

EFFECTS OF PROTON IRRADIATION ON TRIBOLUMINESCENT MATERIALS SUCH AS ZNS:MN

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ABSTRACT

Research has shown that the fluorescence decay time can be used to measure temperatures in adverse environments, such as those found in space. Development of space-based phosphor sensors will depend heavily upon research investigating the resistance of phosphors to ionizing radiation. Research completed at the Alabama A&M University Center for Irradiation of Materials (CIM) shows that a 3 MeV proton fluence as small as $2.28 \times 10^{13} \text{ mm}^{-2}$ statistically reduces the ZnS:Mn decay time for temperatures less than 200 °C. Reductions in decay time appear to be proportional to increasing 3 MeV proton fluence beyond $2.28 \times 10^{13} \text{ mm}^{-2}$. It is possible that radiation induced dislocations in ZnS:Mn or the formation of sooty carbon in the binder could account for some of these reductions.

1. INTRODUCTION

Phosphors are materials doped with trace elements that give off visible light when suitably excited. Many of these phosphors have a ceramic base and can survive and function at high temperatures such as those present during combustion. When the phosphor is applied as a thin coating, it quickly equilibrates to the ambient environment and can be used to measure surface temperature, pressure/impact, or other phenomena.

The basic physics of phosphor thermometry is well established [ref. 1-2]. This method relies on measuring the fluorescence yield decay rate as a function of temperature. Having calibrated the phosphor over the desired temperature range, a small surface deposit is excited with a pulsed light source. The resulting fluorescence decay time is measured to calculate the temperature of the substrate.

For many phosphors, the fluorescence decay time (τ) varies as a function of temperature and is defined by:

$$I = I_0 \exp\left\{-\frac{t}{\tau}\right\}, \quad (1)$$

where:

I	=	Fluorescence light intensity (arbitrary units),
I_0	=	Initial fluorescence light intensity (arbitrary units),
t	=	Time since cessation of excitation source (s), and
τ	=	Prompt fluorescence decay time (s).

The time needed to reduce the light intensity to e^{-1} (36.8%) of its original value is defined as the prompt fluorescence decay time. An example of the fluorescence decay time for several phosphors is shown in Figure 1 [ref. 1-2]. Notice the decay time for $Y_2O_3:Eu$ changes by as much four orders of magnitude when the temperature increases from 600 to 1100 °C.

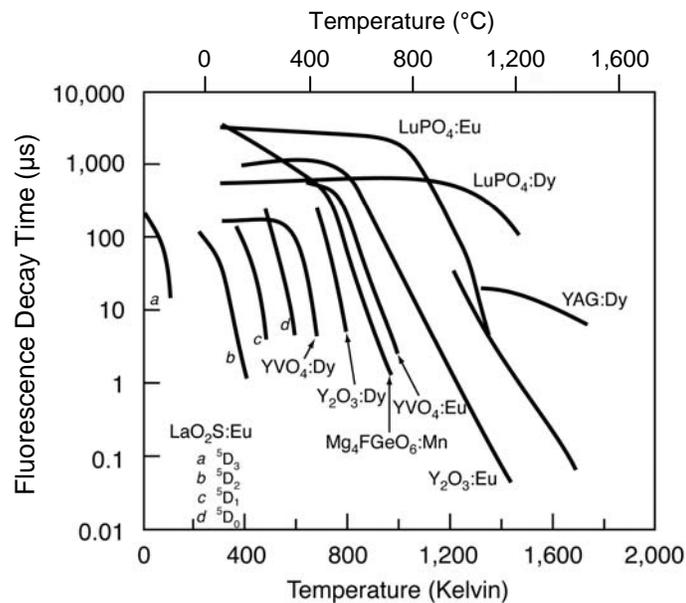


Figure 1. Prompt fluorescence decay time for a selection of phosphors.

Phosphor thermometry can be used in a variety of adverse environments. To be used to measure temperatures in space, any phosphor must also be resistant to ionizing radiation, including protons of all energies. As a rule, it is necessary to test material response to the action of the same type of ionizing radiation existing in the space environment. Research over the last decade has shown that 3 MeV proton irradiation reduces the fluorescence intensity for a variety of inorganic phosphors [ref. 3-5]. This paper will show preliminary results to measure fluorescence decay time as a function of temperature for zinc sulfide doped with manganese ($ZnS:Mn$) and the response of polymer paint samples exposed to 3 MeV protons.

