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# Cathodoluminescent and photoluminescent properties of terbium doped $ZrO_2$ films prepared by pneumatic spray pyrolysis technique

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## Abstract

Terbium doped  $ZrO_2$  cathodoluminescent and photoluminescent films have been prepared by pneumatic spray pyrolysis deposition process. Different substrate temperatures, doping concentrations and the flows of solution in the start spraying solution were studied. It is observed that the crystallinity of the films depends on the substrate temperature during deposition of the films. For substrate temperatures lower than  $400^\circ\text{C}$ , the deposited films are amorphous, whereas for substrate temperatures higher than  $400^\circ\text{C}$  the crystalline structure of the prepared material presents the metastable tetragonal or cubic phases. Preliminary measurements on cathodoluminescent emission are presented. In the case of photoluminescence, the excitation and emission spectra were obtained; for an excitation wavelength of 250 nm, all the photoluminescent spectra show peaks located at 489, 548, 588 and 620 nm. Concentration quenching of the cathodoluminescence and photoluminescence occurs at activator concentration greater than 1.17 and 1.96 atomic percent (a/o), respectively. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Zirconium oxide has attracted much attention in technology and science because of its low thermal conductivity, high melting temperature, high

refractive index, hardness and corrosion barrier properties [1–8]. Relatively little research has been done in the area of luminescent properties of the zirconia in the form of powders and single crystals [9–16]; and the information about zirconia luminescent films is practically non-existent [17].

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

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important microcharacterization tool for the analysis of luminescent materials.

Nowadays, luminescent thin films have a wide range of applications, such as flat panel displays, cathode-ray picture tube screens, AC plasma panels and electroluminescence devices [18–20]. For these applications, it is necessary to be able to deposit good quality coatings emitting in the three basic colors (blue, red and green). A worldwide interest exists in the development of multicolor thin film electroluminescent devices. Rare earth elements have been recognized as most important dopants for multicolor electroluminescent devices since LUMOCEN (Luminescence From Molecular Centers) devices were reported [21]. The potential of the rare earth ions to provide the three basic colors needed in a full color device has led to intensive study of the doping of II–VI compounds with rare earths during the past few years [22]. The studies began with the ZnS matrix and were later extended to alkaline earth sulfides. 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 [23]. Compared to powder phosphors, thin luminescent films offer advantages such as better thermal stability, good adhesion to the substrate, no out-gassing problems and possess uniform properties across the covered area.

Zirconia thin films have been prepared by several techniques [24–27]. Spray pyrolysis technique is relatively simple and probably the least expensive technique suitable for deposition over large areas. This technique has been successfully used in the deposition of luminescent thin films of materials such as ZnO:Tb [28], ZnO:In [29], Al<sub>2</sub>O<sub>3</sub>:Tb [30], ZnS:Mn [31], Al<sub>2</sub>O<sub>3</sub>:CeCl<sub>3</sub> [32], ZnO:Li [33], etc.

The present work reports, for the first time, to the authors best knowledge, the cathodoluminescent (CL) characteristic emission of Tb doped ZrO<sub>2</sub> films as well as the photoluminescent (PL) characteristics of this material deposited by the pneumatic spray pyrolysis deposition process. The role that some deposition parameters play on these characteristics is also reported.

## 2. Experimental details

Pneumatic spray pyrolysis technique was used to prepare terbium doped zirconium oxide films. The experimental arrangement for this technique has been presented elsewhere [34]. In this process, a solution containing the materials to be deposited is sprayed through a spraying nozzle over a hot substrate. The solvents in the solution are vaporized when the mist of the solution gets in touch with the hot substrate leaving a solid coating on the substrate. The substrate is placed on a resistance heated stage and the nozzle is located approximately 25 cm above the stage, all enclosed in an exhaust hood. The spraying solution was 0.05 M solution of zirconium oxichloride (ZrOCl<sub>2</sub>·8H<sub>2</sub>O, Merck) in deionized water. Doping with Tb was achieved by adding TbCl<sub>3</sub>·6H<sub>2</sub>O to the spraying solution in the range from 1 to 20 atomic percent (a/o) in relation to the Zr content in this solution. The gas flow (filtered air) was 10 l/min and the solution flow was varied from 4 to 16 ml/min. The substrate temperature during deposition was in the range from 250°C to 500°C; the substrates used were Corning 7059 glass slides. The deposition time was 5 min. The thickness of the films studied was approximately 5 μm as measured by a Sloan Dektak IIA profilometer. 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 to  $\leq 10^{-3}$  Torr. The electron beam was deflected through a 90° 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. The excitation and emission PL spectra were obtained using the spectrophotometer cited above. All PL spectra were obtained at room temperature and 250 nm light was found to be suitable as excitation source for the PL 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 (Cu K<sub>α</sub>). The chemical composition of the films was

