Available online at www.sciencedirect.com
SCIENCE DIRECT®

ELSEVIER

Optical Materials 22 (2003) 345–351

OPTICAL Materials

www.elsevier.com/locate/optmat

Characterization of europium doped zinc aluminate luminescent coatings synthesized by ultrasonic spray pyrolysis process

M. García-Hipólito [a], C.D. Hernández-Pérez [a], O. Alvarez-Fregoso [a,*], E. Martínez [a], J. Guzmán-Mendoza [a], C. Falcony [b]

[a] *Institute de Investigaciones en Materiales., UNAM, A.P. 70-360 Coyoacán 04510, Mexico*
[b] *Departamento de Física, CINVESTAV-IPN, Apdo. Postal 14-740, 07000, Mexico D.F.*

Abstract

Europium doped zinc aluminate ($ZnAl_2O_4$) photoluminescent films have been deposited by ultrasonic spray pyrolysis deposition process. Different substrate temperatures and doping concentrations in the start spraying solution were studied. It is observed that the crystalline structure of this material depends on the substrate temperature during deposition of the films. For low substrate temperatures, the deposited films are amorphous. When the substrate temperature is increased at 500 °C some peaks corresponding to hexagonal phase of ZnO (zincite) appears. At substrate temperatures of 550 °C, the crystalline structure of the $ZnAl_2O_4$:Eu films presents the close-packed face centered cubic phase. The excitation and emission spectra were obtained; for an excitation wavelength of 260 nm, all the photoluminescence (PL) spectra show peaks located at 589, 615, 652 and 700 nm. Concentration quenching of the PL occurs at activator concentrations greater than 0.85 at.% inside the deposited films. The PL intensity increases as the substrate temperature rises. In addition, the surface morphology features of the films, as a function of the deposition temperature, are shown.

PACS: 78.55.–m; 81.05.Hd; 81.20.Rg
Keywords: Photoluminescence; $ZnAl_2O_4$:Eu films; Spray pyrolysis

---

1. Introduction

Zinc aluminate ($ZnAl_2O_4$) is a well-known wide-bandgap semiconductor with a spinel structure. This material has a close-packed face centered cubic structure with Fd3m space group symmetry [1]. The optical bandgap of polycrystalline $ZnAl_2O_4$ is 3.8 eV [2], this indicates that $ZnAl_2O_4$ is transparent for light possessing wavelengths >320 nm which makes it useful in ultraviolet photoelectronic devices [3]. $ZnAl_2O_4$ is widely used as ceramic, electronic and catalytic materials. This material is used in various catalytic reactions, such as cracking, dehydration, hydrogenation and dehydrogenation, in chemical and petrochemical industries [4,5].

---

[*] Corresponding author. Tel.: +52-55-56224649; fax: +52-55-56161371.
E-mail address: oaf@servidor.unam.mx (O. Alvarez-Fregoso).

0925-3467/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0925-3467(02)00346-4

There has been noticeable investigation involving both experimental and theoretical studies on spinel oxides like magnesium aluminate, but there are scarce works on $ZnAl_2O_4$. The studied properties of these materials are the crystal structure, the optical spectra and the electronic structure [1,6,7]. Regarding to the luminescent properties of $ZnAl_2O_4$ there are very few reported studies [8–10]. These studies have been carried out on powder form samples. There are very scarce studies reporting on the general properties of $ZnAl_2O_4$ films [11]. To the best of our knowledge, it is non-existent the information about $ZnAl_2O_4$ luminescent coatings.

Compared to powder phosphors, thin luminescent films offer advantages such as better thermal stability, good adhesion to the substrate, no outgassing problems and possess uniform properties across the covered area [12].

At the moment the luminescent films can be applied mainly in electroluminescent flat panel displays and color plasma display panels. For these applications, it is necessary to deposit good quality coatings emitting in the three basic colors (blue, green and red). Rare earth doped oxides are some of the most promising luminescent materials in this case. In contrast to sulfur-based luminescent materials, oxides are chemically inert to plasmas commonly used in plasma operated panels and do not contaminate the electron emitters in field emission displays [12]. The potential of the rare earth elements to provide the three basic colors needed in a full color device has led to intensive study of the doping of II–VI compounds activated with rare earths during the past few years [13]. Rare earth ions have efficient visible emissions in 4f shell, which is insensitive at great extent to the influence of surroundings due to the shielding effect of the outer 5s and 5p orbitals [14].

