. The prism (LaSF35, angle 60°) was coupled with a light of He-Ne laser with a wavelength $\lambda = 633 \text{ nm}$ into the waveguide. The morphology of the crystalline films was inspected using a Nanoscope III apparatus in tapping mode. The analyses were carried out in air and at room temperature, and the scan rate was about 1 Hz. Photoluminescence spectra were recorded using a

Spectra Pro fluorometer equipped with an R955 photomultiplier tube (Hamamatsu), at room temperature.

3. Results and discussion

3.1 Thermogravimetric analysis

Figure 2 shows the TGA-DTA curves of the as-prepared $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ xerogel. The study was carried out for the F127/Y = 1.0 sample. Three different stages can be observed. The first stage, from $20\text{--}380^\circ\text{C}$, shows a weight loss of 11% and four endothermic events, at 93, 129, 181 and 304°C . The first event can be attributed to the thermal decomposition of the methanol, the second to the evaporation of the 2-4-pentanedione (b.p. 139°C) used as chelating agent, the third to the combustion of the carbonyl groups, and the fourth one to the pyrolysis of the yttrium (III)-2,4-pentadionate. The second stage, from $380\text{--}450^\circ\text{C}$, shows a significant mass loss of 43%, accompanied with the major endothermic event centered at 394°C . This event can be ascribed to the decomposition of the F127 in only one event, as it has been demonstrated previously for F127.³⁴⁾ The third stage, from 450°C presents a little weight loss of 7%, which is consequence of the final elimination of the remnants carbonyl groups. The last endothermic event, centered approximately at 610°C , corresponds to the crystallization process of the ceramic sample into the cubic phase. These observations are in good agreement with the IR and XRD studies.

3.2 FTIR studies

Figure 3 shows the typical FTIR spectra of the F127/Y = 1.0 sample as function of the annealing temperature. This study was carried on the dried precursor sol to determine the evolution of the decomposed products of the xerogel powders calcined up to the crystallization process. For 100°C , there is a strong presence of the O-H bands because of alcohol groups (methanol),

Fig. 2. DTG and DTA profiles of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ powders obtained from a F127 modified sol.

Fig. 1. Photograph of transparent $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ F127 modified thin films.

characterized for the bands at 3300 cm^{-1} (ν) and 750 cm^{-1} (δ), ascribed to O–H stretching (ν) and deformation (δ) vibrations. These bands almost disappeared at 700°C , indicating that the annealing temperature is enough to volatilize the remnant OH groups of the sample. Strong absorption bands are observed at $\sim 1046\text{--}1003\text{ cm}^{-1}$ and $\sim 952\text{--}918\text{ cm}^{-1}$, which could be attributed to a symmetrical stretching of C–O and deformation vibrations of C–O in CO_3^{2-} , respectively, corresponding to the thermal pyrolysis of the carbon groups of acetic acid methanol. All of the bands observed at $\sim 1560\text{--}1400\text{ cm}^{-1}$ correspond to the asymmetric and symmetric C–H vibrations from the F127.³⁵⁾ All these bands are almost completely removed at 700°C . The bands from $\sim 660\text{--}570\text{ cm}^{-1}$ are ascribed to the stretching vibrations of C=C on acetylacetonates, from de yttrium precursor, and as observed, are completely eliminated from 600°C , indicating that from this temperature the crystallization process began, in concordance of DTA observations. Finally, from 700°C , bands at $\sim 555\text{ cm}^{-1}$ appear which are associated with the crystallization of the Y_2O_3 cubic phase.³⁶⁾

Fig. 3. Infrared spectra $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ F127 modified system, F127/Y = 1.0.

