

TERMOLUMINESCENT PROPERTIES OF HIGH SENSITIVE ZrO₂ FOR UV RADIATION DOSIMETRY

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Abstract

This paper presents the preparation method, luminescent characteristics and the results of thermoluminescence (TL) properties of zirconium oxide (ZrO₂) exposed to 260 nm radiation. The glow curve of ZrO₂+PTFE pellets exhibited one peak centered at 180°C lower than that the commercially available aluminum oxide peak (Al₂O₃:C). TL response of spectral irradiance showed good linear in the range from 2.4 to 3000 μJ/cm² of spectral irradiance. Experimental results of studying the thermoluminescent (TL) properties of ZrO₂+PTFE pellets exposed to ultraviolet radiation allow to propose zirconium oxide as an excellent candidate as ultraviolet dosimeter.

INTRODUCTION

Ultraviolet radiation (UV) emanating from the sun reaches at the Earth's surface after passing through space and the Earth's atmosphere. The level of UV radiation reaching the Earth varies, depending on a variety of factors. In response to the serious public health threat posed by increased UV levels, several research groups are interested in getting environmental personal dosimeters to measure the level of environmental UV radiation. Firstly, the Commission on Illumination (CIE) has conventionally designated the UV radiative category, in order to correlate its increasing on Earth's surface and biological effects on the body as well as skin and eyes part in.

The CIE has categorized 315 to 400 nm as UV-A, 280 to 315 nm as UV-B, and 100 to 280 nm as UV-C. Some authors also may divide the UV-A band into two regions: UV-A1 and UV-A2, with a boundary at about 340 nm [1].

From a biological and chemical point of view, wavelengths below 180 nm (vacuum UV) have a practical significance, since they are readily absorbed in air. UV-C wavelengths are photochemically active because they correspond to the most energetic photons and are absorbed in certain amino acids, i.e. protein [2,4]. UVB wavelengths are biologically active, but more penetrating in most tissues [5-9]. UVA wavelengths are also biologically active, but are still more penetrating than UVB wavelengths and play an interactive role when exposure occurs often UVB exposure [10-13]. Then, from a biological point of view, it is very important to monitor UVB and UVC wavelengths, which has become very

recent years as people become aware of its biological effects either from sunlight or artificial sources. In response to the serious public Health threat posed by exposure to increased UV levels, several research groups are interested in getting environmental and personal dosimeters to measure the level of environmental UV radiation.

The monitoring of ultraviolet radiation (UVR) different thermoluminescent (TL) materials have been used to measure UVR. UV dosimetry using thermoluminescence (TL) has been suggested in the past by several authors [14-19]. This technique has an advantage over others methods due to the readout of the samples. Another advantages of these dosimeters are their small size, portability, lack of any power requirements, linear response to increasing radiation dose and high sensitivity. The new material studied to be used as thermoluminescent dosimeter is zirconium oxide (ZrO_2). Research on this material has been increased due to its high sensitivity compared to that commercially available aluminum oxide.

In our recent paper [20] the general features of ZrO_2 using optically stimulated luminescence (OSL) method were discussed. In that work, it has been showed that optical illumination of the pre-irradiated samples demonstrated to be a good candidate for UV radiation dosimetry by means OSL method. The main aims of the present paper is to study the dosimetric characteristics of ZrO_2 , such as relative sensitivity, linear response, fading and response as a function of the low energy incident radiation using the thermoluminescence method. Results suggest the its application of this material in UV environmental radiation dosimetry.

2 MATERIALS AND SAMPLES

Materials used in this study were constituted by ZrO_2 +PTFE pellets. Powder of ZrO_2 was prepared by the evaporation method from a solution of zirconium hexachloride dissolved in ethanol. The powder obtained was sieved to select grain sizes between 100 and 300 μm . In order to facilitate handling, samples were made in pellet form. Pressing this powder at room temperature in a mixture (2:1) of thermoluminescent material and polytetrafluoroethylene (PTFE), pellets of 5 mm diameter and 0.8 mm thickness were obtained. Sintered ZrO_2 +PTFE pellets of 5 mm diameter and 0.8 mm thickness were obtained by pressing a mixture of ZrO_2 powder with PTFE at room temperature. Then sintering at a temperature slightly lower than that of the PTFE melting, using the technique described in previous works [21,22].

Before exposure of the ZrO_2 +PTFE samples to the UVR they were annealed at 300°C for 10 min in order to erase all possible remaining information. Samples were irradiated individually at 260 nm ultraviolet radiation from a beam from a Xe lamp which was coupled to a monochromator to select desired wavelength. The emission lamp was normalized to a reference light by manufacturer [23].

