UCRL-85608
PREPRINT

CONF-810810--5

MASTER

RADIATION-TO-LIGHT CONVERTERS FOR
NUCLEAR ENVIRONMENTS--DEEP RED EMITTERS

M. D. Rotter, F. Roeske, P. M. Calavan
Lawrence Livermore National Laboratory

and

S. S. Lutz
EG&G, Inc.

This paper was prepared for submittal to
SPIE International Symposium,
San Diego, California, August 24-28, 1981.

June 18, 1981

Lawrence
Livermore
Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISCLAIMER

This paper was prepared as an account of work sponsored by an agency of the United States Government. Therefore, the United States Government and any agency thereof, nor any of those employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, disclosed product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or approval by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Radiation-to-Light Converters For Nuclear Environments--Deep Red Emitters

M. D. Rotter, F. Roeske, P. M. Calavan

Lawrence Livermore National Laboratory
P.O. Box 808, Livermore, CA 94550

and

S. S. Lutz
EG&G, Inc.
130 Robin Hill Road
Goleta, CA 93117

Abstract

This report gives the preliminary results on work done to find a scintillator that is compatible with high-bandwidth, long-distance fiber-optic transmission. The requirements for such a scintillator are 1) emission in the near-IR; 2) linear output over 2-3 decades of input excitation; 3) time response < 2 ns; and 4) immunity to radiation damage. The behavior of single crystal cadmium sulfide (CdS) and cadmium selenide (CdSe) was examined under electron and laser excitation. Both crystals emit in the deep red, however, time response was found to be slower than 2 ns. Neither crystal exhibited good linearity over the entire range of input excitation.

Introduction

In the course of performing diagnostic measurements of nuclear test, one encounters signals with extremely fast rise-times and, consequently, large bandwidths. Coaxial cables can be made to meet the bandwidth requirements over the distances involved (typically 1/2-1 km) only through extensive equalization and resulting loss of amplitude. To help meet this bandwidth requirement (and to remove some undesirable side-effects of coaxial cables), we are experimenting with optical fibers as a replacement for coaxial cable.

Optical transmission modes require new diagnostic methods. For example, the current method used to detect the passage of radiation (e.g. gamma rays) utilizes the Compton Effect to produce a voltage pulse on a coaxial cable. For fiber-optic transmission, an optical analog of the above method must be found.

One such method involves the use of scintillators which emit light whenever radiation is incident upon them. However, most of the currently available scintillators (such as NE-111) emit light in the blue region of the spectrum. Since cable lengths of 1 km are not uncommon in nuclear testing, and fiber attenuation is greatest in the blue, these scintillators are unsuitable for field use.

We will give the preliminary results of our work to find a scintillator that is compatible with long-distance, high-bandwidth, optical-fiber transmission. We will focus on the results obtained with cadmium selenide (CdSe) and cadmium sulfide (CdS). Another paper submitted to this conference shall focus on gallium arsenide (GaAs) and cadmium telluride (CdTe).¹

These semiconductors were chosen for the following reasons: 1) in the case of CdSe, the band-gap energy is of the right value to allow photons in the far-red region of the spectrum to be generated; 2) red emission has been observed in CdS^{2,3}; and 3) both semiconductors were of the direct band-gap type, thus having the potential for very short radiative lifetimes. The CdSe samples were obtained from Eagle-Pitcher Co., and had the dimensions 1 cm x 1 cm x 0.2 cm. The CdS samples were obtained from the II-VI Corporation and had the same dimensions as the CdSe crystals. Excess sulfur (CdS⁰) samples were also obtained from II-VI.

Experimental Configuration

In the course of the experiment, both electron radiation and laser radiation were used. The electron radiation was used for studies of spectra, linearity, and, within the limits of the system, time response. The laser radiation was used for spectral studies and time response only.