3.3 Structural and morphological studies

Figures 4(a)–4(c) and shows the X-ray diffraction patterns of the synthesized $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ F127 modified thin films as function of the annealing temperature for three different F127/Y molar ratio, 0.0, 0.2, 1.0 and 5.0, respectively. All of the diffracted peaks were identified to correspond to the Y_2O_3 cubic structure with a spatial group $\text{I}\bar{a}3$, and a lattice parameter of $10.604\text{ \AA}$ (251200 JCPDS). The results confirm that crystallization seems to start at 600°C when F127 has been added meanwhile, when it is not added, begin at 700°C . This effect has been observed for TiO_2 ³⁷⁾ and it has been explained in terms of the modification of the gelation behavior during the sol–gel process, as consequence of the hydrolysis rates changes, which could be modified with the addition of a polymer during the sol formation.³⁸⁾ For all cases, at higher temperature, more intense and sharp diffraction peaks of Y_2O_3 appear because the increment of the annealing temperature increases the crystallinity of the thin films, as can be deduced by the sharpening of the diffraction lines. The crystallite size (d) at the films was estimated using Scherrer's method, taking into account the broadening line of the diffracted peak.³⁹⁾ The results are presented in Table 1. The average crystalline domain size was found to be from $11.7\text{--}17.0$, $6.9\text{--}14.8$, $7.08\text{--}16.9$ and $12.7\text{--}17.9\text{ nm}$ for F127/Y = 0.0, 0.2, 1.0 and 5.0 samples respectively. There is not obvious evidence that F127 content modifies substantially the crystallite size. On the other hand, since a preferential crystal orientation is a desirable physical property for luminescent materials because it optimizes the optical performance of the films, increasing effectively the light yield.⁴⁰⁾ For the non-modified $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ synthesized films, the increment of the annealing temperature from 800°C produces a preferred (100) orientation. Similar behavior has already been observed for Y_2O_3 sol–gel derived films starting with yttrium acetate as precursors on amorphous substrates.⁴¹⁾ It is demonstrated that a preferential orientation could be consequence of a high heating rate in rapid thermal annealing process,⁴²⁾ and can change when the film was grown by nucleation with the lowest strain energy,⁴³⁾ which could be suppressing the stress and reducing the strain energy adding an organic additive,^{44,45)} like the 2-4-pentanedione, which tends to retard the hydrolysis and condensation of the yttrium (III)-2,4-pentadionate in the course of heating, and therefore suppressing the stress generation. A similar effect has also been observed when it was used 2-(2-methoxyethoxy) for Y_2O_3 sol–gel derived films.⁴⁶⁾ However, as observed, the F127/Y = 5.0 sample shows clearly a (111) orientation. In order to quantify this observation, it

Fig. 4. Structural evolution of $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ films, F127/Y = X, a) X = 0.0, b) X = 0.2, c) X = 1.0 and d) X = 5.0.

Table 1. Preferential orientation parameter α_{hkl} of Y₂O₃:Eu³⁺ films, a) X = 0.0, b) X = 0.2, c) X = 1.0 and d) X = 5.0

Temperature /°C	F127/Y = 0.0		F127/Y = 0.2		F127/Y = 1.0		F127/Y = 5.0	
	α	α	α	α	α	α	α	α
	$\langle 111 \rangle$	$\langle 100 \rangle$	$\langle 111 \rangle$	$\langle 100 \rangle$	$\langle 111 \rangle$	$\langle 100 \rangle$	$\langle 111 \rangle$	$\langle 100 \rangle$
600	—	—	0.33	0.56	0.42	0.46	0.56	0.11
700	0.61	0.39	0.63	0.36	0.31	0.53	0.54	0.11
800	0.06	0.94	0.21	0.78	0.16	0.72	0.52	0.12
900	0.03	0.97	0.16	0.84	0.14	0.81	0.62	0.13

was calculated the preferential orientation parameter α_{hkl} , which is defined as $\alpha_{hkl} = I_{hkl} / \Sigma I_{hkl}$, where I_{hkl} is the relative intensity of the corresponding diffraction peak.⁴⁷⁾ As can be observed, with the increment of the F127 content, the preferential orientation changes from the $\langle 100 \rangle$ to $\langle 111 \rangle$, along with a clearly much polycrystalline structure. This effect can be explained since as the polymer content increases, it tends to modify the chemical structure during the sol-gel process, restricting the formation of the Y–O–Y bonding during the polymerization process, as observed for TiO₂⁴⁸⁾ or Al₂O₃⁴⁹⁾ sol-gel materials modified with PVP, increasing secondary poly-condensations reactions and therefore, multiplying the nucleation sites and limiting the grain growth. Therefore, a polycrystalline structure is produced, which it is oriented to the common less-energy $\langle 111 \rangle$ direction. On the other hand, an excess amount of F127 becomes the a major constituent of the film, causing too much film shrinkage on firing and incrementing the stress over the film which also could lead to the fracture and a poor optical quality, as observed in Fig. 1, where the F127/Y = 5.0 sample is clearly opaque. However, as discussed later, the F127 does effectively increment the thickness of the films.

The morphology of the Y₂O₃:Eu³⁺ modified F127 thin films was evaluated by AFM. **Figure 5** shows the micrographs for the F127/Y = 0.1 and 1.2 sample. As can be observed, in both cases the films are constituted of dispersed grains all over the surface, however, their size varies from 0.1 to 5 μ m, indicating that the F127 tends to agglomerate the particles and promotes their growing, probably because tends to chelating the metal-organic compounds during the xerogel stage. This also affect the roughness of the film, as can be clearly noted on the 3D image of the micrographs, where the lower content presents a particle-rounded morphology, in contrast to the sharpened one for the higher content. The Ra roughness, showed on **Table 2**, increases from 4.5 to 58.6 nm for the F127/Y = 0.1 and 1.2 samples, respectively. However it is important to notice that at lower F127 contents, 0.1 and 0.2, roughness is lower compared with the non-modified F127 sample. Finally, all the samples were homogeneous and crack-free from 0.1 to 1.2 samples.

