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Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Effects of added dibutyl phosphate on the luminescent properties of europium tetrakis dibenzoylmethide triethylammonium

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ARTICLE INFO

Article history:

Received 1 February 2014

Received in revised form

11 October 2014

Accepted 13 October 2014

Available online 22 October 2014

Keywords:

Triboluminescence

Mechanoluminescence

Fractoluminescence

EuD₄TEA

ABSTRACT

Since 2003, the authors have been pushing the boundaries on a special type of functional material, i.e., a material that gives off light when it is stressed, strained, and/or fractured. This unique class of materials has been proposed for the active element of impact sensors, earthquake detectors, and stress sensors. However, in order for this concept to go from the lab to real world applications, the light emission from these functional materials must be bright such that inexpensive light detectors can be used. One of the brightest materials found thus far is europium tetrakis dibenzoylmethide triethylammonium (EuD₄TEA). This material has an emission so bright that it can be observed in daylight. In 2013, the authors discovered that the addition of dimethyl methylphosphonate (DMMP) increased the light emission two fold. As a result, a search for similar compounds was conducted to determine if the emission can be increased further. This paper explores the effects of dibutyl phosphate (DBP) on EuD₄TEA. The effects of DBP on the triboluminescence, photoluminescence, and crystal structure of EuD₄TEA will be determined. This paper will show that DBP has an even greater effect on the properties of EuD₄TEA than DMMP.

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1. Introduction

Functional materials are those whose physical and chemical properties are sensitive to a change in the environment such as temperature, pressure, electric field, magnetic field, optical wavelength, quantity of absorbed gas molecules, and pH [1]. Optical materials can be defined as materials whose function is to alter or control electromagnetic radiation in the ultraviolet, visible, or infrared spectral regions [2]. Such materials can be fabricated into optical elements including lenses, mirrors, windows, prisms, polarizers, detectors, and modulators [2]. Moreover, optical materials can be used to refract, reflect, transmit, disperse, polarize, detect, and transform light [2].

Generally speaking, a phosphor is a substance that emits luminescence that is not caused by incandescence. The word phosphor comes from Greek meaning light bearer [3]. Phosphors are able to emit light owing to the excitation of electrons that are caused by the absorption of energy from an external source such as another electron, photon, or electric field [3]. An excited electron occupies a quantum state whose energy is higher than

the ground state, i.e., minimum energy state [3]. In semiconductors and insulators, the electronic ground state is usually referred to the state that has the electrons at the ground level. Conversely, the state that has the electrons in the excited state is often referred to as the conduction band. These two states, i.e., the conduction and valence bands, are separated by an energy gap known as the band gap [3]. Thus, small continuous changes in the electron energy in the band are not possible, which is contradictory to metals. Instead a minimum energy that is equal to the band gap is required to excite an electron in a semiconductor or insulator. Moreover, the energy released by the de-excitation is nearly always equal to the band gap [3]. In fact, the band gap of a semiconductor material is such that at room temperature very few electrons are able to jump from the valence band to the conduction band thereby leaving holes in the valence band [3].

There are several approaches or methods that are capable of providing the required energy to excite valence electrons into the conduction band. The most common methods along with their process of excitation are shown in Table 1.

Let us consider the case of photoluminescence (PL). When a phosphor absorbs electromagnetic radiation, i.e., a photon, an electron may be excited to a higher energy quantum state by a radiating photon. If the excited electron returns or relaxes to a lower energy quantum state by a radiating photon, the process is known as PL [3–6]. However, some of the quantum state relaxation

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Table 1
Common luminescent methods with their process of excitation [3–6].

Method	Process of excitation
Photoluminescence (PL)	Absorption of light
Electroluminescence (EL)	Electric field
Cathodoluminescence (CL)	Electron beam
Radioluminescence (RL)	Ionizing radiation
Mechanoluminescence (ML)	Mechanical action (e.g., stress, strain, breaking)
Chemiluminescence (CL)	Chemical reaction
Sonoluminescence (SL)	Acoustic cavitation
Thermoluminescence (ThL)	Heat

transitions are not allowed. The allowed transitions are based on the spin and *Laporte* selection rules [3,6]. The photoluminescent intensity depends on the temperature and energy of the exciting source [3]. It should be noted that in general the intensity of the excitation spectrum is higher than that of the emission spectrum [3].

