

Article

Optical Properties of ZrO₂, SiO₂ and TiO₂-SiO₂ Xerogels and Coatings Doped with Eu³⁺ and Eu²⁺

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Eu³⁺ doped bulk monoliths and thin films were obtained by sol-gel methods in the ZrO₂, SiO₂ and SiO₂-TiO₂ systems. Eu³⁺ ⁵D₀ → ⁷F_J emission and decay time characteristics were measured during the entire experimental preparation route from the initial sol to the final xerogels. The crystalline phases identified were tetragonal ZrO₂ and mixtures of rutile and anatase TiO₂ at high temperature treatments in bulk samples. Good quality thin films were obtained for all systems by dip-coating optical glasses (Schott BK270). The same spectroscopic features were observed either for the bulk monoliths or the films. By appropriate heat treatments under H₂ atmosphere Eu²⁺ containing samples could be obtained in the SiO₂-TiO₂ system.

Keywords: rare earths, Eu³⁺ spectroscopy, silica, titania, zirconia, thin films

1. Introduction

Despite the large number of papers dealing with the sol-gel preparation of rare earth containing materials either in the form of bulk monoliths or thin films, relatively few of them deal with the influence of the rare earth neighbourhood on the optical properties and its evolution with the materials preparation. Er³⁺ and Nd³⁺ doped materials have been mostly studied mainly due to their technologically important emission lines in the infrared region of the electromagnetic spectrum¹. Sm²⁺ systems have also been investigated due to their hole burning characteristics².

Eu³⁺ ions have been added to SiO₂³⁻⁸, SnO₂⁹⁻¹² and TiO₂¹³⁻¹⁵ with the main goal to understand the structural features well reflected in the observed spectroscopic characteristics.

In this work we investigate the Eu³⁺ spectral changes as a function of the experimental preparation route in SiO₂, SiO₂-TiO₂ and ZrO₂ prepared by a sol-gel method. The materials were obtained as xerogel monoliths, powders or thin films deposited on glass substrates by the dip-coating

technique. Some preliminary results in the reduction Eu³⁺ → Eu²⁺ are also presented.

2. Experimental

2.1. ZrO₂

Zirconium isopropoxide Zr(OC₃H₇)₄ was dissolved in isopropanol followed by addition of acetic acid. The solution was then treated with ultrasonic irradiation during 20 min. Water or Europium Chloride solution (0.1 M) were added and a clear and transparent sol was obtained. The molar ratio alkoxide:acetic acid:water was 1:7.8:24.8. Samples with 2.7%, 5.4% and 8.1% Eu (mol%) could be prepared.

2.2. SiO₂

Tetraethyl orthosilicate TEOS was diluted in ethanol followed by addition of acetic acid and hydrochloric acid solution (0.1 M), under ultrasonic irradiation. The molar ratio alkoxide:acetic acid: hydrochloric acid solution was 1:4:0.2. Clear sols containing 1.4%, 2.7% and 4.1% (%mol) Eu³⁺ were prepared.

2.3. SiO₂-TiO₂

TEOS was diluted in ethanol followed by addition of acetic acid under ultrasonic irradiation. Titanium ethoxide was then added followed by addition of methanolic solution of europium chloride and hydrochloric acid solutions. The molar ratio TEOS: Titanium ethoxide: acetic acid was 1:0.62:1.3. Clear sols containing 0.5% mol Eu³⁺ were prepared.

2.4. Thin films

Were obtained by dip-coating technique. Optical glass (Schott-BK270) slides (25 mm x 10 mm) were carefully cleaned, sunk in the sols and then withdrawn at a rate of 100 mm/min (for SiO₂-TiO₂ better depositions were achieved at 50 mm/min). The coated substrates were dried for about 15 min at room temperature and then heat treated at 500 °C. The homogeneity of the compositions and thickness were checked by scanning electron microscopy and energy dispersive X-ray (EDX) analysis.

