

Growth and cathodoluminescent characteristics of blue emitting cerium-doped zinc aluminate layers synthesized by spray pyrolysis technique

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Cerium doped ZnAl₂O₄ cathodoluminescent films have been deposited by ultrasonic spray pyrolysis deposition technique. X-ray diffraction measurements on these layers have shown that their crystalline structure depends on the substrate temperature. Cerium ions have been introduced into zinc aluminate films for produce violet-blue cathodoluminescence emissions. The behavior of cathodoluminescence emission intensity has been studied, as a function of the variations on doping concentrations, in the start spraying solution, substrate temperatures and the electron accelerating voltage. Concentration quenching of the cathodoluminescence occurs at about 0.8 percent of activator (Ce) concentrations inside the synthesized films. The surface morphology characteristics of these films, as a function of the substrate temperature, and the chemical composition, as measured by energy dispersive X-ray spectroscopy, are also exhibited.

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1 Introduction

The zinc aluminates (ZnAl₂O₄) belong to the class of inorganic materials called spinels. This material has a closed-packed face centered cubic structure with Fd3m space group symmetry [1]. The spinel zinc aluminates have been widely used as ceramic, electronic and catalytic material, in chemical and petrochemical industries [2, 3] and more recently as transparent conductor. Regarding to the luminescent properties of zinc aluminate there are very few reported studies [4–6]. These studies have been carried out on samples in the form of powder. Also there are very scarce studies reporting on the general properties of zinc aluminate films [7]. The luminescent films can be applied in electroluminescent flat panel displays and color plasma display panels. Rare earth doped oxides are some of the most promising luminescent materials. 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 [8]. The potential of the rare earth to provide the three basic colors needed in a full color device has led to intensive study of these ions in several host lattices [9]. Although, in general, the emission spectra of some rare earth ions remain the same in different hosts, the crystalline field of the matrix can have an influence on frequency radiation of the activators, as well as the luminescent efficiency. Furthermore, the chemical stability and durability largely depend on the physical properties of the selected host lattice. In the case of Ce³⁺ the transition energy of 5d–4f states change significantly when this ion is inserted in different host materials due the orbitals 5d are very sensitive to local environ-

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ment [10]. Due to this characteristic, ultraviolet, violet, blue and green emissions have been observed from luminescent materials doped with trivalent cerium [11]. Up to now it has been difficult to obtain efficient blue emitting materials. Therefore, the search on this type of materials continues growing in the last years. Cathodoluminescence is an important technological phenomenon that is most widely used in modern cathode-ray tube (CRT)-based instruments, and recently it has emerged as an important microcharacterization tool for the analysis of luminescent materials. Spray pyrolysis technique, with ultrasonic generation, is relatively simple and probably the least expensive non-vacuum technique suitable for deposition over large areas. This deposition process has been successfully used in the synthesis of luminescent layers of materials such as $\text{Al}_2\text{O}_3:\text{CeCl}_3$, $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Tb}$, Eu or Ce , $\text{ZrO}_2:\text{Mn}$, Cl , etc. [12] and references therein.

A room temperature violet-blue cathodoluminescence from cerium-doped zinc aluminate coatings growth by the ultrasonic spray pyrolysis technique and its characterization are reported in this contribution. The behavior of the cathodoluminescent spectra has been studied as a function of the substrate temperature during the deposition process, activator concentration, and the electron accelerating potential. In addition, the characteristics of the surface morphology and the crystalline structure of the films, as a function of the deposition parameters, are shown.