The electron radiation scheme is shown in Figure 1. A model 706 Febetron from Field Emission, Inc. produces a pulse of electrons 1.5-2 ns long, full-width half-maximum (FWHM)

with an energy range of 100-600 keV. The electron pulse travels along the beam transfer tube, which has been evacuated and back-filled with 2 torr of nitrogen. This configuration produces a stable, propagating electron beam. After passage through a remotely controlled aperture and an opaque vacuum barrier, the electrons strike the sample in the dewar. The dewar is designed so that the temperature of the sample may be varied between 77°K and 300°K. Light emitted by the sample is lens-coupled into a 1/4-in. fiber bundle. The other end of the bundle may be connected either to an optical multichannel analyzer or a photomultiplier tube. A Faraday cup attached to the dewar monitors the amplitude and the time response of the electron pulse.

Figure 1. Febetron data-acquisition system.

To calculate the sample dose, radiachromic film, which was first calibrated using a standard ^{60}Co source, was used. The Febetron was then fired at film samples and dose or peak Faraday-cup voltage readings were taken. Using the configuration outlined above, a maximum dose of 5×10^5 rads was achieved, with a minimum dose of approximately 100 rads. Thus, we have approximately a 3-decade range of input excitation with which to check linearity.

Since the output pulse from the Febetron is 1.5-2 ns (FWHM), it is difficult to accurately determine time response in fast samples. To determine the time-response of a fast-response sample under electron excitation, the Linear Accelerator (LINAC) at EG&G/Santa Barbara was used. The LINAC produces a continuous train of 40-50 ps pulses of electrons with a nominal energy of 6 MeV. Light from the sample is collected, filtered through a monochromator, and applied to a fast photomultiplier tube. The output from the tube goes to a sampling system, where a computer-aided data acquisition system determines various parameters such as pulse shape, rise-time, etc.

It is conceivable that the time response and emission spectra from a sample depend upon the type of input excitation. Figure 2 shows the laser system used to study the behavior of samples under laser excitation. A Candela model 625-SLL pulsed dye laser is operated with a 5×10^{-5} M solution of Rhodamine 6G and is mode-locked with a 10^{-6} M solution of the saturable absorber DODCI. The Pockel's cell and accompanying optics pick out a single pulse from the pulse train. The peak power in a pulse is from 2 to 20 MW. The light emitted from the sample is collected into a 1/4-in. fiber bundle and is sent either through a monochromator and photomultiplier tube for time response measurements, or to the optical multichannel analyzer for spectral measurements. Because the absorption coefficient of the sample is extremely high for photons with higher energy than the band-gap, the light penetrates only a few microns into the sample. This means the surface must be very clean or else no emission from the sample can be observed. We have found that an etch of 3 HCl to 1 HNO₃ adequately prepares the CdSe surface.⁴

Figure 2. Laser data-acquisition system.

Results

CdSe Spectral Response

Figure 3 shows the results of spectral measurements taken on the Febetron and laser systems. The very broad nature of the spectrum taken with the laser at 300°K is due to the 2-mm input slit used on the monochromator. This gives us a resolution of 12 nm vs 0.6 nm with the 50 μ slit. From this figure, we see that the peak of the emission spectrum for laser excitation at 300°K is at 716.5 nm, which corresponds to a band-gap energy of 1.73 eV, which is in excellent agreement with the literature.⁵

Measurements of the temperature dependence upon the peak wavelength show that the peak wavelength moves linearly with temperature over the range of 77°K < T < 300°K. The linear dependence of the peak wavelength on temperature has a slope of $-1.5 \text{ \AA}/^\circ\text{K}$. This corresponds to a dE_g/dT of $-3.73 \times 10^{-4} \text{ eV}/^\circ\text{K}$, which is in good agreement with existing values.⁶ We have found a similar linear behavior for the Febetron data, but with a smaller slope of $-1.3 \text{ \AA}/^\circ\text{K}$ or $-3.149 \times 10^{-4} \text{ eV}/^\circ\text{K}$.

