Eu³⁺ as optical probe of the structure in amorphous and nanocrystalline TiO₂ films prepared by sol-gel method

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ABSTRACT

In this work the Eu^{3+} ion was used as optical probe, by considering its hypersensitive transitions to follow changes in the local environment. Eu^{3+} ions were incorporated into gel via dissolution of soluble species into the initial precursor TiO_2 sol. The TiO_2/Eu^{3+} films were spin-coated on glass wafers. A spectroscopic study of the Eu^{3+} impurity in function of the heat treatment provided to the TiO_2 matrix was done. Anatase nanophase was obtained after heat treatment at 600°C for 1h and it was detected by X-ray diffraction. An absorption band located in the UV region between 300-360 nm is due to the band gap of the titania host. Results of emission and excitation spectra at room temperature of Eu^{3+} inserted in the TiO_2 matrix are presented. The ratio of the $^7F_2/^7F_1$ transitions was calculated. The evolution of this ratio was interpreted in terms of the Eu^{3+} symmetry site change when the nanocrystalline TiO_2 phase was obtained.

KEYWORDS: sol-gel, rare earth, luminescence, europium, titania, optical probe

1. INTRODUCTION

The study of the luminescent properties of trivalent lanthanides incorporated into several crystalline matrices is strongly motivated because of their technological applications in optoelectronics devices and flat panel displays ¹. Then, it is important the systematic research of the rare earths (RE) hosted in different kind of matrices with good mechanical and thermal properties and chemical stability. Fabrication of new optical devices based upon the incorporation of rare earth ions via sol-gel methods depends on elimination of dopant ion clusters and residual hydroxyl groups from the final material ².

The optical absorption and/or luminescence properties of rare earth ions are influenced by the local bonding environment and the distribution of the rare-earth dopants into the matrix. Many investigations have been performed with Eu^{3+} , Tb^{3+} or Ln^{3+} acting as an optical probe of Ca^{2+} sites in a wide variety of calcium binding proteins. Strek et al. ³ investigated the phase transitions in BaTiO₃ nanocrystalline grains by means of fluorescence using Eu^{3+} ions as an optical probe. An important advantage is that the fluorescence properties of the dopants (rare earths) enable us to study the microstructure of the matrix.

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On the other hand, there are reports on the optical properties of the material and its potential applications, mainly in the form of thin films $^{4-6}$, in which the doped rare earth ions open up new possibilities. The sol–gel method, based on wet chemistry processing, is quite cheap and simple for the fabrication of thin films and bulk samples, where significant RE ion concentrations, in particular Eu³⁺, can be achieved ⁷.

In this paper, the Eu^{3+} ion was used as optical probe, by using its hypersensitive transitions to follow changes in the local environment. Eu^{3+} ions were incorporated into gel via dissolution of soluble species into the initial precursor TiO₂ sol. A spectroscopic study of the impurity Eu^{3+} in function of the heat treatment provided to the TiO₂ matrix was done. Results of emission and excitation studies of Eu^{3+} inserted in the TiO₂ matrix are shown. The ratio of the ${}^7F_2/{}^7F_1$ transitions was obtained. The evolution of this ratio was interpreted in terms of the Eu^{3+} response when the nanocrystalline anatase phase was formed by calcination at 600°C.

2. EXPERIMENTAL

2.1 Synthesis

a) TiO_2/Eu^{3^+} . The Eu³⁺-doped TiO₂ films were synthesized by sol-gel method. Firstly, 2ml of tetrabutyl orthotitanate and 10 ml of ethanol were mixed together. Besides this, a mixture of 1 ml of de-ionized water (DI H₂O), 1 ml of hydrochloric acid (hydrochloric concentration is 37%), and 10 ml of ethanol was prepared. The two solutions and 0.01 M of Eu(NO₃)₃·5H₂O powder were mixed together under vigorous stirring in order to dissolve the Eu(NO₃)₃·5H₂O powder entirely into the sol. The final molar ratio of all components was Ti(OCH₂CH₂CH₂CH₂CH₃)₄:EtOH:DI H₂O:HCI: Eu(NO₃)₃·5H₂O = 1:25.9:9.4:5.6:0.042. The TiO₂/ Eu³⁺ solution has a pH = 6.0.

b) $TiO_2/Eu^{3+}/PF127$. The block copolymer Pluronic F127 (PF127) was added to 20 ml of TiO_2/Eu^{3+} solution prepared in the previous section. The mixture was refluxed at 35 °C for 4 h. The final molar ratio of all components was Ti(OCH_2CH_2CH_2CH_3)_4:EtOH:DI H_2O:HCl: PF127:Eu(NO_3)_3:5H_2O = 1:25.9:9.4:5.6:0.047:0.042.

c) $TiO_2/Eu^{3+}/Al(NO_3)_3$. All components were mixed under nitrogen atmosphere. In a beaker, 10 ml of tetrabutyl orthotitanate and 4.9 ml of ammonium hydroxide were stirred for 10 min at room temperature. After, Eu(NO_3)_3·5H_2O powder and Al(NO_3)_3·9H_2O powder were added to this solution, and it was refluxed at 35 °C for 4 h. The final molar ratio of all components was Ti(OCH_2CH_2CH_2CH_3)_4:NH4OH:Eu(NO_3)_3·5H_2O: Al(NO_3)_3·9H_2O = 1:4.5:0.022:0.067.