2 Experimental details

Ultrasonic spray pyrolysis technique was used to deposit cerium doped zinc aluminate layers. The experimental arrangement for this process has been published elsewhere [13]. In few words, in this technique, a 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 0.5 cm above the substrate. The spraying solution was 0.05 M solution of zinc acetate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, purity 99.99% from the Aldrich Chemical Co.] and aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, purity 99.9% from the Aldrich Chemical Co) in deionized water as solvent. Doping with Ce was achieved by adding $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (purity 99.9% from the Aldrich Chemical Co.) to the spraying solution in the range from 0 to 20 atomic percent (a/o) in relation to the Zn content in this solution. The carrier gas flow (purified air) was 10 liter/minute and the solution flow rate was 3 ml/min. The substrate temperature (T_s) during deposition was in the range from 350 °C to 550 °C; the substrates used were Corning 7059 glass slides and Si (100) single crystals (the samples deposited on glass substrates were only used for the XRD measurements). 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 to 6 minutes) 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 Cambridge-Leica electron microscope mod. Stereoscan 440 equipped with a Beryllium window X-ray detector. Cathodoluminescence (CL) measurements were performed in a stainless steel vacuum chamber with a cold cathode electron gun (Luminoscope, model ELM-2 MCA, RELION Co.). Samples were placed inside the vacuum chamber and evacuated up to 10^{-3} Torr. The electron beam was deflected through a 90-degree angle to bombard the luminescent material normal to the surface. The emitted light from the sample was coupled into an optical fiber bundle leading to a Perkin-Elmer LS50B fluorescence spectrophotometer. All CL spectra were obtained at room temperature. The accelerating voltage of the electron beam used in the measurements reported was varied in the range from 2 kV to 15 kV and the applied current was 0.5 mA. The spot size of the beam on the surface sample was 3 mm in diameter approximately.

3 Results and discussion

XRD measurements showed that the crystalline structure, of the $\text{ZnAl}_2\text{O}_4:\text{Ce}$ films prepared by the ultrasonic spray pyrolysis process, is dependent on the substrate temperature employed during deposition.

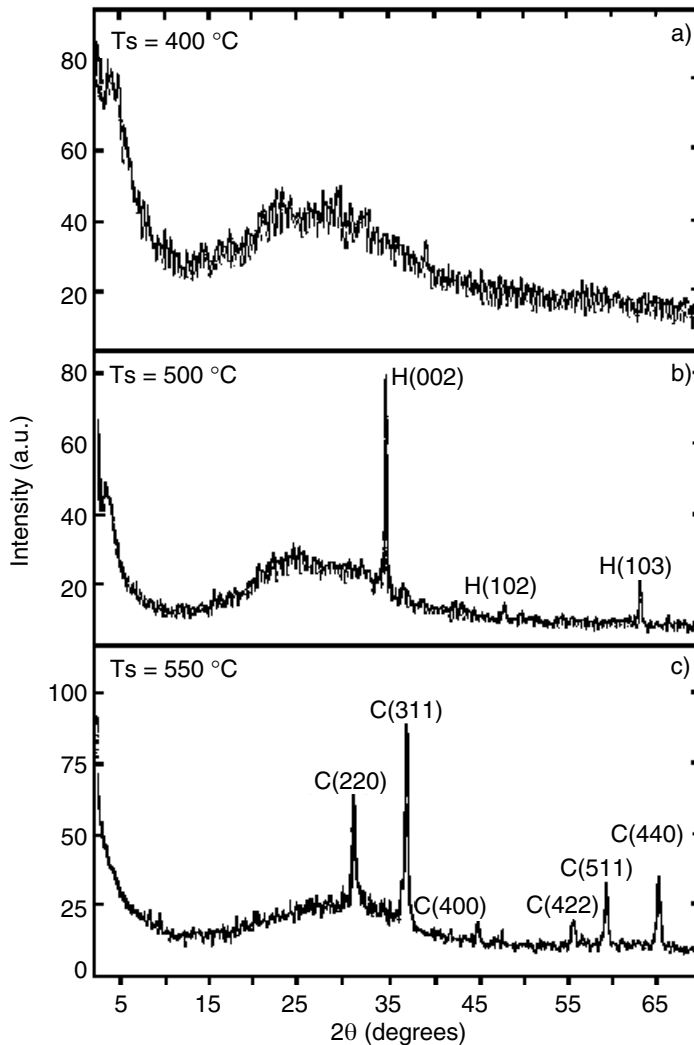


Fig. 1 XRD patterns for cerium-doped zinc aluminate coatings at three different deposition temperature, T_s : 400 °C, 500 °C and 550 °C. (H = hexagonal, C = cubic).

The crystalline characteristics are illustrated in Fig. 1 (a, b, c), here X-ray diffraction patterns for $\text{ZnAl}_2\text{O}_4:\text{Ce}$ (20 a/o in the spraying solution) at three different substrate temperatures, 400 °C, 500 °C and 550 °C, are presented. The $\text{ZnAl}_2\text{O}_4:\text{Ce}$ coatings remain in the non-crystalline state when deposited at substrate temperatures up to 400 °C (Fig. 1 a), as the substrate temperature is increased at 500 °C some peaks corresponding to hexagonal phase of zinc oxide (zincite, ICDD Card File No. 36-1451) are observed (Fig. 1 b). In the case of the samples deposited at 550 °C (Fig. 1 c) only a cubic spinel crystalline phase of ZnAl_2O_4 (gahnite) was observed (ICDD Card File No. 05-0669 [14]). The lattice parameters were calculated ($a = b = c = 8.0859 \text{ \AA}$) for cubic spinel phase in the films deposited at 550 °C and these values are in good agreement with the reported values ($a = b = c = 8.0848 \text{ \AA}$) [14]. In this case, the material grows with a preferential (311) direction normal to the films surface.

