

# Studies on blue and red photoluminescence from $\text{Al}_2\text{O}_3:\text{Ce}^{3+}:\text{Mn}^{2+}$ coatings synthesized by spray pyrolysis technique

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## Abstract

$\text{Al}_2\text{O}_3:\text{Ce}^{3+}:\text{Mn}^{2+}$  films deposited by the spray pyrolysis technique show blue and red emissions under ultraviolet light excitation. The blue emission is due to the de-excitation of  $\text{Ce}^{3+}$  ions from their excited state 5d to the split ground state  $^2\text{F}$ . The usually weak red emission attributed to 3d→3d de-excitation of  $\text{Mn}^{2+}$  is enhanced through an efficient energy transfer from  $\text{Ce}^{3+}$  to  $\text{Mn}^{2+}$  ions. The quantum efficiency of this transfer is near to 100%. SEM and RBS have been used to analyze the surface morphology and chemical composition of Ce- and Mn-doped  $\text{Al}_2\text{O}_3$  films. The films were also characterized by the X-ray photoelectron spectroscopy technique, and it was found that a considerable amount of Mn ions remains linked to chlorine while Ce is mostly in an oxidized state.

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## 1. Introduction

Aluminum oxide coatings have excellent dielectric and mechanical characteristics on many types of substrates, such as hardness, abrasion and scratch resistance as well as corrosion-resistant characteristics. Aluminum oxide films are also able to withstand high temperatures and energetic radiation exposure, besides having low permeability to alkali impurities [1]. Because of its wide energy band gap and chemical stability,  $\text{Al}_2\text{O}_3$  can be an important host for luminescent impurities in the fabrication process of phosphors for thin film electroluminescent devices and optical active layers in flat-panel displays [2]. For instance, the incorporation of rare earth ions such as  $\text{Eu}^{3+}$  [3],  $\text{Tb}^{3+}$  [4,5] and  $\text{Ce}^{3+}$  [6] in  $\text{Al}_2\text{O}_3$  films deposited by means of the spray pyrolysis technique has been reported. Aluminum oxide

coatings have been deposited by many techniques like vacuum evaporation, sputtering, chemical vapor deposition, anodization to form barrier-type coating and a number of methods involving growth from chemical solutions, so-called chemical techniques. Nevertheless, the spray pyrolysis technique, because of its simplicity and low cost, is a technique that has been extensively used for the preparation of thin films [7].

Luminescent materials incorporating more than one center could present energy transfer phenomena from one center to another [8–10]. In particular, it is well known that Ce ions are excellent donors of excitation energy (sensitizers) and Mn ions act as efficient activators or energy acceptors; both have been used as dopants in photoluminescent materials involving energy transfer [11,12] in the quest for efficient blue- and red-emitting materials. In this work, blue and red photoluminescence emissions from  $\text{Al}_2\text{O}_3:\text{Ce}^{3+}:\text{Mn}^{2+}$  coatings synthesized by spray pyrolysis technique are studied, Rutherford backscattering spectroscopy (RBS) studies are used to determine the concentration of the dopants since, for the proper

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assessment of the energy transfer phenomena, it is important to know the chemical composition and spatial distribution of the participant ions ( $\text{Ce}^{3+}$  and  $\text{Mn}^{2+}$ ). Also, high-resolution X-ray photoelectron spectroscopy (XPS) was used to determine the state of bonding for Ce and Mn ions.