The three different solutions were deposited onto glass wafers by the spin-coating technique. The precursor solution was placed on the glass wafers $(2.5 \times 2.5 \text{ cm}^2)$ using a dropper and spun at a rate of 3000 rpm for 15 s.

After coating, all films were pre-annealed in a muffle oven at 100 °C for 0.5 h to remove some of the organic and volatile compounds. Finally, the films were sintered at 600 °C for 1 h in a muffle to produce a crystalline nanophase.

2.2. Characterization

UV-vis absorption spectra were obtained on a Thermo Spectronic Genesys 2 spectrophotometer with an accuracy of ± 1 nm over the wavelength range of 300-900 nm. The structure of the final films was characterized by XRD patterns. These patterns were recorded on a Bruker AXS D8 Advance diffractometer using Ni-filtered CuK α radiation. A step-scanning mode with a step of 0.02° in the range from 1.5 to 60° in 2 θ and an integration time of 2 s was used. Emission and excitation optical spectra were collected at room temperature with a SPEX FLUOROLOG FL111 spectrofluorimeter equipped with a 450W xenon lamp. Excitation and emission wavelengths were selected by two monochromators (SPEX spectrometer 0.34m), and the detection was done with a HAMAMATSU R928 photomultiplier tube.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction. Figure 1 shows the XRD patterns for titania films doped with Eu^{3+} ions, annealed at 600 °C for 1 h. Only the TiO₂/ Eu^{3+} /Al(NO₃)₃ films exhibit some crystallization that corresponds to the anatase phase. The anatase phase was identified by the diffraction peaks located at 20 =25.37, 48.16 and 62.59 which can be indexed as (101), (200) and (204) respectively. The position of the diffraction peaks in the film is in good agreement with those given in ASTM data card (#21-1272) for anatase.



Figure 1. X-Ray diffraction patterns recorded for TiO₂/ Eu³⁺ thin films annealed 1 h at 600° C.

The average crystalline size (D) was calculated from Scherrer's formula ⁸ by using the diffraction peak (101) for anatase phase:

$$D = \frac{0.9\lambda}{B\cos\theta} \tag{1}$$

with $\lambda = 1.54056 \times 10^{-10}$ m. A value of 6.6 nm was obtained for nanocrystallites.

3.2 UV-vis optical absorption. Figure 2 shows the optical absorption spectra of amorphous and nanocrystalline TiO_2/Eu^{3+} films taken at room temperature in the range of 300-900 nm.



Figure 2. Absorption spectra of: (a) Amorphous $TiO_2/Eu^{3+}/PF127$ film, (b) Amorphous TiO_2/Eu^{3+} film and (c) Nanocrystalline $TiO_2/Eu^{3+}/Al(NO_3)_3$.

Table 1 contains the positions of the maximum peaks of all films.

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Film	Band A	Peak B	Peak C	
	TiO ₂	Eu ³⁺	Eu ³⁺	
Amorphous TiO_2/Eu^{3+}	331 nm	-	630 nm	
Amorphous TiO ₂ / Eu ³⁺ /PF127	322 nm	392 nm	633 nm	
Nanocrystalline TiO ₂ / Eu ³⁺ /Al(NO ₃) ₃	364 nm	397 nm	646 nm	

Table 1. Absorption bands of TiO₂ and Eu³⁺.

3.3 Emission and Excitation Spectra. Eu^{3+} has been most often used as an optical probe because of its particularly informative luminescence spectrum ^{2, 9}. The luminescence intensity depends of the local symmetry in the Eu^{3+} site. The relation between the hypersensitive transition ${}^{5}D_{0}$ - ${}^{7}F_{2}$ to the ${}^{5}D_{0}$ - ${}^{7}F_{1}$ determines the centrosymmetry. Increasing ratio corresponds to increasing asymmetry. This section shows the emission and excitation spectra for TiO₂/Eu³⁺, TiO₂/Eu³⁺/Al(NO₃)₃ and TiO₂/Eu³⁺/PF127 films. The spectra were measured before and after the heat treatment of 600 °C. We focus on the luminescent response of the impurity Eu³⁺ inside the TiO₂ matrix.

i) TiO_2/Eu^{3+} film

Figure 3 shows the emission spectra for TiO_2/Eu^{3+} film with $\lambda_{exc} = 394$ nm. Before the heat treatment, the emission is due to the transitions from 5D_0 state to 7F_j (j = 1, 2, 3 y 4) for Eu^{3+} . In Fig. 3 (a) the band located at 601 nm is the superposition of the 7F_1 and 7F_2 transitions; the band at 648 nm corresponds to the 7F_3 transition and the band at 707 nm corresponds to the 7F_4 transition. After the treatment of 600 °C for 1 h (Fig. 3b), the 7F_1 transition is located at 592 nm, the most intense transition 7F_2 corresponds to 612 nm. The 7F_3 transition is located at 644 nm and the 7F_4 transition corresponds to 708 and 723 nm.



