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Ultraviolet Stimulated Thermoluminescent Response Characteristics of Aluminum Oxide

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Western Kentucky University

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ULTRAVIOLET STIMULATED THERMOLUMINESCENT RESPONSE CHARACTERISTICS OF ALUMINUM OXIDE

A Thesis
Presented to
the Faculty of the Department of Physics and Astronomy
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Edward L. Ryan III
December 1976
ULTRAVIOLET STIMULATED THERMOLUMINESCENT RESPONSE CHARACTERISTICS OF ALUMINUM OXIDE

Recommended Nov 24, 1976

William G. Bondman

Approved 12-2-76

Dean of the Graduate College
The author would like to express his appreciation to his wife for her understanding and assistance during the course of this research. The author truly appreciates her efforts in reviewing the manuscript and offering constructive criticism. The author dedicates this thesis, in appreciation of these efforts, to his wife, Martha Ann.

Dr. W. G. Buckman suggested the original thesis problem and was instrumental in the successful completion of this research through his advice at critical phases of the project. For this the author expresses his appreciation.

For their patience and understanding the author would like to express his appreciation to Dr. T. P. Coohill and the personnel of the Biophysics Laboratory.

The author would like to extend his thanks to Dr. J. E. Parks for his assistance in the preparation of this manuscript.

Appreciation and thanks are extended to the Science Library personnel, especially to Mrs. J. Almand for her skillful assistance in the completion of the literature search.

The author would like to thank the Department of Physics and Astronomy for their financial assistance during the course of this research.
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This investigation has demonstrated that some aluminum oxide crystals have high sensitivity and are well suited for detecting and measuring ultraviolet radiation rates significantly less than 0.1 \( \mu \text{W/cm}^2 \).

The thermoluminescent glow curve, linearity of response, and fading of the crystals were determined. An action spectrum was performed to determine the relative sensitivities of several crystals in a range of wavelengths from 230 nm to 546 nm.

The sensitivity of the crystals was found to decrease as a function of exposure. An explanation for the decrease in sensitivity due to the presence of high temperature traps is presented.

This investigation has demonstrated that certain aluminum oxide crystals exhibit ultraviolet response characteristics necessary to meet the criteria set forth by the Occupational Safety and Health Administration for the detection and measurement of low levels of ultraviolet radiation.
INTRODUCTION

In recent years the application of ultraviolet (uv) radiation sources for purposes such as sterilization of instruments and treatment of diseases has increased. This trend can be expected to continue in the future, as evidenced by the current introduction of uv lasers and the greater use of fluorescent dyes. The potential hazard of human exposure to the harmful effects of uv has increased in proportion to the use of these sources. Consequently, the Occupational Safety and Health Administration has recommended that occupational exposure to uv be limited to 0.1 \( \mu W/cm^2 \) during a continuous eight hour period.\(^1\) However, technology to measure ultraviolet energy for compliance with the recommended standard is not now adequate.\(^1\)

Currently, uv rates are measured with photomultiplier tubes (PMT), thermopiles, or photodetectors.\(^2\) These detectors are limited in use by their complex electronics, sensitivity ranges, or their need for delicate handling. Consequently, there is a need for an instrument that is sensitive to low levels (<0.1 \( \mu W/cm^2 \)) of uv, is stable, linear in response, and simple to use. This detector should also be durable and relatively inexpensive.

Many thermoluminescent phosphors have been tested for their ability to meet the above criteria. One such phosphor is crystalline aluminum oxide (Al\(_2\)O\(_3\)). Buckman et al.\(^3\) have shown that nominally pure sapphire crystals with a high concentration of manganese (possibly 1\%) and chromium impurities exhibit sensitivity to low levels (<0.3 \( \mu W/cm^2 \)) of uv. Wells
and Buckman\textsuperscript{4} have reported an increased sensitivity and a linear response for other Al\textsubscript{2}O\textsubscript{3} crystals given a large prior exposure to germicidal uv and subsequent annealing. These results have indicated a need for more detailed information about the response characteristics of aluminum oxide persuant to its use as a simple uv dosimeter.

The following investigation was undertaken to determine the uv-stimulated thermoluminescent response characteristics of aluminum oxide crystals. Based on the results of Wells and Buckman\textsuperscript{4}, the investigation was begun by determining if the degree of sensitivity of these crystals could be selected by varying the amount of prior germicidal uv exposure. In addition, the thermoluminescent glow curve and the linearity of response of the crystals were determined. The decay of sensitivity as a function of total uv exposure was investigated for the crystals, and an explanation for this decay is presented. Fading of the crystals during post-irradiation storage at room temperature was determined for a period of 240 hours. An action spectrum was performed using selected representative crystals to determine their relative sensitivities to a range of wavelengths (230-546 nm). Using x-ray fluorescence an impurity analysis was conducted on selected crystals to determine if the differences in thermoluminescent response could be related to the impurities.

