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Triboluminescent Materials for Smart Optical Damage Sensors for Space Applications

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LIST OF ACRONYMS

GLOW	gross lift-off weight
MSFC	Marshall Space Flight Center
RF	radio frequency
RFID	radio frequency identification
SSTO	single stage to orbit
TL	triboluminescent
TM	technical memorandum

NOMENCLATURE

Ar	argon
CaF_2	calcium fluorite
ΔT	time difference obtained by subtracting Universal Time from Terrestrial Time
Eu^{3+}	europium ion
EuD_4TEA	europium tetrakis (dibenzoylmethide) triethylammonium
nm	nanometer
ZnS	sphalerite

TECHNICAL MEMORANDUM

TRIBOLUMINESCENT MATERIALS FOR SMART OPTICAL DAMAGE SENSORS FOR SPACE APPLICATIONS

1. INTRODUCTION

Future space applications will be using more and more composite material, and the need will arise to tackle the problem of structural health monitoring. The domain of structural health monitoring systems is rapidly expanding beyond the typical sensing elements that glue to the surface or attach externally in some other manner. These older techniques have several draw backs, not the least of which is the cable harness needed to provide power and to route the signals away from the area being monitored. Fortunately, technology has progressed in the area of wireless sensing sufficiently that one may now talk intelligently about monitoring the state of health of a structural element with no strings attached. There are basically two types of applications when it comes to monitoring structural health. One is the solid metal elements, such as bolts, struts, etc., which are so widely used today and for which the older technology of wired, glued on, or bolted on sensors are in broad use. However, these are not the concern of this paper. The tougher and more pressing issue is how to discern internal debonds and/or delaminations in composite structures, such as cryogenic fuel tanks for a space vehicle or other lightweight composite structural applications. The real payoff for wireless sensors will come when it is possible to monitor a large expanse of a composite cryogenic fuel or oxidizer tank, such as liquid hydrogen or liquid oxygen. There is a need for a monitoring system that would detect debonds and/or delaminations at the threshold of critical flaw length and to do it with no wiring harness, either for power or signal. This is the subject to be addressed in part by this technical memorandum (TM).

2. THE PROMISE AND THE PROBLEM WITH COMPOSITES

Although lightweight and relatively strong, the composite structure is intrinsically vulnerable to high ΔT thermal cycling involved in cryogenic tanking and detanking in preparation for the launch of a space transportation vehicle using these lighter weight composite tanks. The ratio of fuel weight in a space launch vehicle compared to the weight of the rest of the entire vehicle (including payload) is known as the "mass fraction." For a single stage to orbit (SSTO), this fraction needs to be close to 90%. With only 10% of the gross lift-off weight (GLOW) allocated to all structures, payload, and other physical systems, lightweight is essential, and composites are mandated. Experience to date with composites shows a very high strength-to-weight ratio; however, little is known about the survivability of a composite structure in a high ΔT thermal cycle environment. It is believed that failures in this environment will be manifested mainly in the form of debonds within the joints and/or in delaminations of the primary composite material itself. For solid structures, there are well known and widely used techniques to determine structural state of health.

One of the more commonly used techniques is that of removing inspection plates and performing dye-penetrate and magnified visual inspections of critical, high stress structural elements. Whereas this is relatively effective and does reveal microcracks indicative of excessive structural stress, it is nonetheless intrusive, laborious, and expensive. Similar techniques for discerning debond and/or delaminations in composites are not possible because they are internal and not visible even under magnification. X-ray examination of smaller composite parts is possible, but likewise intrusive, laborious, and expensive. Therefore, a need exists for sensing techniques that can be embedded along with the lay-up of the composite materials when the structure is fabricated that will be capable of detecting debonds and/or delaminations, will be easily and inexpensively installed, and will be capable of interrogation in a nonintrusive manner. One such sensing capability is offered in the form of embedded specialized triboluminescent (TL) materials described in this TM.

In the present TM, we present our results of the study of this type of TL materials and perform a proof-of-concept study to utilize them in fabricating smart optical damage sensors capable of real-time detection of both the magnitude and location of damage in composite structures, particularly in space applications.

Essentially, a luminescent material is a phosphor that converts certain type of energy into electromagnetic (EM) radiation. Many types of energy can excite luminescence. Photoluminescence is excited by EM (often ultraviolet) radiation, cathodoluminescence by a beam of energetic electrons, electroluminescence by an electric voltage, chemiluminescence by the energy of a chemical reaction, and triboluminescence by mechanical energy.

