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Preparation and study of the titanium oxide thin films doped with Tb^{3+} and Ce^{3+} ions

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ABSTRACT

In this study, we investigated the dependence of the thickness and refractive index of thin films on the withdrawal speed. The films were produced by dip-coating on a glass substrate. The hydrolytic (conventional) sol-gel method was used in the preparation of titanium alkoxide, which were obtained by homogenizing tetraethylorthotitanate stabilized by beta-diketone (2,4-pentanodione) in an alcohol solution. Potential applications, such as active planar waveguides, were evaluated by m-line spectroscopy, electron absorption spectra in the ultraviolet visible region, and photoluminescence. Based on the m-line measurements, the thickness of the films obtained from the homogenized sols were found to be dependent on the withdrawal speed. The thickness range from 400 to 500 nm to the films prepared by withdrawal speed 100 mm/min, 600 to 700nm using 200 mm/min, and 800 to 900 nm to withdrawal speed 300 mm/min. The refractive index is not affected by deposition speed. The photoluminescence of the Tb III ion exhibited lines that were attributed to the transitions characteristic of this ion, i.e., transitions from the $^5D_4$ excited state to the $^7F_{J\ (J=3,4,5,6)}$ fundamental state.

Keywords: titanium dioxide, sol-gel, coating, waveguide

1 INTRODUCTION

The development of techniques based on the production of thin films applied to materials science is one of the major factors responsible for technological advances [1]. There is much interest today in the design of new materials for waveguides. Based on the mechanical and optical properties of films deposited on transparent substrates, these materials are believed to have a wide range of potential applications in the field of optics [2, 3].

Thin films prepared by the sol-gel route have attracted special attention due to the formation of pores in their structure, which may originate applications such as chemical sensors and selective membranes [2], and which may be utilized to produce films with adequate protective behavior on metal substrates [4, 5].

Thanks to the spectral wealth provided by the lanthanide series it is possible to find ions that are perfectly suiTable for the regions of the electromagnetic spectrum used in telecommunications. Thin films doped with rare earth ions to obtain materials with luminescent properties offer unique advantages, such as easy doping and control of the concentrations of dopant [6]. When doped with photoactive organic molecules, these films can be used as optical components due to the transfer of energy.

Various studies have been conducted to obtain information about the morphology, thermal stability and spectroscopic properties of thin films, such as luminescence and life span of excited states [7, 8]. These thin films have engendered much interest due to the variety of possible applications, which include optical [9] and electroluminescent [10, 11] devices, sensors [12, 13], biomaterials [14-16] and others [17].

Ce^{3+} ions have important applications due to their high chemical stability and high diffusion coefficient [18-22]. Tb^{3+} is used in color TV tubes to provide green fluorescence [23, 24]. The transfer of energy between Ce^{3+} and Tb^{3+} ions has been the object of numerous investigations in different matrices [25, 26], because the luminophores that present this phenomenon can be used industrially as green components in low vapor pressure fluorescent lamps, in borax glasses and as X-ray image intensifiers [27-29]. In addition to presenting intense emission in the red region of the electromagnetic spectrum, enabling it to act as a luminophore, the Eu^{3+} ion is also an efficient structural probe [8, 18, 30, 31]. Other rare earths have also been used extensively, particularly those that present emission in the infrared region, such as Er^{3+} ions [32 - 34].

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In this work, titanium oxide thin films were prepared by the conventional sol-gel route, using titanium alkoxide stabilized with beta-diketone. The films, obtained by dip-coating at different withdrawal rates and containing Tb^{3+} only and Tb^{3+} and Ce^{3+} ions, were characterized by m-line measurements, by the photoluminescence of the Tb^{3+} ions, and UV-Vis absorption spectroscopy.

2 MATERIALS AND METHODS

The rare earth oxides were calcined at 900°C for 2h. Then, Ce_2O_3 or Tb_4O_7 was dissolved in H_2O and HCl 6 $mol.L^{-1}$. Excess HCl and H_2O were evaporated. The ethanol was then added and evaporated three times. The final concentration of RE ion in the ethanolic solution was 1.0 x 10^{-1} mol L^{-1}.