The investigation demonstrated that some Al\textsubscript{2}O\textsubscript{3} crystals are highly sensitive to low levels (<0.1 \(\mu\)W/cm\textsuperscript{2}) of uv. Since thermoluminescent phosphors are integrating devices, the high sensitivity of these Al\textsubscript{2}O\textsubscript{3} crystals makes them well suited for detecting and measuring uv rates significantly less than 0.1 \(\mu\)W/cm\textsuperscript{2}. 
Rieke and Daniels\textsuperscript{5} reported the influence of structure and of impurities on the thermoluminescent glow curve of aluminum oxide (Al$_2$O$_3$). They found that most of their powdered Al$_2$O$_3$ samples produced thermoluminescent glow curves after irradiation with $\gamma$-rays. The shape of these curves and the amount of thermoluminescence (TL) varied with the degree of calcination. For synthetic $\alpha$-Al$_2$O$_3$, the associated TL was greatest. They were able to resolve the glow curves into four peaks (103, 123, 164, 236°C), and they attributed the peak at 236°C to the presence of sodium impurities. Gabrysh et al.\textsuperscript{6} reported visually observing two glow peaks when $\gamma$-irradiated Al$_2$O$_3$ was allowed to warm from liquid nitrogen temperature to room temperature. Philbrick\textsuperscript{7} studied the $\gamma$-irradiation-produced centers and optical absorption bands in sapphire and ruby. He showed that a correlation existed between the TL and the optical absorption bands and calculated the thermal activation energies for sapphire. In addition he showed a glow curve dependent on the crystal C-axis orientation and the direction of thermoluminescent emission.

Philbrick et al.\textsuperscript{8} reported a glow curve for $\gamma$-irradiated sapphire that generally agreed with that obtained by Gabrish et al.\textsuperscript{9} who used $\gamma$-irradiated crystals that were uv stimulated. In addition Philbrick et al.\textsuperscript{8} reported that the thermoluminescent emission occurring in the region of 700 nm can be attributed to chromium as an impurity in the nominally pure sapphire.
Van Tricht and Van der Kraay\textsuperscript{10} studied the TL and phosphorescence of $\gamma$-irradiated $\alpha$-$\text{Al}_2\text{O}_3$ on the ascending slopes of the thermoluminescent glow peaks. From a plot of the phosphorescence of these peaks they were able to derive the activation energies directly. McDonald and Rudin\textsuperscript{11} studied the energy response of $\text{Al}_2\text{O}_3$ to $\gamma$-irradiation and found that the response was energy dependent below 1 MeV. They reported that the thermoluminescent response was apparently unaffected by heat treatment, and that the crystals faded about 20\% in 60 days. Cooke and Sutherland\textsuperscript{12} reported x-ray induced thermoluminescent peaks for sapphire (Linde Co.) occurring at 180, 260, and 310$^\circ$C. They reported a large band emission peaking at 330 nm and a chromium R-line emission at 692.9 nm and 694.3 nm. Based on the thermoluminescent emission intensity of the chromium ion, they concluded that there was a high probability that this was the site of recombination or de-excitation for both the ruby and nominally pure sapphire. Cooke \textit{et al.}\textsuperscript{13} reported that ruby, under continuous x-irradiation and continuous heating and cooling, exhibited a glow curve dependent on temperature, chromium ion concentration and crystal C-axis orientation. They also reported that the emission observed at 300 nm was characteristic of either the $\text{Al}_2\text{O}_3$ host lattice or an impurity common to both the sapphire and ruby.

Watson\textsuperscript{14} obtained many of the same results in $\gamma$-irradiated ruby as Cooke \textit{et al.}\textsuperscript{13} who used x-rays. Watson\textsuperscript{14} showed that the thermoluminescent response followed an exponential decrease which was related to the concentration of chromium impurity present in the crystals but failed to specify to which peaks he referred. Also, he presented a model for the influence of chromium on the TL of ruby.
Each of the above investigators was primarily interested in the x-ray or γ-ray thermoluminescent response of Al₂O₃. Some of these investigators also observed a characteristic related to the ultraviolet response of Al₂O₃.

Rieke and Daniels⁵ reported light-induced TL in some crystals which had not received previous x, γ, or other high energy radiation exposure. They showed that a thermoluminescent response could be induced by exposure to room light or light from a mercury source. Coop and Hammond¹⁵ reported on the phosphorescence observed in sapphire at room temperature after exposure to a low pressure mercury source. Gabrysh et al.⁶ observed the response of γ-ray-damaged sapphire to a 100 W tungsten filament lamp. They observed the luminescent buildup and decay characteristics at five temperatures ranging from 5°C to 83°C. In another experiment, Gabrysh et al.⁹ reported a glow curve, similar to the one reported by Rieke and Daniels⁵, for mercury light induced TL in aged γ-irradiated crystals. They also noted that the TL was sensitive to thermal pretreatment and exposure to daylight. Lehman and Gunthard¹⁶ reported a typical glow curve (-60 to 120°C) with glow peaks at -23°C and 82°C, an absorption spectrum (230-500 nm) for flash light excited sapphire. They presented a model for the luminescence process below 67°C.