measured using EDS (Energy Dispersive Spectroscopy) 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.

### 3. Results and discussion

As mentioned above, the thicknesses of the studied films were in all cases approximately 5  $\mu\text{m}$ . The structural characteristics of Tb doped  $\text{ZrO}_2$  coatings deposited by spray pyrolysis method are illustrated in Fig. 1, where X-ray diffraction patterns for  $\text{ZrO}_2:\text{Tb}$  (20 a/o in solution) at four different substrate temperatures, 350°C, 400°C, 450°C and 500°C, are shown. The zirconia coatings remain in the amorphous state when deposited at substrate temperatures up to 400°C, but when the substrate temperature is increased above this value various peaks associated with a metastable tetragonal or cubic of zirconia phase appear. When increasing substrate temperature, the growth of zirconia with a preferential (111) direction normal to the films surface is promoted and sharper diffraction peaks at high substrate temperatures indicate that a fast sintering process

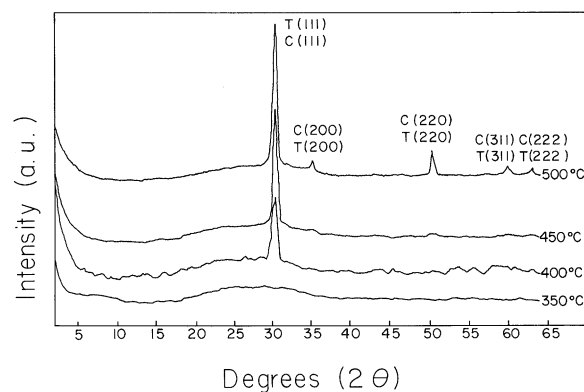


Fig. 1. X-ray diffraction patterns for terbium doped zirconia films (20 a/o, in the spraying solution) at four different deposition temperatures, 350°C, 400°C, 450°C and 500°C. (T = tetragonal zirconia, C = cubic zirconia).

is taking place in this temperature range, leading to an increase in the crystallite size (decreased peak width).

EDS measurements were performed on films deposited on (100) 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 oxygen, zirconium, terbium and chlorine present in the films as a function of the content of the  $\text{TbCl}_3$  inserted into the spraying solution. A reduction of the relative content of oxygen and zirconium and, furthermore, an increase in the relative contents of terbium and chlorine is observed when the doping concentration rises. The substrate temperature, in this case, was 500°C. Table 2 presents results similar to those in Table 1 but as a function of the substrate

Table 1

Atomic percent content of the oxygen, zirconium, terbium and chlorine in the films as measured by EDS for different  $\text{TbCl}_3$  concentrations in the spraying solution. In this case, the substrate temperature was 500°C

$\text{TbCl}_3$ concentration in the spraying solution (a/o)	Oxygen	Zirconium	Terbium	Chlorine
0	60.04	39.21	00.00	00.75
1	59.03	39.71	00.43	00.83
3	58.88	39.11	00.96	01.05
5	58.11	39.46	01.17	01.26
10	57.71	38.65	01.96	01.68
20	57.07	37.14	02.78	03.01

Table 2

Atomic percent content of the oxygen, zirconium, terbium and chlorine in the films as determined by EDS for different substrate temperatures. In this case, the  $\text{TbCl}_3$  concentration in the spraying solution was 10 a/o

