

Thin Film of $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ Synthesized by a non-Alkoxide Precursor Sol-Gel Method

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Filmes de aluminato de zinco dopados com európio ($\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$) foram preparados pelo método sol-gel usando precursores não-alcóxidos em meio etanólico através da técnica de *dip-coating*. Os espectros de fotoluminescência do filme aquecido a 500 °C apresentaram bandas de excitação em 270 e 393 nm e bandas de emissão em 578, 590, 612, 650 e 698 nm, atribuídas às transições $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($J = 0, 1, 2, 3, 4$). Os filmes mostraram-se transparentes acima de 320 nm.

Europium-doped zinc aluminate ($\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$) films were prepared by the dip-coating technique using a non-alkoxide precursor sol-gel method in ethanolic medium. Photoluminescence spectra displayed the main excitation bands at 270 and 393 nm. The emission spectra of the film heated at 500 °C displayed bands at 578, 590, 612, 650 and 698 nm, assigned to the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($J = 0, 1, 2, 3, 4$) transitions. The films are transparent above 320 nm.

Keywords: zinc aluminate, europium, non-alkoxide, sol-gel process, UV-Vis transparent and luminescent films

Introduction

In recent years, spinel-type zinc aluminate (ZnAl_2O_4) has become technologically important due to its peculiar optical properties. With an optical bandgap of 3.8 eV, which results in effective transparency at wavelengths above 320 nm, it is a useful component of photoelectronic devices operating in the ultraviolet region.¹⁻³ Also, its high chemical and mechanical stabilities make it suitable for a variety of applications such as flat panel display electrodes, ceramics, and electronic and catalytic materials.^{4,5} Bulk non-doped ZnAl_2O_4 has been prepared by the sol-gel process employing alkoxides as precursors, as well as by coprecipitation and wet mixing.^{6,7} Phani *et al.*⁸ have obtained ZnAl_2O_4 thin films by utilizing an alkoxide sol-gel route and deposition by spin-coating. Davolos *et al.*⁹ have successfully prepared bulk zinc aluminate by a non-alkoxide sol-gel method. Bulk rare earth (RE)-doped zinc aluminate ($\text{ZnAl}_2\text{O}_4:\text{RE}^{3+}$) has been produced by spray drying, combustion and hydrothermal methods.¹⁰⁻¹⁴ The sol-gel process has also been employed in the preparation of luminescent rare earth-based materials incorporated into inorganic hosts in very mild conditions.¹⁵

The non-alkoxide sol-gel method has the advantage of employing stable and less expensive precursors; alkoxides are very reactive and need special care during manipulation and storage (especially aluminum alkoxides). So far, there has been no study devoted to the preparation of rare earth-doped ZnAl_2O_4 using a non-alkoxide sol-gel process. In the present work, thin films of photoluminescent $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ have been synthesized by a non-alkoxide precursor sol-gel process using the dip-coating technique.

Experimental

Zinc acetate dihydrate (0.329 g, 0.0015 mol) and aluminium nitrate nonahydrate (1.125 g, 0.0030 mol), selected as starting materials, were dissolved in 13.4 mL ethanol. An ethanolic solution of europium chloride (1.6 mL, 0.095 mol L⁻¹, 0.00015 mol) was then added; the resulting solution, containing Al/Zn 2:1 and Eu/Al 5:100 (molar ratios), was refluxed until formation of a homogeneous and stable sol (4 h).

Borosilicate glass substrates were previously washed with sodium dodecylsulfate, treated ultrasonically with deionized water for 30 min, followed by another 30 min treatment with ethanol and dried in ambient conditions. The film was dip-coated on the glass substrate and treated

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at 500 °C for 15 min, and this procedure was repeated ten times. Bulk samples were fabricated by evaporating the initial solution and heating the solid at 500 and 700 °C for 1 h.

The film and bulk material were characterized at room temperature by photoluminescence (PL), using a SPEX TRIAX 550 FLUOROLOG III spectrofluorometer. UV-Vis absorbance spectra of the film on the glass substrate were obtained on an HP 8353 diode array spectrophotometer. The X-ray diffraction (XRD) experiment for the bulk materials (500 and 700 °C) was performed at room temperature with a Siemens/Bruker D.5005 instrument using CuK_α radiation ($\lambda = 1.542 \text{ \AA}$). In order to determine the thickness of the film, the substrate was fractured and imaged on a Zeiss EVO 50 scanning electron microscope (SEM).