Philbrick⁷ reported that the shape of the thermoluminescent glow curve was dependent on whether the thermoluminescent emission was parallel or perpendicular to the C-axis, and whether the C-axis was perpendicular to the face or the edge of the crystal. For the C-axis directed perpendicular to the face of the crystal, there was little difference between the two directions of emission. The glow peaks occurred in the regions 180, 290, and 330°C. When the C-axis was directed perpendicular to the edge of
the crystal, thermoluminescent emission in this direction produced peaks in the regions 130, 190, 260, and 350°C. If the thermoluminescent emission was perpendicular to the face of the crystal, the peaks occurred in the regions 200, 260, and 310°C.

From the results of these investigations it appeared that Al$_2$O$_3$ crystals which respond to uv might be used as uv dosimeters. Buckman et al.\textsuperscript{3} reported small 65°C and broad 165°C thermoluminescent glow peaks for uv-stimulated sapphire. The current integral of the thermoluminescent glow curves for these crystals was stable for as long as eight days. An emission spectrum exhibited peaks at approximately 300, 410, 640, and 690 nm. Exposure of several samples to a cool white fluorescent lamp at a distance of 2.54 cm produced only small 65°C thermoluminescent glow peaks after a 3-hour exposure.

In other studies Buckman\textsuperscript{17,18,19} reported finding that Al$_2$O$_3$ containing titanium as the luminescent center had favorable characteristics for functioning as simple uv dosimeters. They were small in size, easily portable, and sensitive to both low and high levels of uv. Additionally they exhibited a linear response. Wells and Buckman\textsuperscript{4} reported that some Al$_2$O$_3$ crystals initially exhibited a supralinear response but became linear and increased in sensitivity (by a factor of 2000) after receiving a prior exposure to germicidal uv (13.5 hrs at 200 $\mu$W/cm$^2$) and subsequent annealing.

Zinker et al.\textsuperscript{20} reported that x-irradiated Al$_2$O$_3$ samples (grown by vapor transport from ultrapure starting materials) from the NBS and Verneuil crystals (supplied by Krystallos) did not show detectable sensitivity to uv. However, Czochralski-grown crystals (Krystallos) showed sensitivity to uv, and gave a similar glow curve to that of Buckman et al.\textsuperscript{3}. 
Cooke$^{21}$ reported that prior $\gamma$-irradiation of some Al$_2$O$_3$ crystals containing chromium and titanium exhibited increasing sensitivity upon successive uv exposures provided that the annealing temperature was below 600-800$^\circ$C. He suggested that this response may be due to the presence of deep traps. Also, he stated that if the crystals were annealed at 800$^\circ$C for one hour, the sensitivity was no longer dependent on the uv exposure; thereby making them suitable for use as ultraviolet radiation dosimeters.
CHAPTER II

INSTRUMENTATION, MATERIALS, AND METHODS

Instrumentation

Two types of ultraviolet (uv) radiation sources were used in this investigation. A Westinghouse G15T8 sterilamp was used to determine the fading of the crystals and to determine if the degree of crystal sensitivity could be selected by varying the amount of prior germicidal uv exposure, and by subsequently annealing the crystals. A Hanovia Type 929B00070, 2500 watt mercury-xenon high pressure arc was used for determining the thermoluminescent glow curve, linearity of response, decay of sensitivity and the action spectrum. The beam from this lamp was passed through a GM250D double grating monochromator (Schoeffel Instrument Corp.) using gratings with 1180 rulings/mm which were blazed for 240 nm. The system utilized an off-axis Ebert type mount to eliminate reentry spectra, multiple diffraction and reflection. The half-bandwidth of the uv beam was 3.2 nm for entry and exit slits of 2 mm and 6.6 nm for those of 4 mm. The uv beam was turned on and off by use of a camera shutter mounted between the exit slit of the monochromator and the crystal irradiating platform.

The ultraviolet intensity from both sources was measured by a United Detector Technology Inc., series PIN-10 Cal/uv photodetector, calibrated at 250, 320, and 360 nm. The photocurrent was measured by a Keithley Model 610B electrometer operating in the fast mode.

A Harshaw Model 2000A Thermoluminescence Detector (Harshaw Chemical Co.) which employed an EMI 9656 Photomultiplier tube (PMT) operating at 800
volts was used to detect the thermoluminescence (TL). A Harshaw Model 2000B Automatic Integrating Picoammeter was used to record the photocurrent. Since there is evidence in the literature for quenching of TL by water vapor, the crystal sample was continuously flushed with nitrogen during TL readout. Two heating ranges were employed. The heating range during initial experiments was from 20-250°C. The upper limit was subsequently changed to 350°C because an additional glow peak was observed in the 300-320°C region. The heating rate and the thermoluminescent output current were relayed to the X and Y axes, respectively, of a Hewlett-Packard Model 7005 X-Y recorder, thus providing a graphical record of the TL as a function of temperature.