Substrate temperature (°C)	Oxygen	Zirconium	Terbium	Chlorine
250	46.21	43.15	04.11	06.53
300	47.44	42.90	03.85	05.81
350	50.53	42.05	03.16	04.36
400	52.79	41.38	02.80	03.03
450	55.48	40.01	02.23	02.28
500	57.71	38.65	01.96	01.68

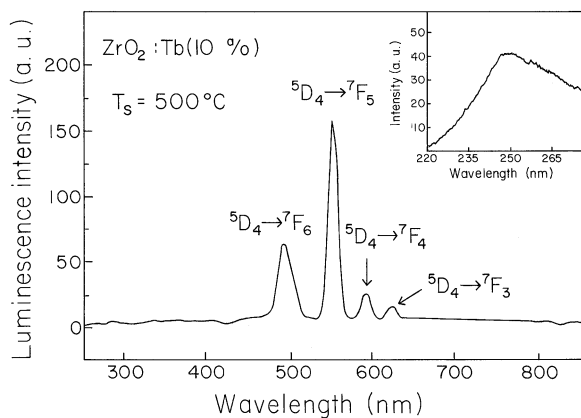


Fig. 2. Room temperature PL emission from zirconia film doped with Tb. The characteristic peaks associated with radiative transitions between the electron energy levels of the rare earth activator involved are shown. The inset shows the excitation spectrum. The optimal wavelength obtained for excitation was 250 nm.

temperature, keeping constant the doping concentration ( $\text{TbCl}_3$ , 10 a/o) in the starting solution. In this case, we observe an increase in the content of oxygen and a reduction in the content of zirconium, terbium and chlorine as the substrate temperature increases. In both cases (Tables 1 and 2), the solution flow was 8 ml/min.

Typical PL emission spectrum for Tb doped zirconia film is shown in Fig. 2. It is possible to distinguish four emission bands centered at 489, 548, 588 and 620 nm which correspond to transitions between the levels  $^5\text{D}_4 \rightarrow ^7\text{F}_6$ ,  $^5\text{D}_4 \rightarrow ^7\text{F}_5$ ,  $^5\text{D}_4 \rightarrow ^7\text{F}_4$  and  $^5\text{D}_4 \rightarrow ^7\text{F}_3$ , respectively, from trivalent terbium ion. The inset shows a typical excitation spectrum; here it is possible to observe that radiation with the wavelength of 250 nm is the optimum in order to excite PL emission from the prepared material. The excitation spectra show a broad band; surely, owing to charge transfer transition (CTT) of the  $\text{Tb}^{3+}$  ion. In these cases, the films were prepared at the substrate temperature of  $500^\circ\text{C}$ , the concentration doping was 10 a/o in the spraying solution and the solution flow was 8 ml/min.

Fig. 3 shows plots of CL spectra measured under steady-state excitation with an accelerating beam voltages from 4 to 12 kV. The observed emission spectra consist of four bands character-

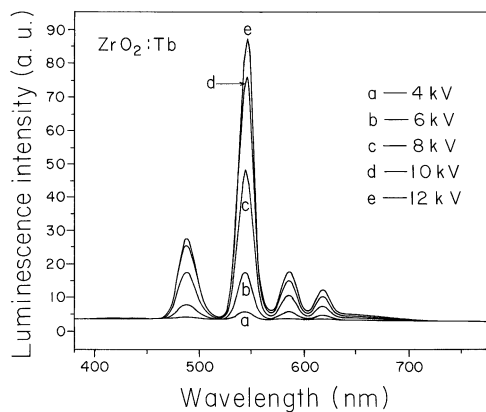


Fig. 3. CL spectra of  $\text{ZrO}_2:\text{Tb}$  films as a function of the electron acceleration voltage.