The ultrasonic spray pyrolysis method is a well-established process for depositing films [15]. The main advantages of this technique are its low cost, a high deposition rate, the possibility to coat large areas, its ease of operation and the quality of the coatings obtained. This technique has been successfully used in the deposition of luminescent films of materials such as ZnO:Tb [16], ZnS:Mn [17], $Y_3Al_5O_{12}$:Tb, Eu or Ce [18], Al_2O_3:$CeCl_3$ [19], Al_2O_3:Eu [20], ZrO_2:Tb [21], ZrO_2:Eu [22], etc.

The present contribution reports on the synthesis and characterization of the photoluminescent Eu doped $ZnAl_2O_4$ coatings synthesized by the ultrasonic spray pyrolysis technique. Also, the role that some deposition parameters (substrate temperature and doping concentration) play on the luminescent characteristics is presented.

2. Experimental

Ultrasonic spray pyrolysis technique was used to synthesize europium doped $ZnAl_2O_4$ films. The experimental arrangement for this technique has been presented elsewhere [23]. In this technique, mist of a solution containing the precursor materials to be deposited is ultrasonically generated and sprayed through a spraying nozzle over a substrate previously heated. The solvents in the solution are vaporized when the mist of the solution gets in touch with the hot substrate producing a solid coating on the substrate. The substrate is placed on a resistance heated stage and the nozzle is located approximately 1 cm above the stage, all enclosed in an exhaust hood. The spraying solution was 0.05 M solution of zinc acetate and aluminum chloride in deionized water as solvent. Doping with Eu was achieved by adding $EuCl_3 \cdot 6H_2O$ to the spraying solution in the range from 0 to 30 at.% (*a*/*o*) in relation to the Zn content in this solution. The carrier gas flow (filtered air) was 10 l/min and the solution flow rate was 3 ml/min. The substrate temperature (T_s) during deposition was in the range from 350 to 550 °C; the substrates used were Corning 7059 glass slides and Si(1 0 0) single crystals. The crystalline structure of the deposited films was analyzed by X-ray diffraction, using a Siemens D-5000 diffractometer with wavelength radiation of 1.5406 Å (Cuk_α). The deposition time was adjusted (4–6 min) to deposit films with approximately the same thickness. The thickness of the films studied was about 5 μm as measured by a Sloan Dektak IIA profilometer. The chemical composition of the films was measured using energy dispersive spectroscopy (EDS) with a Leica-Cambridge electron microscope Mo. Stereoscan 440 equipped with a Beryllium window X-ray detector. The standard used for the EDS measurements was the Multi-element X-ray Reference Standard (Microspec) Serial 0034, part no. 8160-53. The excitation and emission photoluminescence (PL) spectra were obtained using a Perkin-Elmer LS50B fluorescence spectrophotometer. All PL spectra were obtained at room temperature and 260 nm light was found to be suitable as excitation source for these measurements.

3. Results and discussion

As we mentioned above the thickness of the studied films was in all cases approximately 5 μm. The structural characteristics of Eu doped $ZnAl_2O_4$ coatings deposited by spray pyrolysis method are illustrated in Fig. 1a–c where X-ray diffraction patterns for $ZnAl_2O_4$:Eu (30 *a*/*o* in the spraying solution) at three different substrate temperatures, 400, 500 and 550 °C, are shown. The europium doped $ZnAl_2O_4$ coatings remain in the amorphous state when deposited at substrate temperatures up to 400 °C (Fig. 1a), but when the substrate temperature is increased at 500 °C some peaks corresponding to hexagonal phase of ZnO (zincite, ICCD Card File No. 36-1451) are observed (Fig. 1b). In the sample deposited at 550 °C (Fig. 1c) only a cubic spinel crystalline phase of $ZnAl_2O_4$ (gahnite) was found (ICCD Card File No. 05-0669 [24]). The calculated lattice parameters ($a = b = c = 8.0859$ Å) for cubic spinel phase in the films deposited at 550 °C are in good agreement with the reported values ($a = b = c = 8.0848$ Å) [24]. In this case, the material grows with a preferential (3 1 1) direction normal to the films surface.

