ULTRAVIOLET RADIATION DOSIMETRY UTILIZING THERMOLUMINESCENCE

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ABSTRACT

An integrating dosimeter to detect ultraviolet radiation has been developed using the process of "direct" ultraviolet stimulation. This process yields a thermoluminescent signal after an exposure to ultraviolet radiation without prior exposure to ionizing radiation. Various crystals were compared for sensitivity to ultraviolet radiation. The spectral sensitivity, linearity with exposure and long range stability of the stored energy were investigated for MgO crystals which had the most sensitive response. The results of these tests indicate that a sensitive ultraviolet dosimeter can be developed using this phenomenon.

INTRODUCTION

Ultraviolet radiation results from a variety of industrial processes, various kinds of lamps specially designed for ultraviolet emission and natural sources such as sunlight. In addition to the medical therapeutic applications of ultraviolet (u.v.) radiation, there is an increasing application of u.v. radiation for disinfecting and sterlizing[1] materials in industrial and public health areas. The injurious effects of u.v. energy appear to be related to their ability to be absorbed by nucleic acid[2]. Determatologists and skin photobiologists are mainly concerned with the deleterious effects on man, such as erythema (sunburn), painful inflamation of the membrane of the eye, and the possibilities of skin cancer[3]. The actual effectiveness of sunburn is expressed in terms of the "standard erythemal spectrum" covering wavelengths 250 nm to 320 nm. This spectrum and the erythemal effectiveness have been widely studied,[4-7] the most sensitive region of erythema being between the wavelengths of 290 and 320 nm. The smallest amount of ultraviolet energy that will produce visible erythema is called a Minimum Erythemal Dose (MED) and is defined as the minimum amount of energy required to elicit a just barely visually detected reddening of the skin at one particular wavelength. This MED value, however, is dependent on several factors such as the observation time of the erythema and the anatomical site of testing, as well as the irradiation wavelength and other factors. Thus it would be useful to have a convenient dosimeter which would act as an absolute measurement device.

A number of phosphors utilizing the thermoluminescent phenomenon have been studied as possible dosimeters for the ultraviolet region. Thermoluminescence has received extensive study and use in the past for ionizing radiation dosimetry[8]. The low cost per phosphor, the absence of any associated electronics

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at the site of measurement, and the fact that the thermoluminescent phosphor can operate unattended, are some of the advantages in using thermoluminescence. The small size of a solid phosphor allows the possibilities of performing skin transmission studies in vivo and development as a personnel dosimeter.

One of the first thermoluminescent phosphors receiving attention[9,10] for u.v. detection was $CaSO_4$:Mn, but it was not sensitive in the erythemal region. Wilson et.al.[11] studied a natural CaF_2 phosphor using the technique of "transferred thermoluminescence (TL)". The same process was utilized by McCullough and Cameron,[12] and Okuno and Watanabe[13] in natural CaF_2 by Nambi and Higashimura[14] in $CaSO_4$:Tm and $CaSO_4$:Dy. "Transferred Thermoluminescence" involves a sequence of operations. The phosphor is first heated to 700°C to empty deep traps and then is exposed to a "standard" amount of X or γ radiation. The phosphor is then heated to 400°C for 10 minutes (this empties the traps with glow peak temperatures below 400°C but does not empty the deeper traps). Upon exposure to ultraviolet radiation, some of the electrons in the deeper traps are "transferred" to the shallower traps corresponding to lower temperature (<400°C) glow peaks. The glow curve of the transferred thermoluminescence is then measured up to 400°C, and the transferred TL intensity may then be related to the ultraviolet radiation exposure. The transferred TL intensity is also related to the number of traps previously filled by ionizing radiation.

As is evident, this transferred TL process is complex and time consuming. In contrast, the process of "direct" ultraviolet stimulation, with which this work is mainly concerned, yields a thermoluminescent signal after an exposure of ultraviolet radiation, without any prior exposure to ionizing radiation. This simplifies the process and is more convenient for practical use. This paper is concerned with the feasibility of using materials involving the "direct" stimulation process as dosimeters for ultraviolet radiation.

EXPERIMENTAL DETAILS AND MATERIALS SURVEY

An xenon arc lamp (PEK:X-151-1453) was used as a u.v. irradiation source. This type of xenon source was used because its spectral distribution closely resembles that of the sun. Other experiments used a monochrometer (Jarrell-Ash 1/4 meter) with 3 mm exit slits to select a particular u.v. wavelength. All u.v. intensities were measured with a radiometer (YSI-kettering, model 65) at a standard distance of 5mm from the exit slit of the monochrometer. A Harshaw model 2000 thermoluminescence detector was used to record the TL glow curves.

