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THERMOLUMINESCENCE OF Eu-DOPED ZrO_2 THIN FILMS EXPOSED TO ULTRAVIOLET AND VISIBLE LIGHT

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Abstract—This paper reports the experimental results of studying the thermoluminescence (TL) of ZrO_2 doped with Eu exposed to light of wavelength in the range of 200–900 nm. The photoluminescence spectrum induced by 275 nm UV light exhibited three maxima at 588, 612 and 650 nm with the major emission at 612 nm. Among 210, 260 and 320 nm UV light for the same exposures, the 260 nm UV radiation induced the highest TL response. Its glow curve exhibited two peaks at 120 and 290°C for all the wavelengths studied. The 120°C peak faded completely within the first 24 h after exposure. Meanwhile, the 290°C peak shows great stability for a long time. The TL response of Eu-doped ZrO_2 exposed to 260 nm as well as to 320 nm UV light was linear for a wide range of exposure times. The results showed that ZrO_2:Eu films deposited on glass substrates have the potential to be used as UV dosimeters in personal or environmental dosimetry.

1. INTRODUCTION

The monitoring of UV light has become more important in recent years as people become aware of the biological effects of UV radiation either from sunlight or from artificial sources. The use of thermoluminescence (TL) dosimeters of different materials to monitor UV radiation has been reported by many authors (Bassi *et al.*, 1976; Dhar *et al.*, 1976; Nagpal, 1979; Marwaha *et al.*, 1980; Azorín *et al.*, 1993).

Thermoluminescence induced in ZrO_2 irradiated by UV, X-rays or gamma radiation has been also reported by several authors (Iacconi *et al.*, 1978; Bettinali *et al.*, 1969). Some of them have proposed that the impurity Ti could play a major role in the TL emission of ZrO_2. However; other impurities intentionally introduced may also change the TL properties of this material as has been studied by some authors for rare earth oxide impurities used as dopants in single crystals of ZrO_2 (Hsieh and Su, 1994).

This paper reports the experimental results of studying the TL properties of ZrO_2 thin films doped with Eu exposed to light of wavelength in the range of 200–900 nm. Excitation spectra were also obtained.

2. EXPERIMENTAL PROCEDURE

Materials were constituted by $5 \times 5 \times 1\ mm^3$ chips of glass substrate on which a thin film (0.005 mm thickness) of ZrO_2 doped with Eu was coated. The films were made using the ultrasonic spray pyrolysis technique. By this process a solution containing the material 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 touches the hot substrate leaving a solid coating on the substrate. In this case, the spraying solution consisted of a 0.05 M solution of zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$, Merck) in deionized water. Doping with Eu was achieved by adding $EuCl_3$ to the spraying solution in the range of 1–50 atomic percentage in relation to the Zr content in the solution. The substrate temperature during deposition (coating temperature) used was varied in the range of 250–550°C. The thickness of the films were measured by a Sloan Dektak IIA profilometer.

Selected samples of the deposited films were investigated with an X-ray diffractometer Siemmens D-5000 with wavelength radiation of 0.15406 nm, to determine their crystalline structure, by X-ray fluorescence (energy dispersive spectroscopy) (EDS) and neutron activation analysis to determine impurities.

Before exposure of the samples to the UV/vis light they were annealed at 300°C for 10 min in order to erase all previous information.

To investigate the TL response of ZrO_2 doped with Eu, samples were individually exposed to a beam of UV/vis light from a Xe lamp coupled with a monochromator to select different wavelengths between 200 and 900 nm. Samples containing various concentrations of the dopant, produced at different coating temperatures, were compared

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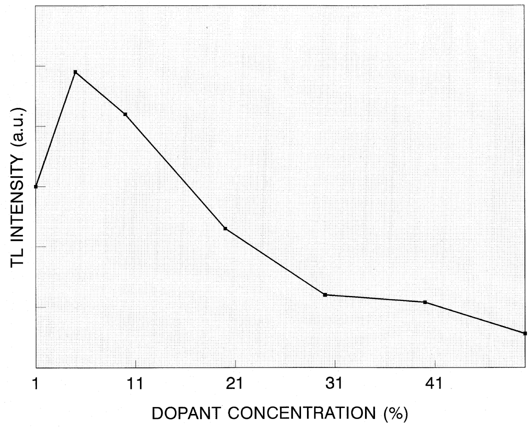

Fig. 1. TL response of Eu doped ZrO_2 films coated on glass substrates exposed to UV light as a function of dopant concentration.

using the UV induced TL response to test the dependence of this response on different crystalline structures and different dopant concentrations.

