

Effects of crystallite grain size on the triboluminescent emission for EuD₄TEA

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ABSTRACT

One of the brightest tested triboluminescent materials is europium dibenzoylmethide triethylammonium (EuD₄TEA). In 2011, the authors discovered that synthesizing EuD₄TEA using europium nitrate instead of chloride significantly increased the triboluminescence yield. In 2012, the authors discovered that anhydrous ethanol is not the best solvent to be used for synthesizing EuD₄TEA. The less expensive acetone increases the triboluminescence and makes the synthesis much easier. However, no study has ever been done on how increasing the crystal size of EuD₄TEA changes its triboluminescence. This paper reports the effect of increasing crystal size on the triboluminescence of EuD₄TEA. The results indicate that acetone can be used to successfully control the grain size of EuD₄TEA and thus increase the amount of triboluminescence emitted. The normalized TL yield is seen to be directly proportional to the square of the average grain size. The fluorescence decay time remains unchanged with an average value of $534.5 \pm 7.3 \mu\text{s}$, with no change in the emission properties of EuD₄TEA. Copyright © 2013 VBRI press.

Keywords: Triboluminescence; mechanoluminescence; europium dibenzoylmethide triethylammonium; EuD₄TEA; europium tetrakis.



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Introduction

If a person is old enough, they can remember observing a small flash of light when chewing real Wint-O-Green Lifesavers® in a darkened room [1, 2]. The emission spectrum for Wint-O-Green Lifesavers® shows a 400 - 500 nm broadband emission from methyl salicylate in the oil of wintergreen [1, 2]. In addition, nitrogen lines due to sparking occur near 350 nm [1, 2]. It should be noted that modern Wint-O-Green® Lifesavers use synthetic chemicals to flavor the candy. As a result, TL is not observed in today's Wint-O-Green® Lifesavers or similar candies.

Other similar materials that demonstrate this unique property are saccharin, tartaric acid crystals, rock salt, glass, and ice [3]. In 1888, Wiedemann and Schmidt called the source of this fascinating light triboluminescence (TL) [3]. Today, TL is defined as light emission resulting from material fracture and is observed in approximately 30% of known organic and in 50% of inorganic crystals [1–5].

One of the brightest triboluminescent materials found to date is europium dibenzoylmethide triethylammonium (EuD_4TEA). In 1966, Hurt *et. al.* synthesized the first EuD_4TEA sample where TL was visible in daylight [6]. However, Hurt's method required the use of anhydrous ethanol and europium chloride as precursors. As a result, the final synthesized EuD_4TEA had to be repeatedly washed to remove the chloride ions that quench the TL [6–8]. Further, repeated washings with alcohol reduced the amount of pure EuD_4TEA obtained after purification. In an effort to increase the yield and minimize purification steps, the authors replaced the europium chloride with europium nitrate hydrate [7]. As a result, the triboluminescent emission yield increased 82% [7,8].

Later, it was decided to see if differences in carrier solvent affected the amount of TL produced by the synthesized EuD_4TEA [8]. Results showed that EuD_4TEA in crystalline form synthesized with lab grade acetone emitted approximately 25% more TL than similar material produced using anhydrous ethanol [8]. This result not only made the synthesis process much cheaper, but also easier due to sample heating being eliminated [8]. In addition, it was found that the solid crystals produced using an acetone carrier produced approximately 110% more TL compared to the EuD_4TEA synthesized from anhydrous ethanol solvent.[8] It appears that the triboluminescent emission yield is proportional to crystal size [8]. This paper will determine the effects of grain size on the triboluminescent emission yield for EuD_4TEA .

Experimental

Materials

Europium nitrate (99.999%) was purchased from Metall Rare Earth, Limited and used without any further purification. Acetone (laboratory reagent, $\geq 99.5\%$), 1,3-diphenyl-1,3-propanedione (98%), and triethylamine ($\geq 99.5\%$) were procured from Sigma Aldrich and used without any further purification.