3.4 Optogeometrical properties

To determine optogeometric parameters of waveguiding thin films, such as refractive index as well as film thickness, an *m-Lines* spectroscopy study was carried out. It is important to notice that the Y₂O₃:Eu³⁺ modified F127 thin films from 0–1.2 F127/Y ratio could be effectively analyzed by this technique, presents at least two TE and two TM modes, indicating the high optical quality of the samples, like transparency, and physical homogeneity. However, it is important to state that the F127/Y = 5.0 sample does not fulfill the requirements since it presents multiple visible cracks. Furthermore, for the F127/Y = 1.0 and 1.2 samples, accomplish the optical quality only after the annealing process at 800 and 900°C, respectively, which indicates that the F127 effectively increases the stress on the samples and, only after

the thermal process, are reduced. **Table 3** summarizes the results obtained for all the samples. On **Fig. 6** it is observed that the F127 content effectively increases the thickness of the sol-gel derived Y₂O₃:Eu³⁺ films. For the 900°C annealed samples, it increases from 881 to 1779, 1843, 1918 and 1937 nm for the F127/Y = 0.0, 0.1, 0.2, 1.0 and 1.2, respectively, and, comparing the F127/Y = 0 to the 1.2 samples, the final thickness is $\approx$ 119%. However, it is also clear that the increment is very small from the F127 lower sample (0.1) to the higher sample (1.2), only about 9%, though this, to obtain thicker films, it's only needed small proportions of F127. On the other hand, the refractive index (**Table 3** and **Fig. 6**), remains similar for the non-F127 modified films and for the two lower F127/Y samples, 0.1 and 0.2; and present evident decrement for the 1.0 and 1.2 samples, as consequence of the same excess of F127. The density (ρ) of the films can be determined by means of the Lorenz-Lorentz equation:⁵⁰⁾

$$\rho = K \frac{n_f^2 - 1}{n_f^2 + 2}$$

Where K is calculated from the bulk material, and n_f is the refractive index of the film. The theoretical pore content (p) is calculated by the Drude's equation:⁵¹⁾

$$1 - p = \frac{n_f^2 - 1}{nb^2 - 1}$$

Where n_b is the refractive index of the bulk material. The results are presented in **Table 4**. It is observed that densification ($\rho_{\text{exp}}/\rho_{\text{the}}$, theoretical density 5.03 g cm⁻³) ranges from 0.982 to 0.986, 0.992, 0.978 and 0.968 g cm⁻³, at 900°C for F127/Y = 0, 0.1, 0.2, 1.0 and 1.2 samples, respectively, demonstrating that the obtained thin films are dense. Also it is show that at lower F127 content, the densification process is better that with higher ones, since the last ones will lose more mass during thermal annealing. The same effect can be observed with the pore content, lower for the 0.1 and 0.2, and higher for the 1.0 and 1.2 samples; the same conclusion regarding the effect on the densification process can be stated.

3.5 Photoluminescent studies

Figure 7 shows a typical excitation spectra ($\lambda_{\text{em}} = 611$ nm) of prepared Y₂O₃:Eu³⁺ film, with a F127/Y = 0.2 molar content, annealed at 700°C. The broad excitation band from 230 to 280 nm can be ascribed to the charge transfer (CT) from the 2p orbital of O²⁻ to the 4f orbital of Eu³⁺ ion. **Figure 8** shows the emission spectra ($\lambda_{\text{exc}} = 253$ nm) for the films as function of the F127/Y content at 700°C, and the ⁵D₀ → ⁷F_J (J = 0, 1, 2, 3, 4) where Eu³⁺ transitions can be observed. On the other hand, as the F127 increases, the light yield of the films is also increased due to the higher thickness of the films, product of the F127 content, the better crystallization process, and the preferential orientation. The most intense line, at around 612 nm, is ascribed to the transition from the ⁵D₀ → ⁷F₂ of the Eu³⁺. The peak centered at 581 is assigned to the ⁵D₀ → ⁷F₀, transition, the band split in three peaks

Fig. 5. AFM micrographs of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ films, F127/Y = X, a) X = 0.1, and b) X = 1.2.

