Fluorescence of Eu^{3+} ions in TiO_2 optical planar waveguides fabricated by the sol-gel method

M. Bouazaoui, M. Bahtat, A. Bahtat, J. Mugnier

► To cite this version:

M. Bouazaoui, M. Bahtat, A. Bahtat, J. Mugnier. Fluorescence of Eu^{3+} ions in TiO_2 optical planar waveguides fabricated by the sol-gel method. Journal de Physique IV Proceedings, 1994, 04 (C4), pp.C4-341-C4-344. 10.1051/jp4:1994481 . jpa-00252744

HAL Id: jpa-00252744

<https://hal.science/jpa-00252744>

Submitted on 1 Jan 1994

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Fluorescence of Eu^{3+} ions in TiO_2 optical planar waveguides fabricated by the sol-gel method

M. BOUAZAOU, M. BAHTAT*, A. BAHTAT** and J. MUGNIER**

Laboratoire de Spectroscopie Hertzienne, URA 249 du CNRS, Université Lille I, Bât. P5, 59655 Villeneuve d'Ascq, France

** Laboratoire du Traitement du Signal et Instrumentation, URA 842 du CNRS, Faculté des Sciences, 23 bd du Dr. P. Michelon, 42023 Saint-Etienne, France*

*** Laboratoire de Physico-Chimie des Matériaux Luminescents, URA 442 du CNRS, Université Lyon I, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne, France*

Abstract

In recent years, rare-earth-doped optical planar waveguides have attracted considerable attention owing to their potential use in the field of integrated optics. To this end, several processes have been employed to produce rare-earth-doped waveguides. Here, we report on the fluorescence of europium trivalent ions in TiO_2 planar waveguides fabricated by using the sol-gel method and the dip-coating procedure. 2-mol % Eu^{3+} : TiO_2 films were deposited on optically polished pyrex substrates. These films are 80 nm thick and their refractive index is ranging from 1.8 to 2.1 depending on the annealing temperature (100°C-600°C). The fluorescence of Eu^{3+} ions was obtained by the excitation in the $^5\text{D}_2$ level with an Argon ion laser (wavelength = 465.8 nm). At room temperature, the fluorescence spectra were recorded for different annealing temperatures. A correlation was seen between the luminescence spectra and the structural evolution of the gel network. Indeed, it was observed that heat treatment increases the Stark splitting which partially removes the transitions J-degeneracy, indicating that Eu^{3+} ions occupy low-symmetry sites and are more embedded in the TiO_2 gel (densification of the TiO_2 gel). Furthermore, it was observed that increasing the annealing temperature entails a high frequency shift and a broadening of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition, which shows that Eu^{3+} ions occupy more distorted sites. These observations are in good agreement with results obtained by waveguide Raman spectroscopy.

Introduction

Optical spectroscopy of the Eu^{3+} ions has been used recently to investigate the structures of silica gels^[1,2] and silica gels evolving toward glasses^[2,3]. Campostrini et al^[1] have reported the study of the Eu^{3+} luminescence in sol-gel derived silica samples. Their work indicates that lifetimes, linewidths and Stark splittings of the Eu^{3+} transitions are an excellent probe for monitoring the densification process of the silica gels on heating.

The present work examines the Eu^{3+} fluorescence from TiO_2 optical planar waveguides prepared by sol-gel process. The luminescence spectra and waveguide Raman spectroscopy were used to follow the structural evolution of the thin films waveguides.

Experimental

The production of planar waveguiding TiO_2 films with a dip-coating method has been described elsewhere^[4]. Briefly, the starting solution was prepared using Titanium isopropoxide ($\text{Ti}(\text{O}^i\text{Pr})_4$ -Aldrich), iso-propanol ($^i\text{PrOH}$ -Merck) and acetic acid (AcOH -Prolabo) with a molar ratio $\text{AcOH}/\text{Ti} = 6$. Eu^{3+} ions were introduced by adding $\text{Eu}(\text{NO}_3)_3$ in a molar ratio $\text{Eu}(\text{NO}_3)_3/\text{Ti} = 2\%$. The mixture obtained was diluted by methyl alcohol. Pyrex substrates (75 mm x 25 mm) were carefully cleaned, then they were sunk into the solution and withdrawn from the bath at a rate of 40 mm mn^{-1} . Hence, the 2-mol% Eu^{3+} : TiO_2 films obtained are first dried at 100°C and then heated at different temperatures (300 °C, 400 °C and 600 °C) in the oven under a constant flow of pure and dry oxygen.