Results and Discussion

Figure 1 shows the PL excitation spectrum of the 10-layered film with emission wavelength at 612 nm. The spectrum presents a wide band below 260 nm, which corresponds to a charge-transfer transition from O²⁻ to Eu³⁺ ions, as well as sharp lines of lower intensity, which correspond to f-f transitions $^7F_0 \rightarrow ^5L_6$ (393 nm) and $^7F_0 \rightarrow ^5D_2$ (462 nm).¹¹ The emission spectrum of the film, obtained with excitation at 270 and 393 nm, 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 centered at 612 nm being the most prominent (Figure 2). Due to the resolution (spectral bandwidth: 1 nm), the only possible consideration about the emission spectrum is that the environment of the Eu³⁺ ion leads to a low symmetry system, as indicated by the high intensity of the $^5D_0 \rightarrow ^7F_2$ electric dipole (ED) transition as compared with the $^5D_0 \rightarrow ^7F_1$ magnetic-dipole (MD) transition.¹¹

The chromaticity coordinates (CIE 1931) were calculated using the Spectra Lux Software.¹⁶ The obtained results demonstrated high color purities: $x = 0.68$ and $y = 0.32$, which are eligible for optical applications.^{11,17,18} The spectra are similar to that obtained by Barros *et al.*,¹¹ who also considered the europium-doped ZnAl₂O₄ as having properties required for display applications. Figure 3 exhibits the emission spectra of the film after each layer transfer from the first until the tenth, and this same figure shows that the luminescence intensity is approximately linear with respect to the number of layers. For comparison purposes, Figure 4 depicts the emission spectra of the powder (700 °C) presenting the same features as the film spectrum. The bulk material obtained at 500 °C remains dark due to carbonaceous impurities,

and it is not appropriate for optical measurements, especially with respect to transparency studies. The close similarity of the emission spectra of the film and bulk samples with that presented by Barros *et al.*¹¹ led us to conclude that Eu³⁺ is embedded predominantly in a *Gahnite* spinel structure.

The UV-Vis spectrum of the ZnAl₂O₄:Eu³⁺ film displays low absorbance from 320 nm to 800 nm (Figure S1, Supplementary Information), resulting in good transparency in a large spectral window. It was not possible to obtain the absorption spectrum of the bulk material obtained at 500 °C. On the other hand, the spectrum of the powder obtained at 700 °C (without carbonaceous material) presented low absorbance above 320 nm, which is very similar to what was observed in the case of the film spectra.

Figure 5 presents the X-ray diffraction patterns of the powder obtained at 500 and 700 °C. The main peaks are

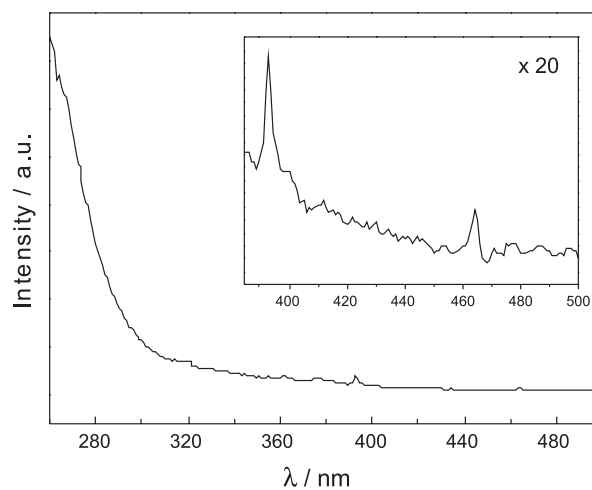


Figure 1. Excitation spectrum of the ZnAl₂O₄:Eu³⁺ film ($\lambda_{em} = 612 \text{ nm}$).