One final point of interest in Figure 3 is the shift in wavelength between laser and electron excitation. Electron excitation produces a shift in the output spectrum of approximately 13 nm towards the red. We believe that, with laser excitation, the depth at which carriers recombine is only a micron or so. Thus, there is very little self-absorption and, consequently, little change in the true emission spectrum. With electron excitation, carriers recombine throughout the entire sample. Since the absorption coefficient is very high ($\sim 10^4 \text{ cm}^{-1}$) for photon energies greater

Figure 3. Relative emission in CdSe.

than the band-gap, the blue part of the emission spectrum is attenuated relative to the red, and so, the output spectrum shifts toward the red.

In Figure 4, we show the absolute output of CdSe under electron excitation at 77°K. The output has been normalized with respect to solid angle (sr), spectral bandwidth (nm), and sample area. At higher doses, the output spectrum assumes the form seen in Figure 5. The extreme narrowing of the spectral output is indicative of stimulated emission.

Figure 4. Absolute emission in CdSe.

Figure 5. Stimulated emission spectrum - CdSe.

CdSe Output vs Dose

We obtained measurements of output vs dose with the Febetron using the peak value of the signal from the photomultiplier tube which was normalized to the peak value of the Faraday-cup reading. Figure 6 shows the output using the entire spectrum. The sharp increase in output at 2×10^4 rads indicates the onset of stimulated emission (cf. Figure 5). Because of this characteristic, the input excitation must be limited to no more than about 10^4 rads if we are to ensure linear behavior. If the spectral region of interest is limited to just spontaneous emission, then we obtain the curve shown in Figure 7. In this case, we have near-linearity over 3 decades of input excitation.

Output amplitude is dependent upon temperature. This relationship for the external efficiency for spontaneous emission may be written in the form

$$\eta_{\text{ext}} = \eta_0 e^{-T/\theta} \quad (1)$$

where θ may take on values between 50 and 110°K.⁷ Our measurements gave a temperature dependence of $3.43e^{-T/62.5}$, the output at 77°K being normalized to 1. Since the output is an exponential function of temperature, the sample must be cooled for efficient operation. This should not be difficult to do in the field.

Figure 6. CdSe linearity.

Figure 7. CdSe linearity - spontaneous emission only.

CdSe - Time Response

In Figure 8(a), we show the time response of CdSe as measured on the Febetron. We note that the $1/e$ decay time of the sample is approximately 30 ns under electron excitation. In Fig. 8(b), we show the time response of CdSe as measured on the laser system. Though the data is noisy, a $1/e$ time of ~ 4 ns may be inferred. To further investigate time response, measurements were taken on the LINAC system. We found that time response depended upon the amount of radiation absorbed by the sample. To test this effect, bursts of 1000 pulses were applied and oscilloscope readings were taken for the first pulse and a pulse near the end of the burst. In Figure 9(a), we show the time response for the first pulse and a pulse near the end. As shown, the $1/e$ decay time changes from 6 to 21 ns. Note that the first value agrees well with that obtained with the laser and the second value agrees well with that obtained with the Febetron.

$1/e$ decay ~ 30 ns 77°K

Figure 8(a). CdSe time response - Febetron system.

$1/e$ decay ~ 4 ns 97°K

Figure 8(b). CdSe time response - laser excitation.

The reason for the difference in time response is not known at present. One possible explanation is that the electron radiation induces trapping levels that are more efficient recombination centers and that lengthen the decay time. The fundamental assumption is that, under laser excitation, only band-band transitions are observed; these transitions are expected to have a fast decay time. To test this, measurements of time response were made under different temperatures following the same procedure as noted above. The ratio of the decay times were taken and the data plotted against temperature, as shown in Figure 9(b).

Figure 9(a). CdSe time response - LINAC system.

Figure 9(b). CdSe temperature dependence of radiation effect.

We note that for temperatures less than 94°K, the ratio between decay times is ~0.4, indicative of the behavior seen in Figure 9(a). At 99°K, the decay times become equal and they have a value of 4 ns. This would indicate that the trapping level, if there is one, thermalizes at 99°K. This places the level at 3.5 meV away from a band edge.