The experimental set-up for waveguide Raman spectroscopy has been described in a previous article^[5]. As shown in Fig.1, the incident beam delivered by a Krypton laser ($\lambda = 647.1$ nm) is coupled into the thin film using either heavy glass or rutile prisms. Light scattered at $\pi/2$ rad from the waveguide was analysed with a Jobin-Yvon model U-1000 double monochromator followed by RCA AsGa photomultiplier tube. The signal was processed by an Ortec photon counting system and recorded under computer control. Europium fluorescence spectra were monitored with the same experimental set-up except for the Krypton laser which was replaced by an Argon ion laser. All the spectra were recorded at room temperature.

FIG.1. Schematic representation of waveguide Raman spectroscopy apparatus.

Results:

The emission spectra of 2-mol % Eu^{3+} : TiO_2 thin films (thickness = 80 nm) heated at various temperatures are shown in Fig.2. These spectra were obtained by the excitation in the $^7\text{F}_0 \rightarrow ^5\text{D}_2$ line with an argon ion laser tuned at $\lambda = 465.8$ nm. The luminescence was detected only from $^5\text{D}_0$ state populated by non radiative relaxations from the excited state $^5\text{D}_2$. The $^5\text{D}_0 \rightarrow ^7\text{F}_{0,1,2,3,4}$ transitions reported on figure 2, shows that heat treatment of samples increases Stark splittings of transitions. This effect is clearly observed for the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition occurring at 16900 cm^{-1} . The full lifting

FIG.3. Luminescence spectra of the $^5D_0 \rightarrow ^7F_0$ transition obtained by excitation in 5D_2 state for different heat treatments : (a) 100°C, (b) 300°C, (c) 400°C, (d) 600°C.

FIG.2. Luminescence spectra of 2-mol-% $\text{Eu}^{3+} : \text{TiO}_2$ thin films waveguides obtained by excitation in 5D_2 state for different heat treatments : (a) 100°C, (b) 300°C, (c) 400°C, (d) 600°C.

degeneracy of the 7F_1 multiplet corresponding to the triplet structure observed, indicates that the Eu^{3+} ions occupy low symmetry sites. Moreover, the increasing of Stark splittings on heating therefore of local crystal field indicates that Eu^{3+} ions are more embedded in the gel network. The $^5D_0 \rightarrow ^7F_{2,3,4}$ transitions occurring respectively at 16200, 15300 and 14200 cm^{-1} , are more broadened at high annealing temperatures which is due to the strong local crystal field, but in this case the Stark components are not resolved. Figure 3 shows the $^5D_0 \rightarrow ^7F_0$ transition. The mean energy of this transition increases with heat treatment and a slightly broadening on heating was observed. All these observations indicates that at high annealing temperatures, Eu^{3+} ions are more embedded in the gel network (gel densification) and occupy low symmetry sites.

Typical Raman spectra of TiO_2 films annealed at various temperatures are shown in figure 4. The Raman spectrum of 2-mol % $\text{Eu}^{3+} : \text{TiO}_2$ thin film heated at 100°C exhibits a broad-bands characteristics of an amorphous structure. The same spectra was observed for an annealing temperature of 300°C. At high annealing temperatures (400°C and 600°C), resolved and narrow bands attributable to an anatase structure were observed at 144, 197, 399, 516 and 632 cm^{-1} .

FIG.4. Raman spectra of 2-mol % $\text{Eu}^{3+} : \text{TiO}_2$ thin films waveguides annealed at : (a) 100°C, (b) 400°C, (d) 600°C.

In conclusion, we have demonstrated that the densification of the gel network in 2-mol % $\text{Eu}^{3+} : \text{TiO}_2$ thin films is monitored through changes in the emission spectra of Eu^{3+} ions. The waveguide Raman spectroscopy of these thin films confirms this correlation.

- [1] R. Campostrini, G. Carturan, M. Ferrari, M. Montagna and O. Pilla. *J. Mater. Res.*, Vol 7, N°3, (1992) 745-753.
- [2] M.J. Lochhead and K.L. Bray. *ICL'93 Technical Digest*, August 9-13, 1993 (University of connecticut).
- [3] X. Fan, M. Wang and G. Xiong. *Materials Science and Engineering*, B21 (1993) 55-58.
- [4] M. Bahtat, J. Mugnier, A. Bahtat, J. Serrughetti. *Treizièmes journées Nationales d'Optique guidée*, INOG 93, 26-27 Mai (1993) 43/2.
- [5] J. Mugnier, B. Varrel, M. Bahtat, C. Bouvier and J. Serrughetti. *J. Mat. Sci. Lett.* 1992, 11, p 875.