EDS measurements were performed on films deposited on (1 0 0) n-type silicon single crystals substrates. The obtained results are shown in Tables 1 and 2. Table 1 summarizes the relative chemical content of the oxygen, zinc, aluminum, cerium and chlorine present into the films as a function of the content of the cerous chloride inserted in the spraying solution. A reduction of the relative content of zinc,

Table 1 Atomic percent content of the oxygen, zinc, aluminum, cerium and chlorine in the cerium-doped zinc aluminate films as measured by EDS for different CeCl₃ concentrations in the spraying solution. The substrate temperature was 550 °C.

CeCl ₃ concentration in the spraying solution (a/o)	oxygen	zinc	aluminum	cerium	chlorine
0	56.00	13.24	27.31	00.00	03.45
3	57.61	12.15	26.16	00.19	03.89
6	58.40	11.59	25.54	00.36	04.11
10	59.82	10.99	23.93	00.81	04.45
20	60.93	09.39	22.35	01.86	05.47

aluminum and an increase in the relative contents of oxygen, cerium and chlorine are observed when the doping concentration is increased. The substrate temperature, in this case, was 550 °C. It seems natural that, as the content of cerous chloride increases in the spraying solution, the cerium and chlorine relative contents are also increased inside the films. At the same time a decrease of the zinc and aluminum relative contents is observed. Presumably the cerium and chlorine ions are incorporated into the host lattice. With the present data it is not possible to elucidate if the cerium and chlorine ions substitute for zinc or aluminum ions or both. Also, it is not clear which is the role of the incorporated chlorine regarding the cathodoluminescent properties. If the trivalent cerium ions substitute zinc ions, the incorporated chlorine ions could act as co-activators to preserve the electrical neutrality. More investigation is in progress to clarify satisfactorily this point.

Table 2 shows similar results to those in Table 1 but as a function of the deposition temperature, keeping constant the doping concentration (CeCl₃, 10 a/o) in the starting solution. Here, we observe that the relative content of zinc is maintained constant, also an increase in the relative contents of oxygen, aluminum and a reduction in the relative content of cerium and chlorine as the substrate temperature increases. At low substrate temperatures the surface thermal energy is probably insufficient to dissociate the initial molecules and to evaporate the solvents and residual gases (H₂O, HCl, Cl, etc.). The above-mentioned fact avoids the beginning of the crystallization of the final material (ZnAl₂O₄) as confirmed by the XRD measurements. This explains the relative high concentrations in cerium and chlorine. As the deposition temperature increases a larger thermal energy is available to reach a complete decomposition and processing of the material arriving to the substrate. This condition promotes the evaporation of the residual products and the formation of the crystallites of zinc aluminate which make that incorporation of cerium and chlorine diminish. With the complete crystallization of ZnAl₂O₄ the relative contents of zinc, aluminum and oxygen spread toward their ideal values: Zn (14%), Al (28%) and O (58%). The deviations of these values are due to the incorporation of the activator ions and possible co-activators.

The CL spectra as a function of activator concentration in the spraying solution are shown in Fig. 2, under 15 kV electron accelerating potential (in these cases $T_s = 550$ °C). These spectra exhibit asymmetrical broad bands centered at approximately 420 nm which are characteristic of the electronic transitions in the Ce³⁺ ion (4f¹). The observed emission bands are originating from the $^2T_{2g}(5d) \rightarrow ^2F_{7/2}, ^2F_{5/2}(4f)$

Table 2 Atomic percent content of the oxygen, zinc, aluminum, cerium and chlorine in the cerium-doped zinc aluminate films as determined by EDS for different substrate temperatures. In this case, the CeCl₃ concentration in the spraying solution was 10 a/o.