Figure 3. Emission spectra of Eu³⁺ in amorphous TiO₂ matrix by using $\lambda_{exc} = 394$ nm (⁷F₂- ⁵L₆). (a) Before heat treatment. (b) After the treatment of 600° C for 1h.

It is notorious that the ${}^{5}D_{0}$ - ${}^{7}F_{2}$ transition has an intense growth with respect to the ${}^{5}D_{0}$ - ${}^{7}F_{1}$ transition. Besides, Eu $^{3+}$ ions show a stronger luminescence after the heat treatment.

Figure 4 shows the excitation spectra of Eu^{3+} with $\lambda_0 = 610$ nm. Fig. 4 (a), the bands located at 393 nm, 467 nm, 482 nm and 543 nm correspond to the ${}^7F_0{}^{-5}L_6$, ${}^7F_0{}^{-5}D_2$, ${}^7F_0{}^{-5}D_1$ and ${}^7F_1{}^{-5}D_1$, respectively. After the treatment of 600 °C for 1 h (Fig. 4b), the band at 376nm is due to the ${}^7F_1{}^{-5}G_3$ transition, the band located at 397 nm corresponds to ${}^7F_0{}^{-5}L_6$, the band at 469 nm is due to ${}^7F_0{}^{-5}D_2$, the band at 484 nm corresponds to ${}^7F_0{}^{-5}D_1$ transition and the band at 563 nm is due to ${}^7F_1{}^{-5}D_1$.



Figure 4. Excitation spectra of Eu^{3+} in amorphous TiO₂ matrix by using $\lambda_0 = 610$ nm. (a) Before heat treatment. (b) After the treatment of 600° C for 1h.

ii) $TiO_2/Eu^{3+}/Al(NO_3)_3$ film

Figure 5 shows the emission spectra for $TiO_2/Eu^{3+}/Al(NO_3)_3$ film $\lambda_{exc} = 397$ nm. Transitions from 5D_0 to 7F_j states are identified for amorphous film (Figure 5 a) and crystalline TiO₂ matrix (anatase) (Fig. 5 b).



Figure 5. Emission spectra of Eu³⁺ in: (a) Amorphous TiO₂/Al(NO₃)₃ film with $\lambda_{exc} = 397$ nm. (b) Crystalline TiO₂/Al(NO₃)₃ (anatase) with en $\lambda_{exc} = 394$ nm.

Figure 6 shows the excitation spectra of Eu^{3+} with $\lambda_o = 612$ nm. Fig. 6 (a) corresponds to the film before heat treatment, and Fig. 6 (b) corresponds to the sample after the treatment of 600 °C for 1 h. The 7F_i to excited states transitions are identified.



Figure 6. Excitation spectra of Eu³⁺ with $\lambda_0 = 612$ nm in: (a) Amorphous TiO₂/Al(NO₃)₃ film. (b) Crystalline TiO₂/Al(NO₃)₃ (anatase).

iii) $TiO_2/Eu^{3+}/PF127$ film

Figure 7 shows the emission spectra for TiO₂/Eu³⁺/PF127 film with $\lambda_{exc} = 394$ nm. Transitions from ⁵D₀ to ⁷F_j states are identified. Fig. 7 (a) presents the results for the amorphous film. Fig. 7(b) shows the results after the treatment of 600 °C for 1 h.



Figure 7. Emission spectra of Eu^{3+} in amorphous TiO₂/PF27 matrix by using $\lambda_{exc} = 394$ nm. (a) Before heat treatment. (b) After the treatment of 600° C for 1h.

Figure 8 shows the excitation spectra of Eu^{3+} with $\lambda_0 = 612$ nm, before heat treatment (Fig. 8 a), and after the treatment of 600 °C for 1 h (Fig. 8b), the ⁷F_i to excited states transitions are identified.



Figure 8. Excitation spectra of Eu³⁺ in amorphous TiO₂/PF127 matrix by using $\lambda_0 = 612$ nm. (a) Before heat treatment. (b) After the treatment of 600° C for 1h.

