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ORIGINAL PAPER

Luminescence in Colorless, Transparent, Thermally Stable Thin Films of Eu^{3+} and Tb^{3+} β-diketonates in Hybrid Inorganic–Organic Zinc-based Sol–Gel Matrix

Renata Figueredo Martins · Rodrigo Ferreira Silva · Rogéria Rocha Gonçalves · Osvaldo Antonio Serra

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Abstract Luminescent zinc-based hybrid inorganic–organic films with rare–earth (RE) complexes have been prepared using a non-alkoxide sol–gel process. The films were fabricated by the dip-coating method starting from zinc acetate dihydrate, rare earth chloride, lactic acid as hydrolytic catalyst, and anhydrous ethanol. The β-diketones thenoylltrifluoroacetone (Httfa) and dibenzoylmethane (Hdbm) were used as ligands to Eu^{3+} and Tb^{3+}, respectively. After deposition of the first layer, the films were fired at temperatures between 50 and 300 °C, in air. Photophysical properties such as excitation, emission and emission, lifetimes were determined for the films obtained in different conditions. Eu^{3+}/ttfa and Tb^{3+}/dbm films fired at 300 and 250 °C, respectively, are still transparent and gave rise to intense emission when excited through the ligand (*antenna* effect).

Keywords Luminescence films · Sol–gel process · β-diketonates · *Antenna* effect · Thermal stability

Introduction

Lanthanide complexes have been shown to be a class of very promising materials for use as emission devices. This is mainly because the rare earth (RE) luminescence intensity can be improved through ligand-assisted energy transfer, namely the *antenna* effect. The forbidden f-f transitions are enhanced by coordination with appropriate ligands (light collectors) such as β-diketonates and criptates, where Eu^{3+} and Tb^{3+} compounds can give emissions with good efficiency in several systems [1]. Another way to enhance the lanthanide emission is to employ embedded inorganic matrices such as the semiconductors GaP [2], ZnO [3], TiO_2 [4], and sol–gel derived glasses [5]. Among various methodologies, the sol–gel process has been widely employed for preparation of luminescent rare–earth based materials in inorganic hosts in very mild conditions. Most studies have reported hydrolysis and polymerization reactions of the alkoxide precursors using europium and terbium complexes containing coordinated organic ligands (β-diketones and aromatic carboxylic acids) to prepare powders, bulk monoliths [6–10], and films [11]. However, the use of non-alkoxide precursors is also desirable due to their low cost and non-toxicity [12]. Luminescent films have potential application as organic light-emitting diodes (OLEDs) in large-area flat panels [13–16]. For full-color applications, a set of red, green, and blue emitters with sufficiently high luminous efficiency and proper chromaticity is necessary.

In recent years, zinc oxide films have also become technologically important because of their range of electrical and optical properties, together with their high chemical and mechanical stabilities, which make them suitable for a variety of applications. The preparation of stable colloidal zinc oxide nanoparticles through sol–gel process from non-alcoxide reagents have been well described by Bahnemann et al. [17] and Spanhel et al. [18]. Thin zinc oxide films have been prepared by Tang et al. [19] and Silva et al. [20], through thermal decomposition of a stable precursor colloidal sol prepared from an ethanolic reflux of zinc acetate and lactic acid as the hydrolysis catalyst. A similar procedure has been reported for the preparation of ZnO:Eu films [21]. However, the efficiency of the emission

R. F. Martins · R. F. Silva · R. R. Gonçalves · O. A. Serra (✉)
Department of Chemistry, FFCLRP-USP,
Av. dos Bandeirantes, 3900,
CEP 14040-901 Ribeirão Preto, SP, Brazil
e-mail: osaserra@usp.br

luminescence of rare earth ions in ZnO matrices is not satisfactory compared with the same ions in other commercialized phosphors. This is due to the large difference in ionic radii between Zn^{2+} and the rare earth ions ($R_{Zn^{2+}} = 0.06$ nm, $R_{RE^{3+}} = 0.10 - 0.12$ nm), which makes penetration of the rare earth ions into the ZnO crystal lattice very difficult [22]. The presence of thermally stable organic ligands capable of acting as an *antenna* and forming an array of strongly absorbing units and a rare earth emitter in an inorganic matrix should produce an efficient light-conversion device. Matrices obtained as described by Tang [19] from non-alkoxide precursors are good candidates to meet such conditions, although no devices have been reported so far.

We describe the fabrication and photophysical properties of colorless, transparent, thermally stable thin films where Eu^{3+}/thenoyltrifluoroacetonate (ttfa) and Tb^{3+}/dibenzoylmethanate (dbm) were embedded in a hybrid inorganic–organic zinc-based sol–gel matrix prepared by a non-alkoxide sol–gel process.