substrate temperature (°C)	oxygen	zinc	aluminum	cerium	chlorine
350	54.84	10.65	18.79	03.53	12.19
400	56.98	11.56	19.08	02.59	9.79
450	57.91	11.88	20.71	01.96	07.54
500	58.87	10.59	22.76	01.41	06.37
550	59.82	10.99	23.93	00.81	04.45

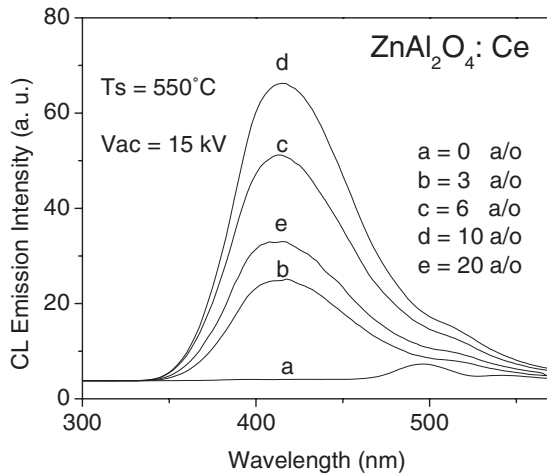


Fig. 2 CL spectra for $\text{ZnAl}_2\text{O}_4:\text{Ce}$ films as a function of the doping concentration, under 15 kV electron accelerating potential. $T_s = 550$ °C.

transitions in the Ce^{3+} ions [15]. These transitions are parity-allowed. The form of the CL bands observed does not show any residual structure which suggest that it is due to one well defined emission center [16]. A concentration quenching of the CL emission intensity is observed at about 0.8 percent of cerium ions inside of the films, as measured by EDS (10 a/o of cerous chloride in the spraying solution). It is believed that concentration quenching of the CL emissions is due to the excess concentration of impurities, which, in this case, interact with each other, generating clusters such as pairs, or triples of Ce ions that favor the dissipation of the energy by non-radiative processes [17]. Another possible effects relative to quenching of CL emissions are: (a) saturation of luminescent centers, whereby the majority of the centers are already in excited states, leaving an insufficient quantity of available centers in the ground state free to accept energy from the excited carriers [18, 19]; (b) thermal quenching, due of the local heating, by energetic electrons, of the luminescent material, and (c) Auger effect which produce ejection of electrons leaving the luminescent centers de-excited [20]. The exact nature of the CL emissions quenching, for this case, is still unknown and needs additional investigation. In absence of activator impurities, Fig. 2 (a), the emission at 420 nm is not present, only a small band centered at approximately 495 nm is appreciated, probably originated at internal transitions within the host lattice.

Figure 3 shows the CL emission intensity behavior, as a function of the deposition temperature. These emissions rise when increasing the substrate temperature, probably due to an improved crystallization of the host lattice, as it is shown by XRD measurements in this range of deposition temperatures, and to the

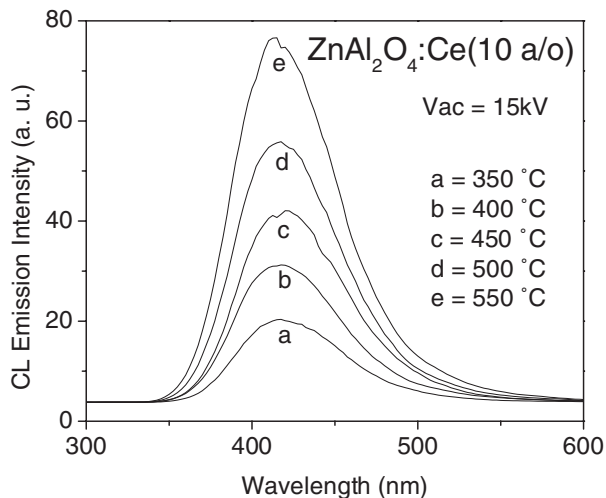


Fig. 3 CL spectra of $\text{ZnAl}_2\text{O}_4:\text{Ce}$ (10 a/o) films as a function of substrate temperature, the electron accelerating voltage was maintained constant at 15 kV.