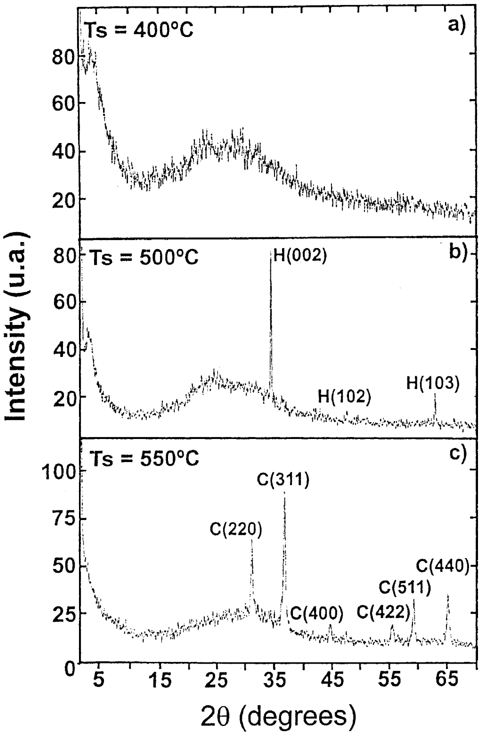

Fig. 1. XRD patterns for $ZnAl_2O_4$:Eu films at three different substrate temperature, T_s: 400, 500 and 550 °C (H = hexagonal, C = cubic).

EDS measurements were performed on films deposited on (1 0 0) n-type silicon single crystals substrates in order to evaluate the oxygen content in the coatings. The obtained results are shown in Tables 1 and 2. Table 1 summarizes the relative chemical content of the oxygen, zinc, aluminum, europium and chlorine present into the films as a function of the content of the $EuCl_3$ inserted in the spraying solution. A reduction of the relative content of zinc, aluminum and an increase in the relative contents of oxygen, europium and chlorine are observed when the doping concentration is increased. The substrate temperature, in this case, was 550 °C. Table 2 presents results similar to those in Table 1 but as a function of the substrate temperature, keeping constant the doping concentration ($EuCl_3$, 10 *a*/*o*) in the starting solution. In this case, we observe an increase in relative the content of oxygen, zinc, aluminum and a reduction in the relative content of europium and chlorine as the substrate temperature increases.

The surfaces morphology of $ZnAl_2O_4$:Eu (10 *a*/*o*) coatings are presented in Fig. 2. It is possible to observe rough but continuous films with good adherence to substrate. SEM micrographs of the samples deposited at 350 °C (a), 400 °C (b), 500 °C (c) and 550 °C (d) are shown. From this figure it is also observed that the surface morphology of the films depends on the substrate temperature. Films deposited at 350 and 400 °C present some cracks. With increasing substrate temperature (500 and

Table 1
Atomic percent content of the oxygen, zinc, aluminum, europium and chlorine in the europium-doped $ZnAl_2O_4$ films as measured by EDS for different $EuCl_3$ concentrations in the spraying solution

$EuCl_3$ concentration in the spraying solution (*a*/*o*)	Oxygen	Zinc	Aluminum	Europium	Chlorine
0	57.44	13.11	27.02	00.00	02.43
5	59.12	12.29	25.16	00.47	02.96
10	61.37	11.85	22.50	00.85	03.43
15	63.66	11.21	18.79	01.03	05.31
20	63.35	09.42	18.45	02.04	06.74
30	63.75	06.75	18.22	02.54	08.74

In this case the substrate temperature was 550 °C.

Table 2
Atomic percent content of the oxygen, zinc, aluminum, europium and chlorine in the europium-doped $ZnAl_2O_4$ films as determined by EDS for different substrate temperatures

Substrate temperature (°C)	Oxygen	Zinc	Aluminum	Europium	Chlorine
350	60.02	09.10	14.88	02.26	13.74
400	60.21	09.39	17.63	01.83	10.94
450	62.75	10.48	18.94	01.38	06.45
500	62.29	11.18	21.10	01.06	04.37
550	61.37	11.85	22.50	00.85	03.43

In this case, the $EuCl_3$ concentration in the spraying solution was 10 *a*/*o*.