Experimental procedure

The colloidal sols were prepared using methodologies described elsewhere [19, 20]. Ethanolic solutions of the rare earth chlorides (0.10 mol L^{-1}) were added separately to an ethanolic suspension of zinc acetate dihydrate (0.44 mol L^{-1}). The system was kept under reflux, and lactic acid was added until complete dissolution of the solid, thus forming a stable and translucent sol. Solid Httfa and Hdbm were added to the sols containing Eu^{3+} and Tb^{3+}, respectively, and agitated at ~25 °C for 30 min. Molar ratios of 1:100 and 1:3 for RE^{3+}/Zn^{2+} and RE^{3+}/β-diketonate, respectively, were employed. The sols were stable in a closed flask for a long period of time (a month or longer).

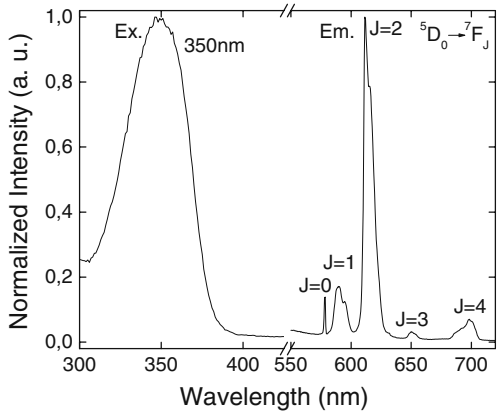

Fig. 1 Excitation spectrum (λ_{em}=612 nm) and emission spectrum (λ_{exc}=350 nm) of the Eu^{3+}/ttfa film annealed at 150 °C for 15 min

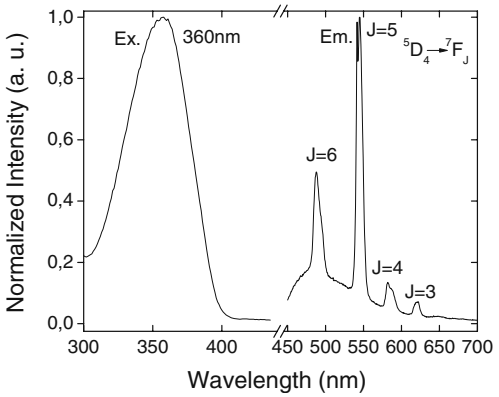

Fig. 2 Excitation spectrum (λ_{em}=543 nm) and emission spectrum (λ_{exc}=360 nm) of the Tb^{3+}/dbm film annealed at 150 °C for 15 min

The films were deposited over borosilicate glass substrates previously washed with a sodium dodecylsulfate detergent, treated ultrasonically with deionized water for 30 min, followed by another 30 min treatment with ethanol, and dried in ambient conditions. As for the transfer process, only one deposition of the 15-day aged sol (~25 °C) onto glass substrates was carried out by dip-coating at 4.0 cm min^{-1}, and the sol was kept immersed for 30 s. The films were thermally treated at 50, 100, 150, 200, 250, 300, and 350 °C for periods of 15 and 30 min. Thermal stability experiments were performed by heating the films at 150 °C for 15 min, then repeating the procedure until 2 h, and the emission spectrum was obtained after each step.

The emission and excitation spectra of the films were measured using a SPEX TRIAX 550 FLUOROLOG III spectrofluorometer with a 450 W xenon lamp and a Hammamatsu R928 photomultiplier. The luminescence of decay curves were measured using a 1934D phosphorimeter accessory with a pulsed xenon lamp. All measurements were accomplished at room temperature.

Results and discussion

Figures 1 and 2 show the excitation and emission spectra of the colorless transparent films annealed at 150 °C for 15 min. The excitation spectra of the materials were obtained by monitoring the emission of the Eu^{3+} and Tb^{3+} ions at 612 nm and 543 nm, respectively. The excitation spectra reveal broad bands with maxima at 350 and 360 nm due to energy transfer from ttfa and dbm to Eu^{3+} and Tb^{3+}, respectively. The emission spectrum (Fig. 1) of the Eu^{3+}/ttfa film displays bands at 578, 590, 612, 650, and 698 nm, assigned to the $^5D_0 \rightarrow ^7F_J$ (J=0,1,2,3,4) transitions with the hypersensitive $^5D_0 \rightarrow ^7F_2$ red emission as the most prominent group. Figure 2 shows the emission and excitation spectra of the Tb^{3+}/dbm film. The emission spectrum

