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Luminescent properties of Tb³⁺ doped ZrO₂ films

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Abstract. In the present work luminescence properties of terbium trivalent (Tb³⁺) doped ZrO₂ were studied. Ultrasonic spray pyrolysis (USP) technique was employed to deposit the films. PL emission of the ZrO₂:Tb³⁺ films exhibits emission peaks around 489, 548, 588, and 620 nm corresponding to transitions ⁵D₄→⁷F₆, ⁵D₄→⁷F₅, ⁵D₄→⁷F₄, and ⁵D₄→⁷D₃ was seen when excited by excitation wavelength 288 nm. TL glow curves for ZrO₂:Tb³⁺ exhibit a glow curve with a well-defined peak centered in around 170°C. TL signal as a function of dopant concentration showed a maximum at 10 at%. The best intensity of TL response as a function of UV radiation wavelength was in 230 nm. TL response fading and reusability were also analyzed. The ZrO₂:Tb³⁺ films has been found to have simple and sharp glow peak which should be considered for dosimetric applications.

1. Introduction

Ceramic thin films are presently used in, and will continue to be developed for, a multitude of devices critical to luminescence and optoelectronics technology. Luminescence properties of many metal oxides [1-3] have attracted considerable interest, because they may be used in many fields. Among these materials, the zirconium oxide (ZrO₂) has been considered as a host material with luminescent characteristics [4-5]. Zirconia in the form of thin film attracts special interest owing to its advantageous properties of being highly homogenous, and transparent for applications in optical devices, scintillators [6] and luminescent detectors [7]. For ZrO₂, the photoluminescence is of much interest for both theoretical and experimental investigations. The PL characteristics of ZrO₂ has been studied by many authors [8], some of them, reported band tail absorption [9]; others, observed broad PL emission centered at 480 nm [10-11]. Several preparation techniques have been proposed to fabricate ZrO₂ thin films by dry processes, such as sputtering [12], chemical vapor deposition (CVD) [13] and atomic layer deposition (ALD) [14] and by moist processes, such as sol-gel [15]. Among these methods, the ultrasonic spray pyrolysis technique has proved to be an efficient and low cost technique to synthesize films of metallic oxides. Due to their relative simplicity and to the possibility of being scalable at industrial level, this process has been used for obtaining films and powders for optical, semiconductor, and magnetic applications. In recent decades, zirconium oxide (ZrO₂) thin films have attracted great interest because of its interesting practical applications as radiation monitoring device [16-17]. Studies on radiation induced defects in insulating materials have been interesting over the last few decades. Thermoluminescence (TL) is one such radiation induced defect



related process in crystalline materials. There are several reports presented in the literature for the optical properties application for ZrO_2 . However, few reports are available on PL and TL properties of terbium trivalent doped zirconia thin films deposited by ultrasonic spray pyrolysis, and in terms of thermally stimulated have not been systematically studied yet.

2. Experimental procedures

2.1. Material preparation.

The zirconium oxide (ZrO_2) films intrinsic and doped with trivalent terbium ($ZrO_2:Tb^{3+}$) were deposited by ultrasonic spray pyrolysis technique on Corning 7059 glass slides substrates. The constituents $ZrOCl_2 \cdot 8H_2O$ (99.99%) Aldrich and $TbCl_3 \cdot 6H_2O$ (99.99%) (Aldrich) were dissolved in deionized water at molar concentration of 0.06M. Substrate temperatures (T_s) during deposition process were in the range from 350°C to 600°C with steps of 50°C. The carrier gas flow (filtered air) was 0.15 l / min. The $TbCl_3 \cdot 6H_2O$ concentration in the spraying solution was in the range from 0 to 15 atomic percent (a/o) in relation to the zirconium content. The deposition time was adjusted to five minutes, in order to obtain similar thickness of all samples.

2.2. Structural characterization.

The prepared host lattice was characterized for their phase purity and crystallinity by X-ray diffraction (XRD) technique using a SIEMENS D-500 diffractometer (Cu-K α radiation) at a scanning step of 0.001, in the 2 θ range from 5 to 70°.

