Using Exotic Materials Like EuD₄TEA and MgD₄TEA to Monitor Damage and Radiation Exposure in Extreme Environments

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Space radiation poses a significant challenge to exploration missions to the Moon, Mars, and beyond. As we consider long duration space missions, the risk from radiation exposure increases. There is no simple technique that is capable of real-time radiation detection. Past research shows that the fluorescence yield and decay time are both functions of temperature and radiation fluence. Each of these parameters need to be investigated separately in order to fully understand the physical properties for any useful phosphor. Once the temperature dependencies are known, then the radiation fluence in the surrounding environment can be estimated. This paper will discuss recent research on europium and magnesium tetrakis dibenzoylmethide triethylammonium (EuD₄TEA and MgD₄TEA) that could be used to measure radiation and temperature in real time. Both of these organic materials have been shown to be sensitive to proton radiation and to changes in temperature.

Introduction

In recent years, luminescent materials have been proposed for use as smart sensors to measure structural damage and to monitor radiation fluence. To sense structural damage using triboluminescence, appropriate materials are embedded in a composite host structure for various applications, such as crew launch or exploration vehicles. When the damage occurs in the host structure, it leads to the fracture of the triboluminescent (TL) crystals resulting in light emission. This process provides a real-time warning that structural damage has occurred. The TL emission of the candidate material has to be sufficiently bright, so that the light signal reaching from the point of fracture to the detector, through a fiber optics cable, is strong enough to be detected. The majority of the known triboluminescent materials do not emit light with sufficient intensity to allow detection with compact and inexpensive detectors. Over the past 40 years, some materials have been reported with TL of sufficient intensity for the light emission to be easily observed with the naked eye. Out of these triboluminescent materials, only few could satisfy the above criterion. Europium tetrakis dibenzoylmethide triethylammonium (EuD₄TEA), one of the brightest known TL materials, is a potential candidate for application to this type of hybrid smart sensor in extreme environments (1). A related material of interest is magnesium tetrakis dibenzoylmethide triethylammonium (MgD₄TEA), which is not triboluminescent but emits a blue fluorescence when excited (2). The purpose of this paper is to present recent results in this area, emphasizing EuD₄TEA and MgD₄TEA.

Theoretical Considerations and Measurements

Ionizing Radiation Effects

Ionizing radiation in the extreme environment of space poses a significant challenge to future human and robotic exploration missions. To be used in space, any intelligent sensor material must also be resistant to ionizing radiation. Sources and types of such radiation include galactic and solar electrons and protons, x-rays, ultraviolet light, and magnetically trapped charged particles in radiation belts. While much research has been devoted to characterizing material degradation due to electron exposure, surprisingly little work seems to have been done on proton damage. Research has shown that proton bombardment in the keV to MeV range, like that occurring in space, reduces the intensity of fluorescence. Thus, proton irradiation will likely reduce the ability of a candidate smart material to emit fluorescence.

Practical space-based sensors based on luminescence will depend heavily upon research investigating the resistance of these materials to ionizing radiation and the ability to anneal or self-heal from damage caused by such radiation. In 1951, Birks and Black showed experimentally that the fluorescence efficiency of anthracene bombarded by alphas varies with total fluence (N) as

$$\frac{I}{I_0} = \frac{1}{1+AN}, \quad [1]$$

where I is the luminescence yield, I_0 is the initial luminescence yield, and A is a constant (3). The half brightness fluence ($N_{1/2}$) is a material figure of merit and is defined as the reciprocal of A . Broser and Kallmann developed a similar relationship to the Birks and Black equation for inorganic phosphors irradiated using alpha particles (4). From 1990 to the present, we have found that the Birks and Black relation describes the reduction in emission yield for every tested luminescent material except one due to proton irradiation (5-9). These results indicate that radiation produced quenching centers compete with emission centers for absorbed energy.

Fluorescence Emission Decay

Decay Time Theory. For many luminescent materials, the reduction in light intensity from the cessation of excitation can be written as:

$$I = I_0 e^{-\frac{t}{\tau}}, \quad [2]$$

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	=	Fluorescence decay time (s) (10-11).