The sols were prepared from titanium isopropoxide stabilized with beta-diketone 2,4-pentanedione (acac) in a molar ratio of 1:1 [35]. The $TbCl_3$ and $CeCl_3$ were add in the sols, 1% compared to titanium oxide.

The films were produced by dip-coating. The borosilicate glass substrates (80 x 20 mm) were carefully cleaned in a solution containing hydrogen peroxide and sulfuric acid (30:70) and then immersed in the sols and withdrawn at withdrawal speeds of 100, 200 and 300 mm/min. The films were dried at 50°C for 2 hours.

The refractive index and film thickness were measured at UNESP's Institute of Chemistry of Araraquara, using an m-line prism coupler refractometer (Metricon model 2110). A gadolinium gallium garnet (GGG) prism with a refractive index of 1.9644 to 632.8 nm was used. The device was equipped with a Si and Ge detector to record visible light and NIR, respectively. Two He-Ne lasers were used, operating at 632.8 and 543.5 nm [18].

The emission and excitation spectra, which were also measured at the Institute of Chemistry of Araraquara, were obtained at room temperature with a 450W continuous Xe lamp in a SPEX Fluorolog F2121 spectrofluorimeter, 2.0 and 0.5 nm slots were used for the excitation and emission, respectively.

The UV-Vis absorption spectroscopy: were measured in a Packard 8453 Diode Array spectrophotometer coupled to a HP KAYAK- XA microcomputer and its respective software.

3 RESULTS AND DISCUSSION

Figures 1 and 2 show the thickness and refractive index of the titanium films containing Tb^{3+} and Tb^{3+}/Ce^{3+} ions, as a function of the different withdrawal speeds.

The films' refractive index varied little, regardless of the withdrawal speed and dopants used, this is an indicative that rare earths ions is not affected by the titanium oxide structure. The refractive index is very important in applications such as waveguides.

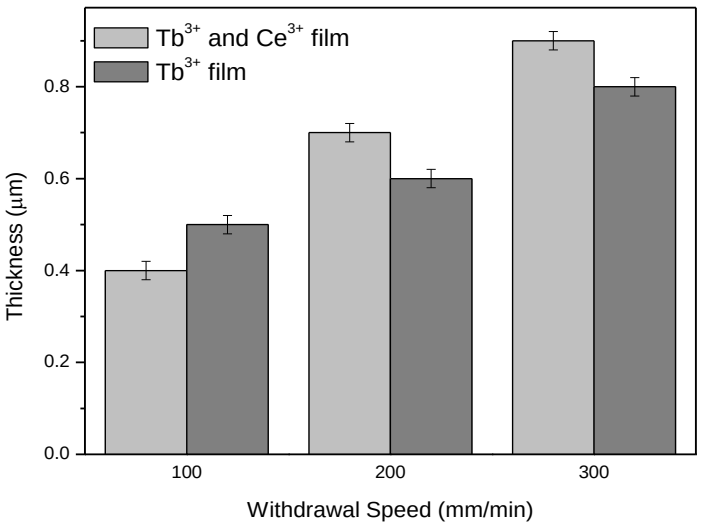

Figure 1: Dependence of the film's thickness on withdrawal speed.

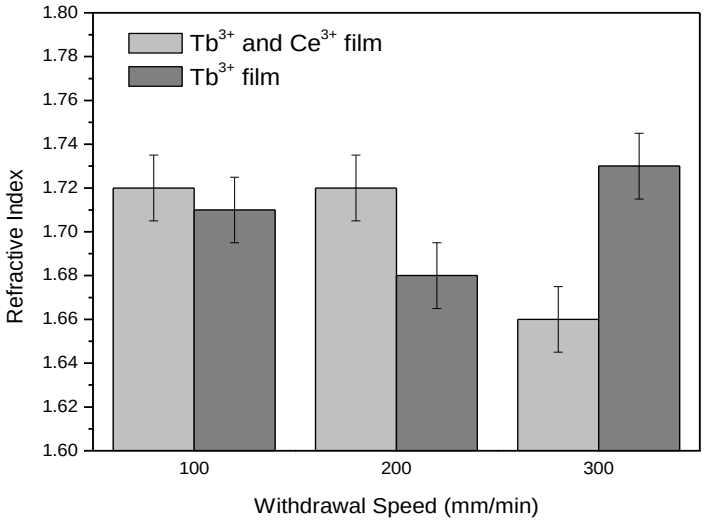

Figure 2: Dependence of the film's refractive index on withdrawal speed.