2.3. Luminescent characterization.

The photoluminescence (PL) emission spectra of the films were recorded using a FluoroMax-P Jobin Yvon Horiba spectrometer, using a beam of Xenon lamp as excitation source. The excitation spectrum of $ZrO_2:Tb^{3+}$ is showed in figure 1. In the figure is clearly showed a maximum centered in 288 nm. All emission spectra were obtained exciting al 288 nm. For TL studies, samples were exposed to ultraviolet radiation (UVR) from a Xenon lamp beam which was coupled to a monochromator to select the wavelength desired. After the desired exposure, TL glow curves were recorded with the help of Bicron model 3500 TL reader, connected to a PC in order to store and to analyze the glow curves. TL readings were carried out at a heating rate of 10 °C s⁻¹. All the measurements were carried out in a nitrogen atmosphere in order to reduce the thermal noise during heating planchet of the TL reader.

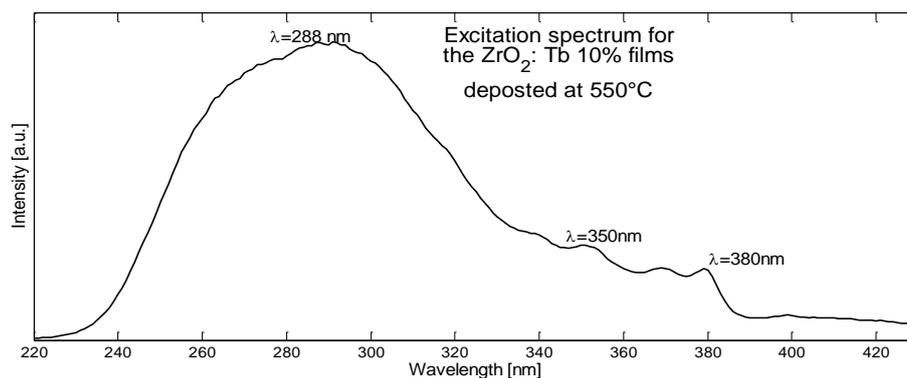


Figure 1. Excitation spectra of Tb^{3+} doped ZrO_2

3. Results and discussion

3.1. Structural characterization

Fig. 2 shows the XRD patterns from pure ZrO_2 films. X-ray diffraction pattern indicates the presence of crystalline ZrO_2 host lattices. The XRD measurements corresponding to ZrO_2 films deposited at substrate temperatures lower than 400°C showed absence of diffraction peaks, indicating that at these substrate temperatures the deposited material have a non-crystalline phase.