Initial annealing of the crystals was performed using a hot plate, with the applied voltage controlled by a variac transformer. The crystals were annealed at 460°C for 15 minutes. During later experiments the annealing was accomplished by placing the crystals in a covered Vitreosil crucible which was then placed in a Type FH2020 Hosking Electric Furnace. The annealing time and temperature were 15 minutes and 575°C. In both annealing procedures the temperature was measured by a chromel-alumel thermocouple connected to a Model 2746 Honeywell potentiometer. The crystals of both annealing procedures were allowed to cool to room temperature in the dark to avoid light induced TL.

Materials

The aluminum oxide (Al₂O₃) crystals (nos. 2-31, Lot 3) were from a boule obtained from Semi-Elements, Inc. in 1972. The dimensions of the crystals were approximately 4 mm x 4 mm x 1 mm. They had been used in a previous investigation.
Method

Since these crystals were observed to exhibit a significant thermoluminescent response after exposure to room light (cool white fluorescent), they were individually wrapped and stored in light-tight containers when not being studied. They were subsequently studied in a dark room. During placement and movement of the crystals for uv irradiation and subsequent thermoluminescent readout, a flashlight with a 600 nm interference filter was used for illumination during placement and movement.

The procedures for crystal irradiation were: 1) turn on the uv source; 2) allow the source to stabilize; 3) thermally bleach (20-350°C) the unirradiated crystal to assure that any TL accrued during storage was removed; 4) make a second thermal bleach (20-350°C) to determine the baseline (blackbody noise level) of the unirradiated crystal and heating planchet; 5) select the desired monochromatic wavelength; 6) adjust the crystal irradiating platform height to achieve the desired uv intensity as determined by the photodetector; 7) center the platform in the uv beam as determined by use of a fluorescent plate; 8) vary the irradiation time from 1 to 100 seconds to achieve the desired exposure; 9) transfer the irradiated crystal quickly to the TL unit and then readout the thermoluminescent glow curve; 10) remeasure the uv beam intensity upon completion of the TL readout. All experiments were conducted at 20°C.
Sensitivity Classes

One assumption for this investigation was that the ultraviolet (uv) sensitivities of crystals could be enhanced by prior exposure to germicidal uv, principally 254 nm, and subsequent annealing. Therefore, the crystals were exposed to 9.2 J/cm$^2$ of germicidal 254 nm uv at an exposure rate of 200 $\mu$W/cm$^2$ for 13.5 hours. The crystals were then annealed at 460°C for 15 minutes.

Two types of thermoluminescent responses were found. One subgroup of crystals was found to have a high uv sensitivity. No sensitivity change was found in the other subgroup. This procedure was repeated several times. Neither subgroup of crystals was found to change in sensitivity during these trials. Based on the thermoluminescent response of the crystals the group was subdivided into two classes, Class H and Class L. Class H crystals were those crystals which exhibited high uv sensitivity, requiring on the order of $\mu$J/cm$^2$ for a significant thermoluminescent response. Class L crystals were those exhibiting low uv sensitivity, requiring on the order of J/cm$^2$ for a significant thermoluminescent response.

Glow Curve

The crystals of primary interest to this investigation were the Class H crystals. Figure 1 is a graph of the typical thermoluminescent
Figure 1. Typical thermoluminescent glow curve for the high sensitivity Class H crystals. The glow peaks occur in the regions of 54°C, 157°C, 224°C, and a band in the region 300-330°C. The exposure was 850 μJ/cm² of 254 nm monochromatic uv.
glow curve of the Class H crystals. These crystals exhibited glow peaks in the regions of 54°C, 157°C, and 224°C. In addition, there was an indication of thermoluminescent response in the region of 300-330°C. The location of the latter peak could not be defined for the uv exposure. The response appeared as a band in this region, but the signal-to-noise ratio was too low to allow its resolution. In some of these crystals the 54°C peak resolved into two peaks. One peak centered about 45°C and the other centered about 72°C.

Figure 2 is a graph of the typical thermoluminescent glow curve for the Class L crystals. These crystals exhibited thermoluminescent glow peaks in the regions of 54°C, 142-152°C, 195-205°C, and 320-350°C. When the thermoluminescent glow curve was readout at a slow heating rate (1.45°C/sec), two shoulders appeared in addition to the normal peaks. One was located at 165°C and the other at 245°C. During initial experiments the maximum thermal bleaching temperature was 230°C. Under these conditions the glow peaks occurred at the lower value of the given ranges. Due to the observation that the Class L crystals exhibited a supralinear response upon successive exposure to uv radiation (1 J/cm²), the thermal bleach temperature was raised to 380°C. A crystal was exposed to 3 J/cm² of 254 nm monochromatic uv and the thermoluminescent glow curve determined. A thermoluminescent glow peak was found to occur in the 320-350°C region. The crystal was then reexposed to 3 J/cm². Upon readout of the thermoluminescence (TL) the other peaks were found to be greatly reduced and shifted to the higher value of the ranges previously given. The 330-350°C peak was shifted from a center about 330°C to a center about 360°C. The Class L crystals did not exhibit a supralinear response after the thermal bleach
Figure 2. Typical thermoluminescent glow curve for the low sensitivity Class L crystals. The glow peaks occur in the regions of 54°C, 142-152°C, 195-205°C, and 320-350°C. The exposure was 3 J/cm² of 254 nm monochromatic uv.
GLOW CURVE