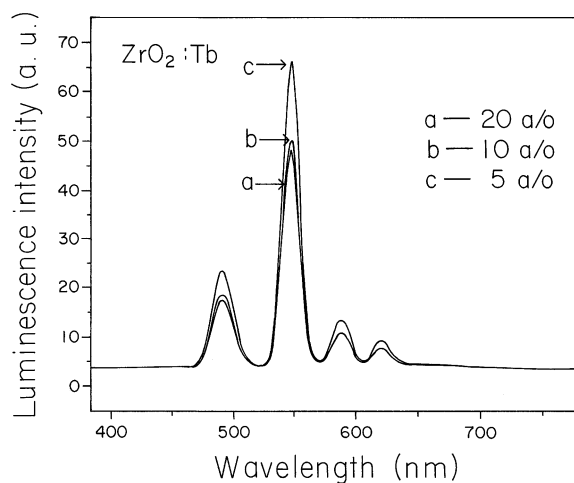


Fig. 4. CL spectra for Tb doped  $\text{ZrO}_2$  films as a function of the activator concentration, under 12 kV electron accelerating potential.

istic of the trivalent terbium ion, occurring within the 4f shell (f–f transition). In this case, the higher electron accelerating voltage produces the best emission intensity. We did not use electron accelerating potentials higher than 12 kV to avoid radiation damage to the samples. The CL spectra as a function of activator concentration in the spraying solution are shown in Fig. 4, under 12 kV electron accelerating potential. A concentration quenching of the CL emission is shown. The maximum intensity emission is obtained for 5 a/o

of terbium ions in the spraying solution. In rare earth activated luminescent materials, the optimum activator concentration occurs at different values for different types of excitation, e.g., cathode-ray excitation, host photoexcitation and direct activator photoexcitation [35]. The concentration dependence curves of luminescent materials excited by cathode rays are almost identical to the curves obtained for host photoexcitation, except for the fact that the optimum concentration under cathode-ray excitation is always lower [36].

Impurities adsorbed at the surface of luminescent materials, as well as surface defects often become quenchers and may, by quenching the emission near the surface, produce a “dead-voltage layer”. The thickness of this layer must be exceeded by the incident electrons to excite luminescence in the deeper active region. In the case of rare earth activators, the migration of excitation by resonant energy transfer between the rare earth activators can be so efficient in such a way that it may carry the energy to a distant killer existing at the surface of the luminescent material. Thus, the aggregation of activator impurities at high concentration may change some activators to quenchers and induce the quenching effect [37]. Other effects relative to quenching of luminescence are: (a) thermal quenching, due of the local heating, by energetic electrons, of the luminescent material, (b) 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 [37,38] and (c) Auger effect which produces ejection of electrons leaving the luminescent centers de-excited [39]. The exact mechanism of the luminescence quenching for this case is still unclear and needs additional investigation.

Fig. 5 shows the 548 nm emission intensity behavior 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 shown by X-ray diffraction measurements in this range of deposition temperatures, and to the reduction of chlorine left in the sample. Both effects will produce a better incorporation and

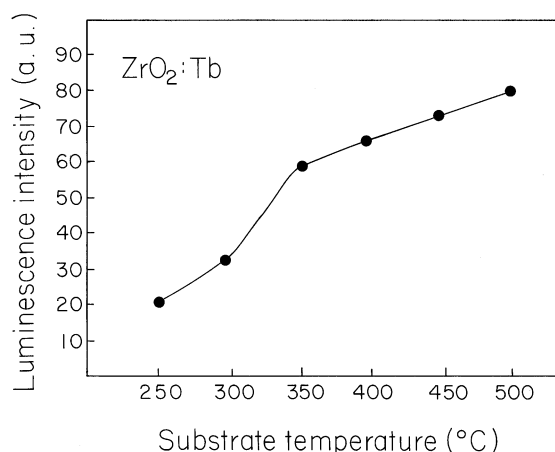


Fig. 5. The PL emission intensity for the main peak centered at 548 nm for Tb doped zirconia films as a function of the deposition temperature. The excitation wavelength was 250 nm.

distribution of the rare earth ions as an atomic impurity in 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 concentration impurities, in the spraying solution, was 10 a/o and the flow of spraying solution was 8 ml/min. In accordance with the observed tendency, films deposited at substrate temperatures higher than 500°C would have a more intense emission; however, films deposited at substrate temperatures higher than 500°C (550°C and 600°C) resulted in a material 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.

