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## Characterization of Al<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> Luminescent Coatings Prepared by Spray Pyrolysis Technique

E. MARTÍNEZ (a), M. GARCÍA (a), F. RAMOS-BRITO (a), O. ALVAREZ-FREGOSO<sup>1</sup>) (a), S. LÓPEZ (a), S. GRANADOS (a), J. CHAVEZ- RAMÍREZ (a), R. MARTÍNEZ M. (a), and C. FALCONY (b)

(a) *Instituto de Investigaciones en Materiales, UNAM, A.P. 07300, Coyoacán 04510, México D.F., México*

(b) *Departamento de Física, Cinvestav – IPN, A.P. 07300, México D.F., México*

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Europium doped Al<sub>2</sub>O<sub>3</sub> photoluminescent coatings have been prepared by an ultrasonic spray pyrolysis process, using a solution of 0.05M of AlCl<sub>3</sub> · 6H<sub>2</sub>O as starting material and EuCl<sub>3</sub> as doping. These films were deposited on Pyrex glass substrates at atmospheric pressure using purified air as a carrier gas. All films were amorphous in structure. The photoluminescence spectra were measured at room temperature as a function of substrate temperature and doping concentration. For an excitation wavelength of 395 nm, all the photoluminescent spectra show bands located at 587, 600, 612 and 648 nm, characteristics of the trivalent europium ion. We observed a concentration quenching of the photoluminescence at values of activator concentration above 10 at% in the starting solution.

**Introduction** Spray pyrolysis is a very low cost process for preparing thin films from a wide variety of materials. Hill and Chamberlain developed this process in the early 1960s, for preparing thin polycrystalline films of binary photoconductors such as CdS, CdSe and their solid solutions [1]. The spray pyrolysis process involves the spraying of solutions, usually aqueous, containing soluble salts of the desired compounds onto a heated substrate. The equipment is simple and inexpensive to construct and operate and does not require an expensive vacuum apparatus or exotic gas [2]. More recently, a worldwide increasing interest exists in the development of thin film electroluminescent devices and large-area flat-panel display applications, which require thin films with good luminescent properties and inexpensive techniques suitable for deposition over large areas. Spray pyrolysis is a technique especially suited for these types of requirements [3, 4]. The present work reports the photoluminescent characteristics of Eu doped aluminum oxide films deposited by ultrasonic spray pyrolysis technique (Pyrosol [5]) and the role that the deposition parameters play in these characteristics. No post-deposition annealing was given to these films and all characteristics studied were in as-grown samples.

**Experimental Procedures** Ultrasonic spray pyrolysis technique was used to prepare europium doped aluminum oxide films. The experimental arrangement for this technique has been presented elsewhere [6]. In this process a solution containing the materials to be deposited is sprayed through a spraying nozzle over a hot Pyrex glass sub-

<sup>1</sup>) e-mail: oaf@servidor.unam.mx; Tel.: (5) 5622 4649

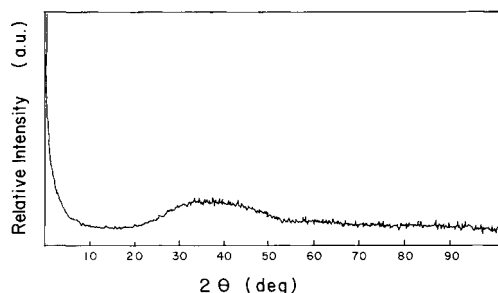


Fig. 1. Typical XRD spectrum of  $\text{Al}_2\text{O}_3:\text{Eu}^{3+}$  coatings deposited by ultrasonic spray pyrolysis

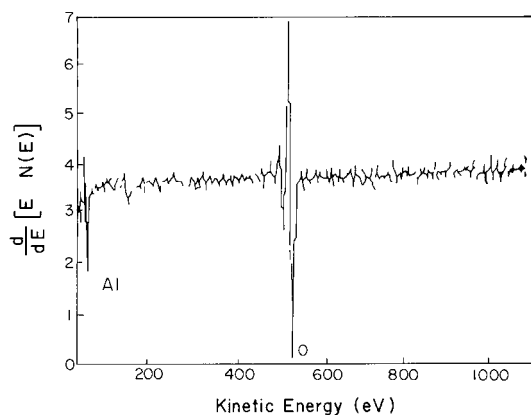
strate. The solvents in the solution are vaporized when the mist of the solution gets in touch with the hot substrate leaving a solid coating onto it.