## 2. Experimental

$\text{Al}_2\text{O}_3$  films doped with  $\text{Ce}^{3+}$  and/or  $\text{Mn}^{2+}$  ions were prepared using the spray pyrolysis technique [13]. In this technique, a solution with proper reactive materials is sprayed through a spraying nozzle over a hot substrate at atmospheric pressure. The spraying solution was a 0.07 M solution of  $\text{Al}_2\text{Cl}_3 \cdot 6\text{H}_2\text{O}$  dissolved in de-ionized water (18 M $\Omega$ /cm), and  $\text{CeCl}_3$  and  $\text{MnCl}_2$  (Aldrich Chemical Co.) were added as doping materials. The spray was produced by means of an ultrasonic generator at a frequency of 0.8 MHz. Filtered air was used as transport gas at a flow rate of 10 l/min. The solution was sprayed at a rate of 1 ml/min. Corning 7059 glass slides were used as substrates. The substrate temperature during the deposit of the films was 300 °C. The time of synthesis was 6 min for a film thickness of about 5  $\mu\text{m}$  and surface roughness of  $0.66 \pm 0.03$   $\mu\text{m}$ , as measured with a profilometer Sloan Dektak IIA. The crystalline structure of the sample (found to be amorphous) was analyzed by X-ray diffractometry (XRD) using a 1.540 Å ( $\text{CuK}\alpha$ ) Siemens D5000 diffractometer, which was operated at 30 keV. The chemical composition of the films was measured using energy-dispersive spectroscopy (EDS) with a Leica Cambridge Electron Microscope model StereoScan 440 equipped with a beryllium window X-ray detector (this microscope was used to obtain the SEM micrographs) [14]. The Rutherford backscattering (RBS) was performed with  $^4\text{He}$  ions of several energies from the Physics Institute (UNAM) 9SDH-2 Pelletron Accelerator at a scattering angle of 168°. For X-ray photoelectron spectroscopy (XPS), a system of ultrahigh vacuum VG-Scientific Microtech Multilab ESCA2000 was used with a  $\text{MgK}\alpha$  X-ray source 8025 in a photoelectron spectrometer. The X-ray generator was operated at 15 kV and 20 mA to achieve high energies ( $h\nu = 1253.6$  eV), and the XPS spectra were obtained at a take-off angle of 55°

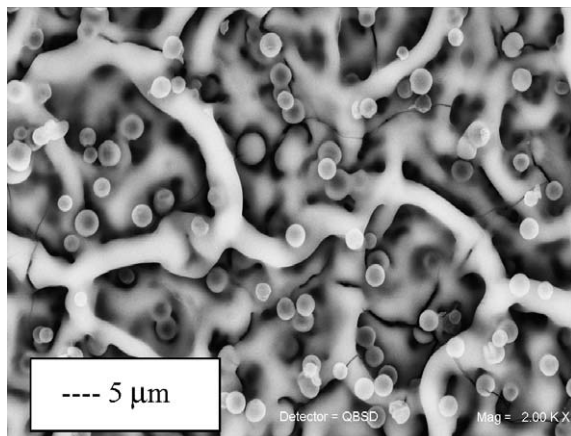


Fig. 1. SEM image from  $\text{Al}_2\text{O}_3:\text{Ce}^{3+}$  (10%): $\text{Mn}^{2+}$  (3%) coatings deposited at 300 °C.

Table 1  
Chemical composition of the films as measured by EDS

Sample	Solution concentration (at.%)		Chemical composition (at.%)				
	$\text{CeCl}_3$	$\text{MnCl}_2$	$\text{O}^{2-}$	$\text{Al}^{+3}$	$\text{Cl}^-$	$\text{Ce}^{3+}$	$\text{Mn}^{2+}$
M1	5	0	55.5	34.5	6.6	3.4	0.0
M2	10	0	47.9	38.3	9.0	4.8	0.0
M3	5	1	57.7	33.3	6.1	2.7	0.2
M4	10	1	57.9	31.3	7.6	3.0	0.2
M5	10	3	50.5	37.1	7.5	4.0	0.9

with respect to surface. The peak position was referenced to the background of  $\text{Ag } 3d^{5/2}$  photo peak at 368.7 eV, with a resolution of the FWHM at 1.0 eV. The pressure stayed constant during the measurement at  $5 \times 10^{-9}$  mb. The surface of the films was etched for 1 min with 4.5 kV  $\text{Ar}^+$  at 4  $\mu\text{A}$  on 12  $\text{mm}^2$ . The analysis of the spectra obtained was performed by means of a software SDPv4.1®.

Luminescence emission spectra were obtained with a Perkin Elmer LS-50B spectrometer using as excitation source the 254-nm line of an 8-W UV mercury lamp model UVGL-25. An optical fibre was used to take the luminescence emission into the spectrometer operated in the bioluminescence mode.