The photoluminescence spectrum induced by 275 nm UV light was measured with a Perkin–Elmer 650-10 S fluorescence spectrophotometer.

Thermoluminescence readings were made in a Harshaw 4000 TL analyzer connected to a PC to obtain and analyze the glow curves, digitizing both TL and temperature signals by means of two channels of an RS 232C interface. All TL measurements were made in nitrogen atmosphere in order to reduce the thermal noise from the heating planchet of the TL reader. Glow curves were registered from room temperature to 300°C at a heating rate of 10°C/s.

3. RESULTS

Optimum concentration of Eu in ZrO_2 determined on the basis of the maximum TL response was 5% in the spraying solution (see Fig. 1). This sample was also measured using DES and found to be 1.8 atomic %. All results were then reported for this concentration.

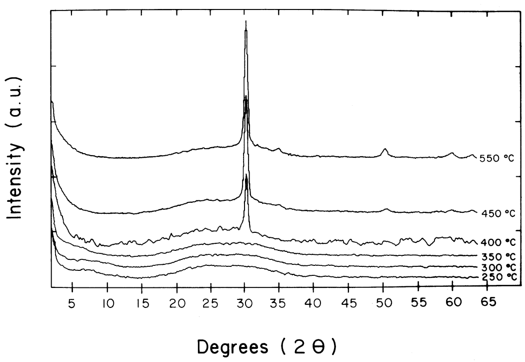

Fig. 2. X-ray diffraction patterns of Eu doped ZrO_2 coatings obtained for different coating temperatures.

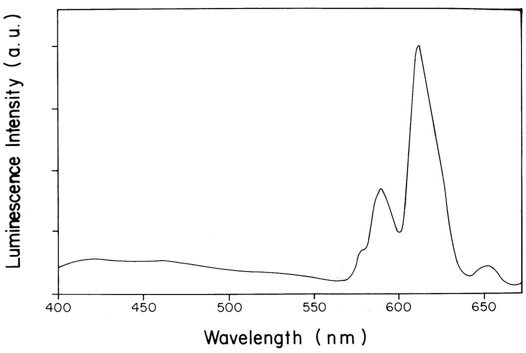

Fig. 3. Photoluminescence spectrum of UV irradiated ZrO_2:Eu films coated on glass substrates excited with 275 nm UV light.

Figure 2 is representative of the structural characteristics of the Eu doped ZrO_2 films studied. X-ray diffraction patterns of undoped and Eu-doped ZrO_2 were very similar and demonstrate metastable tetragonal crystalline structure for coating temperatures higher than 400°C. These X-ray spectra obtained for different coating temperatures showed similar shapes too, and it was found that all diffraction peaks appeared with higher peak heights and narrower peak widths as the coating temperature became higher.

The results of the experimental tests on TL response of Eu doped ZrO_2 films coated at different temperatures showed that a close relation exists between the TL phenomenon and the coating temperature. Thus, combining the results of X-ray diffraction and TL response of Eu doped ZrO_2 films coated at different temperatures, it was found that the optimum coating temperature was 550°C.

The photoluminescence spectrum induced by 275 nm UV light, shown in Fig. 3, exhibited three maxima at 588, 612 and 650 nm with the major emission at 612 nm. These correspond to $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^5F_3$ transitions respectively,

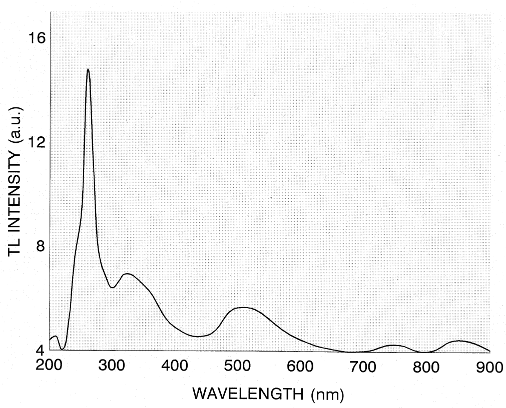

Fig. 4. TL response of Eu doped ZrO_2 films coated on glass substrates exposed to UV light as a function of the wavelength of the light.