2.5. Gels and Xerogels

Bulk monoliths were obtained drying the sols at room temperature (≈25 °C). In general zirconia sols gelify in 2-3 months. Silica and silica-titania systems gelify in 1-2 weeks. The monoliths were then further heat treated at 120, 500, 600, 800 and 950 °C. Some samples were also heat treated under H₂ atmosphere at 800 °C for 5, 10 and 24 h.

2.6. Optical and structural properties

Room temperature excitation and emission spectra were obtained under both continuous (450 W) and pulsed (5 mJ/pulse, 3 μs bandwidth) Xe lamps excitation with a SPEX Fluorolog F212I spectrofluorimeter. The spectra were all corrected for spectrometer optics, lamps output and detector response, and were obtained with typically 1nm bandwidth. Decay curves were processed with the SPEX 1934 phosphorimeter. X-ray diffractograms were obtained with a Siemens D5000 X-ray Diffractometer. Electron Microscopy (MEV) and chemical analysis (energy dispersive X-ray analysis) were performed with a ZEISS DSM960 Microscope.

3. Results and Discussions

Clear sols were obtained for all systems studied. With drying at room temperature, transparent monolithic xerogels could be obtained with typically 1 cm diameter in size. At 500 °C, SiO₂ and SiO₂-TiO₂ transparent monoliths were still obtained. ZrO₂ pieces appear grey in colour. Higher temperatures treatments gave transparent silica pieces and white ones for SiO₂-TiO₂ and ZrO₂.

Homogeneous films with the same compositions as the nominal ones have been obtained from dip coating. Thick-

ness in the range between 0.5 and 1 μm were routinely obtained for the 3 systems.

Figure 1 shows room temperature Eu³⁺ emission spectra, obtained throughout the experimental preparation route, from the stable sol to the xerogel heat treated at 950 °C, for the samples containing 8.1 mol% Eu³⁺ in the ZrO₂ system. No significant changes were observed for samples with lower Eu³⁺ concentrations. The spectra were obtained by exciting the ⁵L₆ level of the Eu³⁺ 4f⁶ configuration at 394 nm. One observes emission transitions arising mainly from the ⁵D₀ level to the ⁷F_J (J = 0-4) manifolds and similar spectra were observed for the starting sol (Fig. 1(a)) and the transparent wet gel (Fig. 1(b)). Eu³⁺ ions seem to strongly interact with the large scale polymeric chain networks assumed to exist in the zirconia colloidal system¹⁶. This feature is observed even for the initial sol, contrary to what is observed in silica systems where Eu³⁺ neighbouring is considered to be water-like in nature³⁻⁸.