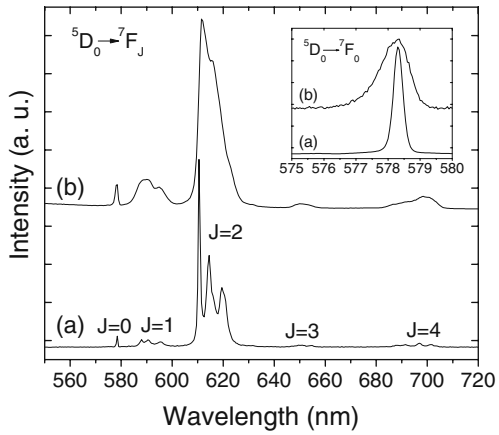

Fig. 3 Emission spectra of (*a*) $Eu(ttfa)_3.2H_2O$(s) and (*b*) Eu^{3+}/ttfa film annealed at 150 °C for 15 min (λ_{exc}=350 nm)

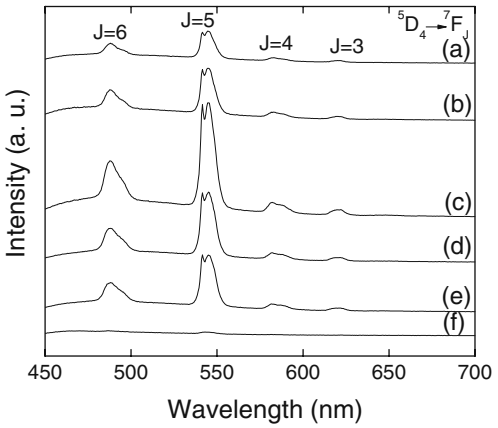

Fig. 5 Emission spectra (λ_{exc}=360 nm) of the Tb^{3+}/dbm film annealed at (*a*) 50 °C, (b) 100 °C, (*c*) 150 °C, (*d*) 200 °C, (*e*) 250 °C, and (*f*) 300 °C

consists of the typical emission bands of Tb^{3+}, at 488, 543, 581, and 622 nm, which are assigned to the $^5D_4 \rightarrow ^7F_J$ (J= 6,5,4,3) transitions. The strongest $^5D_4 \rightarrow ^7F_5$ green emission is observed at 543 nm. Excitation in the absorption bands of the ligands results in the strong emission of Eu^{3+} and Tb^{3+}, indicating that an efficient intramolecular energy transfer occurs from the organic ligands to the emitting ions. For the Eu^{3+}/ttfa film, the emission intensity of the forbidden $^5D_0 \rightarrow ^7F_0$ transition (578 nm) is indicative of the absence of an inversion center in the emitting system.

The emission spectra of the $[Eu(ttfa)_3.2H_2O]$ powder (a) and Eu^{3+}/ttfa film (b) excited at 350 nm (Fig. 3) have a similar feature; that is, there is broadening of the bands in the film, as expected for such a system. As shown in the inset, the $^5D_0 \rightarrow ^7F_0$ transition presents a width of 10 cm^{-1} at half height for the $[Eu(ttfa)_3.2H_2O]$ powder (a), and ~35 cm^{-1} for the Eu^{3+}/ttfa film (b). According to Bünzli et al. [23], when a typical $^5D_0 \rightarrow ^7F_0$ transition presents a sharp component (width ~ 2 cm^{-1} at half height), it reflects the presence of an only chemical environment for the Eu^{3+} ion. A very broad $^5D_0 \rightarrow ^7F_0$ band with a width >10 cm^{-1} at half height suggests that the system has polymeric-like nature or several and very similar environments [24].

In order to study the thermal stability of the films, we investigated the emission intensity as a function of the temperature. Figure 4 presents the emission spectra of the Eu^{3+}/ttfa films heated at 50, 100, 150, 200, 250, 300, and 350 °C for 15 min. The films heated at 150, 200, and 250 °C presented higher emission intensities than those heated at lower temperatures, probably because of the release of water and ethanol from the ion neighborhood, which promote quenching as a result of their high vibrational frequency modes. On the other hand, the films heated at temperatures over 300 °C have a large decrease in the emission intensity, probably because of the ttfa decomposition. A similar behavior is observed for the Tb^{3+}/dbm films (Fig. 5), where the ligand decomposition starts at lower temperatures.