Thermoluminescent readings were carried out by using a analyzer Harshaw model 4000 connected to a PC in order to store and to analyze the glow curves, digitizing both TL and temperature signals by means of two channels of an RS232C interface. The heating rate of the TL analyzer was kept at 10°C per second for all the TL readings, which were made integrating the signal from 50 up to 350°C. All TL measurements were made in nitrogen atmosphere in order to reduce the thermal noise from the heating planchet of the TL reader and chemiluminescence effects.

RESULTS AND DISCUSSION

TL properties of the UVR induced from ZrO_2+PTFE discs were also studied in relation to the well-known UV sensitive dosimeter material $Al_2O_3:C$. A main feature of ZrO_2 is its very high TL sensitivity compared to that of $Al_2O_3:C$. Figure 1 shows the glow curve of ZrO_2+PTFE discs (glow curve 1) and $Al_2O_3:C$ single crystal (glow curve 2). The ZrO_2+PTFE glow curve has a single peak centered in the region of $180^\circ C$ with the full width at half maximum (FWHM) about $45^\circ C$. For comparison, a glow curve of the single crystal $Al_2O_3:C$ detector measured in similar conditions is also presented in figure 1 (curve 2). The FWHM of the TL peak in ZrO_2+PTFE is fifteen degrees narrower than that of $Al_2O_3:C$. The temperature peak of the maximum in ZrO_2 about the former is also $30^\circ C$ lower than in $Al_2O_3:C$. A low temperature peak of ZrO_2+PTFE at around $100^\circ C$ is sometimes observed often decays at room temperature some minutes after irradiation and does not introduce errors in the measurements. The ZrO_2+PTFE shows a sensitivity more times than $Al_2O_3:C$ obtained after $50 \mu J/cm^2$ UV radiation dose. In figure 1 $Al_2O_3:C$ glow curve is scaled times more than ZrO_2+PTFE glow curve, it is in order to compare both maximum temperature peak and the full width of half maximum for both materials. This effect shows that integral response of ZrO_2+PTFE is higher than Al_2O_3 obtained at the same condition of irradiation. Besides, as seen in the figure, there is a great differences in the glow curves shapes.

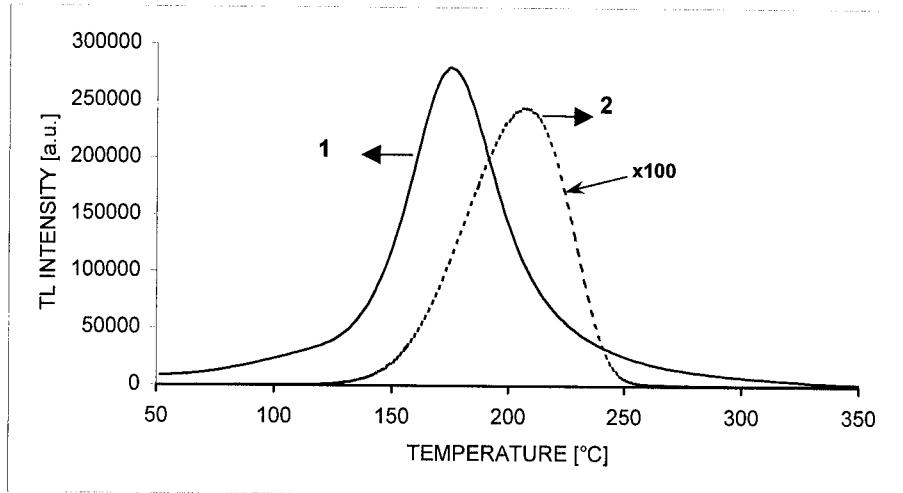


Figure 1. The typical glow curves of ZrO_2+PTFE discs (glow curve 1) and $Al_2O_3:C$ single crystal (glow curve 2) after a test UV radiation of $50 \mu J/cm^2$ of spectral irradiance, using a heating rate of $10^\circ C/s$.

The measured glow peak temperature and relative peak height are shown in Table 1 for ZrO_2+PTFE discs and $Al_2O_3:C$ single crystal. Figure 2 shows the TL response of ZrO_2+PTFE exposed to UV radiation as a function of wavelength. Among 230, 260 and 300 nm UV radiation for the same exposures, the 260 nm UV radiation induced the highest TL response. The TL response of $Al_2O_3:C$ exposed to UV radiation as a function of the same region wavelength exhibited two peaks at 230 and 310 nm. As seen in the figure, the TL integral response of ZrO_2+PTFE is higher than that of $Al_2O_3:C$ at 260 nm UV radiation dose for both dosimeters. The measured TL response as a function of wavelength is shown in Table 2. As seen in the table 2, ZrO_2+PTFE values obtained from 280 to 340 are also higher than that of $Al_2O_3:C$ obtained from the wavelengths.