This paper will focus on the luminescence induced by any mechanical action on solids, which is known as mechanoluminescence (ML) [7]. ML can generally be divided into two categories: (1) light emitted during elastic and plastic strain, which is known as deformation luminescence (DL), and (2) light emitted during fracture, which is known as triboluminescence (TL) [7]. The mechanoluminescent intensity depends on a large number of factors, including stress, strain, strain rate, pressing rate, temperature, atmospheric pressure, dielectric constant, mobility, particle/crystal, sample mass, trap-depth, piezoelectric constant, trap concentration, radiation fluence, dopant type and concentration, sample firing temperature, sample sintering temperature, sample annealing temperature, firing time, sintering time, charge carrier capture cross-section, number of successive pressings, efficiency for the conversion of mechanical energy into light energy, crystal-structure, crystallographic direction, piezoelectric constant, dislocation density, area of newly created surfaces, dislocation charge, sample hardness, and sample age [8]. As a result, the exact cause of ML is unknown [7]. Despite this limitation, great progress has been made to increase our understanding of ML [7]. However, since 1888, several facts have been discovered [7]:

- TL occurs more often in crystals lacking a center of symmetry [7,9–11].
- If a compound is optically active and one of the isomers emits TL, the other one may not be triboluminescent [7,12].
- With certain compounds, the TL activity may diminish a few weeks or months after the crystals have been grown. Some common examples of these phenomena are arsenic trioxide [7] hexaphenylcarbodiphosphorane [13], and triphenylphosphine [14].
- The triboluminescent intensity is dependent upon the crystallization conditions [7,15].
- For every material, there exists a minimum crystal size that does not produce TL [7,15,16].
- Elements by themselves are not triboluminescent [7,15].
- TL can originate from the dielectric breakdown of the surrounding gas during fracture [7,17–20].

Recently, it has been suggested that triboluminescent materials be placed in composites to detect structural damage [7,21–24]. Because composites tend to be strong, stiff, and lightweight, they are being applied to aircraft, spacecraft, and even high performance cars. Typically composites are constructed from layers of epoxy resin reinforced with carbon fibers that are made into panels. One problem with this is that these panels are prone to deformation or fracture upon heavy impact. In addition, the damage caused is not always visible from the exterior surface if

the panels spring back into its original shape. Thus, even if there is no visible damage, the strength of the composite may be greatly reduced. As a result, serious safety issues can arise. The current methods for monitoring damage detection include acoustic based methods, electro-imaging, ground penetrating radar, radiography, and fiber optics methods [21]. However, none of these methods provide in-situ and distributive sensing. In addition, current methods require large downtimes to inspect the structure [21]. Due to location and types of structures, the current methods are quickly becoming insufficient or impossible to conduct.

Triboluminescent based sensors should be able to overcome all of these challenges and provide wireless, in-situ, and distributed sensing with real time continuous monitoring [21]. If these sensors are to be reality, however, they must be inexpensive and easy to integrate. One current challenge with triboluminescent sensors is that most triboluminescent materials are not very bright. In 1966, Hurt et al. synthesized a material that is bright enough to be easily seen in daylight [25]. This material is known as europium tetrakis dibenzoylmethide triethylammonium (EuD_4TEA). This material with modified synthesis discovered by the authors in 2011 has 206% triboluminescent yield than the more commonly known inorganic manganese-doped zinc sulfide (ZnS:Mn) [26–31]. Recently, the authors have been investigating the effects of additives on the TL of EuD_4TEA . Their studies have determined that the best additive to date for EuD_4TEA is dimethyl methylphosphonate (DMMP). This additive increased the TL by nearly 200%, i. e., it had a triboluminescent yield of 300% to the pure version of EuD_4TEA [32].

Due to the success of DMMP, we decided to investigate dibutyl phosphate (DBP) as a possible additive because DBP is similar to DMMP. DBP is a pale-amber colorless medium strong acid that is used as a catalyst in organic synthesis [33–35]. However, DBP can be a dangerous material since it reacts with strong oxidizers and attacks many metals forming flammable and explosive hydrogen gas [34,35]. DBP also reacts with the moisture in the air by releasing acid fumes due to the formation of phosphoric acid with water [34]. As a result, it is often used as a catalyst in the manufacture of phenolic and urea resins and in the separation and extraction of metals [33,34]. This paper investigates the effects of DBP on the crystal structure, PL, and TL of EuD_4TEA .

2. Experimental methods

2.1. Synthesis of materials

The synthesis of EuD_4TEA with added DBP was based on procedures used in Ref. [27]. The process began by pouring 25 mL of reagent grade anhydrous denatured ethanol (Sigma-Aldrich, 277649) into an Erlenmeyer flask. The desired amount of DBP, which ranged from 0 to 5 mL, was then added to the ethanol. The DBP and ethanol mixture was then heated on a hotplate. Afterwards, 4 mmol of europium (III) nitrate hexahydrate was added to the hot solution. This addition caused the solution to turn from clear to white. Once the solution became clear again, 13 mmol of 1,3-diphenyl-1,3-propanedione also known as dibenzoylmethane (DBM) was added. Finally, once the DBM was dissolved, 14 mmol of triethylamine (TEA) was added. The solution was then kept aside to cool at ambient temperature. The pure EuD_4TEA powder that formed were light yellow in color and very sparkly as shown in Fig. 1(a). It should be noted that violent reactions occur when DBP is mixed with bases, amines, and amides. As such, the mixing order is vital to avoid such reactions.

For small concentrations of DBP (≤ 0.5 mL), the final EuD_4TEA product looked and behaved like the pure material, i.e., a fluffy sparkly light yellow powder, as shown in Fig. 1(a). However, when

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