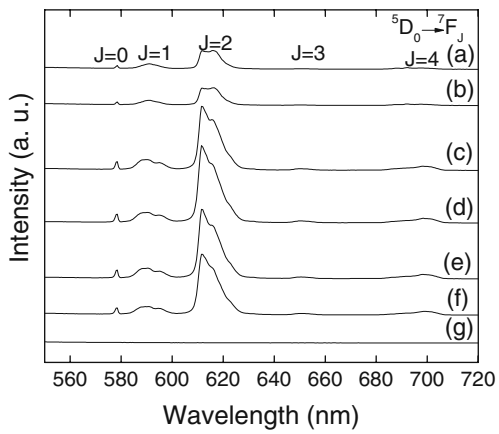

Fig. 4 Emission spectra (λ_{exc}=350 nm) of the Eu^{3+}/ttfa film annealed at (*a*) 50 °C, (*b*) 100 °C, (*c*) 150 °C, (*d*) 200 °C, (*e*) 250 °C, (*f*) 300 °C, and (g) 350 °C

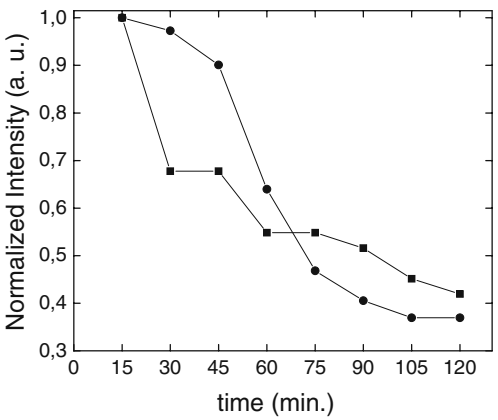

Fig. 6 Relationship between the emission intensities of the $^5D_0 \rightarrow ^7F_2$ transitions for the (●) Eu^{3+}/ttfa and $^5D_4 \rightarrow ^7F_5$ (■) Tb^{3+}/dbm films heated at 150 °C, and heating time

Emissions ($^5D_0 \rightarrow {}^7F_2$ for Eu^{3+}/ttfa and $^5D_4 \rightarrow {}^7F_5$ for Tb^{3+}/dbm) were measured after the films were heated at 150 °C for 15 min, and this procedure was repeated up to 2 h. The final results are depicted in Fig. 6. The emission intensity of the Eu^{3+}/ttfa film decreases more slowly than that of the Tb^{3+}/dbm film, probably because of the lower thermal stability of dbm.

The decay associated with the emissions from the excited states of Eu^{3+} ($^5D_0 \rightarrow {}^7F_2$) and Tb^{3+} ($^5D_4 \rightarrow {}^7F_5$) to the respective ground state in the films were analyzed, and it consists of exponential decays. The lifetimes of the Eu^{3+}/ttfa films are better fitted through a monoexponential decay, giving an average value of 0.7 ms; for a biexponential decay, the lifetime values were found to be τ_1=0.2 and τ_2=0.7 ms. For the Tb^{3+}/dbm films, only a second-order exponential fitting gave better results with average τ_1 and τ_2 values of 0.2 and 0.9 ms, respectively. Low emission lifetimes (<0.1 ms) were assigned to radiationless transitions caused by vibrational modes from the surrounding medium and also to amplified stimulated emissions in Eu^{3+}/β-diketonates under special conditions [25]. Deviations from the determined lifetimes (~0.1 ms) are also in agreement with the broadening of the $^5D_0 \rightarrow {}^7F_0$ transition in the Eu^{3+}/ttfa emission spectra, probably due to a multicomponent environment around the ions in the film. A lifetime value of 0.26 ms for [Eu(ttfa)$_3$.2H$_2$O] is reported in the literature [26, 27], and we found a lifetime of 0.30 ms. As for [Tb(dbm)$_3$.2H$_2$O], a value of 0.60 ms was determined. The lifetimes were calculated by using the Origin® graphics software.

Both the Eu(ttfa)$_3$.2H$_2$O powder and the Eu^{3+}/ttfa film show high color purities (x = 0.66 and y = 0.34), which is a consequence of the intense bands of the $^5D_0 \rightarrow {}^7F_2$ transitions. For the [Tb(dbm)$_3$.2H$_2$O] powder and Tb^{3+}/dbm film, the *Commission Internationale de l'Eclairage* (CIE) color parameters are determined as x = 0.23 and y = 0.50. The CIE chromaticity coordinates were obtained through the Spectra Lux software [28]. The standard coordinates accepted by the *National Television Standard Committee* (NTSC) for red are x = 0.67 and y = 0.33 [29], and for green the values are x = 0.21 and y = 0.71 [30].

Conclusions

Luminescent zinc-based hybrid inorganic–organic films with Eu^{3+} and Tb^{3+} complexes can be successfully prepared from non-alkoxide reagents through a sol–-gel process. Such thin films are a very promising transparent luminescent material due to the efficient energy transfer from the ligands ttfa and dbm to the Eu^{3+} and Tb^{3+} ions, respectively, and to their high thermal stability. Furthermore, the current synthesis method can be easily applied to other ligands and luminescent rare earths.

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