2. SAMPLE PREPARATION

The phosphor used in this research consists of a paint containing 80% poly (phenyl methyl) siloxane (PPMS) and 20% $ZnS:Mn$ powder by volume. This formulation was found to give a tough and wear resistant paint. A $ZnS:Mn$ powder (GL25/N-U1) was purchased from

Phosphor Technology, Ltd. of Great Britain. Individual ZnS:Mn grains have a hexagonal structure where manganese dopant atoms replace zinc in the lattice. The typical emission spectrum for ZnS:Mn collected with a Perkin Elmer LS50B luminescence spectrometer with a wavelength of 355 nm is shown in Figure 2. When excited, ZnS:Mn emits bright yellow light with a broad emission peak centered at 585 nm and a full width at half maximum (FWHM) of about 125 nm.

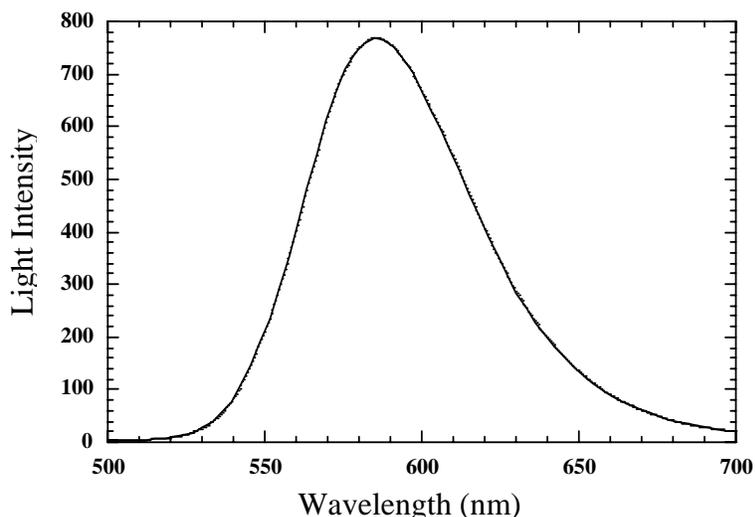


Figure 2. ZnS:Mn emission spectrum excited with a 355 nm xenon lamp.

A crystalline sample of PPMS was obtained from Techneglas Technical Products of Ohio. This polymer was chosen for its coating stability under potentially adverse thermal and mechanical conditions [ref. 3-5]. By itself, PPMS does not emit fluorescence when excited by 3 MeV protons [ref. 3-5]. A PPMS monomer consists of phenyl and methyl groups bonded to a silicon-oxygen chain. The liquid solution was made by dissolving PPMS crystals in butanol, which contains 50% polymer by mass. In each case, the PPMS and ZnS:Mn paint was sprayed on a 625 mm² aluminum substrate using a commercial airbrush. Each painted sample was heated in an oven to 160 °C for 20 minutes to crosslink the PPMS polymer. The PPMS and ZnS:Mn paint was sufficiently thin to allow most of the 3 MeV protons pass completely through and stop in the aluminum substrate.

3. EXPERIMENTAL METHODS

A. Proton Irradiation

Paint samples were exposed to 3 MeV protons using the 5SDH-2 tandem Pelletron accelerator, located at the Alabama A&M University Center for Irradiation of Materials (CIM). A 3 MeV proton beam was selected to make these results consistent with earlier research [ref. 3-5]. Samples for irradiation were mounted on an electrically isolated, four-sided holder located in the implantation beam line at CIM. A total of three samples can be irradiated before opening the chamber to atmospheric pressure. The remaining fourth side of the CIM holder was left empty to periodically adjust the incident current. A current integrator was used to measure total

collected proton charge during each irradiation sequence. The entire holder was biased to +200 V to minimize secondary electron emission.