The time needed to reduce the light intensity to e^{-1} (36.8%) of its original value is defined as the fluorescence decay time (τ). Luminescence can be divided into two groups: fluorescence and phosphorescence. Phosphorescence, also known as delayed emission, has a much longer decay lifetime than fluorescence. Typical phosphorescence lifetimes can

vary from 100 ms up to many seconds in duration, while the lifetimes of fluorescent materials usually range from 1 ns to 10 ms. More specifically, phosphorescence is the emission of light from a triplet excited state, which is where the electron in the ground state and excited state has the same spin orientation. The triplet state is due to the fact that the spin flips take more time to complete. Fluorescence occurs in singlet states, with the excited electron having the opposite spin of the paired ground state, resulting in a short emission time for photons. The fluorescence decay time is unique to each material. It might be possible to use the fluorescence decay time as an indicator to gauge the production of TL from impacts. Some materials such as ZnS:Mn,Cu have multiple decay times. Equation (2) would be valid over a limited range of times.

Past research shows that the fluorescence yield and decay time are functions of temperature and radiation fluence (5-10). Both of these parameters need to be investigated separately in order to fully understand the physical properties for any useful phosphor. Once the temperature dependencies are known, then you can estimate the radiation fluence in the surrounding environment.

The phosphor thermometry method measures the rate of decay of the fluorescence yield as a function of temperature. A small surface deposit of phosphor is excited with a pulsed light source. The resulting fluorescent decay (typically in less than 1 ms) time is measured to calculate the temperature of the substrate. In many instances, (e.g., in a continuous steel galvanneal process) a simple puff of powder onto the surface provides an adequate fluorescent signal (10-11).

Measurement Method. In 2013, Emerging Measurements Company (EMCO), developed a new instrument to measure fluorescence decay time. EMCO is a small business specializing in research and development projects in the physical, engineering, and life sciences. In fact, several colleagues at Oak Ridge National Laboratory came together to form EMCO. *LabKit* is a revolutionary research and educational instrument designed to study and characterize luminescent materials.

Figure 1 shows a picture of the exterior of the first generation EMCO *LabKit*. EMCO sold the first generation *LabKit* apparatus to UL Lafayette for \$7,500, which is 25% below the suggested retail price. The front panel of the *LabKit*, has the control and readout for the heating and cooling of the phosphor sample (left section), the photomultiplier control, including the power switch and gain adjustment (upper center section), and the control for the pulse width and repetition rate of the pulser driving the light source (just below the photomultiplier controls).

Figure 1. Picture of a display oscilloscope and the exterior of the first generation EMCO *LabKit* apparatus purchased during the early phases of this research program.

Figure 2 shows an interior view of the EMCO *LabKit*. This apparatus is designed to measure the temperature-dependent fluorescent rise and decay times as well as the total light yield. Collected data is displayed on an attached oscilloscope and can be saved for future analysis using a standard personal computer. This instrument is unique in the field as being the only turn-key method that is currently available that can measure the prompt fluorescent decay and rise times over a temperature range of -5 to 90 °C.

Figure 2. Picture of the interior of the first generation EMCO *LabKit* apparatus showing: 1) Pulsed 365nm LED light source, 2) Circuit board to provide power and control, 3) Phosphor sample holder clamped to a Peltier cooler/heater, 4) Narrow band filter and holder, 5) Photomultiplier tube detector, 6) Cooling fan, and 7) Removable panels to allow external access.

Figure 3 shows the back panel of the *LabKit*. Seen there are the main power plug for 120 VAC, on/off switch (lower center), the switch to select external or internal triggering of the light source pulser, and three BNC plugs. The upper BNC is the signal output from the photomultiplier. It is a high impedance signal that should be terminated at the recording electronics (typically, an oscilloscope). The middle BNC is the internal trigger output pulse from the light source pulser, available when the switch selects internal trigger. The lower BNC allows a pulse to trigger the light source when the switch is in the external position.