## 3. Results and discussion

The XRD measurements of all the samples showed a typical pattern of an amorphous material, with a very broad band without any clear indication of crystallinity. The typical morphology of the samples studied is illustrated in Fig. 1, which shows the SEM observed surface morphology of a sample deposited at 300 °C. It is possible to observe a rough but continuous film with good adherence to the substrate. The chemical composition of the films studied, determined by EDS for samples deposited with solution concentrations of 5 and 10 at.% of  $\text{CeCl}_3$  (samples M1 and M2), with 5 at.% of  $\text{CeCl}_3$  and 1 at.% of  $\text{MnCl}_2$  (M3), 10 at.% of  $\text{CeCl}_3$  and 1 and 3 at.% of  $\text{MnCl}_2$  (M4 and M5), and with 5 at.% of  $\text{MnCl}_2$  (M6) with

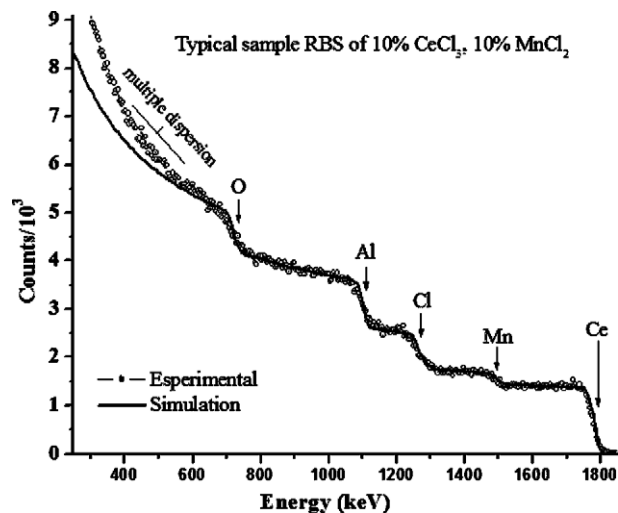


Fig. 2. Backscattered 2 MeV  $^4\text{He}$  spectrum of a 10%  $\text{CeCl}_3$ , 10%  $\text{MnCl}_2$  sample.

respect to the Al content, is summarized in Table 1. It was found that the relative amount of chlorine in the films increases as the amount of  $CeCl_3$  and  $MnCl_2$  does in the start solution.

Fig. 2 shows a typical RBS spectrum for these samples, where the Ce, Mn, Cl, Al and O steps are identified. The full line represents the simulated spectra assuming that Ce, Mn and Cl are distributed homogeneously throughout the film. In general, the chemical composition determined by RBS spectra was in agreement with that determined by EDS [15]. Fig. 3 shows the XPS spectra and a deconvolution fit for the Ce 3d doublet and for Mn 2p. In the case of Ce  $3d^{3/2}$ , the fitted peaks are  $CeCl_3$  at 908.00 eV,  $Ce_2O_3$  at 904.02 eV,  $CeO_2$  at 899.04 eV and satellite peaks of the  $Ce_2O_3$  at 916.94 eV. For Ce  $3d^{5/2}$  the fitted peaks are as follows:  $CeCl_3$  at 888.30 eV,  $Ce_2O_3$  at 885.80 eV,  $CeO_2$  at 882.40 eV and satellite at 900.80 eV. In the case of Mn 2p, the associated peaks are  $MnO_2$  at 642.60 eV,  $MnCl_2$  at 641.90 eV and metallic Mn at 640.70 eV [16]. The uncertainty on the results for binding energy by XPS is estimated to be within 5% of the reported value. From the relative size of the fitted contributions, it is clear that a considerable amount of Mn remains bonded to Cl while Ce is mostly oxidized. From the