On the other hand, their thickness proved dependent on the speed of deposition since, as can be seen in Figure 1, all the films showed increasing thickness as the withdrawal speed increased. This was probably due to the fact that when the substrate is removed rapidly from the solution, the small amount of solution on it does not flow off but remains adhering to the substrate. In contrast, when the substrate is removed slowly the solution has more time to flow off, thereby reducing the film's final thickness. These results can happen depending on the parameters that influence the deposition [17]. The control of the thickness could be determining the applications of the films, the sensors, device, and several other applications.

Figure 3 shows the profile of the refractive index of the film's surface, reconstructed from the effective indices measured at 633 nm by means of the inverse method of Wentezel-Kramers-Brillouin [34] for the sample obtained at a withdrawal speed of 300 mm/min, where the index is usually lower the closer it is to the substrate. The highest refractive index is at the surface of the film, while the lowest is on the surface of the substrate. The profile for the others samples, 200 and 100 mm/min, was not presented, because they showed two and one guided modes, respectively.

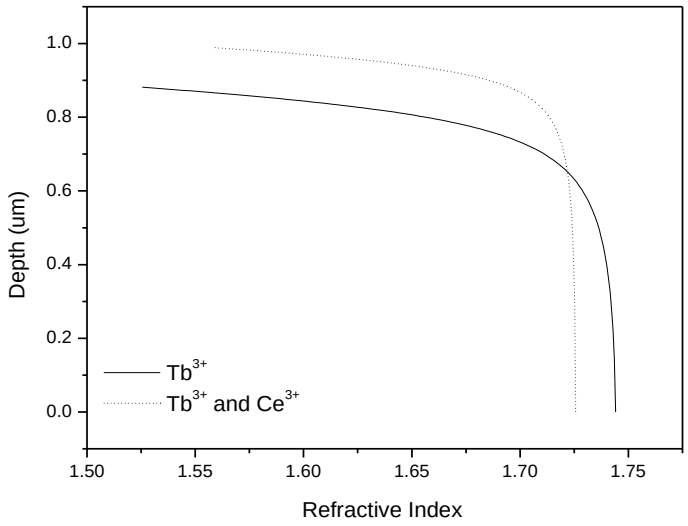

Figure 3: Profile of the refractive index for the film deposited at a speed of 300mm/min, reconstructed from modal measurements taken at 633nm.

The number of the guided modes can be related to the homogeneity and uniformity of the films, in this work we observed 3, 2 and 1 guided modes to samples prepared by 300, 200 and 100 mm/min, respectively. The TiO_2 films deposited at a speed of 300 mm/min were more homogeneous and uniform (Fig. 3) than those deposited at 100 and 200 mm/min.

The excitation spectrum of the Tb^{3+} ion in the films deposited at different speeds were obtained when the maximum emission fixed in the $^5D_4 \rightarrow {}^7F_5$ transition at 544 nm. The spectrum exhibits a very broad band ranging from 250 to 350 nm with the maximum excitation wavelength centered at 280 nm for the sample with only Tb^{3+}, which can be attributed to a charge transfer band. The sample with Tb^{3+}/Ce^{3+} the spectra exhibit a broad band at around 328 nm in the three film samples and a band of lower intensity at 277 nm, which can be ascribed to Ce^{3+} ions and a charge transfer band.

Figures 4 and 5 shows the emission spectra of Tb^{3+} ions in the films with Tb^{3+} only and Tb^{3+}/Ce^{3+}, deposited at different speeds with excitation in the charge transfer band at 280 nm and 328 nm, respectively.

