

Evidence of Annealed Proton Damage From a ZnS:Mn-Based Phosphor Paint

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Abstract. Phosphors are materials that are doped with trace elements that give off visible light when excited. Many phosphors have a ceramic base and can survive and function at high temperatures. 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 and the ability to anneal damage caused by ionizing radiation. Preliminary results indicate that a consistent increase in the fluorescence decay time after thermal cycling was observed at two measured 3 MeV proton fluences. This “annealing” of proton damage was observed over the entire measured temperature range. The more heavily irradiated ZnS:Mn samples did not have annealed decay times that were as large as those that received lesser radiation fluences.

INTRODUCTION

The dependence of the phosphor fluorescence decay time to its the environmental conditions has proven useful to researchers performing non-contact measurements. 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 (Allison and Gillies, 1997; Allison et al., 2003). 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:

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

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 temperature dependent fluorescence decay time for ZnS:Mn is shown in Figure 1 (Hollerman, 2004).

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.

Recently, the authors measured the relationship between 3 MeV proton fluence and fluorescence decay time for ZnS:Mn (Hollerman, 2004). This research found that a 3 MeV proton fluence as small as $2.28 \times 10^{13} \text{ mm}^{-2}$

statistically reduces the ZnS:Mn fluorescence decay time for temperatures less than 200 °C. Reductions in decay time appear to be proportional to increasing fluence beyond $2.28 \times 10^{13} \text{ mm}^{-2}$. One of the unanswered questions resulting from this research was the effect of thermal annealing on the proton damaged ZnS:Mn paint samples. Understanding the role of annealing will help researchers design practical phosphor sensors for space applications. The objective of this paper is to show preliminary annealing results from 3 MeV proton irradiated ZnS:Mn, as evidenced by restoration of the prompt fluorescence decay time.

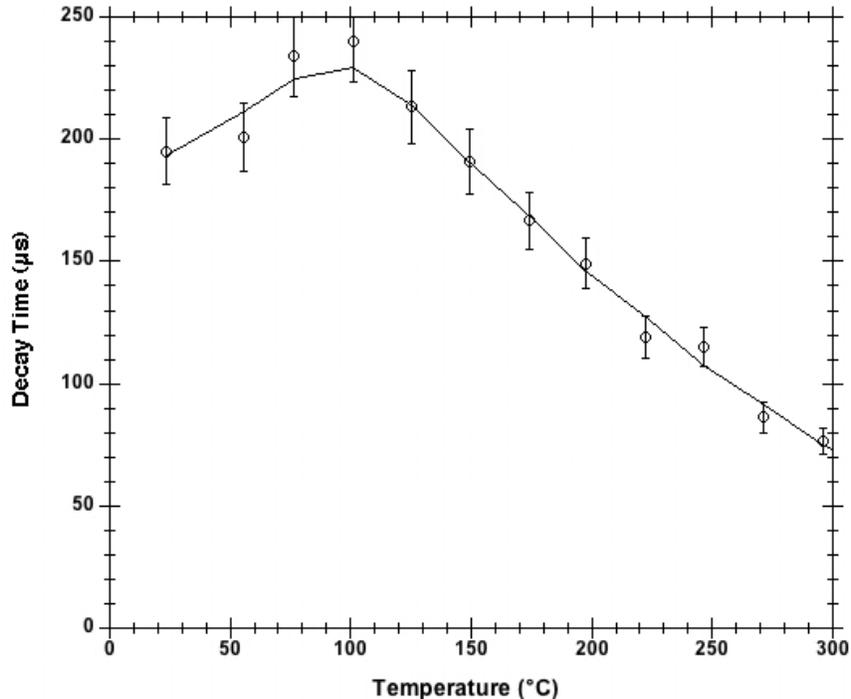


FIGURE 1. Measured Prompt Fluorescence Decay Time for ZnS:Mn (Hollerman, 2004).

SAMPLE PREPARATION

The coating used in this research consist of a paint containing 80% poly (phenyl methyl) siloxane (PPMS) and 20% ZnS:Mn powder by volume. This formulation was found to give a durable 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. 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.

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 (Womack, 2004). By itself, PPMS does not emit fluorescence when excited by 3 MeV protons (Womack, 2004). 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 mm^2 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.

EXPERIMENTAL METHODS

The main purpose of this research was to determine the relationship between environmental temperature and fluorescence decay time for two ZnS:Mn paint samples, each irradiated with 3 MeV protons at different fluences. In

the course of testing, it was noted that decay time of the dosed samples was matching the unirradiated values under certain conditions. This observation lead to the hypothesis that annealing was occurring. Additional details into these efforts are discussed in the sections that follow.

Proton Irradiation

Paint samples were exposed to 3 MeV protons using the 5SDH-2 tandem Pelletron accelerator, located on the campus of Alabama A&M University at the Center for Irradiation of Materials (CIM). Samples for irradiation were mounted on a 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 side of the CIM holder was left empty to periodically adjust the incident current. A picture of the CIM irradiation chamber is shown in Figure 2. The four-sided sample manipulator is mounted to the top arm of a Conflat cross as shown in Figure 2. Beam from the CIM Pelletron enters from the left branch of the Conflat cross.