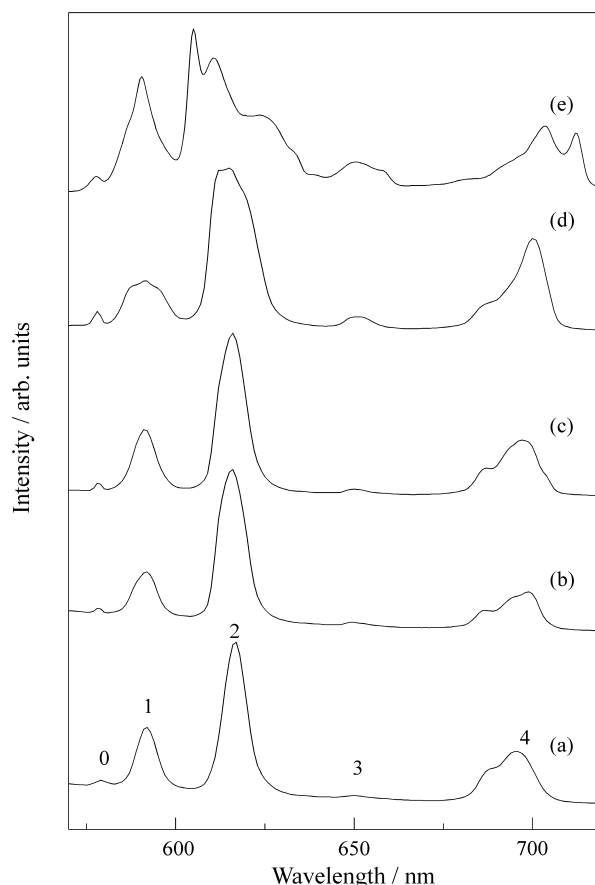


Figure 1. Eu³⁺ ⁵D₀ emission spectra in the ZrO₂ system (8% mol Eu³⁺) under ⁵L₆ excitation (395 nm). (a) Sol (τ(⁵D₀) = 0.52 ms); (b) Wet gel (τ(⁵D₀) = 0.52 ms); (c) Dried gel 50 °C (τ(⁵D₀) = 0.52 ms); (d) Dried gel 130 °C (τ(⁵D₀) = 0.84 ms) and (e) Xerogel 950 °C (τ(⁵D₀) = 3.57 ms). The numbers refer to the J values of the final level of the emission transitions ⁵D₀ → ⁷F_J.

Eu³⁺⁵D₀ measured lifetimes values are presented in the caption of the figure. Considering only radiative and non-radiative processes involved in the ⁵D₀ excited state depopulation, the rates for these two processes were evaluated from the measured decay times and transition intensities. The transition occurring at ≈590 nm (⁵D₀ → ⁷F₁) is known to be magnetic dipolar in character and therefore does not depend on the matrix nature. It can be taken as a reference ($A_{\text{rad}} = 50 \text{ s}^{-1}$ where A_{rad} is the spontaneous emission coefficient). The total radiative rate was estimated by considering the intensities ratios between this transition and the other ones arising from the ⁵D₀ level. The non-radiative transitions obtained with this procedure could then be related mainly to multiphonon processes through OH oscillators of water molecules in the first coordination sphere of the Eu³⁺ ions^{4,5}. From the results presented in the caption of Fig. 1 it is clear that the non-radiative decays become less and less important upon heating the samples. After a 120 °C heat treatment the emission spectrum closely resembles spectra obtained for Eu³⁺ containing oxide glasses, where the lines are inhomogeneously broadened and fully splitted³⁻¹². At this stage the samples lose their transparency although no crystalline phase could be detected by X-rays diffraction. If one relates the measured lifetimes with the number of coordinated water molecules¹⁷ the sample dried at 90 °C ($\tau = 0.84 \text{ ms}$) would present only one molecule of water for each Eu³⁺ ion. These results are largely encouraging regarding technological applications where water molecules are not welcome.

In zirconia systems the crystallisation process is known to occur at 500 °C¹⁸. All our samples heat treated at 500 °C became black, probably because of incomplete burning of organic residues, hindering spectroscopic measurements to be made. By increasing the temperature the samples became white powders and by X-ray diffraction we could identify the tetragonal ZrO₂ phase. At our knowledge there is no study on the limits of solubility for Eu³⁺ in this phase. As X-ray diffraction did not reveal other crystalline phase, we speculate at this stage that spectrum (e) in Fig. 1 is related to the Eu³⁺ doped tetragonal ZrO₂.

Figure 2 presents Eu³⁺ emission spectra for the sol, gel and heat treated samples in the SiO₂ system. Contrary to what was observed in the zirconia systems, good optical quality, transparent samples could be obtained for heat treatment temperatures up to 800 °C. This system is well studied in the literature, and our results agree with the previous published results³⁻⁸. The emission spectrum and the Eu³⁺⁵D₀ decay time ($\tau = 0.14 \text{ ms}$) obtained for the sol, are similar to the results observed for Eu³⁺ in water, and are a clear indication of a water-like neighbouring. With gelation the spectrum hardly changes and the decay time increased to 0.26 ms, reflecting water losses.