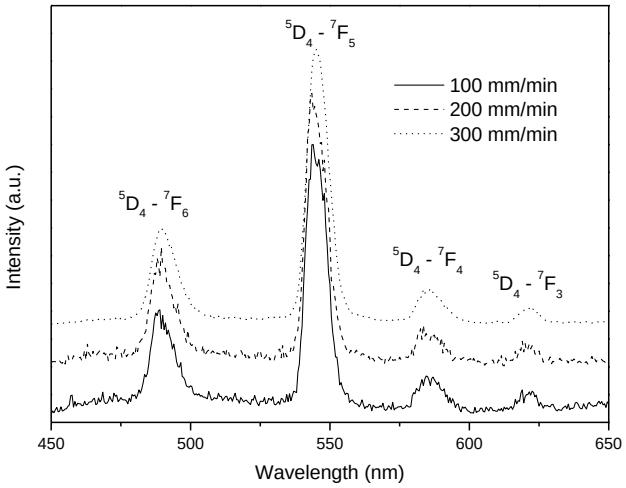

Figure 4: Emission spectra of Tb^{3+} ions in films deposited at different speeds and excited in the charge transfer band at 280 nm.

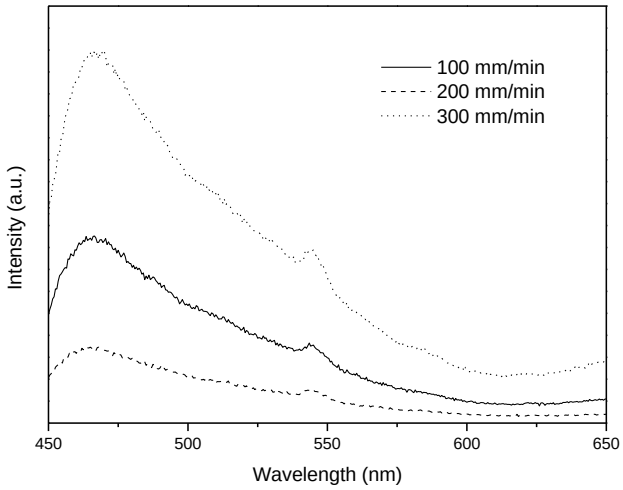

Figure 5: Emission spectra of Tb^{3+}/Ce^{3+} ions in films deposited at different speeds and excited at 328 nm.

In the lines attributed to the transitions characteristic of the Tb^{3+} ion at 487 nm ($^5D_4 \rightarrow {}^7F_6$), 543 nm ($^5D_4 \rightarrow {}^7F_5$), 583 nm ($^5D_4 \rightarrow {}^7F_4$) and 621 nm ($^5D_4 \rightarrow {}^7F_3$), note that the noise-to-signal ratio of the emission spectrum for the ion in the film deposited at a speed of 300 mm/min is smaller than that of the other spectra. This difference may indicate the existence of a larger quantity of emitting ions in the film. A comparison of the results obtained by m-line indicates that this film is thicker, and therefore contains a larger quantity of Tb^{3+} ions.

Excitation at 328 nm, however, clearly favored emission from the matrix itself, a broad band in the blue spectrum of the electromagnetic spectrum. An energy transfer from Ce → Tb was not observed in these samples, where Ce was used in order to intensify the Tb emission. In addition to the non-occurrence of this phenomenon, the Ce ended up by interfering in the emission of Tb, causing suppression of the luminescence.

Figure 6 illustrate the emission spectra of the three films excited at 277nm for the sample contend Tb^{3+}/Ce^{3+}.

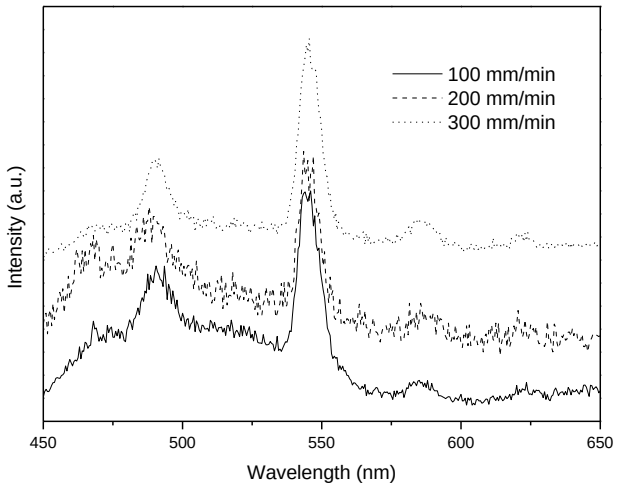

Figure 6: Emission spectra of Tb^{3+}/Ce^{3+} ions in films deposited at different speeds and excited at 277 nm.