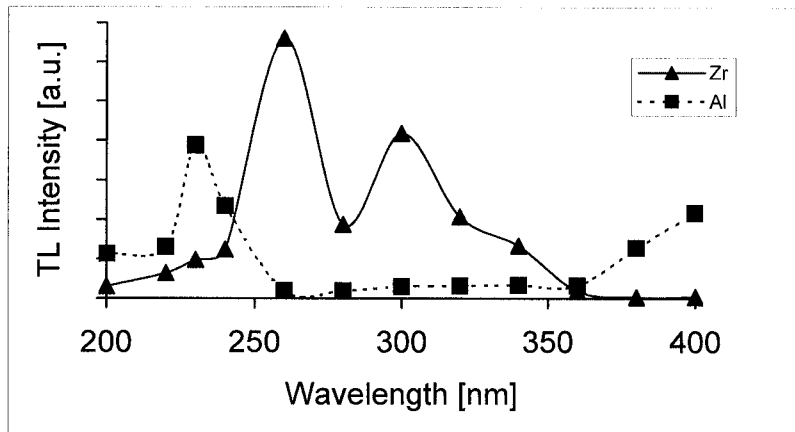


Figure 2. TL response of ZrO_2+PTFE (solid line and $Al_2O_3:C$ (dotted line) as a function of different wavelength in the range from 200 to 400 nm.

DOSIMETER	PEAK TEMPERATURE (°C)	RELATIVE PEAK HEIGHT	TOTAL DOSE
ZrO_2+PTFE	180	3507	100
$Al_2O_3:C$	208	1	1

Table 1. Peak temperature and relative peak heights of ZrO_2+PTFE and $Al_2O_3:C$

WAVELENGTH	ZrO_2+PTFE	$Al_2O_3:C$
200	30673.8	1131.99
220	64437.5	1306.25
230	98067.8	3879.88
240	124345.3	2337.61
260	660553.7	188.69
280	187455.5	193.67
300	418127.7	303.26
320	2071	323.56
340	133701.4	334.12
360	18925.6	321.17
380	2958.6	1283.11
400	4078.8	2170.35

Table 2. TL response measured of ZrO_2+PTFE as a function of different wavelength in the range from 200 to 400 nm.

The relative sensitivities per unit mass of these materials are listed in Table 3. The pre-irradiations annealing, namely 300°C for 10 min for ZrO_2+PTFE and 300°C for 30 min for $Al_2O_3:C$ were used. The readout programs was applied for measured of integral glow curves was heating rate 10°C/s, using a linear heating from 50 to 350°C.

DOSIMETER	RELATIVE SENSITIVITIES
ZrO_2+PTFE	20642.3
$Al_2O_3:C$	6.279

Table 3. Relative sensitivities per unit mass of ZrO_2+PTFE discs and $Al_2O_3:C$ single crystal.

The linearity of the TL response of the ZrO_2+PTFE to UV radiation dose is one of the most important properties of this material. To obtain the plot of the TL responses as a function of the UV radiation dose, the detectors were irradiated at 2.4, 5, 10, 100, 1000, 3000, 5000 and 10000 $\mu J/cm^2$ of spectral irradiance, at room temperature. Figure 3 shows the relationship between the dose and the TL response of ZrO_2+PTFE dosimeter. It can be seen that the TL response as a function of the UV radiation dose is linear in the range from 2.4 to 3000 $\mu J/cm^2$. Saturation plot is appear at about 3000 $\mu J/cm^2$.

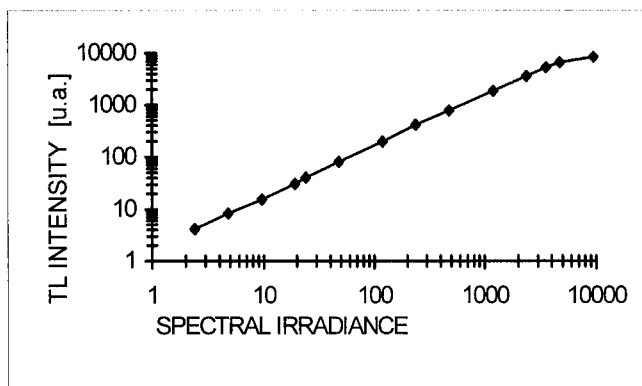


Figure 3. UVC dosimeter response of ZrO_2+PTFE as a function of spectral irradiance in the range from 2.4 to 1×10^4 $\mu J/cm^2$. The relationship between the UV radiation dose and TL response is linear up to 3×10^3 $\mu J/cm^2$.