The spraying solution was 0.05M solution of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  in deionized water (18 MΩ). Doping with Eu was achieved by adding  $\text{EuCl}_3$  to the spraying solution in the range of 0 to 40% in relation to the Al content in this solution. The gas flow consisted in purified air at 10 l/min and the solution flow was constant at 11 ml/min. The Pyrex glass substrate temperature was varied from 350 to 540 °C, in 30 K steps. The deposition time was 5 min and constant for all samples. The thickness of the films was about 5 to 7 μm as measured by a Sloan Dektak IIA Profilometer. The crystalline structure of the samples was analyzed by X-ray diffractometry (XRD) using  $\text{CuK}_\alpha$ , Siemens D5000 diffractometer, operated at 30 keV.

The emission spectra were obtained with a Perkin Elmer LS50B fluorescence spectrophotometer. All photoluminescence spectra were obtained at room temperature and 395 nm light was found to be suitable as excitation source for the photoluminescence measurements. The chemical composition of the films was measured using energy dispersive spectroscopy (EDS) with a Leica Cambridge electron microscope Stereoscan 440. The standard used for EDS measurements was the multi-element X-ray reference Standard Microspec serial 0034, part No 8160-53.

Auger electron spectroscopy (AES) Perkin Elmer PHI-595 was used to determine the homogeneity and stoichiometry of the aluminum oxide samples.

**Experimental Results and Discussion** Figure 1 is representative of the structural characteristics for all  $\text{Al}_2\text{O}_3:\text{Eu}^{3+}$  coatings deposited by ultrasonic spray pyrolysis method.



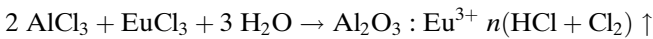
The XRD spectra consist of one very broad peak without any sharp peak, which is normally termed amorphous structured material. It is clear that aluminum oxide films remain in the non-crystalline state for all substrate temperatures used.

Fig. 2. Auger spectrum of  $\text{Al}_2\text{O}_3$  without europium

Table 1  
Chemical composition of Al<sub>2</sub>O<sub>3</sub>: Eu<sup>3+</sup> samples

Eu <sup>3+</sup> in start solution	0 at%	1 at%	5 at%	10 at%	20 at%	30 at%	40 at%
oxygen	70.27	70.59	69.98	71.25	71.69	70.16	70.47
aluminum	28.13	27.60	27.42	25.40	23.60	22.19	19.99
chlorine	1.60	1.66	1.77	1.92	2.51	4.55	5.01
europium	0.00	0.15	0.83	1.43	2.20	3.10	4.53
luminescence intensity (a.u.)	0.00	20	53	100	25	17	5

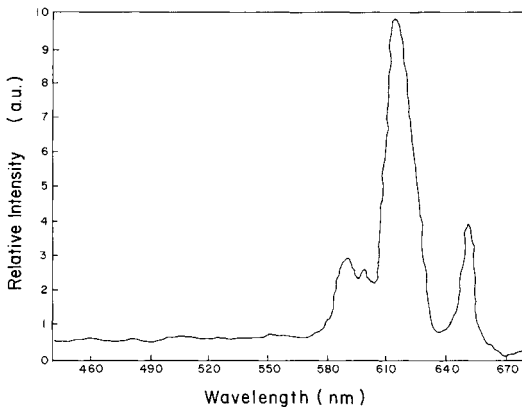
Samples for EDS measurements were prepared at 540 °C substrate temperature (constant) and we varied the atomic percentage of the europium in the start solution from 0 to 40 at%. EDS measured results are summarized in Table 1. The relative amount of chlorine in the samples increases as the amount of europium in the start solution increases. This is due to the chemical reaction on the substrate surface during the solvent evaporation process, i.e.



with chlorine as a remanent impurity.

Figure 2 shows the Auger spectrum for the Al<sub>2</sub>O<sub>3</sub> without europium to determine the homogeneity and stoichiometry of the material deposited. It is observed that the amplitude of the oxygen and aluminum peaks compare well with those reported for Al<sub>2</sub>O<sub>3</sub> in the Handbook of AES. In consequence, the as-deposited samples are almost stoichiometric in composition.