Note that exciting the samples at different wavelengths produced emission spectra favoring different emitting species. Using a wavelength of 277 nm, which was the same one as that applied to the films containing only Tb^{3+}, produced emission bands characteristic of the ion but with a very high noise to-signal ratio.

Figure 7 presents the absorption spectra in the UV-Vis region of the titanium oxide films containing Tb^{3+}/Ce^{3+} ions.

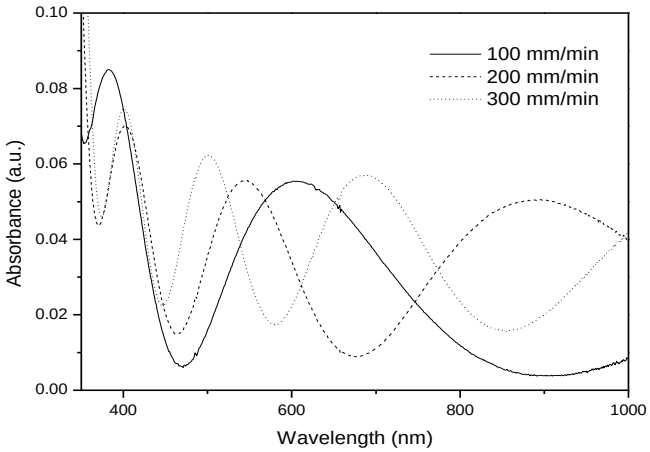

Figure 7: UV-Vis absorption spectra of the TiO_2 film doped with Tb^{3+}/Ce^{3+}, deposited at speeds of 100, 200 and 300 mm/min**.**

The film's thickness and index of refraction can be determined quantitatively by the transmission or absorption spectrum. Qualitatively, the above Figures demonstrate that the number of interference fringes increase as a function of the deposition speed, indicating an increase in the film's thickness [36], which is confirmed by the data obtained through the m-line technique.

4 CONCLUSION

TiO2 films were deposited using the sol-gel route. This study demonstrated that the use of a very simple technique such as dip-coating enables one to control the thickness of films according to the withdrawal speed. The higher withdrawal speed the greater amount of the liquid is pulled which results in a thicker film. This is an indicative that the gravity effect must be considered in the dip-coating process. This was confirmed by m-line.

Based on the films' photoluminescence, we noted transition lines characteristic of Tb3+, where the expected Ce3+ → Tb3+ energy transfer did not occur, probably due to the TiO2 structure.

5 ACKNOWLEDGEMENTS

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6 BIBLIOGRAPHY

[1] ALVES, O.A., RONCONI, C.M., GALEMBECK, A., "Decomposição de precursores metalorgânicos: uma técnica química de obtenção de filmes finos", *Química Nova*, v. 25, n. 1, pp. 69-77, fevereiro 2002.

[2] REISFELD, R., ZELNER, M., PATRA, A., "Fluorescence study of zirconia films doped by Eu^{3+}, Tb^{3+} and Sm^{3+} and their comparison with silica films", *Journal of Alloys and Compounds*, v. 300-301, pp. 147-151, April 2000.

[3] ETIENNE, P., COUDRAY, P., PORQUE, J., *et al*., "Active erbium-doped organic–inorganic waveguide", *Optical Communication*, v. 174, n. 5-6, pp. 413-418, February 2000.

[4] NASSAR, E.J., CIUFFI, K.J., GONÇALVES, R.R., *et al*., "Filmes de titânio-silício preparados por "spin" e "dip-coating"", *Química Nova*, v. 26, n. 5, pp. 674-677, 2003.

[5] SANCHEZ, C., JULIÁN, B., BELLEVILLE, P., *et al*., "Applications of hybrid organic–inorganic nanocomposites", *Journal of Materials Chemistry*, v. 15, n. 35-36, pp. 3559-3562, 2005.