Figure 3. Picture showing the back panel of the EMCO *LabKit* apparatus showing: 8) External trigger input for LED pulser, 9) Internal trigger output from LED pulser, 10) Photomultiplier tube output, 11) Trigger source switch to select internal or external triggering of the LED pulser, and 12) On/off power switch.

Tetrakis Materials

Europium Based Phosphor

In 1966, Hurt *et al.* first synthesized EuD₄TEA, which is also known as europium tetrakis (12). EuD₄TEA is an organic material where bright red triboluminescence can be observed in daylight (1). Detailed information on synthesizing EuD₄TEA can be found in Reference (1). Pictures of some EuD₄TEA crystal samples that were synthesized using 10 to 40 mL of carrier acetone, in 5 mL increments, are shown in Figures 4(a) to 1(f) (13). Note the crystals appear to be monoclinic in shape (13). This finding is consistent with earlier research completed by L.M. Sweeting and A.L. Rheingold who showed that EuD₄TEA crystals are monoclinic (14).

Figure 4. Close-up pictures of synthesized yellow EuD₄TEA crystals using: (a) 10, (b) 15, (c) 20, (d) 30, (e) 35, and (f) 40 mL of carrier acetone. Note the crystal grain size is proportional to acetone carrier volume (4).

Initially, an attempt was made to synthesize EuD₄TEA with 5 mL of carrier acetone was attempted. However, there was not enough liquid solvent present to dissolve the europium. As a result, the amount of carrier acetone was increased slowly until everything was dissolved. It appears that the minimum amount of solvent required to synthesize EuD₄TEA using this method is 10 mL. Small grains of EuD₄TEA precipitated almost immediately when 10 mL of carrier acetone was used in this process. The crystals were light yellow in color as shown in Figure 4(a). As the quantity of carrier acetone was increased beyond 10 mL, the synthesized EuD₄TEA crystals were darker yellow in color. As shown in Figures 4(b) to 1(f), the grain size for the precipitated EuD₄TEA crystals also appears to be proportional to the volume of carrier acetone that is used in the process (13). Synthesizing larger crystals of EuD₄TEA is possible but is not probable based on the quantities of required pre-cursor chemicals.

A great quantity of research into the properties of tetrakis materials have been completed by the authors over the last decade. A small portion of this research is described in References (1), (2), and (13).

Magnesium Based Phosphor

The synthesis of MgD_4TEA was based on procedures developed in Reference (2). The process began by pouring 50 mL of 95% denatured ethanol into an Erlenmeyer flask. The ethanol was heated to boiling by setting a hot plate to 250°C , and the stirring set to maximum. Then, 4 mmol of magnesium nitrate hexahydrate was added to the hot solution. Once the magnesium salt dissolved, 13 mmol of 1,3-diphenyl-1,3-propanedione also known as dibenzoylmethane (DBM) was added to the hot solution. A funnel was then placed on top of the flask, and the solution was left for 20 minutes. Afterwards, the stirrer was removed and 14 mmol of triethylamine (TEA) was added. The solution was then kept aside to cool at ambient temperature. The MgD_4TEA crystals that formed were light yellow in color and clumpy as shown in Figure 5(a). Figure 5(b) shows a picture of synthesized MgD_4TEA illuminated by ultraviolet light.

Figure 5. Pictures of synthesized MgD_4TEA shown in: (a) Standard room light and (b) Ultraviolet light.

Figure 6 shows the resulting MgD_4TEA photoluminescent emission spectrum. The resulting broadband peak is centered in the blue at 492 nm with a FWHM of about 67 nm. MgD_4TEA exhibits a bright blue emission that is comparable in intensity to that emitted from EuD_4TEA , i.e., one of the brightest known triboluminescent materials (2). Unfortunately, MgD_4TEA did not exhibit any measurable or observable TL (2).

Figure 6. Photoluminescent spectrum showing the emission peak for synthesized MgD_4TEA is centered in the blue at 492 nm with a FWHM of about 67 nm.