A general survey of the u.v. response of various materials was performed first to find those showing the greatest promise for direct sensitizations. Fifteen different materials were tested by irradiating for 10 minutes with the light directly from the xenon lamp, so that the samples were exposed to a range of wavelengths. The materials did not receive any other radiation prior to u.v. irradiation. The resultant response of the materials tested is shown in Table I, where MgO and magnesium silicate doped with terbium seem to be the most sensitive to direct u.v. stimulation. The results indicate that MgO crystals annealed in an argon atmosphere at 2000°C for 24 hours have more thermoluminescent sensitivity than the as received or nonannealed MgO crystals; this annealing procedure affects the defect structure of the crystal, which in turn affects the thermoluminescence. The results of this survey also indicated that the total impurity content in MgO plays a significant role in thermoluminescence, since impure MgO has less thermoluminescent sensitivity than the purer MgO.

RESULTS AND DISCUSSION

After these initial tests it was decided to experiment further with MgO

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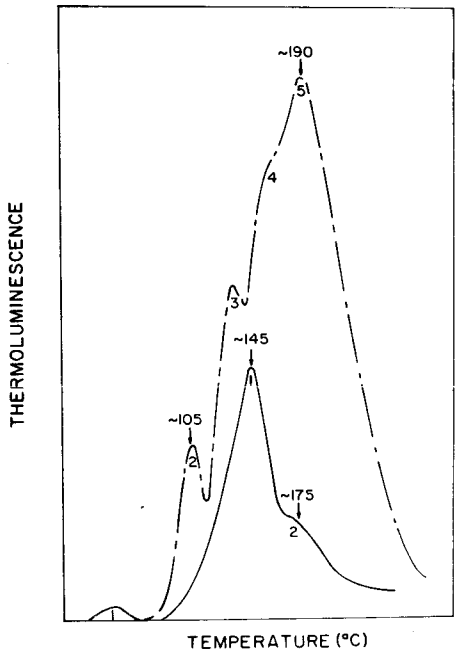

Fig. 1. Thermoluminescent glow curve of MgO-PA type crystal (—) exposed to 3 x 10^4 μW-sec/cm^2 at 296.7 nm and LiF (TLD-100) single crystal (---) exposed to 100R of 250 kVp x-rays (thoreas III filter) Peak height of LiF peak 5 is 2.2 times higher than peak 1 in MgO.

crystals since they responded with the greatest sensitivity. Spectral sensitivity, linearity with exposure and the short range stability of the stored energy was studied. Two sets of MgO crystals, designated as PA and NB, were studied. PA crystals have a total impurity content of 255 ppm and NB crystals have total impurities of 815 ppm; more details on these samples are given by Srinivasan et.al[15].

Figure 1 shows a typical glow curve of a PA crystal, with a main glow peak at about 145°C designated as peak 1. Peak 2 and peak 3 (not shown) are at about 175°C and 325°C respectively. For comparison, a glow curve of X-irradiated LiF (TLD-100) is also shown. In PA crystals, peak 2 is small and not very distinctive, and peak 3 is very broad. Peak 1 and peak 2 were completely absent if there was no prior u.v. irradiation. The most effective peak for dosimetry is peak 1 at 145°C and therefore, all further tests concentrated on this peak. Glow curves of NB crystals show peaks at the same temperature as in PA crystals and an additional peak at 120°C.

The MgO crystals were observed to exhibit a sensitization phenomenon. Untreated crystals irradiated only at one particular wavelength of u.v. radiation show much less TL than similar crystals which have been previously irradiated with whole u.v. (mixed wavelengths) for 10 minutes before exposure to a particular wavelength. The thermoluminescent intensity of the untreated crystals after such a preliminary exposure followed by an exposure at a particular wavelength was similar to that of the crystals which previously had been treated with whole u.v. exposure. The minimum amount of time required for sensitization for PA crystals was found to lie between 10 and 15 minutes; a 20 minute sensitization period shows a drastic reduction in thermoluminescent sensitivity. This sensitization period of 15 minutes was found to give a maximum response for a number of MgO crystals with different impurity levels. The greatest sensitivity however, was for the purest material (PA crystals).