In recent years, TL materials have been proposed as smart sensors of structural damage.[1–6] To sense damage, these materials are embedded in a composite host structure for various applications, such as crew launch vehicles and crew exploration vehicles. When the damage/fracture occurs in the host composite structure, it will lead to the fracture of the TL crystals resulting in a light emission. This will warn in real time that a structural damage has occurred. The TL emission of the candidate phosphor 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 sufficiently strong to be detected. The majority of the known TL 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 that triboluminesce with sufficient intensity for the light emission to be easily observed with the naked eye.[7–8] Out of these TL materials, only few could satisfy the above criterion. Europium tetrakis (dibenzoylmethide) triethylammonium (EuD_4TEA), one of the brightest TL phosphors, is a potential candidate for application to this type of damage sensor.

TL materials possess the property of fracture induced light emission. TL materials produce luminescence due to the creation of new charged surfaces during the fracture of a solid. Its other names are fracto-,[9] piezo-,[10] and mechanoluminescence.[11] This phenomenon can be demonstrated readily by crushing crystalline sugar in a darkened room; after their eyes have adjusted to the darkness, observers will detect the resulting bluish-white light.[12] This triboluminescence phenomenon—defined as the light emitted when a material is stressed to the point of fracture—has been known since the sixteenth century, although serious investigations of the phenomenon were only begun in the 20th century.[13]

A large number of organic and inorganic materials are known to exhibit triboluminescence.[8,13,15] This phenomena occurs more frequently in crystals whose structure lacks a center of symmetry. This fact points to the piezoelectric origin of the phenomenon. Recent studies attempted to establish a relation between crystal structure and triboluminescence.[16] They reported that noncentrosymmetric crystal structure is necessary, but not sufficient, for TL materials. However, the exact physical mechanism that is responsible for the emission of light during mechanical fracture is not fully understood.

There is a large number of materials that show this property only in a small range of environmental conditions of low temperature and gas pressure. Stranski, et al.[14] investigated some 1700 organic and inorganic substances and found 356 to exhibit triboluminescence. This property is exhibited by materials such as calcium fluorite (CaF_2), sphalerite (ZnS), and wintergreen Life Savers™. Special impact mechanisms and complete darkness are required to observe the TL emission from these materials. We have explored some materials that can emit an intense visible light at room temperature.

A TL material embedded in or attached onto a composite structure could act as a real-time damage sensor.[1] Since the triboluminescence light emission is fracture-initiated, no signal would be generated by a TL sensor until damage occurred. An array of TL sensors may allow real-time damage location monitoring simply by determining the wavelength of the emitted light.

In our laboratory, synthesis of a europium complex has been carried out by reacting anhydrous europium chloride with dibenzoylmethane and triethylamine in ethyl alcohol. This complex shows intense triboluminescence, which has also been verified in our laboratory. We plan to investigate if similar complexes can be formed using other trivalent rare earth ions, such as terbium and other ion complexes.

Attempts are being made on an international level to use this phenomenon to obtain information about the basic physical processes taking place in the material and to apply this phenomenon to develop sensor devices to monitor stress and damage within the structure of/composites in real time applications. Currently, there are no simple sensing techniques for determining in real time both the location and magnitude of structural damage in a composite caused by a dynamic impact event. Such a sensor, were it available, could act as a sensor for real-time information to the user on the health and safety condition of the structure.

3. REQUIREMENTS FOR TRIBOLUMINESCENT OPTICAL DAMAGE SENSORS

It is worthwhile to identify the specific prerequisite properties of the TL materials needed to fabricate a successful optical damage sensor.

The main requirements for any candidate TL material that may be used for smart optical sensors are as follows:

(1) It should be highly efficient (allowing detection using inexpensive, compact detectors) and that it should emit light over a discrete, and thus characteristic, wavelength range (allowing integration into an array of sensors to monitor damage location).

(2) The TL light must be emitted only upon crystalline fracture and that the sensors may be embedded within or attached to a composite.

(3) The TL material should have a melting point greater than the cure temperature of the composite (>120 °C) to maintain the required TL particle size distribution and that the material be chemically compatible with the composite resin.

(4) Desirable smart optical sensor TL materials should generate no false alarms. This is to say that the sensor must only yield a signal when the damage has actually occurred. Also magnitude of the sensor output must be indicative of the extent of damage.

Based on the above requirements, an effort was made at Alabama A&M University (AAMU) to develop new and improved TL materials that could act as optical damage sensors. Since no light is emitted until the crystalline TL material has actually fractured, no false alarm would be generated. For a luminescent sensor embedded in or attached to a composite structure, fracture of the TL material would be induced by composite damage. The magnitude of the TL intensity will be directly related to the degree of fracture or the extent of the damage in the composite.[17] Thus, a TL sensor could yield a signal not only when damage has occurred, but additionally and simultaneously give information on the degree of damage.