Spectral Response - CdS

As mentioned previously, red emission in CdS has been observed by a number of authors. The assignment of various impurities to account for the emission is complex. Excess sulfur, sulfur and cadmium vacancies, silver and copper impurities all give rise to red emission bands.⁸ Our investigations centered on the red emission in undoped CdS and CdS with excess sulfur (CdS⁺).

Figure 10 shows the relative output from CdS⁺ and CdS, as taken on the Febetron. The CdS⁺ has enhanced the red emission approximately an order of magnitude over the CdS. The output spectrum is extremely broad; the FWHM for CdS⁺ is 134 nm and, for CdS, it is 150 nm. Our equipment resolution was too poor to determine if there was any fine structure in the emission band. We were also unable to obtain a spectrum under laser excitation due to the very low output from the sample.

Several authors have also observed IR emission near 1 μ.⁹ We plan to investigate this luminescence with respect to output brightness and time response in the future.

Output vs Dose and Time Response of CdS

The result of the linearity measurements, using electron excitation, is shown in Figure 11(a). We integrated the area under the emission spectrum curve to obtain the values shown. A least-squares fit to the data is also indicated on the figure. No

Figure 10. CdS - spectral response.

evidence of stimulated emission was observed. Measurements were also made of output variance on temperature. Over the range of 77°K to 300°K, no appreciable variation in output could be found.

The time response of CdS is shown in Fig. 11(b). As shown, the 1/e decay time is approximately 5 μ s under electron excitation. Due to the low output mentioned above, no time response was obtained under laser excitation.

Figure 11(a). CdS - linearity.

Figure 11(b). CdS - time response.

Conclusions

CdSe was found to be a very bright scintillator operating in the 680-720 nm region of the spectrum. Comparison with the plastic scintillator NE-111, which has a slightly faster time response but emits in the blue, shows that CdSe is brighter by a factor of 8. The time response was deemed too slow for nuclear test applications (> 5ns). However, the turn-on time is extremely fast, less than 1 ns (cf. Fig. 7(b)).

CdSe's output characteristics of the spontaneous emission were found to be near-linear over a 3-decade range of input excitation, up to 10^5 rads. If the entire output spectrum is considered, the presence of stimulated emission at approximately 10^4 rads input limits the usefulness of material up to this level.

CdS was found to have an output that is bright, but exceedingly slow (~5 μ s). Its main characteristic is a broad output spectrum covering the deep-red to near IR (670-1000 nm). This would make CdS a good candidate for an imaging system that requires a broad-spectrum source.¹⁰

Acknowledgments

This work was performed under the auspices of the U. S. Department of Energy under contract No. W-7405-Eng-48.

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government thereof, and shall not be used for advertising or product endorsement purposes.

References

1. Roeske, F., et al. "Radiation-to-Light Converters for Nuclear Environments - Near Infrared Emitters," paper submitted to this conference.
2. Vuylsteke, A. A., and Sihvonen, Y. T., "Sulfur Vacancy Mechanism in Pure CdS," Physical Rev., Vol. 113, No. 1, pp. 40-42. 1959.
3. Sihvonen, Y. T., Boyd, D. R., and Woelke, C. D., "Some Properties of Green and Red-Green Luminescing CdS," Physical Rev., Vol. 113, No. 4, pp. 965-968. 1959.
4. Ray, B. II-VI Compounds, Pergamon Press 1969.
5. Sze, S. M., Physics of Semiconductor Devices, Wiley, Inc. 1969.
6. Pankove, J., Optical Processes in Semiconductors, pp. 412-413, Prentice-Hall 1971.
7. Pankove, Optical Processes in Semiconductors, p. 231.
8. Stanley, A. G., Cadmium Sulfide, Jet Propulsion Laboratory Publication 78-77, Vol. 2, pp. 7-14 through 7-17. 1978.
9. Stanley, Cadmium Sulfide, p. 7-18.
10. Reedy, R. P., Two-Dimensional Image Transmission Through Optical Fibers by Wavelength Multiplexing, Lawrence Livermore National Laboratory Technical Report UCRL-85142. 1980.