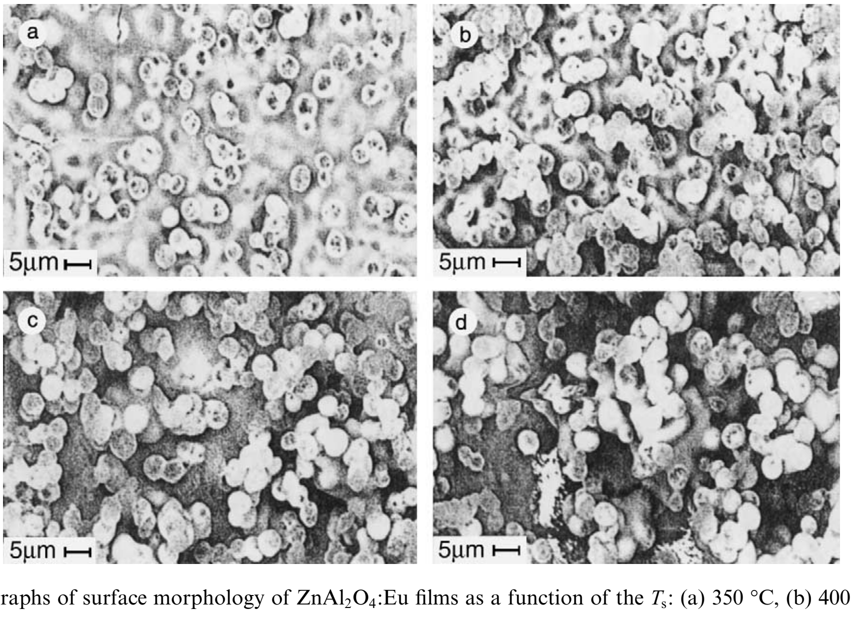

Fig. 2. SEM micrographs of surface morphology of $ZnAl_2O_4$:Eu films as a function of the T_s: (a) 350 °C, (b) 400 °C, (c) 500 °C and (d) 550 °C.

550 °C), cracks disappear and apparently a relatively more dense material is reached.

Fig. 3 shows the excitation spectrum for the red luminescence of the $ZnAl_2O_4$:Eu coatings synthe-

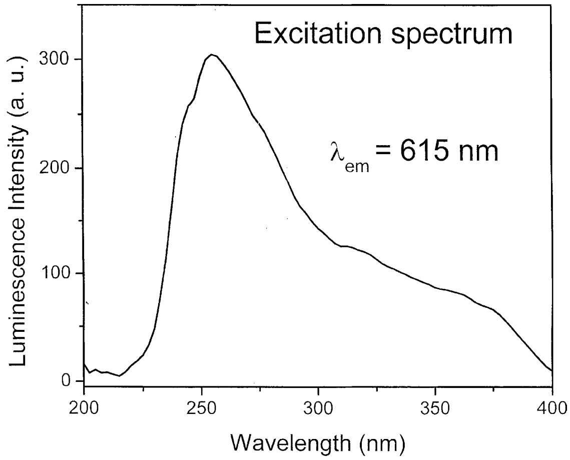

Fig. 3. Excitation spectrum of $ZnAl_2O_4$:Eu (10 *a*/*o*) films deposited at $T_s = 550$ °C, $\lambda_{em} = 615$ nm.

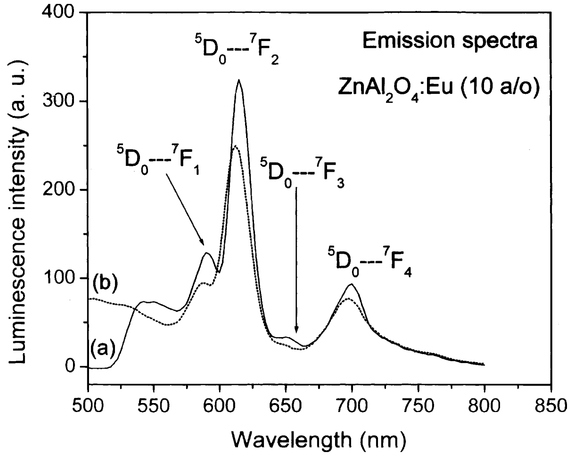

Fig. 4. (a) Typical PL spectrum for $ZnAl_2O_4$:Eu (10 *a*/*o*) films synthesized at $T_s = 550$ °C, $\lambda_{exc} = 260$ nm. (b) PL spectrum for $ZnAl_2O_3$:Eu (10 *a*/*o*) powders.