The sensitivity of PA and NB crystals as a function of wavelength for the u.v. region is shown in Figure 2. All the crystals received the same exposure of 3 x 10^4 μW-sec/cm^2 at all wavelengths. This value is the Minimum Erythermal Dose (MED) at 296.7 nm based on the standard erythemal curve. PA crystals have a completely flat response over the entire wavelength region; thus no wavelength corrections are necessary for this kind of a crystal. NB crystals, on the other hand, show an increase in thermoluminescence at 285 nm followed by a continuous decrease in thermoluminescence to 305 nm and then a uniform response to 325 nm. Thus if NB crystals were to be used for dosimetry purposes, corrections for this wavelength dependence would have to be made. The results shown in Figure 2 are for PA crystals that were sensitized about nine months before this study was done, and for PA and NB crystals sensitized before the experiment. These results show that this sensitization procedure, discussed previously, decreases

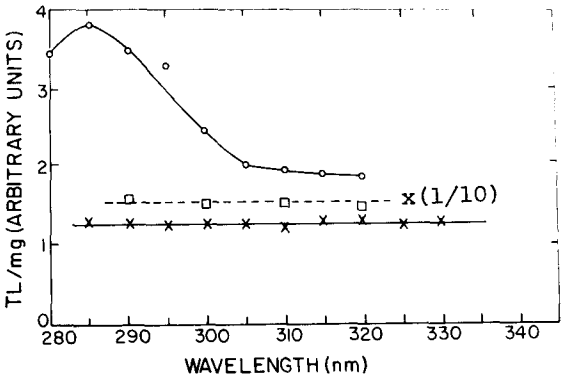

Fig. 2. Thermoluminescent output (TL/mg) for MgO PA and NB crystals as a function of wavelength of irradiation. The circles represent NB immediately after sensitization. The squares connected by the dashed line represent PA immediately after sensitization, whereas the crosses connected by the solid line are for PA sensitized 9 months before the tests.

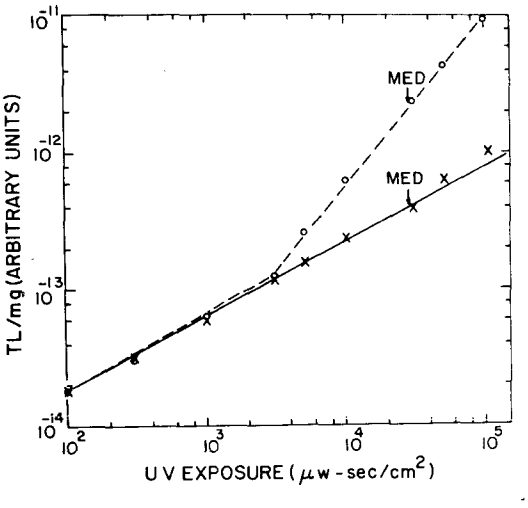

Fig. 3. Thermoluminescent output (TL/mg) for MgO-PA(x) and NB (o) crystals as a function of u.v. exposure at 295 nm. Arrows indicate the MED value at 295 nm.

approximately an order of magnitude in effectiveness in a nine month period. The sensitization decreases by 20% within 15 days. Thus, elapsed time after the sensitization procedure is an important variable requiring attention. Further studies to delineate an optimum time are in progress.

The response of the MgO crystals as a function of ultraviolet exposure at 295 nm is shown in Figure 3. The exposure was determined up to an order of magnitude above the minimum erythemal dose (MED indicated in Figure 3). The linear relationship with exposure shown by PA crystals over the entire region would be extremely useful for dosimetry purposes. The relationship between TL/mg and exposure for NB crystals shows two regions of linearity. This kind of MgO crystal could also be used for dosimetry purposes provided the region of operation is roughly known.