In the emission spectra for the three films, the bands corresponding to the ${}^{7}F_{2}$ transition show a slight increase for crystalline samples. It is possible the Eu³⁺ ions formed aggregates in amorphous films, therefore the luminescence is weaker. After the heat treatment, the aggregates were dissolved and the Eu³⁺ ions were incorporated into crystalline network of TiO₂ matrix, then the luminescence of Eu³⁺ increases (Fig 5 b).

The luminescence of ${}^{7}F_{4}$ for crystalline TiO₂/Eu³⁺/Al(NO₃)₃ film has a little decrement respect to the rest of films. Then the heat treatment induced two effects: i) the ions were incorporated into the titania matrix, ii) the ions are well separated, the aggregates were destroyed. Therefore the concentration quenching was avoided in the crystalline film. It shows that the Eu³⁺ ion can be used as optical probe, by using its hypersensitive transitions to follow changes in the local environment.

Figure 9 shows the unit cell for anatase phase (TiO₂). The Eu³⁺ will replaced the Ti⁴⁺, then for each two Eu³⁺ ions should be generated one O vacancy to neutralize the charge. The Eu³⁺ has positive charge, and the O vacancy has an excess of positive charge, therefore the Eu³⁺ ion moves rejected by the vacancy generating a non-centrosymmetric place.



Figura 9. Unit cell of anatase TiO₂.

It is well known that ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ emission is a hypersensitive transition, it means its intensity depends of the environment symmetry around the europium ion. It is very intense in asymmetric site. The intensity ratio of ${}^{5}D_{0}$ - ${}^{7}F_{2}/{}^{5}D_{0}$ - ${}^{7}F_{1}$ can be used as optical probe to determine the symmetry site where the Eu³⁺ ion is inserted. If this ratio increases then the symmetry site will decrease 10 .

Table 2 contains the positions for ${}^{5}D_{0}-{}^{7}F_{1}$ y ${}^{5}D_{0}-{}^{7}F_{2}$ transitions from emission spectra, and the intensity ratios for all films.

Sample	$\lambda_{ex} [nm]$	${}^{5}\text{D}_{0} - {}^{7}\text{F}_{1} \text{ [nm]}$	${}^{5}D_{0}-{}^{7}F_{2}[nm]$	${}^{5}D_{0}-{}^{7}F_{2}/{}^{5}D_{0}-{}^{7}F_{1}$
Amorphous TiO ₂ /Eu ³⁺ (No heat treatment)	394	591	612	1.00
Amorphous TiO ₂ /Eu ³⁺ (600 °C, 1h)	394	592	612	3.18
Amorphous TiO ₂ /Eu ³⁺ /PF127(No heat treat)	394	592	613	1.10
Amorphous TiO ₂ /Eu ³⁺ /PF127 (600 °C, 1h)	394	591	614	1.31
Amorphous TiO2/Eu3+/Al(NO3)3	397	592	613	3.36
Anatase TiO2/Eu3+/ Al(NO3)3	394	592	612	2.84

Table 2. Intensity ratios of the ${}^{5}D_{0}$ - ${}^{7}F_{1}$ y ${}^{5}D_{0}$ - ${}^{7}F_{2}$ transitions.

For $TiO_2/Eu^{3+}/Al(NO_3)_3$ film, the ${}^7F_2/{}^1F_2$ ratio decreases from 3.36 to 2.84 when the amorphous changes to crystalline phase (Table 2). This indicates that the Eu^{3+} changes from an asymmetric site (amorphous films) to a symmetric site (in crystalline film) with the heat treatment. This means europium position is not close to the oxygen vacancy required as charge compensator when substituting Ti^{4+} in the anatase phase.

For the other two films, TiO_2/Eu^{3+} and $TiO_2/Eu^{3+}/PF127$, the intensity ratios changed from 1.00 to 3.18 and from 1.10 to 1.31, respectively. This fact indicates that the europium ions are in a more asymmetric site after heat treatment, even titania phase was not formed.

4. CONCLUSIONS

Three different titania films doped with europium were obtained by sol gel method. After the heat treatment at 600°C for 1h, anatase phase was produced only in the $TiO_2/Eu^{3+}/Al(NO_3)_3$ films, which was identified by X-ray diffraction studies.

 Eu^{3+} ion was used as optical probe of the crystallization process by using its hypersensitive transitions. Even the small amount of material into the films and the weakness of the rare earth signal, the Eu^{3+} transitions were identified. After the heat treatment, the Eu^{3+} luminescence increases.

The ${}^{7}F_{2}/{}^{1}F_{2}$ ratio decreases when the film changed from amorphous to crystalline phase. This indicates that the Eu^{3+} is in an asymmetric place in the amorphous film, and this site changes to a symmetric one in the crystalline case. Therefore the europium moves to a more symmetric place far from the oxygen vacancy required as charge compensator when Eu^{3+} substituting Ti^{4+} in the anatase phase.

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