sized at 550 °C, with 10 *a*/*o* of $EuCl_3$ in the spraying solution (the emission wavelength considered was 615 nm). It is possible to distinguish a broad band centered at 260 nm. This band is originated by transitions to the charge transfer state due to europium–oxygen interactions [25]. Charge transfer state is normally the most intense excitation mechanism and this region is expected to occur around 250–300 nm. In consequence, excitation in the charge transfer state with a mercury lamp at 254 nm is very efficient.

Typical PL emission spectrum for Eu doped $ZnAl_2O_4$ films is shown in the Fig. 4(a). It is possible to distinguish four emission bands centered at 589, 615, 652 and 700 nm which correspond to transitions between the levels $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$, respectively, from trivalent europium ion. In these cases, the films were prepared at substrate temperature of 550 °C, the concentration doping was 10 *a*/*o* in the spraying solution and $\lambda_{exc} = 260$ nm. The hypersensitive forced electric dipole transition $^5D_0 \rightarrow {}^7F_2$ at 615 nm is the strongest emission band observed. For applications it is necessary that the main emission is concentrated in this transition. The broad band centered at approximately 540 nm is associated to the host lattice as can be observed in Fig. 6 (curve f) which correspond to the sample without europium doping. For comparison purposes the spectrum obtained from similar material in form of powders (these powder samples were synthesized in identical conditions to that of the reference [9]) is shown in the Fig. 4(b). It is clear that the emission from the films is overall more intense than that coming from the powders. This result could be an indication that the PL sensitivity of the films is better than that of the powders in general. The PL emission from the samples (films and powders) studied is easily observed at naked eye in normal room lightening, when excited with a portable 4 W UV–mercury lamp (254 nm).

Fig. 5 shows PL emission spectra of $ZnAl_2O_4$:Eu coatings, as a function of the deposition temperature. The PL emissions rise when increasing the deposition temperature, probably due to an improved crystallization of the host material, as it is shown by X-ray diffraction measurements in this range of deposition temperatures, and to the reduction of chlorine left into the sample. Both effects will produce a better incorporation and distribution of the europium ions as an atomic impurity inside the host film, which will result in an increase of the PL emission as the deposition temperature is increased. In this case, the value of doping concentration, in the deposited film was 0.85 *a*/*o* and $\lambda_{exc} = 260$ nm. In accordance with the observed tendency, films deposited at substrate temperatures higher than 550 °C would have a more intense emission; however material deposited

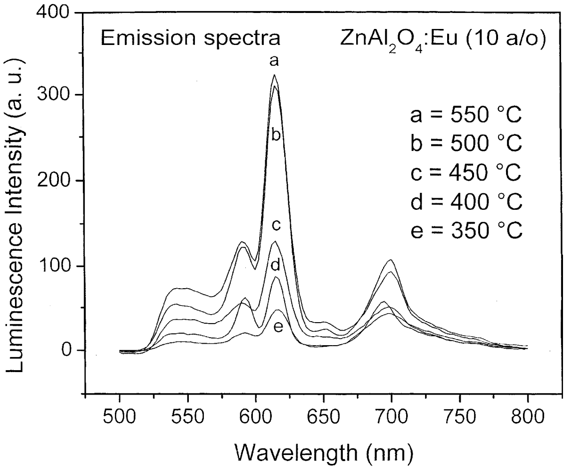

Fig. 5. PL spectra of $ZnAl_2O_4$:Eu (10 *a*/*o*) films as a function of substrate temperature, $\lambda_{exc} = 260$ nm.