Synthesis of EuD_4TEA

The synthesis of EuD_4TEA was based on the method described in Reference [7]. The synthesis of EuD_4TEA

involved the dissolution of 4 mmol of europium nitrate hydrate in laboratory grade acetone purchased from Sigma Aldrich [7, 8]. To this solution, 13 mmol of 1,3-diphenyl-1,3-propanedione also known as dibenzoylmethane (DBM) was added, followed by the addition of 14 mmol of triethylamine (TEA). The solution was left overnight at ambient temperature to precipitate the crystals. The synthesized EuD_4TEA crystals were collected under suction [7]. Pictures of the resulting EuD_4TEA crystal samples that were synthesized using 10 to 40 mL of carrier acetone, in 5 mL increments, are shown in Figs. 1(a) to 1(f). Note the crystals appear to be monoclinic in shape. This finding is consistent with earlier research results as reported by L.M. Sweeting and A.L. Rheingold [9].

Initially, an attempt was made to synthesize EuD_4TEA with 5 mL of carrier acetone. However, there was not enough liquid solvent present to dissolve the europium and DBM. 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 EuD_4TEA using this method is 10 mL. Small grains of EuD_4TEA precipitated almost immediately when 10 mL of carrier acetone was used in this process. The crystals were light yellow in color as shown in Fig. 1(a). As the quantity of carrier acetone was increased beyond 10 mL, the synthesized EuD_4TEA crystals were darker yellow in color. As shown in Fig. 1(b-f), the grain size for the precipitated EuD_4TEA crystals also appears to be proportional to the volume of carrier acetone that is used in the process. Synthesizing larger crystals of EuD_4TEA is possible, but is not probable based on the quantities of required pre-cursor chemicals.

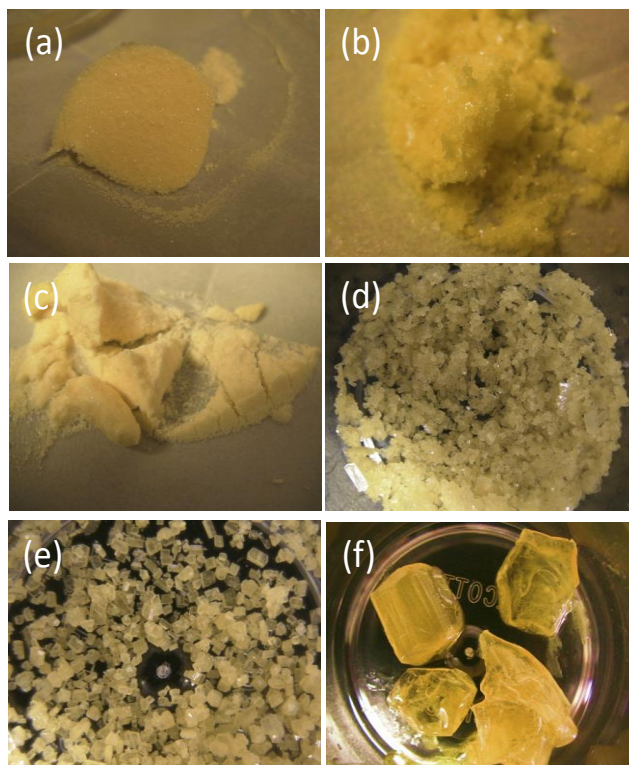


Fig. 1. Close-up pictures of synthesized yellow EuD_4TEA crystals using: (a) 10, (b) 15, (c) 20, (d) 30, (e) 35, and (f) 40 mL of carrier acetone. Note the crystal grain size is proportional to acetone carrier volume.