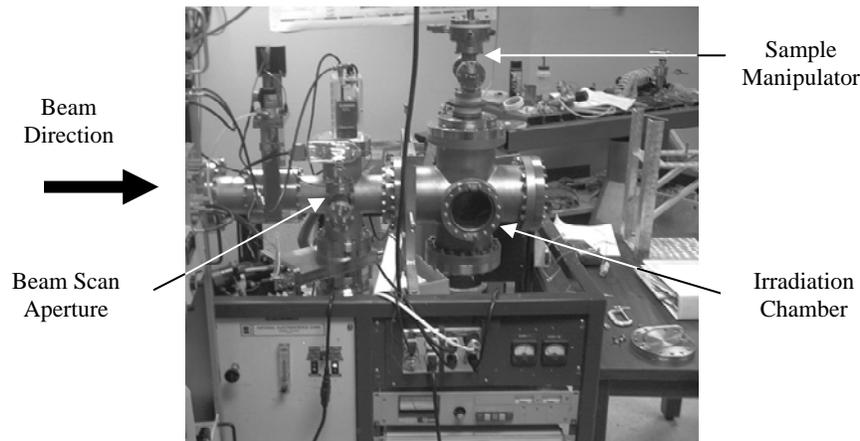


FIGURE 2. Picture of the CIM Irradiation Chamber.

The incident particle fluence n (mm^{-2}) at a given time is

$$n = \frac{Q}{q e A}. \quad (2)$$

Protons have an incident charge state of one ($q = 1$). A current integrator was used to measure total collected proton charge (Q) during each irradiation sequence. Beam currents on the order of 250 nA provided 3 MeV proton fluences (n) of 2.28×10^{13} and $7.39 \times 10^{13} \text{ mm}^{-2}$ to individual ZnS:Mn paint samples. The incident proton beam was randomly scanned, with a duty factor of about 50%, over an aperture positioned just upstream of the sample irradiation position. Scanning a random proton beam over the aperture resulted in a reasonably uniform fluence ($\pm 6\%$) to the sample surface. The target beam spot was measured to be circular with an irradiation area of 460 mm^2 . The entire holder was biased to approximately +200 V to minimize secondary electron emission. The pressure in the irradiation chamber was measured to be less than 10^{-6} Torr for the entire test sequence.

Fluorescence Decay Time

At the conclusion of the irradiation sequence, samples were taken to Oak Ridge National Laboratory (ORNL) to measure the fluorescence decay time. Figure 3 shows the experimental arrangement that was used to measure the decay time. A painted sample was placed in a Thermolyne 46900 furnace at a 45° angle with respect to the top and back walls. 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 of the LSI laser. A computer-based LabVIEW virtual instrument collected and stored signals (using a GPIB interface) that were averaged over thirty-two laser pulses. A type K thermocouple was used to monitor the sample temperature. Measurements of decay time were initially taken at room temperature (approximately 25 °C), and recorded every 25 °C until temperatures of 350 °C were achieved.

To determine the effects of annealing, it was decided to measure the ZnS:Mn decay time twice. The first decay time measurement slowly heats the ZnS:Mn paint sample from room temperature to 350 °C. Approximately eight hours were needed to raise the sample temperature and collect the decay time data in 25°C increments. Once the decay time for ZnS:Mn was measured at 350 °C, the sample was slowly allowed to cool. The second decay time measurement was completed under identical conditions the day following the initial measurements. This procedure should show any differences in decay time resulting from the initial thermal cycling.

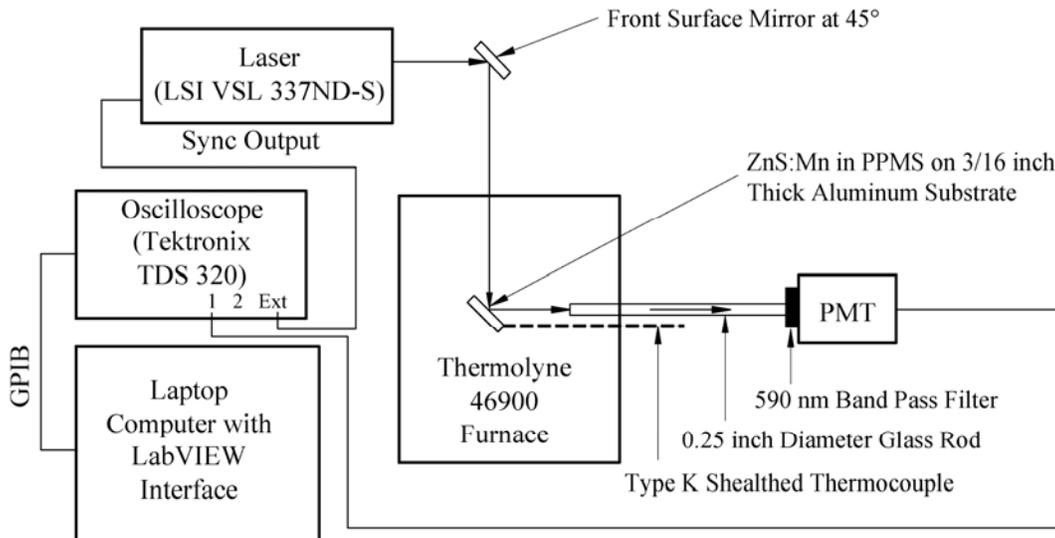


FIGURE 3. Apparatus Used to Measure Fluorescence Decay Time.