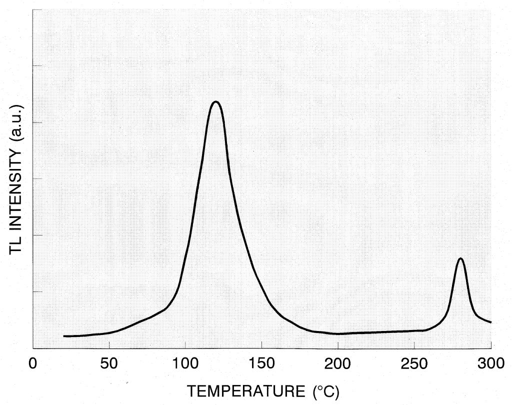

Fig. 5. Glow curve of UV irradiated ZrO_2:Eu films coated on glass substrates.

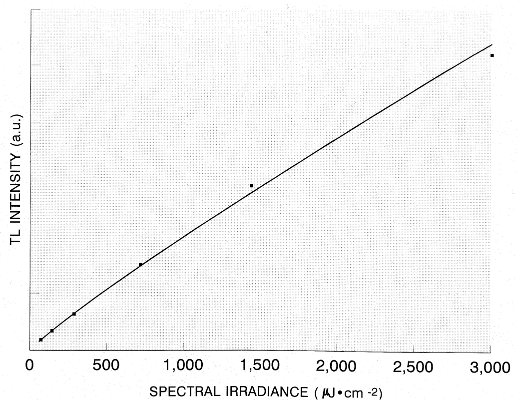

Fig. 6. TL response of Eu doped ZrO_2 films coated on glass substrates as a function of spectral irradiance of UV light.

which are characteristics of the f–f luminescence of the Eu^{3+} ion.

Figure 4 shows the TL response of Eu doped ZrO_2 exposed to UV light as a function of wavelength. Among 210, 260 and 320 nm UV light for the same exposures, the 260 nm UV radiation induced the highest TL response. Its glow curve, shown in Fig. 5, exhibited two peaks at 120 and 290°C for all the wavelengths studied. The intensity of the low temperature (120°C) glow peak was almost the same that of an undoped sample. For the 290°C peak the doped sample had an intensity five times higher than the undoped one. The 120°C peak faded completely within the first 24 h after exposure. Meanwhile, the 290°C peak shows great stability for a long time, exhibiting a fading of 7% in 6 months.

The TL response of Eu-doped ZrO_2 exposed to 260 nm as well as to 320 nm UV light was linear from $70–3 \times 10^3$ $\mu J \cdot cm^{-2}$ of spectral irradiance as is shown in Fig. 6.

4. CONCLUSIONS

The coating temperature of ZrO_2 films plays an important role in the TL response. Then, using the appropriate temperature during the coating process we can conclude that ZrO_2-:Eu films deposited on glass substrates have the potential to be used as UV dosimeters in personal or environmental dosimetry.

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REFERENCES

Azorín, J., Rubio, J., Gutiérrez, A., González, P. and Rivera, T. (1993) Dosimetric characteristics and glow curve kinetic analysis of α-Al_2O_3:C thermoluminescence detectors. *Journal of Thermal Analysis* **39,** 1107–1116.

Bassi, P., Busuoli, G. and Rimondi, O. (1976) UV dosimetry by intrinsic TL of CaF_2:Dy. *Health Physics* **31,** 179–182.

Bettinali, C., Ferraresso, G. and Manconi, J. W. (1969) Thermoluminescence of ZrO_2. *Journal of Chemical Physics* **50,** 3957–3961.

Dhar, A., Dewerd, L. A. and Stoebe, T. G. (1976) Direct-response ultraviolet thermoluminescence dosimeter. *Medical Physics* **3,** 415–417.

Hsieh, W. C. and Su, C. S. (1994) UV induced thermoluminescence in ZrO_2 doped by Er_2O_3. *Journal of Physics D: Applied Physics* **27,** 1763–1768.

Iacconi, P., Keller, P. and Caruba, R. (1978) Traps and emission centres in thermoluminescent ZrO_2. *Physika Status Solidi A* **50,** 275–283.

Marwaha, G. L., Singh, N., Vij, D. R. and Mathur, V. K. (1980) UV dosimetry by thermoluminescence of bismuth doped CaS. *Journal of Physics C: Solid State Physics* **13,** 1559–1563.

Nagpal, J. S. (1979) Ultra violet dosimetry using thermoluminescence phosphors rate dependence. *Radiation Effects Letters* **43,** 173–178.