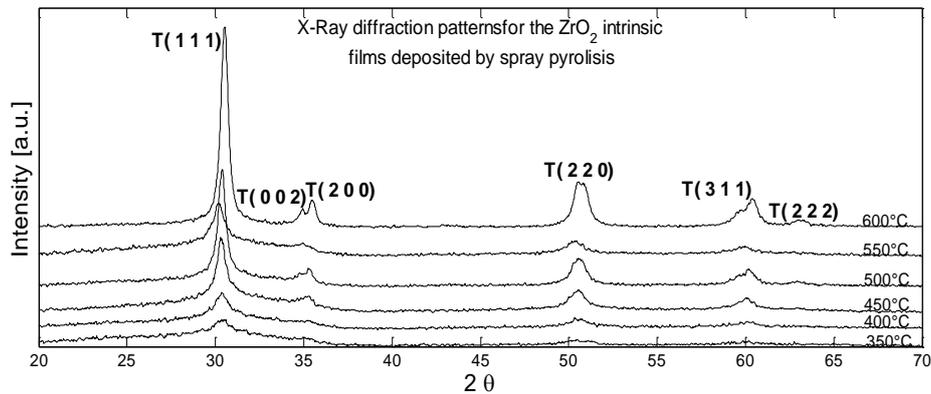


Figure 2. X-ray diffraction pattern of Tb^{3+} ion in ZrO_2 host lattice

The XRD-patterns corresponding to films deposited at higher substrates temperature, over $400^\circ C$, showed defined peaks, which indicates that films acquired a crystalline structure. The decrease in the width of the peaks, as temperature increases, indicates a growth in the crystal sizes constituent of films. The diffractogram of films deposited at $500^\circ C$ with Miller indexes of corresponding planes is shown in figure 2. These peaks appropriately correspond to zirconium oxide composed phase (tetragonal phase). These patterns are very agreement with PCPDFWIN card file number 340104. The crystals size in the film deposited at $600^\circ C$, was estimated by means of Scherer's equation, considering the most intense peak located in 28.43° , corresponding to plane (111).

3.2. Luminescent studies.

3.2.1 PL Study of $ZrO_2:Tb^{3+}$

The PL emission spectra of $ZrO_2:Tb^{3+}$ (10 at%) films excited at 288 nm are shown in Fig. 3. The spectra shows four groups of emissions centered at 489, 548, 588, and 620 nm, which correspond to the transitions of $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, and $^5D_4 \rightarrow ^7D_3$ respectively, similar than that obtained by others authors [18, 19] obtained with others synthesis techniques. It can be observed that PL emission spectrum was recorded as function of substrate temperature during the deposition. The spectrum shows the effect of deposition temperature on the PL emission intensity. It is possible to observe, that PL emission intensity increases as the substrate temperature increase still the emission reaches its highest intensity for the films deposited at $550^\circ C$, since for higher deposition temperatures the photoluminescent emission decreases.

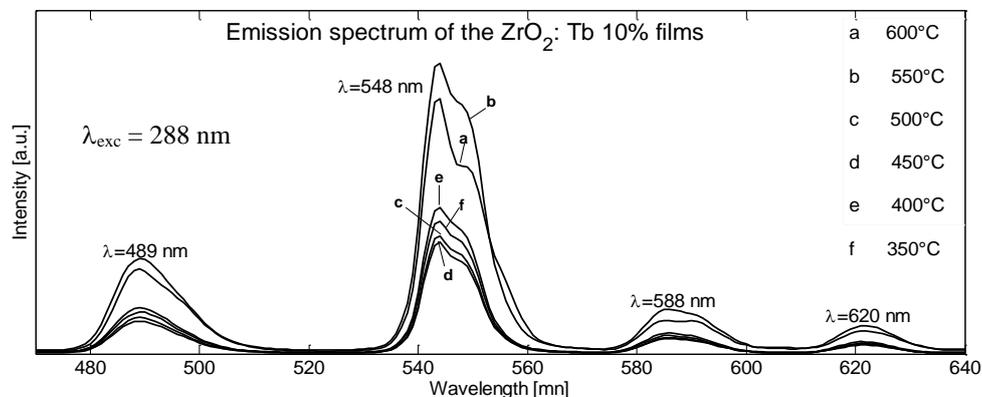


Figure 3. Emission spectra of $ZrO_2:Tb^{3+}$ at $\lambda_{exc}=288$ nm

3.3. TL Studies

3.3.1. TL Glow curve of $ZrO_2:Tb^{3+}$

Thermoluminescence is a very common and simple technique used for estimation of doses of ionizing radiations absorbed by materials. As-prepared $ZrO_2:Tb^{3+}$ films did not show any thermoluminescence response (samples obtained below $400^\circ C$). However, films exposed with visible ultraviolet radiation (UVR) showed good TL response. Fig. 4 shows a glow curve for the films (deposited at $550^\circ C$) exposed to UV radiation. TL glow curves of $ZrO_2:Tb^{3+}$ film showed a glow curve, consisting of one well defined peak, indicating that one type of trap are being activated within the particular temperature range with its own value of activation energy (E) and frequency factor (s). The shape of the glow curve remains almost the same for different UVR dose but the height of the glow peak was increased as UVR dose increased. The sensitivity of main glow peak was increasing as concentrations of Tb^{3+} ion in ZrO_2 was increased as well as increasing of crystallinity. The increase in glow peak sensitivity was increased up to 10 % concentration of Tb^{3+} ion (the maximum concentration used in this study was 15%) and this was favorable for future TL studies. The increase in the intensities of the glow peaks with increase of dopant concentration can be understood by the fact that more and more defects were created. After the maximum intensity (10 %), TL intensity was decreased as impurity concentration was increased. TL decreasing of the emission intensity can be attributed at the quenching concentration phenomena. This behavior was observed for PL emission as a function of Tb^{3+} ion concentration, the maximum PL intensity was also at 10 a/o. Therefore, we can conclude that the distributions of traps produced by the irradiation of UVR can be altered greatly by the change in the concentrations of Tb^{3+} ion doped in ZrO_2 phosphor.