RESULTS

Results of the two successive ZnS:Mn decay time measurements for 3 MeV proton fluences of 2.28×10^{13} and $7.39 \times 10^{13} \text{ mm}^{-2}$ are shown in Figure 4. For both fluences, a consistent increase in the temperature dependent fluorescence decay time was observed during the second thermal cycle. When other irradiated samples were subjected to the same procedure, it was discovered that the temperature dependent fluorescence decay time was greater during the second thermal cycle than during the first measurement. As annealing became evident when the irradiated ZnS:Mn was subjected to thermal cycling, so did a particular characteristic of that data. For the conducted thermal cycles, the more heavily irradiated samples did not have annealed fluorescence decay times that were as large as those that received smaller radiation fluences, as evidenced in Figure 4. Another noticeable difference was the thermally cycled samples lacked the small peak in fluorescence decay time that was observed at approximately 100 °C for both sets of data as shown in Figure 4. As of now, a workable explanation for this phenomenon does not exist. Additional research will be completed to quantify these results.

CONCLUSIONS

To be used in space, a phosphor must be resistant to ionizing radiation. Potentially it would be useful for some of the radiation damage to be annealed by a controlled temperature increase. To that end, samples of ZnS:Mn exposed to 3 MeV proton fluences of 2.28×10^{13} and $7.39 \times 10^{13} \text{ mm}^{-2}$ were subjected to two thermal cycles determining fluorescence decay time versus temperature. A consistent increase in the temperature dependent fluorescence decay time was observed at both fluences during the second thermal cycle. The temperature dependent decay time was greater during the second thermal cycle than was measured during the first. The more heavily irradiated samples did not have annealed decay times that were as large as those that received lesser radiation fluences. This result could

mean that the annealing temperature was not reached or the sample did not stay at the elevated temperature long enough for complete annealing to take place. These discoveries provide a better understanding of 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.

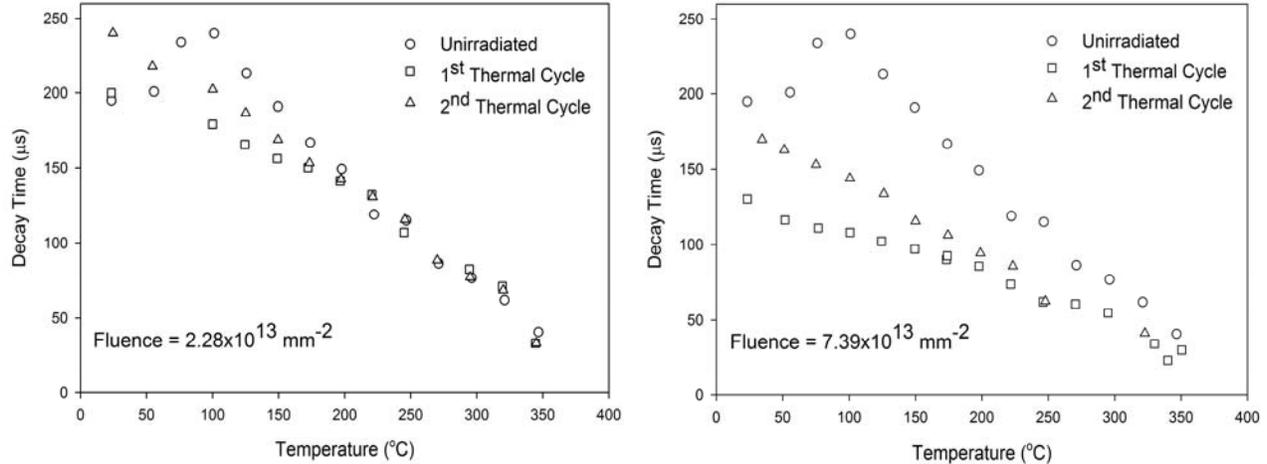


FIGURE 4. Thermal Annealing Decay Time Data Collected at Two Different 3 MeV Proton Fluences.

NOMENCLATURE

A	=	Sample irradiation area (mm ²)
e	=	Electronic charge (1.6021 x 10 ⁻¹⁹ C)
I	=	Fluorescence light intensity (arbitrary units)
I ₀	=	Initial fluorescence light intensity (arbitrary units)
n	=	Incident particle fluence (mm ⁻²)
t	=	Time since cessation of excitation source (s)
τ	=	Prompt fluorescence decay time (s)
q	=	Charge state of the incident proton (q = 1)
Q	=	Total integrated beam charge (Q)

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