The dependence of PL intensity on the 548 nm peak for Tb doped zirconia films, as a function of concentration impurities, is shown in Fig. 6. The emission intensity as a function of the relative doping concentration shows a maximum at 10 a/o of TbCl<sub>3</sub> in the spraying solution (1.96 a/o as measured by EDS); here a concentration quenching is observed [40,41]. The deposition temperature in this case was 500°C and the flow of the spraying solution was 8 ml/min.

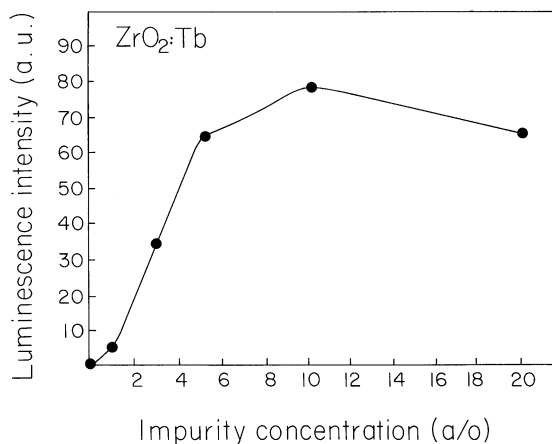


Fig. 6. The PL emission intensity for the main peak for Tb doped zirconia films as a function of the activator concentration in the spraying solution, under an excitation wavelength of 250 nm.

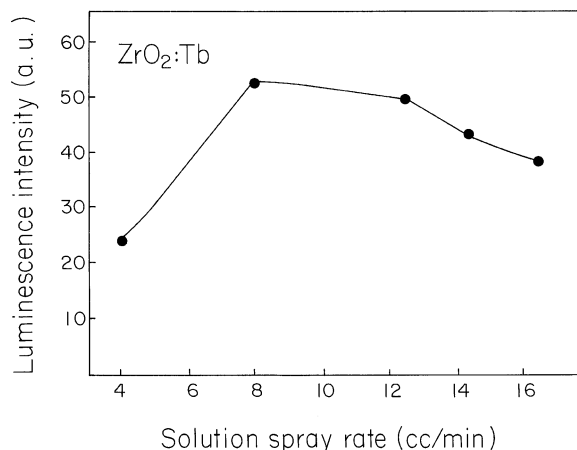


Fig. 7. The PL emission intensity for the main peak for terbium doped zirconia films as a function of the solution spray rate. The excitation wavelength was 250 nm.

Fig. 7 shows the dependence of the intensity of the PL emission (peak centered at 548 nm) as a function of the spraying solution flow. An optimal value of the solution flow (8 ml/min) can be observed. Considering values of the solution flow lower than 8 ml/min, it could happen that the mixture (solution plus carrier gas) is rich in air and less mass arrives at the substrate surface. This mixture is more easily evaporated and species related to terbium could be evaporated together with air. This process will produce a terbium deficient film. With regard to the values of the solution flow higher than 8 ml/min, we have more abundance of mass arriving on the substrate, which can produce clusters not completely processed, probably rich in chlorine and not well crystallized. This could originate a quenching of the PL emission similar to the case described above (concentration quenching). The other process conditions were fixed at optimal conditions.

#### 4. Conclusions

Green CL and PL emissions from pneumatic spray pyrolysis deposited zirconia films doped with Tb have been observed. The X-ray diffraction measurements of these films show that its crystal-

linity depends on the deposition temperature; at low temperatures they are in the amorphous state and when increasing the deposition temperature they get transformed to tetragonal or cubic phase. The luminescence emission of Tb doped zirconia films is characteristic of the Tb(III) ion. A concentration quenching was observed if the activator concentration increases above the optimum concentration of 1.96 a/o as measured by EDS. An increase of the PL emission as the substrate temperature increased was observed. Furthermore, a quenching of the PL emission as a function of the solution flow was observed, the optimum value of this parameter was 8 ml/min. In addition, a high deposition rate up to 1  $\mu\text{m}$ /min was observed. It was shown that zirconia is an excellent host for rare earth ions as active center to get luminescence emission. Finally, it has been shown that the versatile and low cost spray pyrolysis technique is able to produce high quality films.

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