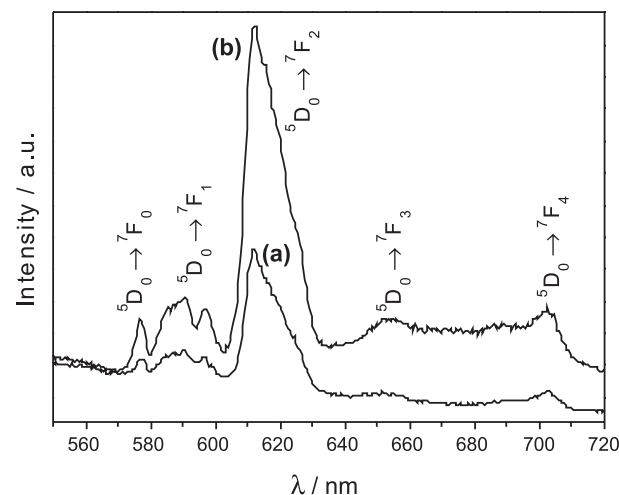


Figure 2. Emission spectra of the ZnAl₂O₄:Eu³⁺ film: (a) $\lambda_{exc} = 393 \text{ nm}$ and (b) $\lambda_{exc} = 270 \text{ nm}$.

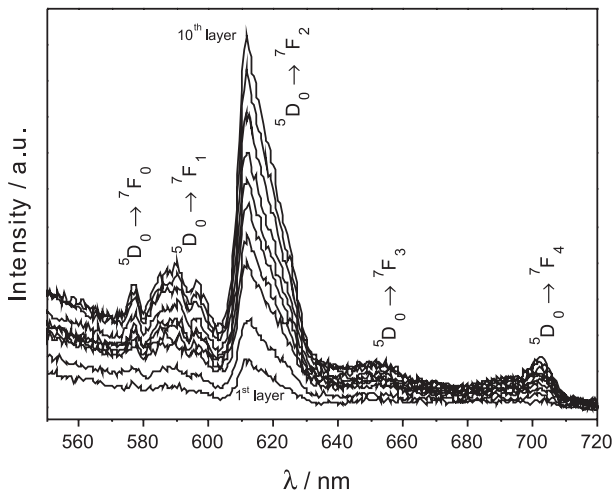


Figure 3. Emission spectra ($\lambda_{exc} = 393$ nm) of the $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ film from one to ten layers.

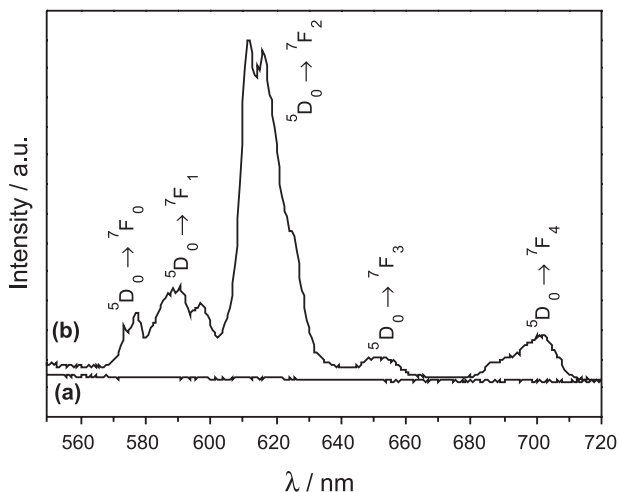


Figure 4. Emission spectra of the $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ powder annealed at 500 °C (a) and 700 °C (b).

in agreement with the *Gahnite* spinel crystalline phase (JCPDS 01-082-1043). Analysis of the X-ray pattern depicts the formation of the main crystalline planes (220), (311), (511) and (440) at $2\theta = 31, 37, 59$ and 65 , respectively, and it is evident that (311) is the preferential orientation, as previously reported by Barros *et al.*¹¹ Some less intense peaks due to ZnO are also present in the sample patterns, as described in Barros' paper.