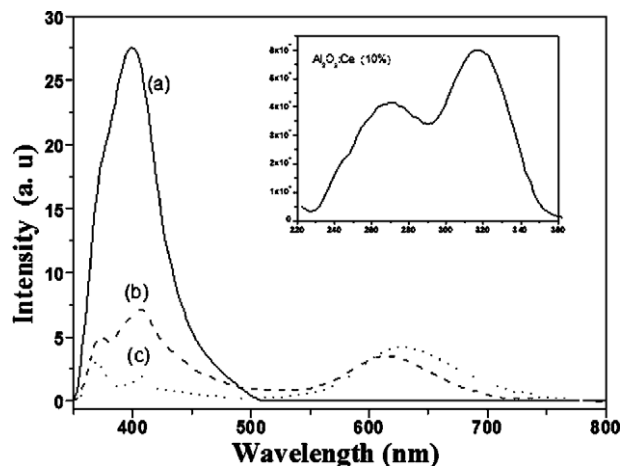


Fig. 4. Emission spectra of the (a) M2, (b) M4 and (c) M5 films excited with a UV mercury lamp at 254 nm. The inset shows the excitation spectrum of the  $Al_2O_3:Ce^{3+}$  film with 10% concentration in the solution.

point of view of charge compensation, this was somehow expected since the  $Mn^{2+}$  requires the charge compensation of the chlorine ion.

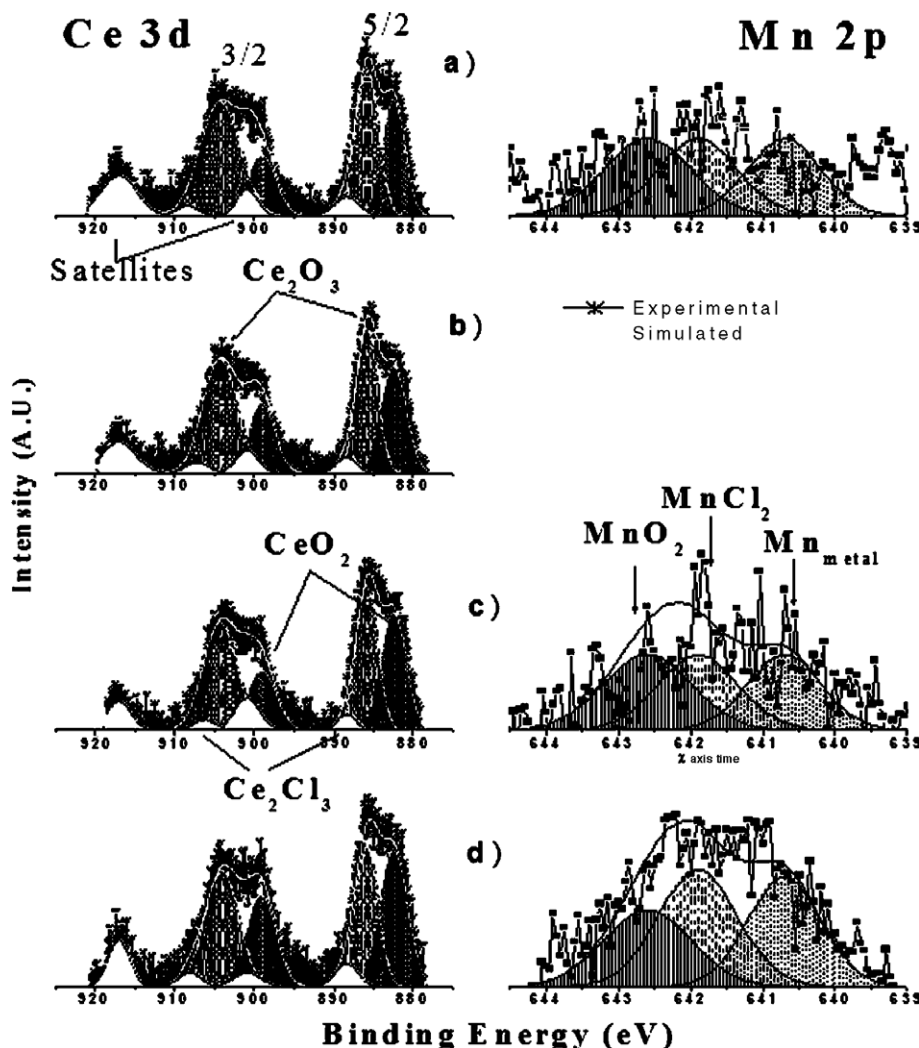


Fig. 3. Core-level XPS spectra for Ce  $3d^{5/2}$ , Ce  $3d^{3/2}$  and Mn 2p and their deconvolution peaks. Ce 3d and Mn 2p include spectra for the following samples: (a) M4; (b) M2; (c) M5; (d) M6.