[6] ZHANG, H.J., FU, L.S., WANG, S.B., *et al*., "Luminescence characteristics of europium and terbium complexes with 1,10-phenanthroline in-situ synthesized in a silica matrix by a two-step sol–gel process", *Materials Letters*, v. 38, n. 4, pp. 260-264, 1999.

[7] MENG, Q.G., FU, L.S., WANG, S.B., *et al*., "Preparation and optical characterization of an organoeuropium-doped sol–gel transparent luminescence thin film", *Thin Solid Films*, v. 1-2, n. 1, pp. 87-92, 2001.

[8] ROCHA, L.A., CIUFFI, K.J., SACCO, H.C., *et al*., "Influence on deposition speed and stirring type in the obtantion of titania films", *Materials Chemistry Physcs*, v. 85, n. 2-3, pp. 245-250, 2004.

[9] QUE, W., SUN, Z., ZHOU, Y., *et al*., "Optical and mechanical properties of TiO_2/SiO_2/organically modified silane composite films prepared by sol–gel processing", *Thin Solid Films*, v. 359, n. 2, pp. 177-183, 2000.

[10] UEKAWA, M., MIYAMOTO, Y., IKEDA, H., *et al*., "Synthesis and properties of europium complexes with β-diketone ligands for organic electroluminescent devices", *Bulletin Chemistry Society Japan*, v. 71, pp. 2253-2258, 1998.

[11] ZHANG, R.J., YANG, K.Z., YU, A.C., *et al*., "Fluorescence lifetime and energy transfer of rare earth *β*-diketone complexes in organized molecular films", *Thin Solid Films*, v. 363, n. 1-2, pp. 274-278, 2000.

[12] KUMAR, A., MALHOTRA, R., MALHOTRA, B.D., *et al*., "Co-immobilization of cholesterol oxidase and horseradish peroxidase in a sol–gel film", *Analytical Chimica Acta*, v. 414, n. 1-2, pp. 43-50, 2000.

[13] GOUDA, M.D., KUMAR, M.A., THAKUR, M.S., *et al*., "Enhancement of operational stability of an enzyme biosensor for glucose and sucrose using protein based stabilizing agents", *Biosensors and Bioelectronics*, v. 17, n. 6-7, pp. 503-507, 2002.

[14] RODDICK-LANZILOTTA, A.D., MAQUILLAN, A.J., "An *in situ* infrared spectroscopic investigation of lysine peptide and polylysine adsorption to tio$_2$ from aqueous solutions", *Journal of Colloid and Interface Science*, v. 217, n. 1, pp. 194-202, 1999.

[15] HAMADA, K., KON, M., HANAWA, T., *et al*., "Hydrothermal modification of titanium surface in calcium solutions", *Biomaterials*, v. 23, n. 10, pp. 2265-2272, 2002.

[16] HANAWA, T.,"In vivo metallic biomaterials and surface modification", *Materials Science and Enginnering A*, v. 267, n. 2, pp. 260-266, 1999.

[17] BRINKER, C.J., SHERRER, G.W., In: Sol-gel science: *The physics and chemistry of sol-gel processing*, Academic Press, New York, 1990.

[18] NASSAR, E.J., GONÇALVES, R.R., FERRARI, M., *et al*, "Titania-based organic–inorganic hybrid planar waveguides", *Journal of Alloys and Compounds*, v. 344, n. 1-2, pp. 221-225, 2002.

[19] TRINCHI, A., LI, Y.X., WLODARSKI, W., *et al*, "Investigation of sol–gel prepared CeO_2–TiO_2 thin films for oxygen gas sensing", *Sensors and Actuators B: Chemical*, v. 95, n. 1-3, pp. 145-150, 2003.

[20] MURATA, T., SATO, M., YOSHIDA, H., *et al*., "Compositional dependence of ultraviolet fluorescence intensity of Ce^{3+} in silicate, borate, and phosphate glasses", *Journal of Non-Crystalline Solids*, v. 351, n. 4, pp. 312-318, 2005.

[21] TAGO, T., TASHIRO, S., HASHIMOTO, Y., *et al*., "Synthesis and optical properties of SiO_2-coated CeO_2 nanoparticles", *Journal of Non-Crystalline Solids*, v. 351, pp. 312-315, 2005.