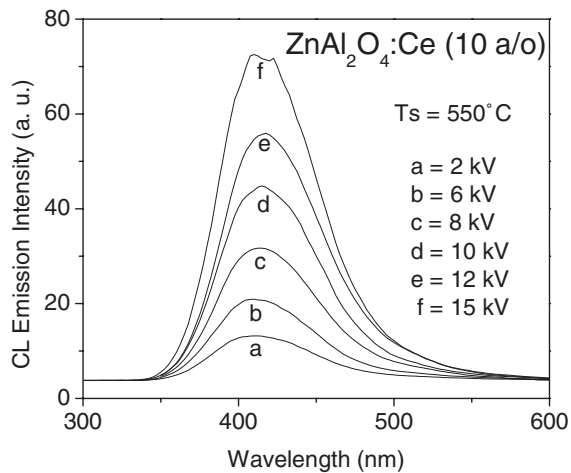


Fig. 4 Behavior of CL emission intensity for $\text{ZnAl}_2\text{O}_4:\text{Ce}$ (10 a/o) layers synthesized at $T_s = 550^\circ\text{C}$, as a function of the electron accelerating potential.

reduction of chlorine and residual impurities left into the crystallized samples. Both effects will produce a better incorporation and distribution of cerium ions as an atomic impurity into the host lattice, which will result in an increase of the CL emission as the deposition temperature is increased. In this case, the value of concentration activators in the spraying solution was fixed at 10 a/o and the electron accelerating potential was 15 kV. In accordance with the observed tendency, films deposited at substrate temperatures higher than 550°C would have larger emission intensity; however, it was not possible to deposit films at substrate temperatures higher than 550°C , since the resulting material was powdery and non-adherent to the substrate. This is probably due to a sudden evaporation of the solvent because at these relatively high temperatures the chemical reaction of the generated aerosol is carried out in the vapor phase before the mist touch the substrate, producing in this way, only a fine powder and not a solid layer. It should be noted that CL emissions exhibited by the films deposited at low temperatures, in despite of their poor crystallinity (coatings deposited at 350°C are non-crystalline or amorphous), already show the characteristic emission from the trivalent cerium ion, as observed for layers deposited at higher substrate temperatures (500 and 550°C) which exhibit crystalline structures corresponding to zinc oxide (hexagonal phase) and zinc aluminate (cubic phase), respectively. Even though for high substrate temperatures the emission intensity is larger.

Figure 4 shows plots of CL spectra measured under steady-state excitation with an electron accelerating voltages ranging from 2 kV to 15 kV. In this case, the highest electron accelerating voltage produces the strongest emission intensity. In principle, it is assumed that in ordinary CL study, the incident electron beam reach and penetrates the luminescent material to generate the secondary electrons and electron-hole pairs which excite the activator ions in the host lattice and so generate CL emissions. The penetration depth of the incident electrons into the film is dependent on the energy E of the electron beam which is given by $E = eV$, where V is the anode voltage and e is electron charge. As the electron accelerating voltage increases, the penetrating electrons produce more electron-hole pairs due to the interaction with a larger volume of the luminescent material, resulting in much more intense activator luminescence due to the recombination of the electron-hole pairs [21]. This is possible if the luminescent material contains activator ions distributed through the whole body of the film acting as radiative recombination centers for electron-hole pairs. The increment in the CL emission intensity, as the electron accelerating potential increases, could indicate that the activators ions are indeed distributed throughout the body of the coatings.

The surfaces morphology of $\text{ZnAl}_2\text{O}_4:\text{Ce}$ (10 a/o) coatings are presented in Fig. 5. It is possible to observe rough but continuous films with good adherence to the substrate. SEM micrographs of the samples deposited at 400°C (a), 500°C (b) and 550°C (c) are shown in this figure. It is also observed that the surface morphology of the films depends on the substrate temperature. Layers deposited at 400°C present some cracks. With increasing substrate temperature (500°C and 550°C), cracks are not appreci-