Table 2. Ra roughness of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ films F127 modified-films

	F127/Y				
	0.0	0.1	0.2	1.0	1.2
Ra/nm	10.2	4.5	9.2	47.8	58.6

centered at 588, 594 and 600 nm is ascribed to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$, whereas the ones centered at 650 and 690 nm are ascribed, to the $^5\text{D}_0 \rightarrow ^7\text{F}_3$ (≈ 630 nm) and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions. The dominance of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ electric dipole transition over the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ magnetic dipole transition confirms that the Eu^{3+} ions are preferably located at the non-centrosymmetrical C_2 site in the Y_2O_3 cubic matrix. Therefore the transitions ratio $R = I(^5\text{D}_0 \rightarrow ^7\text{F}_2)/I(^5\text{D}_0 \rightarrow ^7\text{F}_1)$ can be used as a reference of the site symmetry. High values of ratio R are related with the purity of the color.⁵²⁾ The R ratios obtained for F127/Y = 0, 0.1, 0.2, 1.0 and 2.0 were 1.52 ± 0.03 , 4.02 ± 0.08 , 1.61 ± 0.02 , 3.96 ± 0.06 and 5.95 ± 0.02 respectively, and these results confirm that in the mostly of the cases the F127 content is proportional to the site

Fig. 6. Evolution of thickness and refractive index at 633 nm of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ modified thin films as function of F127/Y molar ratio, $T = 700^\circ\text{C}$.

Table 3. Thickness and refractive index of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ films F127 modified-films

F127/Y molar content	Temperature /°C	Thickness /nm	Refractive index/a.u
0.0	600	1225	1.852
	700	1136	1.896
	800	917	1.890
	900	881	1.907
0.1	600	2235	1.889
	700	1956	1.896
	800	1776	1.901
	900	1779	1.913
0.2	600	2337	1.882
	700	1901	1.893
	800	1843	1.902
	900	1864	1.912
1.0	600	—	—
	700	—	—
	800	1885	1.900
	900	1918	1.896
1.2	600	—	—
	700	—	—
	800	—	—
	900	1937	1.887

Table 4. Density and Porosity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ films F127 modified-films

F127/Y molar content	Temperature /°C	Densification / $\rho_{\text{experimental}} \cdot \rho_{\text{theoretical}}^{-1}$	Porosity /%
0.0	600	0.940	10.1
	700	0.974	3.9
	800	0.970	4.8
	900	0.982	2.5
0.1	600	0.968	4.9
	700	0.974	4.0
	800	0.976	3.9
	900	0.986	1.5
0.2	600	0.964	6.0
	700	0.972	4.4
	800	0.978	3.1
	900	0.992	0.7
1.0	600	—	—
	700	—	—
	800	0.976	3.5
	900	0.978	3.4
1.2	600	—	—
	700	—	—
	800	—	—
	900	0.968	25.12

symmetry decreasing. Our best R value film obtained at F127/Y = 1.0 ratio are similar to the one obtained by J. Su et al. for polycrystalline powders.⁵³⁾

Finally, the study of the effect of annealing temperature on the luminescence was carried out in the range of 600–900°C. **Figure 9** shows the variation of the luminescence emission with the temperature for a F127/Y = 1.0. As observed, the emission intensity presents a direct relationship with respect to the annealing temperature; these results can be explained with the increment of the size of crystallite that can be observed in Fig. 4. The R ratios obtained at 600, 700, 800 and 900°C where 1.57 ± 0.04 , 3.96 ± 0.06 , 5.18 ± 0.05 , 3.98 ± 0.08 and there confirm that the site asymmetry can be related with the emission intensity.

Fig. 7. Excitation spectra ($\lambda_{\text{em}} = 612$ nm) of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, F27/Y = 0.2 thin film. Fig. 8. Emission spectra ($\lambda_{\text{exc}} = 254$ nm) of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ F127 modified thin films as a function of F127/Y molar ratio at annealing temperature of 700°C. Fig. 9. Emission spectra ($\lambda_{\text{exc}} = 254$ nm) of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ F127 modified thin films, F127/Y = 1.0, as a function of annealing temperature.

4. Conclusion

Dense and transparent $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ thin films were prepared by means of the sol-gel method and the dip-coating procedure, starting with a F127 modified sol. With a small F127 content

(0.1), it is possible to increase the thickness more than 100% compared with a non-modified sample, with high quality and physical homogeneity, however, further increments on the F127 content (0.2–1.2) doesn't increase significantly the thickness but tends to increment the pore content and dismissing the density and the optical quality of the films. The XRD results confirm that the films with lower F127 present a highly 100 preferential orientation, whereas higher concentrations tends to promote multiple oriented materials. Luminescence studies showed a strong Eu^{3+} 611 nm emission that increases with the F127 content due to the higher thickness and density of the films as well as the asymmetry.

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