The incident proton beam was randomly scanned over a 22.2 mm diameter aperture positioned just upstream of the sample irradiation position. The target beam spot was measured to be circular with an irradiation area of 460 mm². Scanning a random proton beam over the aperture resulted in a reasonably uniform fluence ($\pm 6\%$) to the sample surface. Pressure in the irradiation chamber was measured to be less than 10⁻⁶ torr for the entire test sequence. A beam scan duty factor of 50% was used for this research.

B. Fluorescence Decay Time

At the conclusion of the irradiation sequence, samples were taken to Oak Ridge National Laboratory to measure the fluorescence decay time. Figure 3 shows the experimental arrangement that was used to measure the fluorescence decay time. A painted sample was placed in a Thermolyne 46900 furnace at a 45° angle with respect to the top and back of the wall. Light from a LSI 337-NDS pulsed nitrogen laser was directed through the furnace top and was incident on the painted sample. The pulse frequency of the laser was approximately 10 Hz. Emitted fluorescence from the sample was then collected using a quarter inch diameter glass rod placed directly in front of the sample. A Hamamatsu H5783 photomultiplier tube (PMT) was placed directly at the end of the glass rod. A 590 nm narrow band pass filter was positioned between the PMT and the end of the glass rod to remove stray light. The measured potential from the PMT was displayed using a Tektronix TDS 320 digital oscilloscope. The TDS-320 oscilloscope was synchronized to the internal clock to the LSI laser. A GPIB-based LabVIEW virtual instrument collected and stored signals that were averaged over thirty-two laser pulses. A type K thermocouple was used to monitor sample temperature.

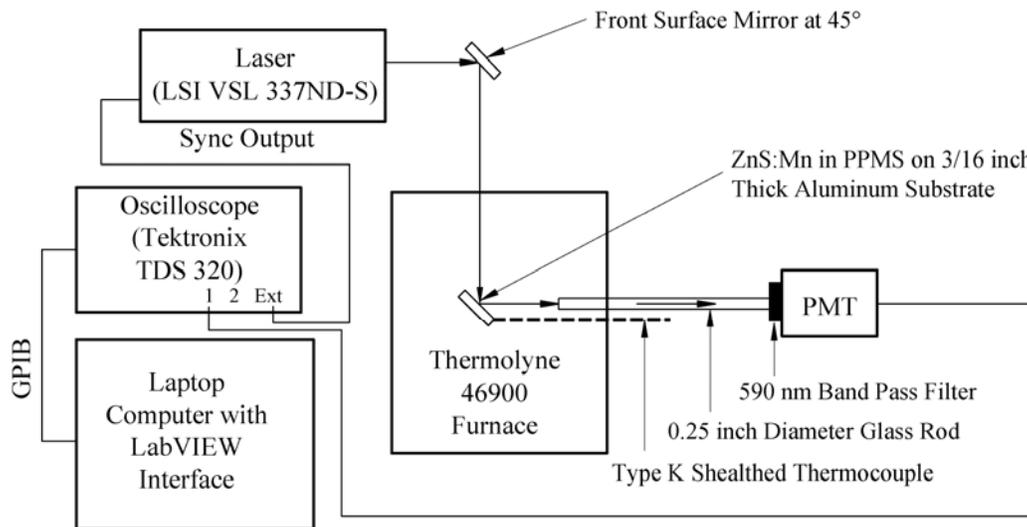


Figure 3. Apparatus used to measure fluorescence decay time.

4. RESULTS

A plot of the temperature-dependent fluorescence decay time as a function of 3 MeV proton fluence is shown in Figure 4. The error bars shown in Figure 4 for the measured decay

times were calculated using standard uncertainty propagation techniques. The temperature dependent decay times for the unirradiated (zero fluence) sample is completely consistent with earlier measurements as discussed in reference 6.

Results from Figure 4 indicate that a 3 MeV proton fluence as small as $2.28 \times 10^{13} \text{ mm}^{-2}$ statistically reduces the ZnS:Mn decay time for measurement temperatures of less than $200 \text{ }^\circ\text{C}$. The unirradiated and $2.28 \times 10^{13} \text{ mm}^{-2}$ decay time curves appear to be statistically identical after this temperature.