Thermoluminescent reproducibility, another important dosimetric consideration, has been checked several times under various conditions. The repeated thermoluminescent measurements yielded a standard deviation of less than ±5%. This 5% reproducibility in the PA crystals was obtained without any intermediate heat treatments or sensitization procedures; this could be a big advantage of using this system, since no annealing treatments are needed for repeated use of these crystals such as those required for LiF (TLD-100) crystals after each thermoluminescent measurement. The effect of storage at room temperature and of room light, which are other important aspects of the reproducibility of these crystals, was studied for a number of crystals. The crystals were u.v. irradiated to an exposure of 3×10^4 μW-sec/cm^2 and the thermoluminescence was measured. The crystals were then cycled through the readout procedure a few times after the first thermoluminescent measurement to assure that there was no thermoluminescence left in these crystals. Then half of the samples were left in room light and the other half was wrapped in a black paper and left in a drawer. After 24 hours, all the crystals were read out again. Crystals which were left in black paper did not show any thermoluminescence whereas those left in room light had a response which was less than 0.5% of the original thermoluminescence, corresponding to an exposure of 1.5×10^2 μW-sec/cm^2. Thus

under normal use, care must be exercised to avoid unnecessary exposure to room light although the response after 24 hours may be considered negligible. If u.v. irradiated crystals are stored at room temperature wrapped in black paper, the response decreases exponentially with time; peak 1 has a half life of 192 hours (8 days).

Two regions of sensitivity and linearity were noted above (Figures 2 and 3) for the impure NB crystals. Since thermoluminescence in MgO may be correlated with the valence changes of Fe and Cr,[16,17] it is probable that these two phenomena might be related to the impurity defect structure within the crystals. The impurity defect structure is affected by annealing, and thus the presence of certain defect structures might yield greater u.v. sensitivity as mentioned previously. Reactions between vacancies and impurities, and the effects of their concentrations in MgO have been studied as a function of temperature using optical methods[18] and ionic conductivity techniques[19]. Irradiation with u.v. light or heating in oxygen or magnesium vapor to change the valence state of the impurities will produce optical absorption bands in MgO crystals which contain no intentionally added foreign ions. Wertz et.al.[20,21] presented evidence for changes in valence of various foreign ions in MgO during irradiation and other treatments. Hansler and Segelken[16] have reported that the amount of Fe^{3+} could be changed during ultraviolet irradiation depending on the previous treatment. These changes could be reversed during thermoluminescence. The same effects have been observed with Cr^{3+}. Therefore it was suggested that thermoluminescence might be correlated with the valence changes of impurities in MgO. Further investigations are in progress to attempt to correlate changes in the defect structures with maximum thermoluminescent response to ultraviolet irradiation.

CONCLUSIONS

On the basis of these results, MgO-PA crystals have been found to be feasible for u.v. dosimetry in the erythemally effective region of 290 to 320 nm. MgO crystals of lesser purity, represented by NB crystals in this paper can also be used but require more care. These MgO crystals yield a thermoluminescent signal after a "direct" u.v. radiation stimulation without any prior exposure to ionizing radiation. For the greatest response, the crystals should be sensitized by irradiating them with whole u.v. (mixed wavelengths) for 15 minutes before using them. MgO-PA crystals are independent of the wavelength of irradiation and have a linear relationship of thermoluminescence as a function of exposure. Thus these crystals can be used without any corrective procedures. The crystals also can be reused immediately with a reproducible response to within ±5%. However, these crystals are slightly affected by room light and as such, precaution should be taken to prevent the crystals from receiving unnecessary prolonged exposure to room light.

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TABLE I

Thermoluminescent response of various materials after exposure to the entire spectrum of a xenon lamp for 10 minutes.

Sample	Peak Temperature (C°)	Thermoluminescent Peak Height
MgO		
(1) Annealed Pure PA Crystal[a]	145	0.61×10^{-8}
	175	0.15×10^{-8}
(2) Unannealed Pure Crystal[a]	136	0.22×10^{-8}
(3) NB Crystal (Lower Purity)[b]	120	0.26×10^{-8}
	145	0.39×10^{-8}
Magnesium Silicate: Terbium[c]	190	0.17×10^{-8}
Magnesium Borate: Terbium[c]	115	0.12×10^{-11}
Calcium Fluoride[d]		
(1) CaF_2:Mn	153	0.62×10^{-11}
	185	0.35×10^{-11}
(2) CaF_2:Dy	170	0.43×10^{-11}
	215	0.33×10^{-11}
Calcium Sulphate[d]		
(1) $CaSO_4$:Mn	120	0.23×10^{-12}
(2) $CaSO_4$:Dy	190	0.12×10^{-12}
Lithium Borate[e]	119	0.76×10^{-11}
	165	0.40×10^{-11}
LiF (TLD-100)	No Detectable Response	

a Oak Ridge
b Norton Company
c Dai Nippon Toryo Co., Ltd.
d Harshaw Chemical Company
e Grown in this laboratory