In order to estimate the thickness of the 10-layered film, the fractured cross-section of the substrate was imaged by SEM (Figure 6). A 300 nm thickness was observed, which led us to infer that each deposited layer has a thickness of approximately 30 nm. From this value, we can estimate that the size of the particles forming the film is less than 30 nm. Recently, Kapilashrami *et al.*¹⁹ used the same technique (cross-section) to determine the thickness of ZnO films measuring between *ca.* 150 and 1000 nm.

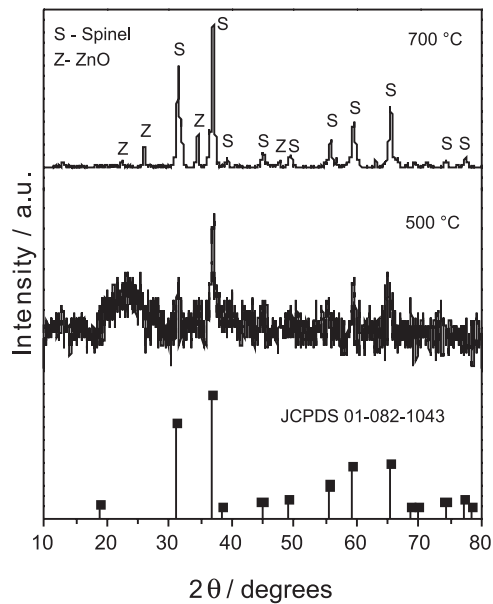


Figure 5. X-ray diffraction pattern of the $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ powder annealed at 500 and 700 °C, together with the reference *Gahnite* ZnAl_2O_4 spinel (JCPDS 01-082-1043).

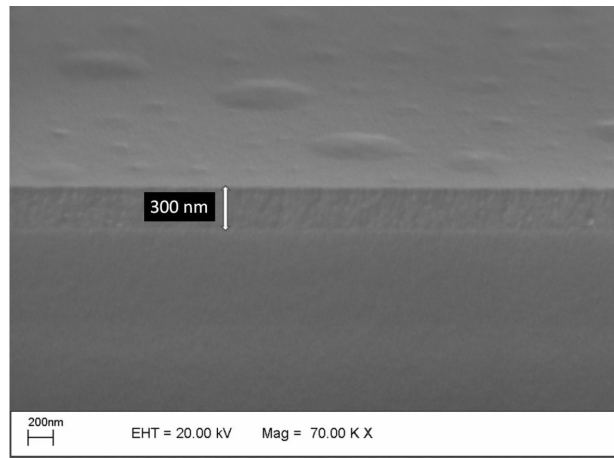


Figure 6. SEM image (cross-section) of the ten-layered $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ film annealed at 500 °C.

Conclusions

We have successfully fabricated $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ films with nanosized thickness by the dip-coating technique using a non-alkoxide sol-gel method. The films are transparent above 320 nm, and the close similarities between the emission spectra of the film and those of the bulk samples (known to have a *Gahnite* spinel structure as evidenced by XRD) have led us to conclude that it consists mainly of the *Gahnite* structure, where Eu^{3+} is embedded. Also, the determined CIE 1931 chromaticity coordinates $x \cong 0.68$ and $y \cong 0.32$ make this very thin film a possible component for photoelectronic devices transparent in the UV-Vis region.

Supplementary Information

The UV-Vis absorbance spectrum of the ZnAl₂O₄:Eu³⁺ film (Figure S1) is available free of charge at <http://jbcs.sbq.org.br>, as a PDF file.