Photoluminescence spectra for Eu doped Al<sub>2</sub>O<sub>3</sub> are shown in Fig. 3; it is possible to distinguish four emission bands centered at 587, 600, 612 and 648 nm, which correspond to transitions between the levels <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>0</sub>, <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub>, <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> and <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub>, respectively, from the trivalent europium ion. The best luminescence relative intensity was shown by the sample with 1.43 at% of europium (see Table 1). The variation in relative intensity for the 612 nm (maximum) luminescent peak as a function of the substrate temperature is indicated in Fig. 4. It is observed an increase in luminescent intensity as the substrate temperature increases in the range 300 to 450 °C and then a saturation process with constant intensity in the range 450 to 540 °C. This no incremental intensity behavior is probably due to the increase in chlorine content in the samples. Similar results have been reported in the literature [7].



In Fig. 5 is shown the behavior of the

Fig. 3. Photoluminescence spectrum for Eu doped Al<sub>2</sub>O<sub>3</sub>

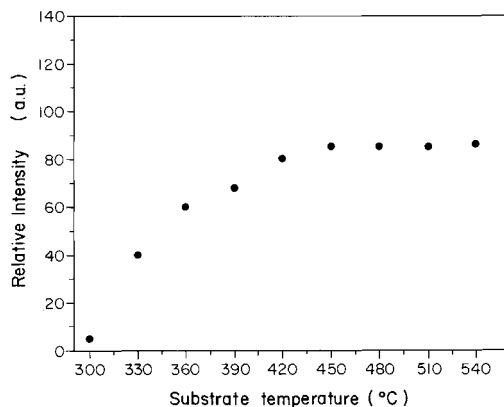


Fig. 4. Relative intensity of the 612 nm peak as function of temperature

relative luminescence intensity as a function of europium atomic percentage in the samples. The intensity of the 612 nm emission raises rapidly as the amount of Eu increases from 0 to 1.5 at%. At higher Eu concentration, the intensity decreases drastically. This quenching effect with the Eu concentration has been observed previously in Tb doped  $\text{Al}_2\text{O}_3$

and Mn doped ZnS, and it has been subject of exhaustive studies, although the exact mechanism for the occurrence of this quenching is still a matter of controversy. It is generally accepted that the quenching effect is associated with interaction among Eu ions at the nearest, the second nearest and probably even at the third nearest neighbor sites [8].

**Conclusions** Europium doped aluminum oxide films have been deposited by ultrasonic spray pyrolysis technique. The films were deposited at different substrate temperature in the range 300 to 540 °C and with an Eu concentration in the spraying solution in the range 0 to 40 at%. The material deposited was non-crystalline in all cases.

The chemical composition analyses of these samples show that the amount of Cl in the films increases as the  $\text{EuCl}_3$  amount in the start solution increases, see Table 1. The luminescence spectra showed four peaks, associated with the  $\text{Eu}^{3+}$  transitions. The maximum relative luminescence intensity was observed at 612 nm. The luminescence intensity shows a saturation effect as a function of substrate temperature. In the range 300 to 450 °C, the relative intensity increases as the temperature increases and at higher substrate temperatures, the intensity remains almost constant, probably due to the chlorine content in the films. The maximum luminescence intensity starts to increase as the Eu concentration increases and above a certain concentration there is a quenching

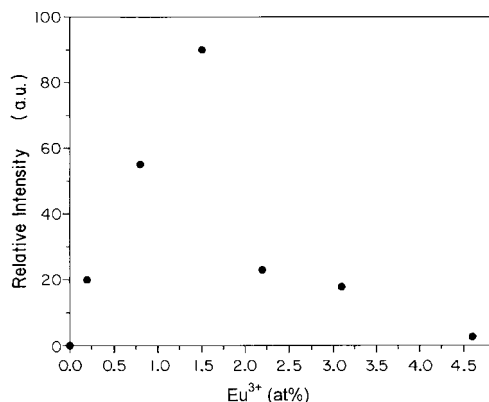


Fig. 5. Relative intensity of the 612 nm peak as function of  $\text{Eu}^{3+}$  amount in the solid coating as measured by EDS

effect of the luminescence. This effect is similar to that reported to occur in Mn doped ZnS samples deposited by similar technique [8].

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