Low energy triboluminescent test

Once the EuD₄TEA crystals were completely dried, they were placed in a clear round wide-mouth jar for storage. Using a custom-built drop tower, the triboluminescent emission yield was measured for the synthesized EuD₄TEA samples. Specific design and operational information on the constructed drop tower can be found in References [10] and [11]. The measurement began by placing 0.03 g of a sample powder on a plexiglass plate. A 130 g steel ball is positioned 1.1 meters above the pile of sample powder. When the ball is released, its impact with the EuD₄TEA crystals produces TL that is measured using a United Detector photodiode positioned 2.25 cm below the sample. The corresponding detector signal generated during an impact is adjusted using a Melles Griot large dynamic range linear amplifier set to a gain of 200 μ A. The TL signal from an impact is recorded using a Tektronix 2024B oscilloscope in single sequence mode with a 0.5 second measurement time. Once the signal is acquired, it is analyzed using custom LabVIEW program that integrates the area under the curve and calculates the decay time for the particular emission [10,11]. For many luminescent materials, the reduction in light intensity from the cessation of excitation can be written as:

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

Where,

I=Fluorescence light intensity (arbitrary units),
 I₀=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 (1) would be valid over a limited range of times.

Results and discussion

The main advantage of using acetone instead of ethanol during the synthesis process was that the crystal size could be easily controlled. Both DBM and europium nitrate are

highly soluble in acetone and require no heating. As a result, the crystal size could be easily controlled by varying the amount of acetone. The smaller amount of acetone produced a very quick precipitation due to the solution being super saturated. However, as the amount of acetone was increased in 5 mL increments, the precipitation slowed due to the time needed for super saturation to take place. As a result, the crystals had more time to form and thus became larger. This is likely the greatest advantage to this method as no other dopants are introduced into the crystal matrix as compared to other methods such as the solid state method of creating manganese doped zinc sulfide that introduces oxygen dopants as the firing time is increased to create larger crystals.

In order to better determine the effect of crystal size on TL yield, the assorted EuD₄TEA samples were sifted using 120, 80, 60, 45, 35, and 25 U.S. standard mesh sieves [12]. Table 1 shows the relationship between U.S. standard sieve number and the mesh opening size expressed both in inches and millimeters. For example, a crystal that has a maximum size of 0.30 mm would pass through a number 45 U.S. standard mesh sieve (0.355 mm opening size), but would be caught and not passed through a number 60 standard mesh sieve (0.250 mm). Based on earlier research [9], it is likely the crystal structure for these EuD₄TEA samples is monoclinic. Therefore, the maximum "grain size" that would pass through a sieve opening is likely equivalent to a "body diagonal" for the monoclinic system and would be somewhat larger than the actual crystallographic dimensions for the EuD₄TEA samples.

After all the samples were synthesized, the resulting EuD₄TEA crystallites of different sizes were mixed together and the entire sample was sifted using the number 25 sieve. This process caused all EuD₄TEA crystallites smaller than 0.710 mm to pass through the number 25 sieve and into a clean container. The crystallites larger than 0.710 mm were left on the sieve and were removed. The pass-through crystallites were then sifted again with the number 35 sieve, causing the particles smaller than 0.500 mm to be separated. Particles with sizes larger than 0.500 mm and smaller than 0.710 mm were left on the number 35 sieve. This process was repeated for the rest of the sieves shown in **Table 1**. In all cases, the EuD₄TEA crystallites left on sieves 45, 60, 80, and 120 had sizes between 0.355-0.500, 0.250-0.355, 0.177-0.250, and 0.125-0.177 mm respectively. This sifting process generated five samples ranked by grain size. Due to the small quantity of size-sorted crystallites, 0.030 g of EuD₄TEA was used for each TL drop trial. In addition, three drops were completed on each size-sorted EuD₄TEA sample to give an average TL emission yield. The triboluminescent emission yield for each size bin was normalized to the 0.250 – 0.355 mm value.

Table 2 shows the results of this analysis. Notice the normalized TL yield appears to increase as a function of the average grain size. The measurement uncertainties for the triboluminescent emission yields were estimated to be 7%, based on earlier research [13]. The estimated uncertainties shown in the square of the average grain size from **Table 2** were calculated using standard error propagation techniques [14].