4. CHARACTERIZATION OF EuD$_4$TEA TRIBOLUMINESCENT MATERIAL

To demonstrate the use of TL materials as smart optical damage sensors we have to perform the following experiments and give proof of concept:

(1) Prove that light is only emitted upon fracture, which would mean that TL damage sensors will only emit light when damage has actually occurred.

(2) Prove that the relationship exists between the applied impact energy (thus damage) and the resulting TL intensity.

(3) Demonstrate that the material can be put in an epoxy or composite and still retain its TL properties.

Initially, these materials were developed at AAMU in collaboration with scientists from Naval Surface Warfare Center; preliminary synthesis was successfully accomplished, and properties were measured at Alabama A&M University. The future plan is to further improve these materials by embedding these materials in composites and test them in practical applications useful for Department of Defense and NASA space applications.

The triboluminescence emission spectrum of TL material EuD$_4$TEA is shown in Fig. 1. The dominant emission in triboluminescence peaks about 614 nm, which is responsible for the orange red color. Minor emission peaks are seen between 575-590 nm, at 650 nm, and at 700 nm. A minor peak below 550 nm observed in freshly prepared samples was not seen in the samples stored for six months. This may be due to some impurity that evaporated with time as product dries further.

The observed peaks in the TL spectrum can be attributed to the emission from the Eu^{3+} ion. This correlation was obtained by examining the photoluminescence spectrum of EuD$_4$TEA excited by 363 nm line of an argon (Ar) ion laser. The main emission peak in photoluminescence occurs at 609.5 nm and other peaks are seen at 576.5 nm, 589 nm, 649 nm, and 700 nm. The most intense peak matches with our clearly observed orange red color and is close to the spectrum peak of 614 nm.

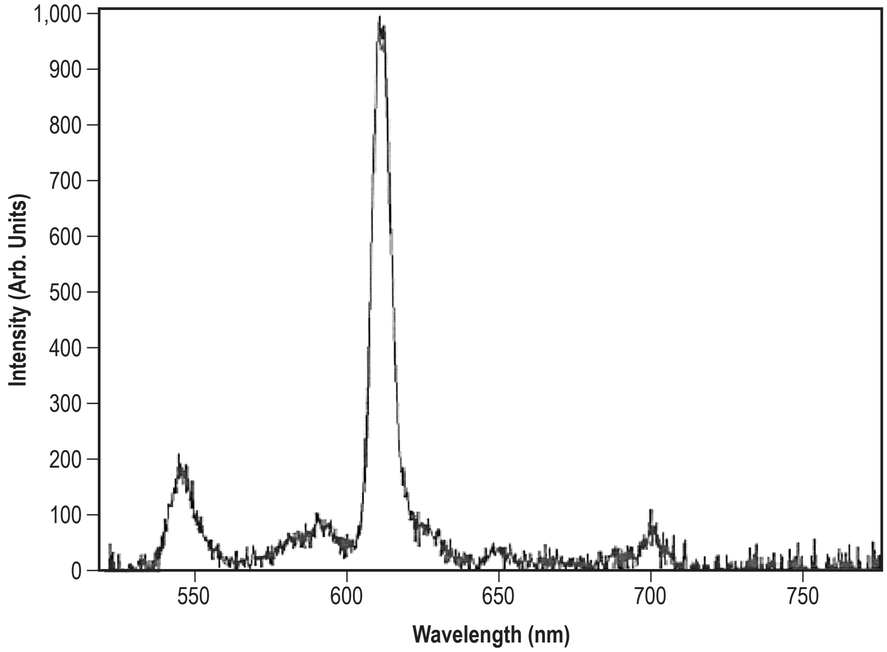

Figure 1. Triboluminescence spectrum of EuD_4TEA.