Fig. 4 shows the luminescent emission spectra, excited with 250 nm light, for the M2 (10 at.% of CeCl<sub>3</sub>, 0 at.% MnCl<sub>2</sub>), M4 (10 at.% of CeCl<sub>3</sub>, 1 at.% MnCl<sub>2</sub>), M5 (10 at.% of CeCl<sub>3</sub>, 3 at.% MnCl<sub>2</sub>) and M6 (10 at.% of CeCl<sub>3</sub>, 5 at.% MnCl<sub>2</sub>) deposited at substrate temperature  $T_s=300$  °C. The peak at 400 nm is associated with Ce<sup>3+</sup> emission while the peak at 620 nm is related to Mn<sup>2+</sup> emission. The inset shows the excitation spectra for the 400 nm (Ce) emission of sample M2 with two wide bands centered at 270 and 317 nm. The behavior of the blue emission is similar to that previously reported from aluminum oxide films doped with similar cerium concentrations [6]. Thus, the blue emission can be attributed to the de-excitation of Ce<sup>3+</sup> ions from the <sup>2</sup>D<sub>3/2</sub> excited state to the split ground state into their <sup>2</sup>F<sub>5/2</sub> and <sup>2</sup>F<sub>7/2</sub> components. Fig. 4 shows, besides the blue emission of Ce<sup>3+</sup> ions, a red emission at ~600 nm associated with the incorporation of Mn<sup>2+</sup> ions since it is observed only after the film was simultaneously doped with MnCl<sub>2</sub>. Therefore, it can be attributed to the Mn<sup>2+</sup> <sup>4</sup>T<sub>1g</sub>(G)→<sup>6</sup>A<sub>1g</sub>(S) transition. It is also observed that as the content of Mn is increased, the red emission intensity increases at the expense of the blue emission. It has been proposed that an energy transfer mechanism between the Ce<sup>3+</sup> and Mn<sup>2+</sup> ions is taking place. A detailed analysis of this energy transference process has been published elsewhere [17], in which a short-range interaction mechanism was proposed to take place between these ions. The short lifetime measured for the Ce<sup>3+</sup> emission (2.4±0.5 and 2.6±0.4 μs for M1 and M2) proves that the 4f→5d absorption transition of the Ce<sup>3+</sup> ions via electric dipole is allowed. On the other hand, the long lifetime measured for the Mn<sup>2+</sup> emission (1.7±0.3 and 1.3±0.2 ms for M3 and M5) reveals the forbidden nature of the 3d→3d transitions. Therefore, it is expected that the Ce<sup>3+</sup>→Mn<sup>2+</sup> energy transfer could occur via an electric dipole–quadrupole interaction mechanism, with quantum efficiency for this transfer process estimated as being near to 100%. These large transfer efficiency values suggest that Ce ion is a good sensitizer to Mn-red emission in aluminum oxide films [17].

#### 4. Conclusions

Al<sub>2</sub>O<sub>3</sub>:Ce<sup>3+</sup>:Mn<sup>2+</sup> films deposited by the spray pyrolysis technique have been observed to present blue–red emission under ultraviolet light excitation. SEM, EDS, RBS and XPS techniques have been used to analyze Ce- and Mn-doped Al<sub>2</sub>O<sub>3</sub> films. It was found that there is a homogeneous distribution of the activators and a high concentration of Cl. In particular, a considerable amount of Mn remains linked to chlorine while Ce is mostly in an oxidized state. The blue emission is a broad band associated with Ce<sup>3+</sup> transitions from

the 5d excited state to the <sup>2</sup>F<sub>5/2</sub> and <sup>2</sup>F<sub>7/2</sub> levels of the ground state. The red emission observed from manganese-doped samples is very weak, and it is strongly enhanced with the simultaneous addition of Ce through an efficient energy transfer mechanism from Ce<sup>3+</sup> to Mn<sup>2+</sup> ions.

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