The important property of a TL detectors is its fading, which should be as low as possible, mainly in environmental application. In order to determine this characteristic, a set of 24 ZrO_2+PTFE discs were exposed at 50 $\mu J/cm^2$ of UV. Then, the set was divided into six groups of four discs for each group. The first group was readout immediately after irradiation. The other groups were placed in a dark place. The Second group was readout 1 day after irradiation; the third to the sixth groups were readout 2, 10, 20 and 30 days after irradiation respectively. At the end of one month under same experimental conditions a 1.8% fading value was obtained. The data obtained are shows in figure 4.

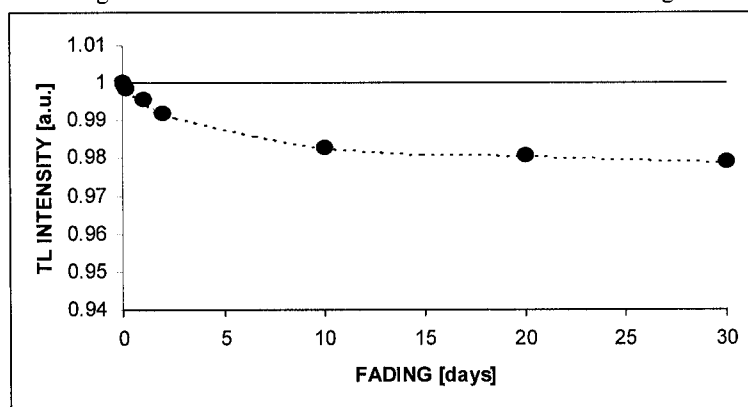


Figure 4. UVC dosimeter response of ZrO_2+PTFE as a function of the storage time. The pre-dose of 50 $\mu J/cm^2$ of 260 nm UV radiation was delivered at room temperature at different readout time after

UV irradiation. Each data point is the mean at four TL signal from four different dosimeters. The standard deviation from the mean was 1%.

The reproducibility of the TL was tested as it follows: ZrO_2+PTFE discs was first annealed at $300^\circ C$ for 10 min before irradiation to $5 \mu J/cm^2$ of UV radiation and subjected to ten readout exposure cycles. The mean value of results of reproducibility tests of ZrO_2+PTFE phosphors at $300^\circ C$ reading temperature are showed in figure 5. The TL read out values at $350^\circ C$ are reproducible within a coefficient of variation of 2% over ten re-use cycles.

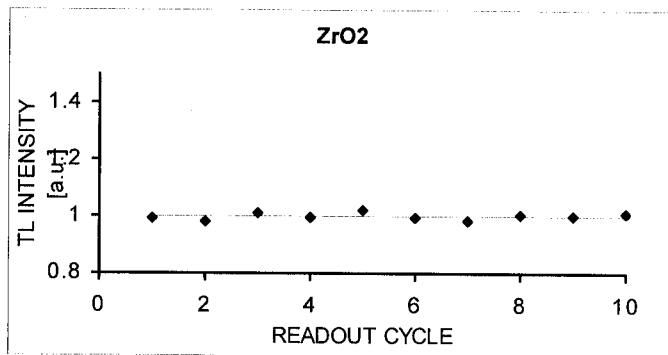


Figure 5. UVC dosimeter response of ZrO_2+PTFE values obtained after irradiated with an intensity of $50 \mu J/cm^2$ before being heated at $10^\circ C/s$. Symbols represents a different experimental data point of each readout cycle. Solid line mean TL signal with ± 2 standard deviation

CONCLUSION

The ZrO_2+PTFE discs detectors that have been developed, possess a set of unique dosimetric characteristics superior to the parameters of the analogues known. The detectors are suitable for UV radiation dosimetry mainly centered at 260 nm.

In summary, the luminescent emission (LE) observed in ZrO_2+PTFE samples, excited by heating phenomena, yields a transient, time dependent UV luminescence signal. Re-irradiation after annealing caused a reappearance of the luminescence. This effect confirms that the stimulated luminescence from irradiated samples is a result of the interaction of UV radiation with matter.

Thermo-stimulated luminescence signal is proportional to UV radiation dose, the feasibility of using ZrO_2+PTFE in UV radiation dosimetry by means of TL method is well demonstrated. May be is important to remark for UV radiation application dosimetry mainly for the region between 200 to 400 nm. That it is possible the using of both dosimeters as practical complementaries due that $Al_2O_3:C$ highest luminescent response is appeared in 230 nm, while ZrO_2+PTFE highest TL response is centered at 260 nm UV radiation wavelength. Thus, to application in UV radiation field is suggestion to use both dosimeters.

The experimental results obtained for ZrO_2+PTFE showed that this material could be useful for detection of UV using thermoluminescence (TL) method. Taking into account special care of exposure to light, this material can be used in to personal UV dosimetry.

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