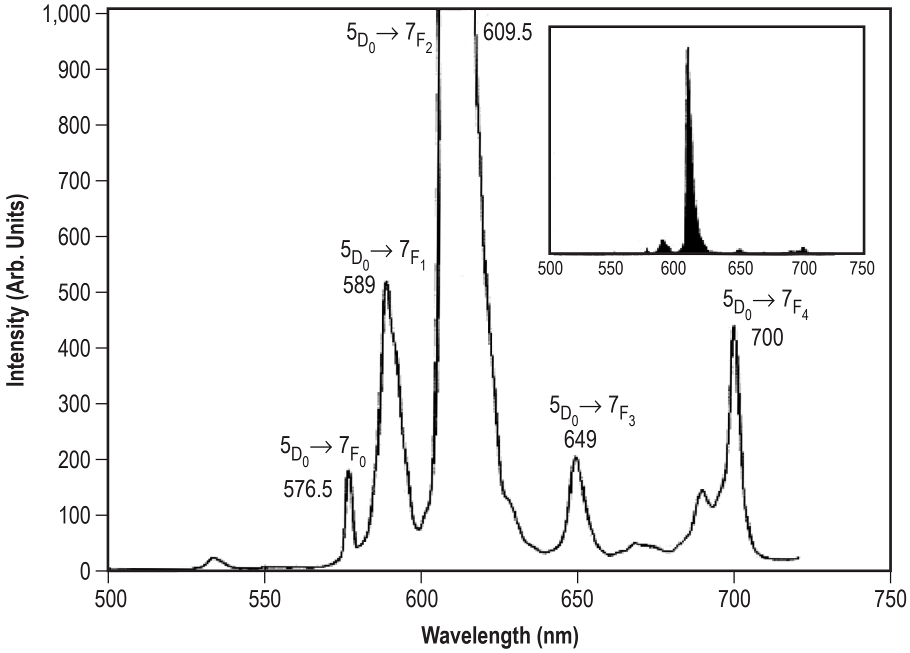

Figure 2. Photoluminescence of EuD_4TEA excited by 363 nm line of Ar ion laser.

In summary, EuD_4TEA exhibits strong triboluminescence, which makes it a potential candidate for use in a sensor to detect a fracture in real time in a composite structure for space applications.

These sensors can be made wireless with the use fiber optics, photodetectors, and radio frequency (RF) as transmission medium. Essentially, radio frequency identification (RFID) technology can be utilized, which is an automatic identification method, relying on storing and remotely retrieving data using RFID transponders. An RFID tag can be incorporated into the sensor for the purpose of identification using radio waves. Chip-based RFID tags contain silicon chips and antennas. Passive tags require no internal power source, whereas active tags require a power source. Active tags are typically more reliable, transmit at higher power levels and are more effective in RF-challenged environments, like water, metal (vehicles), or at longer distances. These active RFID tags have the potential to function as low cost remote sensors that broadcast relevant data back to the desired base station. Application of tagometry data could include embedded triboluminescence sensor data in the composite structure.

5. WHAT A SYSTEM WOULD LOOK LIKE AND HOW IT WOULD WORK

The huge advantage of a fully embedded structural health-monitoring system is that one could discern the structural state of health with only a minor weight increase. Due to inherent system properties, the TL sensor system will sense the nature and magnitude of structural damage as the damage occurs in real time and will send out the damage level information. The “fingerprint” of the received data would need to be correlated to known damage levels in order to determine the specific structural state of health. Comparison of the real-time data can be compared to that of known damage levels in ground-based systems if desired or, for more sophisticated systems, these may be placed in space along with the rest of the structure being monitored. This is especially true of Lunar based systems.

Clearly, one cannot embed a sensor element in a composite structural element without some means of communication and interrogation. This is where the wireless attribute becomes valuable. As stated earlier, a bundle of wires needed to power and interrogate an array of sensors would be awkward at best and totally unacceptable at worst. However, with advancements in microcomputers and micro-communications, it is potentially feasible to incorporate all structural integrity sensing and computational capability totally within the structure, so that no external wiring is involved. This would constitute a truly “smart” structure, capable of self-diagnostics and with no wiring to external entities (no strings attached). Normally, this type system is totally passive. However, if a small amount of electrical energy is required, this could be provided by a small, minimally intrusive source, such as a nuclear beta cell of some type or energy-scavenging device. The algorithm to convert received signals from the sensing elements into an intelligent understanding of the nature and magnitude of structural damage could be accomplished via a small, embedded CPU chip, along with internal printed-circuits for the signal flow paths. The readout to the outside world must then be radiated via micro transmitters/antenna units also embedded within the structure. The electrical energy requirement could be very small, since power would be required only when a structurally damaging event is in progress. Also, the radiated output would not need to be great, because of the close proximity of the interrogation units.

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13. ABSTRACT *(Maximum 200 words)*

There is a need to develop a new technique of damage detection for composites, which could detect cracking or delamination from any desired location within a material structure in real time. Recently, triboluminnescent materials have been proposed as smart sensors of structural damage. To sense the damage, these materials can be epoxy bonded, coated in a polymer matrix, or embedded in a composite host structure. When the damage or fracture takes place in the host structure, the resultant fracture of triboluminescent crystals creates a light emission. This will warn in real time that structural damage has occurred. The triboluminescent emission of the candidate phosphor has to be bright enough that the light reaching from the point of fracture to the detector through a fiber optic cable is detectable. There are a large number of triboluminescent materials, but few satisfy the above criterion. The authors have synthesized an organic material known as Europium tetrakis (dibenzoylmethide) triethylammonium (EuD4TEA), which is a potential candidate for application as a damage sensor and could be made into a wireless sensor with the addition of microchip, antenna, and electronics. Preliminary results on the synthesis and characterization of this material are presented.

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