A 3 MeV proton fluence of $2.28 \times 10^{13} \text{ mm}^{-2}$ corresponds to one quarter of the half brightness “dose” for ZnS:Mn as measured in reference 5. The half brightness dose can be used as a figure of merit for radiation hardness and is defined as the proton fluence required to reduce the fluorescence intensity to half its original value [ref. 5].

Figure 4 also shows that 3 MeV proton fluences greater than of $2.28 \times 10^{13} \text{ mm}^{-2}$ uniformly reduce the ZnS:Mn decay time over all tested temperatures. It appears that reductions in temperature dependent decay time appear to be proportional to fluences larger than $2.28 \times 10^{13} \text{ mm}^{-2}$. It is possible that radiation induced dislocations in ZnS:Mn and the formation of sooty carbon in the PPMS could account for these effects.

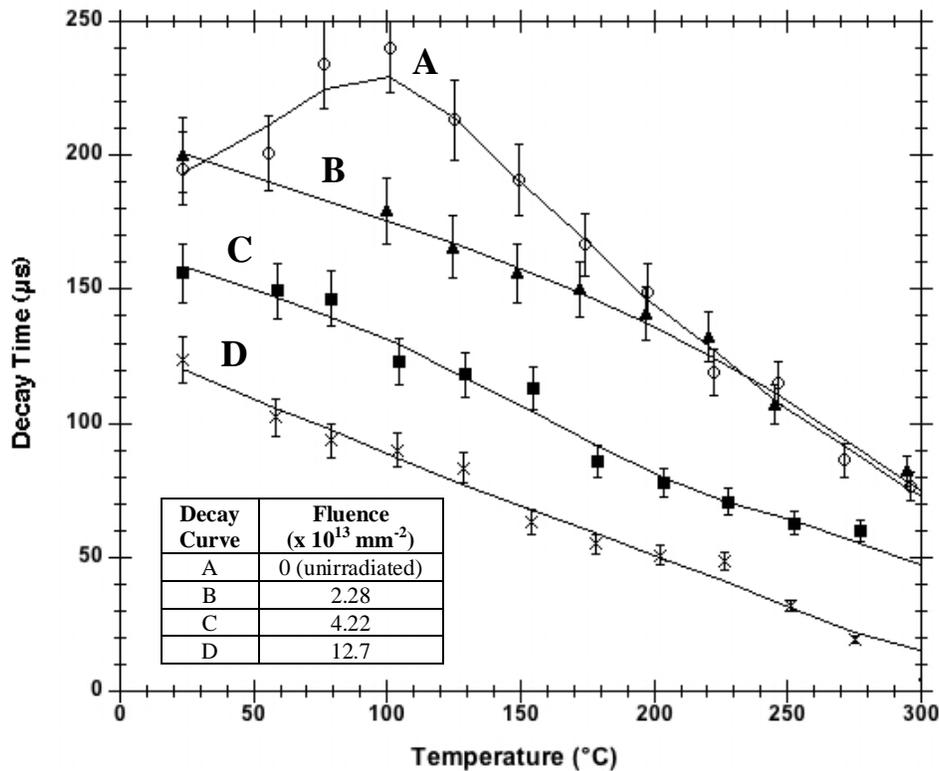


Figure 4. Comparison of temperature dependent decay times measured at a selection of 3 MeV proton fluences

5. CONCLUSIONS

To be used in space, a phosphor must be resistant to ionizing radiation, including protons of all energies. A 3 MeV proton fluence as small as $2.28 \times 10^{13} \text{ mm}^{-2}$ statistically reduces the ZnS:Mn decay time for temperatures less than $200 \text{ }^\circ\text{C}$. Reductions in decay time appear to be

proportional to increasing 3 MeV proton fluence beyond $2.28 \times 10^{13} \text{ mm}^{-2}$. It is possible that radiation induced dislocations in ZnS:Mn or the formation of sooty carbon in the PPMS could account for this difference. This discovery will allow greater understanding into the behavior of phosphors exposed to ionizing radiation, and coupled with previous research into high temperature phosphor thermometry, aids in the development of sensors appropriate for space environments. Additional research is planned and will be completed to verify these results.

6. ACKNOWLEDGEMENTS

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