[22] JIA, P.Y., YU, M., LIN, J., "Sol–gel deposition and luminescent properties of $LaMgAl_{11}O_{19}$:Ce^{3+}/Tb^{3+} phosphor films", *Journal of Solid State Chemistry*, v. 178, n. 9, pp. 2734-2740, 2005.

[23] PIVIN, J.C., GAPONENKO, N.V., MOLCHAN, I., *et al*., "Comparison of terbium photoluminescence from ion implanted and sol–gel-derived films", *Journal of Alloys and Compounds*, v. 341, n. 1-2, pp. 272-274, 2002.

[24] ISMAIL, A.A., ABBOUDI, M., HOLLOWAY, P., *et al*., "Photoluminescence from terbium doped silica–titania prepared by a sol–gel method", *Materials Research Bullitin*, v. 42, n. 1, pp. 137-142, 2007.

[25] REISFELD, R., HORMADALY, J., "Quantum yield of Ce^{3+} and energy transfer between Ce^{3+} and Tb^{3+} in borax glasses", *Journal of Solid State Chemistry*, v. 13, n. 4, pp. 283-287, 1975.

[26] FINKE, B., SCHWARZ, L., GURTLER, P., *et al*., "Optical properties of potassium rare earth orthophosphates of the type $K_3RE(PO_4)_2$", *Journal of Luminescence*, v. 60-61, pp. 975-978, 1994.

[27] HOLSA, J., LESKELA, M., NIINISTO, L., "Sensitization of Tb^{3+} luminescence with Ce^{3+} in LaOBr: Tb^{3+}, Ce^{3+}", *Journal of Solid State Chemistry*, v. 37, n. 3, pp. 267-270, 1981.

[28] SERRA, O.A., NASSAR, E.J., ZAPPAROLLI, G., *et al*., "Photophysical properties of Ce^{3+}:Tb^{3+} supported on silicas and zeolites", *Journal of Alloys and Compounds*, v. 225, n. 1-2, pp. 63-65, 1995.

[29] YOU, H., WU, X., CUI, H., *et al*., "Luminescence and energy transfer of Ce^{3+} and Tb^{3+} in $Y_3Si_2O_8Cl$", *Journal of Luminescence*, v. 104, n. 3, pp. 223-227, 2003.

[30] PILLONNET, A., MUGNIER, J., LE BIHAN, V., *et al.*, "Rare-earth-based nanoclusters embedded in sol–gel waveguiding thin films", *Journal of Luminescence*, v. 119-120, pp. 560-564, 2006.

[31] ROCHA, L.A., MOLINA, E.F., CIUFFI, K.J., *et al*., "Eu (III) as a probe in titania thin films. The effect of temperature", *Materials Chemistry Physics*, v. 101, n. 1, pp. 238-241, 2007.

[32] AFIFY, N.D., GRISENTI, R., DALBA, G., *et al*., "Short-range order around Er^{3+} in silica waveguides containing aluminium, titanium and hafnium", *Optical Materials*, v. 28, n. 6-7, pp. 864-867, 2006.

[33] HUONG, T.T., ANH, T.K., NAM, M.H., *et al*., "Preparation and infrared emission of silica–zirconia–alumina doped with erbium for planar waveguide", *Journal of Luminescence*, v. 122-123, pp. 911-913, 2007.

[34] SIGOLI, F.A., GONÇALVES, R.R., MESSADDEQ, Y., *et al*, "Erbium- and ytterbium-doped sol–gel SiO_2–HfO_2 crack-free thick films onto silica on silicon substrate", *Journal of Non-Crystalline*, v. 352, n. 32-35, pp. 3463-3468, 2006.

[35] DUVERGER, C., FERRARI, M., MAZZOLENI, C., *et al*., "Optical spectroscopy of Pr^{3+} ions in sol–gel derived GeO_2–SiO_2 planar waveguides", *Journal of Non-Crystalline Solids*, v. 245, n. 1-3, pp. 129-134, 1999.

[36] KUBINYI, M., BENKÖ, N., GROFESIK, A., *et al*., "Determination of the thickness and optical constants of thin films from transmission spectra", *Thin Solid Films*, v. 286, n. 1-2 , pp.164-169, 2006.