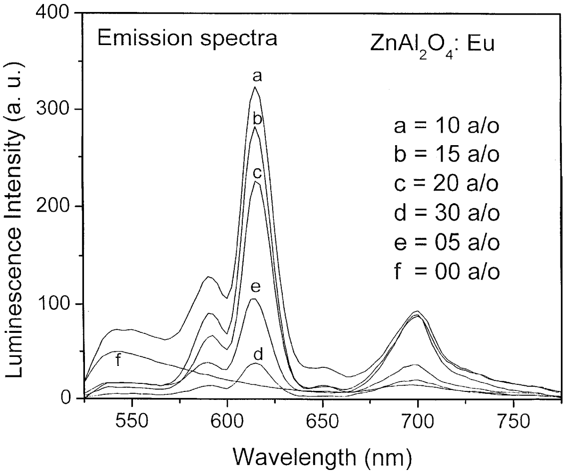

Fig. 6. PL spectra for $ZnAl_2O_4$:Eu films as a function of the doping concentration, $T_s = 550$ °C, $\lambda_{exc} = 260$ nm.

at substrate temperatures higher than 550 °C (600 °C) resulted in a sample that was powdery, porous and non-adherent to the substrate. This is probably due to a sudden evaporation of the solvent because at those relatively high temperatures the chemical reaction is carried out in the vapor phase in a nearby region to the substrate, producing in this way only a fine powder, which falls on the substrate, and not a solid film. In any event, the luminescent emissions are always observed in despite of the crystalline structure of films studied. The characteristic emission from the trivalent europium ion is similar for films deposited at 350 °C (amorphous) and for films deposited at higher substrate temperatures (500 and 550 °C) which exhibit polycrystalline structures corresponding to zinc oxide (hexagonal phase) and $ZnAl_2O_4$ (cubic phase), respectively. Although, the highest emission intensity corresponds to the sample deposited at 550 °C. At this point it is convenient to note that the luminescence spectrum of trivalent europium ion is only slightly influenced by surrounding ligands of the host lattice, since the electronic transitions of Eu involve only a redistribution of electrons within the inner 4f sub-shell [26].

The PL emission spectra for Eu doped $ZnAl_2O_4$ films, as a function of doping concentration, is shown in the Fig. 6. $T_s = 550$ °C and $\lambda_{exc} = 260$ nm. These emission spectra show a maximum at 10 *a*/*o* of $EuCl_3$ in the spraying solution (0.85 *a*/*o* as measured by EDS). Here it is observed a concentration quenching. In the case of rare-earth activators, the migration of excitation by resonant energy transfer between these ions can be so efficient in such way that it may carry the energy to a distant killer in which this energy can be dissipated non-radiatively. Probably the aggregation of activators at high concentration may change some activators to quenchers and induce the quenching effect [27]. This type of concentration quenching does not appear at low concentrations because the average distance between activators is so large that the migration is prevented and the killers are not reached [25].

4. Conclusions

Red PL emissions from ultrasonic spray pyrolysis deposited zinc aluminate films doped with Eu have been observed. The luminescence emission of Eu doped $ZnAl_2O_4$ films is characteristic for the Eu^{3+} ion. The hypersensitive forced electric-dipole emission ($^5D_0 \rightarrow {}^7F_2$) was dominant. This characteristic is required for display applications. A concentration quenching with increasing activator concentration was observed above the optimum doping concentration (0.85 *a*/*o*, as measured by

EDS). A continuous increase of the PL emission intensity as the substrate deposition temperature rises was observed in the range of substrate temperatures studied (up to 550 °C). Comparative PL measurements show that the sensitivity of films is better than that of powders in this case. The X-ray diffraction measurements of these films show that their crystalline structure depends on the deposition temperature; at low temperatures they are in an amorphous state and when the deposition temperature is increased they are transformed to a polycrystalline cubic phase of the $ZnAl_2O_4$ (gahnite). In addition, it was observed a high deposition rate up to 1 μm/min. SEM micrographs showed that these films are rough but dense and continuous. It was reasserted that $ZnAl_2O_4$ is a good host for rare earth ions as active center to generate luminescence emission. To our best knowledge, this is the first time that a characterization on luminescent $ZnAl_2O_4$ films is reported.

Acknowledgements

The authors would like to thank to Leticia Banos for X-ray diffraction measurements, Sara Jimenez, Marcela Guerrero and Juan García-Coronel for their technical support.