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References

1. Sampath, S. K.; Cordero, J. F.; *J. Am. Ceram. Soc.* **1998**, *81*, 649.
2. Khenata, R.; Sahnoun, M.; Baltachea, H.; Rérat, M.; Reshak, Ali H., Al-Douri, Y.; Bouhafs, B.; *Phys. Lett. A* **2005**, *344*, 271.
3. Mathur, S.; Veith, M.; Hass, M.; Shem, H.; Lecerf, N.; Huch, V.; Hufier, S.; Haberkorn, R.; Beck, H. P.; Jilavi, M.; *J. Am. Ceram. Soc.* **2001**, *84*, 1921.
4. El-Nabarawy, T.; Attia, A. A.; Alaya, M. N.; *Mater. Lett.* **1995**, *24*, 105.
5. Girgis, B. S.; Youssef, A. M.; Alaya, M. N.; *Surf. Technol.* **1980**, *10*, 105.
6. Duan, X.; Yuan, D.; Wang, X.; XU, H.; *J. Sol-Gel Sci. Technol.* **2005**, *35*, 221.
7. Valenzuela, M. A.; Bosch, P.; Aguilar-Rios, G.; Montoya, A.; Schifter, I.; *J. Sol-Gel Sci. Technol.* **1997**, *8*, 107.
8. Phani, A. R.; Passacantando, M.; Santucci, S.; *Mater. Chem. Phys.* **2001**, *68*, 66.
9. da Silva, A. A.; Gonçalves, A. S.; Davolos, M. R.; *J. Sol-Gel Sci. Technol.* **2009**, *49*, 101.
10. García-Hipólito, M.; Hernández-Pérez, C. D.; Alvarez-Fregoso, O.; Martinez, E.; Guzmán-Mendoza, J.; Falcony, C.; *Opt. Mater.* **2003**, *22*, 345.
11. Barros, B. S.; Melo, P. S.; Kiminami, R. H. G. A.; Costa, A. C. F. M.; de Sá, G. F.; Alves Jr., S.; *J. Mater. Sci.* **2006**, *41*, 4744.
12. Streck, W.; Deren, P.; Bednarkiewicz, A.; Zawadzki, M.; Wrzyszczyk, J.; *J. Alloys Compd.* **2000**, *300*, 456.
13. Yanga, C.-C.; Chena, S.-Y.; Cheng, S.-Y.; *Powder Technol.* **2004**, *148*, 3.
14. Singh, V.; Natarajan, V.; Zhu J.-J.; *Opt. Mater.* **2007**, *29*, 1447.
15. Chea, P.; Meng, J.; Guoa, L.; *J. Lumin.* **2007**, *122*, 168.
16. Santa-Cruz, P. A.; Teles, F. S.; *Spectra Lux Software v.2.0, Ponto Quântico Nanodispositivos/RENAMI* (Brazil), 2003.
17. Sousa Filho, P. C.; Serra, O. A.; *J. Lumin.* **2009**, *129*, 1664.
18. Wang, Z.; Liang, H.; Gong, M.; Su, Q.; *J. Alloys Compd.* **2007**, *432*, 308.
19. Kapilashrami, M.; Xu, J.; Ström, V.; Rao, K.V.; Belova, L.; *Appl. Phys. Lett.* **2009**, *95*, 033104.

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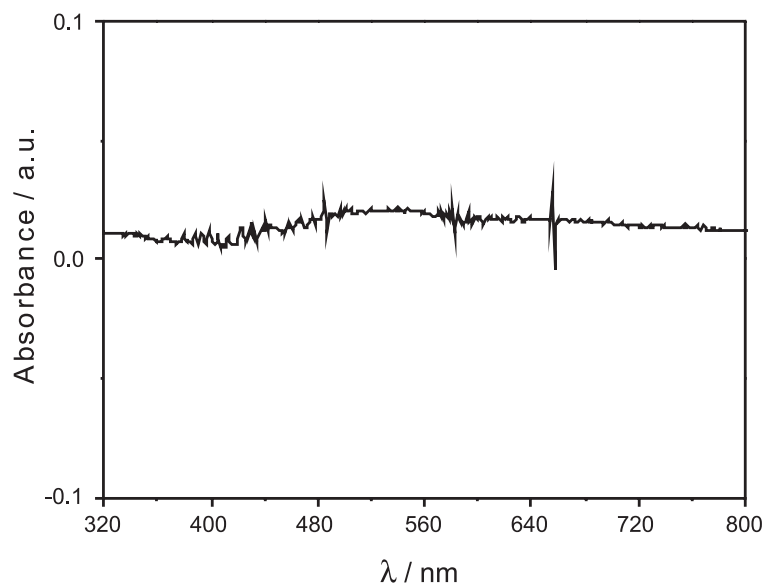


Figure S1. UV-Vis absorbance spectrum of the $\text{ZnAl}_2\text{O}_4:\text{Eu}^{3+}$ film formed onto a glassy substrate.

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