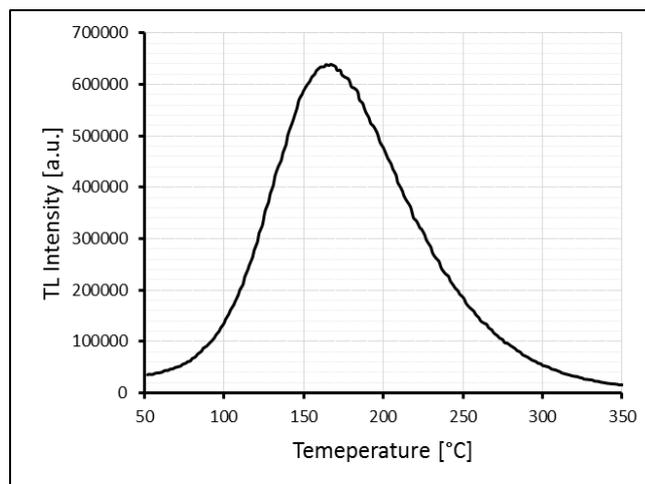


Figure 4. TL glow curve of $ZrO_2:Tb^{3+}$ films deposited at $550^\circ C$

3.3.2. Reusability, linearity, and TL as function of wavelength

Reusability is one of the most useful property that sample should possess in order to find a place in any environmental application. If the sensitivity of a sample does not change after several cycles of exposures and readouts then it is termed as a phosphor with good dosimetric characteristics. For studying the reusability of the films, samples were given exposure of 100 mJ.cm^{-2} and TL glow curve was recorded. TL signal as a function of UV light wavelength is showed in fig. 5. In this figure the TL response of films as a function of UVR wavelength exhibit a maximum in 230 nm. Several such cycles of exposures and glow curve recordings were executed. The present material UV light irradiated and analyzed after 10 cycles showed a standard deviation value of 2.8%.

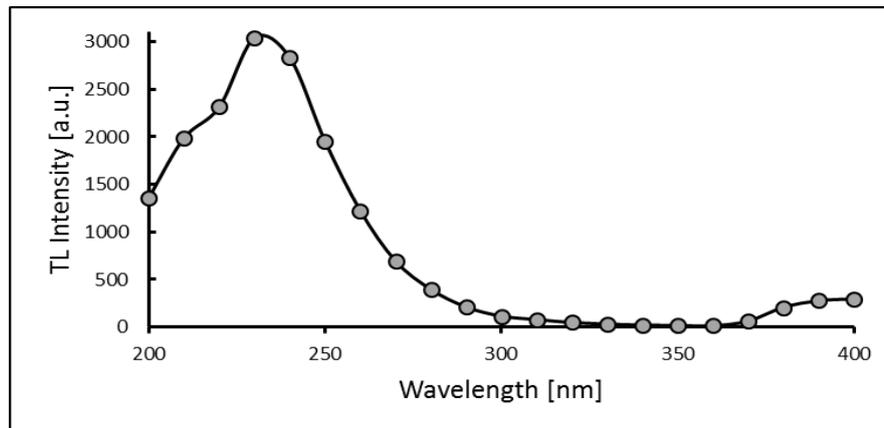


Figure 5. TL response of films as a function of UV wavelengths

The TL intensity of glow peak increases linearly with variation in the dose from 100 up to 400 $\text{mJ}\cdot\text{cm}^{-2}$ and is shown in Fig. 6. The increase in the intensities of the glow peaks with increase of ultraviolet radiation dose suggests that more and more traps, responsible for these glow peaks, were getting filled with the increase of UV radiation dose and subsequently these traps releases the charge carriers on thermal stimulation, to finally recombine with their counterparts, thus giving rise to glow peaks of different intensities.