References

[1] R.J. Hill, J.R. Craig, G.V. Gibbs, Phys. Chem. Minerals 4 (1979) 317.

[2] S.K. Sampath, J.F. Cordaro, J. Am. Ceram. Soc. 81 (1998) 649.

[3] S. Mathur, M. Veth, M. Mass, H. Shen, N. Lecerf, V. Huch, S. Hufiier, R. Haberkorn, H.P. Beck, M. Jilabi, J. Am. Ceram. Soc. 84 (2001) 1921.

[4] T. El-Nabarawy, A.A. Attia, M.N. Alaya, Mater. Lett. 24 (1995) 319.

[5] B.S. Girgis, A.M. Youssef, M.N. Alaya, Surf. Technol. 10 (1980) 105.

[6] S. Itoh, H. Toki, Y. Sato, K. Morimoto, T. Kishino, J. Electrochem. Soc. 138 (1991) 1509.

[7] S.K. Sampath, D.G. Kanhere, R. Pandey, J. Phys.: Condens. Matter. 11 (1999) 3635.

[8] H. Matsui, C.N. Xu, H. Tateyama, Appl. Phys. Lett. 78 (2001) 1068.

[9] M. Zawadski, J. Wrzyszcz, W. Strek, D. Hreaniak, J. Alloy Compounds 323/324 (2001) 279.

[10] W. Strek, P. Deren, A. Bednarkiewicz, M. Zawadski, J. Wrzyszcz, J. Alloy Compounds 300/301 (2000) 456.

[11] A.R. Phani, M. Passacantando, S. Santucci, Mater. Chem. Phys. 68 (2001) 66.

[12] G.A. Hirata, J. McKittrick, M. Avalos-Borja, J.M. Siqueiros, D. Devlin, Appl. Surf. Sci. 113/114 (1997) 509.

[13] C.N. King, in: Conference Record of the International Display Research Conference, San Diego, 1985, p. 155.

[14] G.H. Dieke, Spectra and Energy Levels of Rare Earth Ions in Crystals, Interscience, New York, 1968.

[15] J.C. Viguie, J. Spitz, J. Electrochem. Soc. 122 (1975) 585.

[16] A. Ortiz, C. Falcony, M. García, A. Sánchez, J. Phys. D: Appl. Phys. 20 (1987) 670.

[17] C. Falcony, M. García, A. Ortiz, J.C. Alonso, J. Appl. Phys. 72 (4) (1992) 1525.

[18] A. Esparza, M. García, C. Falcony, Thin Solid Films 325 (1998) 14.

[19] C. Falcony, M. García, A. Ortiz, O. Miranda, I. Gradilla, G. Soto, L. Cota-Araiza, M.H. Farías, J.C. Alonso, J. Electrochem. Soc. 141 (1994) 2860.

[20] E. Martínez, M. García, F. Ramos-Brito, O. Alvarez-Fregoso, S. López, S. Granados, J. Chavez-Ramírez, R. Martínez, C. Falcony, Phys. Stat. Sol. (b) 220 (2000) 667.

[21] M. García-Hipólito, R. Martínez, O. Álvarez-Fregoso, E. Martínez, C. Falcony, J. Lumin. 93 (2001) 9.

[22] M. García-Hipólito, E. Martínez, O. Álvarez-Fregoso, C. Falcony, M.A. Aguilar- Frutis, J. Mater. Sci. Lett. 20 (2001) 1799.

[23] M. Langlet, J.C. Joubert, in: C.N.R. Rao (Ed.), Chemistry of Advanced Materials, Blackwell Science, Oxford, England, 1993, p. 55.

[24] Powder Diffraction File Card No. 05-0669, International Center for Diffraction Data, Newtown Square, PA, 1990.

[25] G. Blasse, B.C. Grabmaier, Luminescent Materials, Springer-Verlag, Berlin, 1994.

[26] S.A. Studenikin, M. Cocivera, Thin Solid Films 394 (2001) 264.

[27] T. Hase, T. Kano, E. Nakasawa, H. Yamamoto, Phosphors Materials for Cathode-Ray Tubes, in: Advances in Electronics and Electron Physics, vol. 79, Academic Press, 1990, p. 271.