TEMPERATURE (CENTIGRADE)

PEAK HEIGHT (AMPS)

NOISE LEVEL
temperature was raised to 380°C. The response was linear. When the thermoluminescent response was rechecked after a period of about two months from the last annealing, the response was found to be non-linear. When the Class L crystals were re-annealed they again exhibited a linear response.

One crystal exhibited a response entirely different from the Class H and Class L crystals. This crystal exhibited three thermoluminescent glow peaks. The glow peaks were centered in the regions of 100°C, 160°C, and 225°C. Sensitivity of these crystals was determined to be intermediate to that of the Class H and Class L crystals.

*Thermoluminescent Response After Storage*

The Class H crystals were observed to exhibit a thermoluminescent glow peak centered in the 160°C region after storage at room temperature. These crystals had been exposed to uv radiation but had been thermally bleached to 350°C prior to storage. To determine if this response was real and not spurious, three crystals were given an exposure to monochromatic 254 nm uv radiation. Glow curves for each crystal were readout, the crystals were allowed to cool to room temperature, and the glow curves were readout again. This was done to determine if there was any residual TL; none was present. Crystals were then stored wrapped in tissue in individual light-tight containers for a period of 13 days. This procedure was also followed for one crystal which was stored for a period of 57 days. Figure 3 shows the relative responses for the three crystals stored for 13 days, and for the one crystal which had been stored for 57 days. The relative magnitude of uv energy necessary to give a similar response is on the order of <0.5 μJ/cm² for the 13-day responses and <1 μJ/cm² for the 57-day response.
Figure 3. Spontaneous thermoluminescent response after storage of three crystals for a period of 13 days and for one crystal stored for a period of 57 days.
Linearity of Response

The response of the crystals was investigated as a function of uv exposure; and it was determined that the Class L crystals exhibited reasonable linearity after annealing, but became non-linear after storage for moderate to long periods of time (weeks to months). Class H crystals were found to exhibit a highly linear response for exposures ranging from an energy density of 0.4 μJ/cm² to over 1000 μJ/cm². Figures 4, 5, and 6 show the linear nature for the response of three representative Class H crystals. Figure 4 shows the highly linear nature of crystal 12H for three trials from a series of seven trials. The energy density to which the crystal was exposed varied from 0.4 μJ/cm² to about 50 μJ/cm² of monochromatic 254 nm uv, at a rate of 0.4 μW/cm². Each point represents the average of three responses. That the slope of the response decreases for successive trials is readily apparent. In each trial the crystal was exposed to a total energy density of about 500 μJ/cm². Figure 5 shows the linear nature of the response for crystal 1911 for three trials from a series of six trials. Again, it is readily apparent that the thermoluminescent response is proportional to the uv exposure, and that the response decreases with successive exposures. This crystal was exposed to a total energy density of about 500 μJ/cm² for trial 1 and was exposed to an additional 500 μJ/cm² between trial 1 and 3. During trial 3 the crystal received a total energy density of about 300 μJ/cm². Figure 6 shows the linear nature of the thermoluminescent response for crystal 2H during two successive trials, trials A and B, to about 1.2 mJ/cm², on the same scale as Figures 4 and 5. Figure 7 is expanded for clarity. Trial C was obtained after the crystal had been annealed at 575°C for 15 minutes.
Figure 4. Linearity of response for crystal 12H at a constant exposure rate of 0.4 μW/cm². The energy density was varied from 0.4 μJ/cm² to about 50 μJ/cm² of 254 nm monochromatic uv.
A TRIAL 1
B TRIAL 2
C TRIAL 7

PEAK HEIGHT ($10^{-10}$ AMPS)

EXPOSURE IN MICROJOULES/CM$^2$
Figure 5. Linearity of response for crystal 19 at a constant exposure rate of 0.6 $\mu$W/cm$^2$ for trial 1 and 0.56 $\mu$W/cm$^2$ for trials 3 and 4. The energy density was varied from 0.56 $\mu$J/cm$^2$ to about 50 $\mu$J/cm$^2$ of 254 nm monochromatic uv.
Figure 6. Linearity of response for crystal 2H. Trial A and B were for exposure rates of 10 μW/cm$^2$, and for trial C 46 μW/cm$^2$. Exposure for trials A and B was 1200 μJ/cm$^2$, and for trial C 580 μJ/cm$^2$.