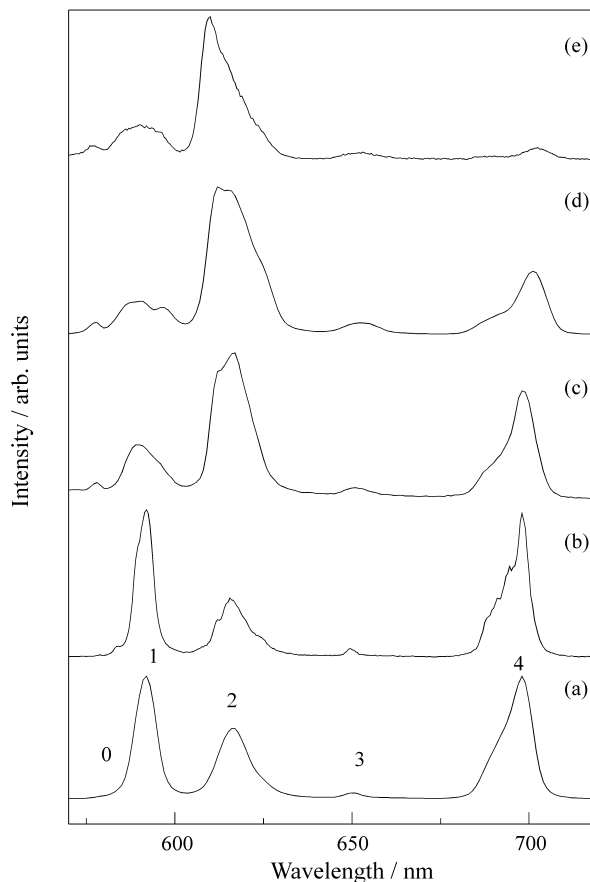


Figure 2. Eu³⁺⁵D₀ emission spectra in SiO₂ system under ⁵L₆ excitation (395 nm). (a) Sol ($\tau(^5\text{D}_0) = 0.14 \text{ ms}$); (b) Wet gel ($\tau(^5\text{D}_0) = 0.26 \text{ ms}$); (c) Dried gel 120 °C ($\tau(^5\text{D}_0) = 0.70 \text{ ms}$); (d) Dried gel 500 °C ($\tau(^5\text{D}_0) = 1.35 \text{ ms}$) and (e) Dried film 500 °C ($\tau(^5\text{D}_0) = 1.35 \text{ ms}$). The labels refer to the J values of the final level of the emission transitions ⁵D₀ → ⁷F_J.

For the sample heat treated at 120 °C the intensities ratio between the hypersensitive ⁵D₀ → ⁷F₂ transition (≈620 nm) and the magnetic dipolar ⁵D₀ → ⁷F₁ increases drastically and an inhomogeneous broadening typical of oxide glasses is observed which is a clear indication of lower symmetry for the Eu³⁺ surroundings. 1.2 neighbouring water molecules may be inferred from the decay time results ($\tau = 0.70 \text{ ms}$). The broadening of emission lines is still increased with 500 °C treatment (Fig. 2(d)) and from the Eu³⁺⁵D₀ decay time of 1.35 ms the number of OH oscillators at the Eu³⁺ surrounding may be estimated to be < 0.4. No crystalline phase could be detected.

Figure 2 also displays the emission spectrum obtained for the film submitted to the same 500 °C heat treatment (Fig. 2(e)). It shows differences in comparison with the spectrum obtained for the bulk sample mainly related to the relative transition intensity of the ⁵D₀ → ⁷F₄ transition at about 700 nm. The ⁵D₀ measured decay time of 1.35 ms is the same of the one obtained for bulk sample.

Figure 3 displays Eu^{3+} the emission spectra obtained for the system $\text{SiO}_2\text{-TiO}_2$. As for SiO_2 systems sol and wet gel present Eu^{3+} spectra very similar to the one observed for the aqua ion³⁻⁸ although decay times suggest about 4 water molecules for the Eu^{3+} surroundings. With heat treatments the structural changes are more spectacular than those observed in silica. The relative increase in intensity for the hypersensitive ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ is more important and the measured decay times are considerably longer. The same features are observed for the films (Fig. 3(c)). All these features must be related with the enhanced interactions of Eu^{3+} ions and the colloidal $\text{SiO}_2\text{-TiO}_2$ particles compared with the SiO_2 .