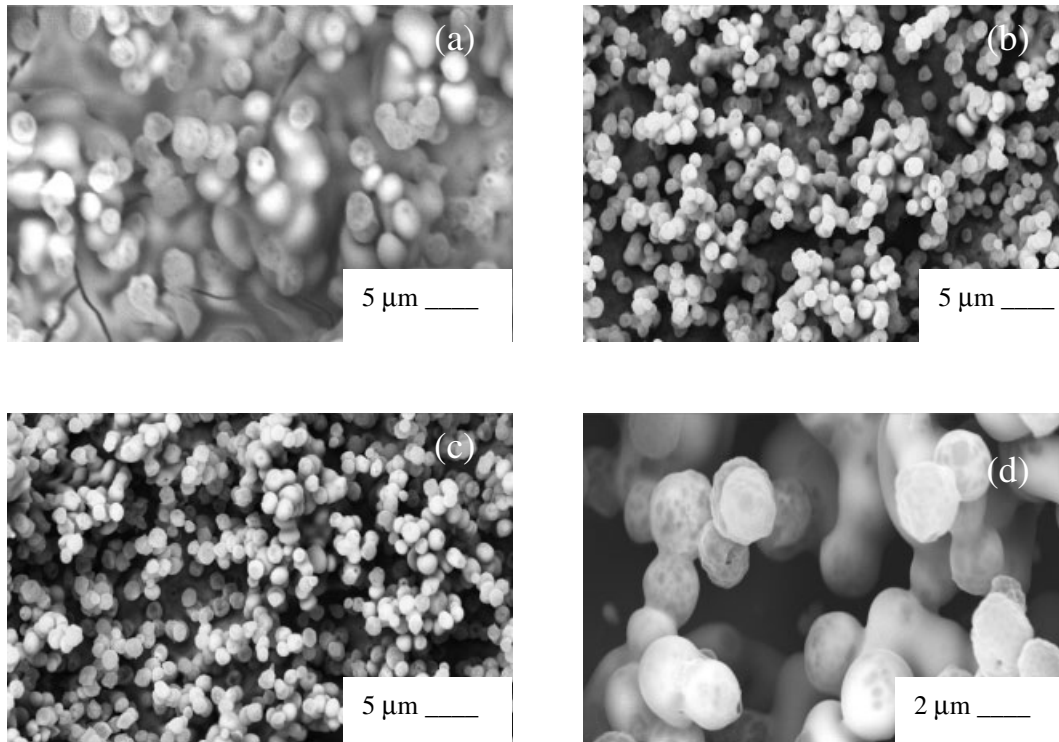


Fig. 5 SEM micrographs of surface morphology of $\text{ZnAl}_2\text{O}_4:\text{Ce}$ coatings as a function of the T_s : (a) 400 °C, (b) 500 °C and (c) 550 °C. Figure 5(d) shows detailed features of the sample deposited at 550 °C.

ated. Probably these characteristics are obtained because that at higher deposition temperature the deposited precursors have bigger surface kinetic energy, which permits them a better accommodation and in consequence to produce a better processed material. In addition, in the samples deposited at 500 °C and 550 °C it is possible to distinguish rough and continuous surfaces but more finely granulated; also, the surface particles have a more spherical form that those of the layers deposited at 400 °C. Figure 5(d) shows some details of the sample deposited at 550 °C, here it is observed the granular growth of the material and the cavernous nature of the top of the surface.

The CL emission from the samples studied is easily observed at naked eye (through the window of the vacuum chamber) in normal room lightening, when excited with electron accelerating voltage through the 2 kV to 15 kV range.

In recent contributions [22, 23], it has been determined that the luminescent characteristics of europium and terbium doped zinc aluminate, are the red and green emissions usually associated with electronic transitions of the respective trivalent ions. The results reported in the present work complete the three basic colors necessary in a multicolored display device. Taking into account that it is difficult to obtain a single phosphor host that can accommodate the three different luminescence centers which emit in the primary colors red, green, and blue, the luminescent emissions from $\text{ZnAl}_2\text{O}_4:\text{Ce}^{3+}$ have a strong potential CL-based display applications. These results demonstrate the versatility and utility of zinc aluminate as host to generate luminescent materials.

4 Conclusions

Violet-blue CL emissions from cerium-doped ZnAl_2O_4 coatings, synthesized by the ultrasonic spray pyrolysis, have been obtained. The XRD analysis 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). The CL emission of Ce doped zinc aluminate films is characteristic of the Ce^{3+} ion. A concentration quenching with increasing activator concentration was observed at about 0.8 percent of cerium ions inside the films, as measured by EDS. A continuous increase of the CL emissions intensity, as the substrate deposition temperature rises, was appreciated in the range of substrate temperatures studied (up to 550 °C). In addition, an increment in the CL emission intensity as the electron acceleration voltage increases was also observed. The spray pyrolysis technique used in this work is capable to render high deposition rates (up to 1 μm per minute). SEM micrographs showed that these films are rough but dense and continuous. It was confirmed that zinc aluminate is a good matrix for rare earth ions as active center to generate strong luminescence emissions. Finally, it should be stressed that there are no reports in the literature, to our best knowledge, about the cathodoluminescent features of blue emitting cerium-doped zinc aluminate films.

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