Figure 7. Linearity of response expanded for clarity. This graph demonstrates the difference in sensitivity from trials A and B for which the crystal had been annealed at 460°C, and for trial C for which the crystal had been annealed at 575°C.
PEAK HEIGHT ($10^{10}$ AMPS)

Exposure in microjoules/cm$^2$
Previously this crystal had been annealed at only 460°C for 15 minutes. As is apparent from the graph, the crystal increased in sensitivity after being annealed at 575°C.

**Decay of Sensitivity**

The decreasing slope for the response trials prompted an investigation of the decay of sensitivity of Class H crystals. Certain representative crystals were repeatedly exposed to an energy density of 500 µJ/cm² of 254 nm monochromatic uv radiation.

An initial assumption was that the decrease in response could have been due to the length of time which had elapsed since these crystals were reannealed. Crystal 19H was, therefore, reannealed at 460°C for 15 minutes in the Hoskins Furnace. Figure 8 is a plot of the response for crystal 19H given repeated exposures of 500 µJ/cm². As can be seen, the response exhibits very close agreement with an exponential decrease in sensitivity as a function of uv exposure.

Crystal 19H was then reannealed at 575°C for 15 minutes. This temperature was selected from annealing temperature data presented by Wells and Buckman⁴. Figure 9 shows the results of the change in annealing temperature. As can be seen, the thermoluminescent response still exhibits an exponential decrease as a function of uv exposure. In this case, however, the first two points on the curve are decreasing at a rate greater than exponential. The effect of the increased annealing temperature on crystal 19H was to increase the sensitivity by an order of magnitude. Figure 10 shows the response for two other Class H crystals. These crystals also decrease exponentially with exposure. Figure 11 is a plot of the thermoluminescent response obtained by exposing the crystal and then waiting five minutes for the phosphorescence of the low temperature
Figure 8. Decay of sensitivity of crystal 19H after annealing at 460°C and repeated exposures to 500 μJ/cm² of 254 nm monochromatic uv.

Figure 9. Decay of sensitivity of crystal 19H after annealing at 575°C and repeated exposures to 500 μJ/cm².
Figure 10. The graphs of the decay of sensitivity for two other Class H crystals are shown. The top graph is for crystal 14H given repeated exposures of 850 μJ/cm$^2$. The bottom graph is for crystal 2H given repeated exposures of 545 μJ/cm$^2$. 
Figure 11. Decay of sensitivity for crystal 1911 as determined by waiting five minutes after the crystal was irradiated for the phosphorescence of the low temperature traps to terminate. Each exposure was 500 μJ/cm².
traps to terminate. It was observed that this procedure produced a
greatly reduced peak at 54°C and a slightly reduced peak at 165°C. As
can be seen the sensitivity of the crystal does not decrease as rapidly.

Figure 12 shows a graph of the initial thermoluminescent response
after each annealing at 575°C. The crystals were found to exhibit a net
loss in sensitivity after each annealing. This loss of sensitivity closely
follows a log-log decay.

**Fading of the Thermoluminescent Response**

Figure 13 shows the fading characteristics of a representative Class
H crystal as determined for a period of 240 hours. The greatest amount of
fading occurred during the first 32 hours. Fading during this period
amounted to about 7.5%. During the next 208 hours the fading amounted
to an additional 1.5%.

**Action Spectrum**

During preliminary experiments some of the crystals were observed to
exhibit a significant response at a distance of 2 m from a cool white
fluorescent lamp. Therefore, an action spectrum was performed at 20 wave-
lengths in the 230-546 nm range to determine the relative sensitivities
of selected representative Class H crystals. The action spectrum is shown
in Figure 14. The procedure for obtaining the data points was to anneal
each crystal at 575°C prior to each exposure. The data was normalized
allowing the response at 254 nm to have a value of one. The relative
sensitivities of the crystals are presented in Table 1.

**Impurity Analysis**

An x-ray fluorescence impurity analysis of selected representative
crystals produced inconclusive information about the impurities. Therefore
Figure 12. This graph shows the initial thermoluminescent response obtained after each annealing at 575°C for 15 minutes. The peak heights for crystals 12H and 19H are $10^{-8}$ amps and $10^{-10}$ amps for crystal 2H.
Figure 13. Fading of crystal 2H determined for a period of 240 hours. Exposures were 3800 μJ/cm² of 254 nm monochromatic uv.
Figure 14. Action spectrum for three representative Class II crystals. Wavelength range is from 230 nm to 546 nm. Each crystal received an energy density of 850 μJ/cm² at each wavelength.
### TABLE 1