An 800 °C heat treatment results in the crystallisation of a mixture of rutile and anatase TiO_2 , as revealed by X-ray diffraction. Eu^{3+} seems to segregate in different phases as different emission spectra could be obtained just by changing the excitation wavelength. Figure 3 (d) pre-

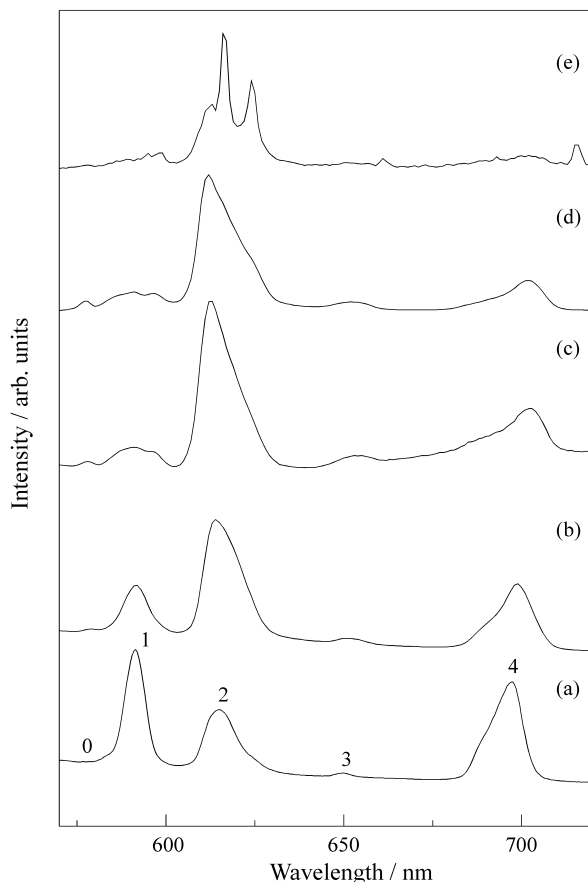


Figure 3. $\text{Eu}^{3+} {}^5\text{D}_0$ emission spectra in the $\text{SiO}_2\text{-TiO}_2$ system (0.5% mol Eu^{3+}). (a) Wet gel ($\tau({}^5\text{D}_0) = 0.24$ ms); (b) Dried gel 130 °C ($\tau({}^5\text{D}_0) = 0.92$ ms); (c) Dried film 500 °C ($\tau({}^5\text{D}_0) = 2.40$ ms); (d) Dried gel 800 °C ($\tau_1({}^5\text{D}_0) = 1.80$ ms; $\tau_2({}^5\text{D}_0) = 2.35$ ms) obtained under excitation at ${}^5\text{L}_6$ level (395 nm) and (e) Dried gel 800 °C ($\tau = 1.80$ ms) (excitation at 340 nm). The labels refer to the J values of the final level of the emission transitions ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$.

sents the spectrum obtained by excitation at 395 nm. This spectrum is very similar to the one obtained for the samples heat treated at lower temperatures, indicating Eu^{3+} ions statistically distributed in an amorphous matrix. Decay times could not be fitted by a single exponential law. Instead, the contribution of at least two components was necessary to well fit the curves. In the caption of the Fig. 3(d) decay times for these two components are denoted τ_1 and τ_2 . By changing the excitation wavelength to 340 nm a completely different spectrum is obtained as shown in Fig. 3(e). The increased decay time and the reduced bandwidths suggest the presence of Eu^{3+} in one of the crystalline phases detected by the X-ray diffraction. Further measurements are needed to completely characterise the Eu^{3+} neighbouring in this composite matrix.

Figure 4 shows the results obtained for some Eu^{3+} reduction experiments under N_2/H_2 atmosphere, for the $\text{SiO}_2\text{-TiO}_2$ system. Eu^{2+} may be easily identified by the broad emission band observed at around 500 nm and assigned to the $4f^65d \rightarrow 4f^7$ electronic transition. An increase in Eu^{2+} concentration is observed with longer treatments.