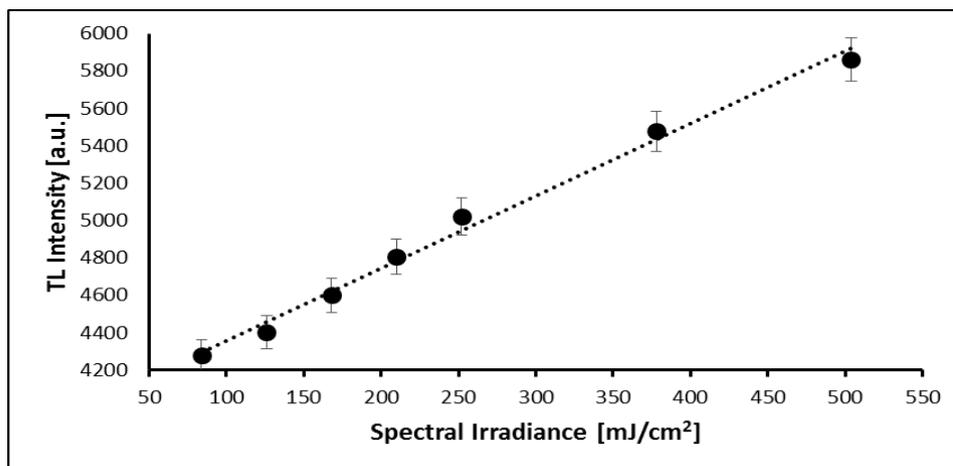


Figure 6. TL response of $\text{ZrO}_2:\text{Tb}^{3+}$ films as a function of UV dose

In order to make samples films useful in ultraviolet radiation dosimetry their TL should be stable and should not die away upon storage after exposure to ionizing radiations. The present material was stored for a few days without taking any protection to shield it from light and humidity and it was found that glow peak was reasonably stable. The fading observed was about 5% during a period of 5 hours.

4. Conclusion

Therefore, we can conclude that PL emission intensity increases as the substrate temperature increases until the emission reaches its highest intensity for the films deposited at 550°C ; the maximum PL emission is observed at 548 nm, as it can be seen in fig. 3. This behavior should be related to crystal size as showed in fig. 2, when the films are deposited above 500°C . The TL glow curve of $\text{ZrO}_2:\text{Tb}^{3+}$ shows a simple glow curve well defined similar than that reported by the same authors for undoped ZrO_2 [20]. This single glow curve form in samples is attributed to one type of traps. The maximum

temperature indicates that the position of dosimetric peak shifts slightly toward the low temperature side compared with undoped samples [20]. The shift of the position dosimetric peak could be attributed on the type of activator present in the phosphor, if the present results are compared with those doped samples with europium and gadolinium impurities [17, 20]. TL intensity of dosimetric peak of undoped ZrO_2 , $\text{ZrO}_2:\text{Tb}^{3+}$ is found to be 1.23 times more sensitive. The position temperature peak revealed about the stability of the traps. In our case, the maximum of temperature peak is centred in around 160°C , then the glow peak occurs at a relatively lower temperature and the corresponding trap is unstable. When the phosphors show unstable information, this affect the storage information on the TL signal at room temperature. The post-irradiation fading of this peak at room temperature is also 5% in five hours. The UVR dose response of this peak is linear in the dose range 100 up to 400 mJ/cm^2 . At present days, there is a great demand of the dosimetric phosphors which exhibit simple and sharp glow curves for UV radiation dosimetry purposes. The $\text{ZrO}_2:\text{Tb}^{3+}$ films have been found to have simple and sharp glow peak and moreover it can be prepared very easily. Further work is in progress to clarify details of the defect within the material and glow curve structure.

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