**RELATIVE CRYSTAL SENSITIVITY FOR VARIOUS WAVELENGTHS**  
NORMALIZED TO THE RESPONSE AT 254 NM

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Relative Crystal Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12H</td>
</tr>
<tr>
<td>203.2</td>
<td>0.811</td>
</tr>
<tr>
<td>232.3</td>
<td>0.627</td>
</tr>
<tr>
<td>235.2</td>
<td>1.01</td>
</tr>
<tr>
<td>239.9</td>
<td>0.765</td>
</tr>
<tr>
<td>244.6</td>
<td>0.836</td>
</tr>
<tr>
<td>248.2</td>
<td>0.985</td>
</tr>
<tr>
<td>253.7</td>
<td>1.000</td>
</tr>
<tr>
<td>265.2</td>
<td>0.775</td>
</tr>
<tr>
<td>269.9</td>
<td>0.658</td>
</tr>
<tr>
<td>280.4</td>
<td>0.357</td>
</tr>
<tr>
<td>289.3</td>
<td>0.352</td>
</tr>
<tr>
<td>296.7</td>
<td>0.282</td>
</tr>
<tr>
<td>302.1</td>
<td>0.250</td>
</tr>
<tr>
<td>312.5</td>
<td>0.158</td>
</tr>
<tr>
<td>334.1</td>
<td>0.015</td>
</tr>
<tr>
<td>365.0</td>
<td>0.001</td>
</tr>
<tr>
<td>390.6</td>
<td>0.0001</td>
</tr>
<tr>
<td>404.6</td>
<td>0.0001</td>
</tr>
<tr>
<td>435.8</td>
<td>--</td>
</tr>
<tr>
<td>546.0</td>
<td>--</td>
</tr>
</tbody>
</table>
it was necessary to rely on the results obtained in a previous investigation. The crystals used in that investigation were other crystals from the same boule. Table II shows the results from a spectrographic analysis conducted by the Battelle Institute.

<table>
<thead>
<tr>
<th>Element</th>
<th>Lot #3 Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>0.004</td>
</tr>
<tr>
<td>Ba</td>
<td>0.003</td>
</tr>
<tr>
<td>Si</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Ti</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0005</td>
</tr>
<tr>
<td>Ga</td>
<td>&lt;0.0003</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;0.0001</td>
</tr>
</tbody>
</table>
Sensitivity Classes

Two major sensitivity classes were found to occur in the investigated Al$_2$O$_3$ crystals. The two classes exhibited glow curves similar to those reported by Philbrick for different crystal C-axis orientations. The Class H crystals had glow curves in close agreement with the glow curves reported by Philbrick for crystals with the TL emission and C-axis perpendicular to the face of the crystal. Class L crystals had glow curves that were in agreement with those reported by Philbrick for crystals having the TL emission and C-axis perpendicular to the crystal edges.

The high sensitivity of the Class H crystals, in addition to their capacity for giving an integrated response to uv radiation, shows that these crystals are well suited for detecting and measuring extremely low levels of uv radiation.

Spontaneous TL Response After Crystal Storage

An interesting observation for the Class H crystals was their capacity for producing a low level TL response without uv stimulation after they had been stored for a period as short as 13 days. There are three possible mechanisms that could produce this TL. First, the crystals could be responding to stray uv radiation in the dark room. This possibility can be eliminated since no similar low level response was observed when
the crystals were given mock irradiations. Second, the crystals could be responding to the low level environmental background x or γ ray radiation. This can be considered a feasible explanation since several studies have shown Al₂O₃ crystals to respond to these particular radiations. This hypothesis can be tested by shielding several crystals and determining if a thermoluminescent response occurred after storage. If a response occurred, then the third possibility would most likely explain the effect. The third possibility is that the crystals could be responding to the decay of higher temperature traps (>350°C).

Decay of Sensitivity

The Class H crystals have been shown to be linear in their response from 0.4 μJ/cm² to over 1000 μJ/cm². Unfortunately these crystals have also been shown to decrease in sensitivity by as much as 33%, in some crystals, over a series of four linearity of response trials. At this point it must be remembered that the data points for the linearity of response were determined by taking the average of three exposures with a total energy density of about 2000 μJ/cm². When the decrease in response as a function of exposure was determined, the crystals received an energy density of about 500 μJ/cm² and the maximum decrease observed was about 6% per trial.

The decay of sensitivity demonstrated by these crystals can be explained by the presence of high temperature traps. The data presented showed that the sensitivity decreased exponentially. As the crystals were irradiated a small number of electrons were being lost from the photoelectron pool. These electrons were being trapped by the high temperature traps. Thus, there were fewer electrons in the photoelectron pool
and the thermoluminescent response decreased. When the annealing temperature was raised from 460°C to 575°C many of the electrons that had been lost to the high temperature traps were recovered. This is demonstrated by the greatly increased sensitivity of crystals that were annealed at 575°C (see Figures 7, 8, and 9). This indicates that at least some of the high temperature traps are in the region of 460°C to 575°C.