Results and Conclusions

Half Brightness Fluence Measurements

In 2015-2016, the $N_{1/2}$ for EuD_4TEA irradiated with 3 MeV protons was measured to be about $3 \times 10^{10} \text{ mm}^{-2}$ (9). These measurements were collected using specialized hardware and a 5SDH-2 Pelletron accelerator located on the campus of the University of Louisiana at Lafayette (UL Lafayette) (9). ZnS:Mn compounds tested were found to have $N_{1/2}$ values for 3 MeV protons that are nearly one thousand times larger ($\sim 10^{13} \text{ mm}^{-2}$) (9). According to Tribble, a spacecraft at 1 AU from the Sun will receive a 1 MeV proton fluence of less than 10^{11} mm^{-2} from a large solar event (15). Likewise, 1 MeV proton fluences in the Earth's radiation belts and the Earth-Moon-Sun Lagrange points will be even less than the 10^{11} mm^{-2} value from large solar events (15). For this reason, EuD_4TEA might be a candidate sensor material to monitor large-scale solar events for astronauts in vehicles flying in near earth space. Since their $N_{1/2}$ values are larger, ZnS:Mn compounds are more suited for use as sensors in higher radiation environments or for very long duration space missions.

Getting reasonable $N_{1/2}$ data for MgD_4TEA from 3 MeV proton irradiation was quite difficult. When irradiated, MgD_4TEA samples were quite dim. In fact, it was difficult to measure the radioluminescence emission yield using the existing measurement hardware. No specific $N_{1/2}$ data was obtained when MgD_4TEA was irradiated with 3 MeV protons. Because of this limited success, a rough $N_{1/2}$ of between about $(6-12) \times 10^9 \text{ mm}^{-2}$ was measured for MgD_4TEA . The experimental uncertainty for this measurement was a factor of two in $N_{1/2}$, mainly because the magnitude of the radioluminescence emission yield was small. Additional research needs to be completed to better quantify these results.

Fluorescence Decay Time Measurements

Figure 7 shows an example plot of the photoluminescent light yield (intensity) as a function of time for sample lot 476 of an undoped MgD_4TEA sample. This data was collected using the EMCO LabKit at a temperature of 19.9°C . MATLAB was used to calculate the prompt fluorescence decay time using the form of Equation (1). The measured decay time for this sample was $155.7 \mu\text{s}$ with an estimated uncertainty of 5%. The *LabKit* was used to measure the photoluminescent light yield as a function of time and temperature for the remaining samples.

Figure 7. Plot of the PL light yield as a function of time for sample lot 476 of an undoped MgD_4TEA .

Figure 8 shows a plot of the photoluminescent light yields as a function of time for sample lot 476 of the undoped MgD₄TEA measured at 2.7, 25.0, and 111.3 °C. This data was collected using the EMCO *LabKit*. The measured decay times at 2.7 and 25 °C are both about 160 μs with an estimated uncertainty of 5%. The measured decay time at 111.3 °C was difficult to measure since the light yield was small. The results from Figure 7 indicate that the fluorescence emission yield from undoped MgD₄TEA decreases as a function of temperature. Additional research will be completed to fully understand this phenomenon.

Figure 8. Plot of the photoluminescent light yield versus time for the undoped lot 476 MgD₄TEA sample measured with *LabKit* at 2.7, 25.0, and 111.3 °C.

The Cajun Advanced Picosatellite Experiment (CAPE) is a non-profit organization that develops and builds small satellites along with a host of small aerospace related systems such as high-altitude balloons and sensor buoys. CAPE is associated with the college of Engineering at UL Lafayette and has already launched successful CubeSats in 2007 and 2013. In October 2018, the CAPE-3 satellite will be launched. This 1U CubeSat will orbit the Earth carrying an innovative first-generation sensor to monitor radiation fluence and a student designed and built Geiger counter. This flight experiment is a natural outgrowth of earlier ground-based radiation exposure measurements that will be used to determine if EuD₄TEA-based materials can be used as a real-time structural damage and/or radiation sensor for applications in space or other extreme environments. The secondary mission for CAPE-3 is to take pictures of the Earth using active attitude control for stabilization, as well as getting K-12 schools interested in space science.

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