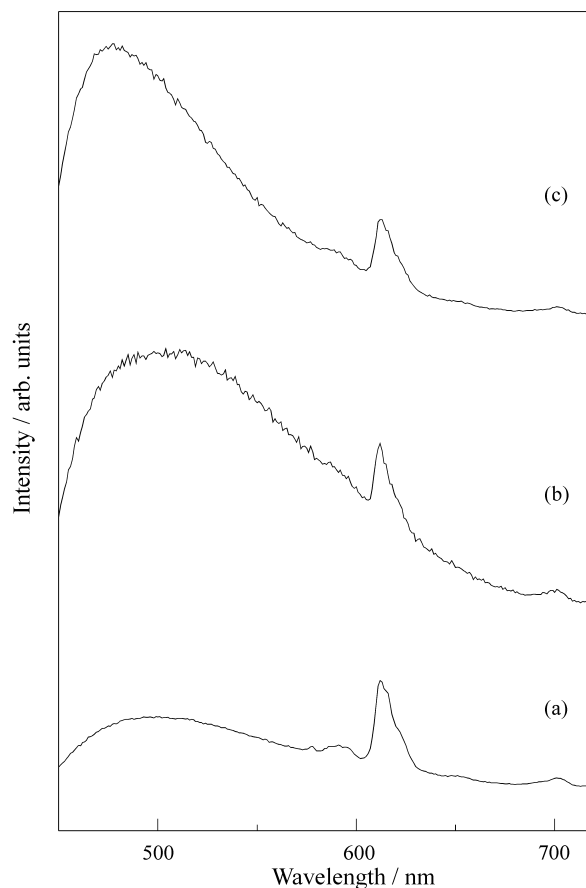


Figure 4. $\text{Eu}^{3+,2+}$ emission spectra in $\text{SiO}_2\text{-TiO}_2$ (0.5% mol Eu^{3+}) xerogels obtained after 800 °C heat treatment under H_2 atmosphere (excitation at 340 nm). (a) 5 h; (b) 10 h and (c) 24 h.

However, as the figure shows, a mixture of Eu³⁺ and Eu²⁺ is always obtained for treatments up to 24 h.

4. Conclusions

Clear gels containing Eu³⁺ have been obtained by the sol-gel process in the systems ZrO₂, SiO₂ and SiO₂-TiO₂. Eu³⁺ characteristic luminescence spectra have been measured after all processing steps.

In the case of silica and silica-titania systems a water like environment could be suggested for the Eu³⁺ neighbourhood in the initial sol and the wet gel. Spectra typical of silica glasses were obtained for silica xerogels treated at 500 °C with a ⁵D₀ level lifetime of 1.35 ms. For the silica-titania system the same observations could be done for heat treatments up to 500 °C. However a longer lifetime for the ⁵D₀ level is observed ($\tau = 2.40$ ms) denoting the enhanced interaction between Eu³⁺ ions and the colloidal matrix. The crystallization of a mixture of rutile and anatase TiO₂ is observed for 800 °C treatments. Eu³⁺ ions segregate in different phases as indicated by emission spectra.

In zirconia systems Eu³⁺ strongly interacts with the colloidal particles even in the initial sol. After 120 °C treatment spectra typical of oxide glasses are obtained.

The long ⁵D₀ decay times obtained after appropriate heat treatments suggest that low multiphonon decay for Eu³⁺ excited states are achieved in low phonon oxides such as ZrO₂ or TiO₂.

Good optical quality films were obtained for these systems and the easy for eliminating water molecules from the lanthanide neighbourhood is largely encouraging for utilization in optical devices.

A mixture of Eu³⁺ + Eu²⁺ was obtained from Eu³⁺ samples for preliminar experiments with heat treatments up to 24 h long under H₂/N₂ atmosphere.

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