From the data presented in Figure 12 it can be concluded that other high temperature traps exist. The presence of these traps then explains the net log-log decrease in sensitivity after each annealing at 575°C. Data presented in Figure 9 indicated that after the initial annealing at 575°C the decrease in sensitivity, initially, progressed at a rate greater than exponential. This indicates that a certain saturation level of electrons trapped in the high temperature traps must be achieved before the decrease in response becomes well behaved.

The highly linear nature of the Class II crystals can now be explained. The number of low temperature traps, responsible for the thermoluminescent response at 157°C, must be less than the number of electrons in the photoelectron pool. Now for a unit energy density of exposure a probability for trapping an electron in the various traps can be assigned. From the experimental results it can be assumed that the probability of the low temperature trap capturing an electron is much larger than the probabilities of the high temperature traps. The presence of at least two high temperature traps has been verified, but there may be more. As the crystal is exposed to larger amounts of uv radiation the response is supralinear. This response can be explained by considering the low temperature traps to be saturated by the photoelectrons, implying that the number of these traps
is less than the photoelectron population. Initially the number of
electrons lost to the high temperature traps is a negligible fraction of
the total photoelectron population and saturation of the low temperature
traps can occur. Consequently, the response is supralinear. As the
accumulated total exposure of the crystal increases a significant number
of the electrons from the photoelectron pool are lost to the high temp-
perature traps. When enough of these electrons have been lost to the high
temperature traps saturation of the low temperature traps no longer occurs,
and the response becomes directly proportional to the energy density of
the exposure. This description can be used to explain the results of
Wells and Buckman.4

These results indicate that the linear nature of these crystals is
dependent on the level of saturation of the high temperature traps. Once
the necessary level of saturation has been reached the number of electrons
in the photoelectron pool has been reduced to a sufficiently low level so
that saturation of the low temperature traps does not occur, and the response
is linear.

By a judicious determination of the uv energy density required to
saturate the high temperature traps, crystals that are highly linear in
nature and have a high sensitivity can be generated. The variable of
greatest significance for production of this response is the distribution
of the impurities. Considering that the total integrated level of exposure
of greatest interest is on the order of a few μJ/cm² or less, the decrease
in sensitivity will be negligible. Therefore, these crystals can be ex-
pected to give reproducible results within experimental error.
Fading

Fading of the thermoluminescent response has been shown to be most significant during the first 32 hours after exposure, decaying about 7.5% in this period. During the next 208 hours the decay was only about 1.5%. This shows that after an initial rapid decrease in response the fading is relatively small, less than 10%, for a 10-day period.

Action Spectrum

Action spectrum results show that the Class H crystals are definitely sensitive to wavelengths in the visible spectrum. The response, although small, (less than .01% of the response at 254 nm), extends to 546 nm. The predominant response for the wavelengths studied is between 230 nm and 334 nm. Peaks in the thermoluminescent response occur at the wavelengths 235 nm, 254 nm, 289 nm, 334 nm, and 365 nm. The response of the 334 nm and 365 nm peaks are on the order of 2% of the response at 254 nm.

These results indicate that these crystals can be used for measuring the uv component below 300 nm by comparing the thermoluminescent response for the total uv environment to the thermoluminescent response produced after simple filtering with glass.

Conclusions

This investigation has demonstrated that certain Al₂O₃ crystals exhibit the characteristics necessary to meet the criteria set forth by the Occupational Safety and Health Administration for the detection and measurement of low level uv radiation. These crystals can detect and measure levels of uv radiation significantly below 0.1 µW/cm². In addition, these crystals are linear, stable, relatively inexpensive, and well suited for use in hostile environments.
The data presented in this investigation suggest that the sensitivity of the Class H crystals can be selected, to some degree, by the temperature at which these crystals are annealed.

Since these crystals were used in another investigation, it was not possible to determine if the response observed with the Class H crystals was inherent or due to previous treatment as reported by Wells and Buckman. The data obtained suggest that the sensitivity of the crystals is dependent on the number of low temperature traps and the relative saturation of the high temperature traps. The sensitivity of Class H crystals can be influenced by changing the annealing temperature. The supralinear response observed by Wells and Buckman was observed in this investigation only with Class L crystals when the thermal bleach temperature was limited to $210^\circ C$. When the thermal bleach temperature was raised to $380^\circ C$, an additional peak was observed in the region of $330$-$360^\circ C$. This peak was found to be responsible for the supralinear response. If this peak was thermally bleached upon thermoluminescent readout, the Class L crystals gave a linear response.

Should further investigations of this phosphor be undertaken, it is suggested that virgin crystals be used. These crystals should be subdivided such that one group of crystals is exposed to uv to determine their native response and one group should be exposed to x or y rays and their response determined. In this manner it may be determined which type of crystal has the best uv response characteristics. The energy density required to produce the necessary saturation of the high temperature traps could then be determined. By increasing the thermal bleach temperature the location and number of high temperature traps could be determined.
BIBLIOGRAPHY