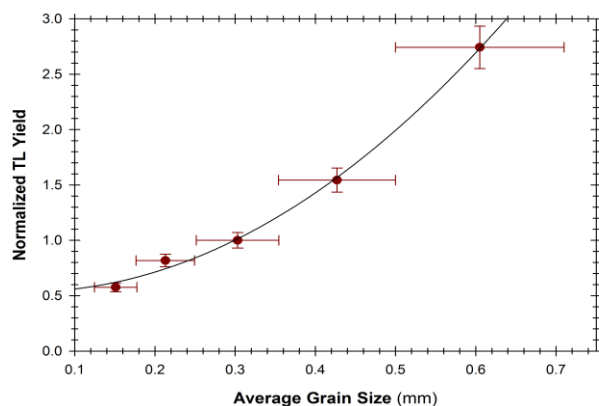
Table 1. Comparison of U.S. standard sieve number and standard opening sizes for several common meshes [12].

U.S. Standard Mesh Sieve Number	Standard Opening Size	
	(inches)	(mm)
120	0.0049	0.125
80	0.0070	0.177
60	0.0098	0.250
45	0.0139	0.355
35	0.0197	0.500
25	0.0278	0.710

Table 2. Measured triboluminescent yield results for EuD₄TEA samples sorted by grain size.

EuD ₄ TEA Grain Size Limits (mm)	Average Grain Size (mm)	Normalized TL Yield
0.125 – 0.177	0.151 ± 0.026	0.576 ± 0.040
0.177 – 0.250	0.213 ± 0.037	0.817 ± 0.057
0.250 – 0.355	0.303 ± 0.052	1.000 ± 0.070
0.355 – 0.500	0.427 ± 0.073	1.544 ± 0.108
0.500 – 0.710	0.605 ± 0.105	2.743 ± 0.391

A plot of the normalized TL yield versus the average grain size for EuD₄TEA is shown in Fig 2. Notice that the TL yield appears to be directly proportional to the square of the average grain size as shown by the square fit.

**Fig. 2.** Plot of the normalized TL yield versus the square of the grain size for the tested EuD₄TEA samples.

What does this mean? It is logical to assume that the number of luminescent centers that generate TL should be proportional to the average effective surface area of the individual EuD₄TEA crystallites. During these measurements, each size-sorted sample of EuD₄TEA was spread evenly on the clear plexiglass plate in the drop tower. When the ball bearing was dropped, a relatively uniform layer of EuD₄TEA was available at the impact location to produce TL. Since each sample was sorted for size, the “average effective surface area” for the individual EuD₄TEA crystallites was relatively constant. Since the exact crystallographic information on each EuD₄TEA crystallite is not yet known, it is not possible to directly measure the surface area for all the grains in each sample. This process is made more difficult by the fact that the crystallites are positioned randomly on the drop tower plate and have no preferred orientation. However, the average

surface area for the crystallites in each sample should be proportional to the square of the effective grain size. Remember this grain size is equivalent to the body diagonal for the monoclinic EuD₄TEA crystallites. Although Fig. 2 does not directly show that the normalized TL yield for EuD₄TEA is proportional to the average effective surface area, it does strongly suggest this is likely the case. The square of the data is remarkable, with a calculated goodness-of-fit or R² value equal to 0.997. This result matches the prediction of Chandra *et al.* as discussed in Reference [15]. The prompt fluorescence decay times for the acetone-synthesized EuD₄TEA samples were measured as shown in Table 3. From this data, it appears as though increasing the volume of acetone used during synthesis does not change the triboluminescent decay time for EuD₄TEA. Over all drops, the average measured triboluminescent decay time for EuD₄TEA was found to be 534.5 ± 7.3 μs, which is consistent with earlier results [8, 11, 16, 17].

Table 3. Fluorescence decay times (e⁻¹) as a function of acetone volume used during synthesis of EuD₄TEA.

Amount of Acetone (mL)	Average (μs)
10	516.6 ± 18.0
15	548.6 ± 21.1
20	518.3 ± 13.0
25	546.5 ± 16.1
30	518.1 ± 15.2
35	527.4 ± 13.0
40	566.0 ± 13.9

Conclusion

EuD₄TEA crystallites can be synthesized using 10 to 40 mL of acetone. Visual inspection indicates that the EuD₄TEA grain size appears to be proportional to the volume of carrier acetone used in this process. Synthesizing larger crystals of EuD₄TEA is possible, but is not practical based on the quantities of the required pre-cursor chemicals. All of the synthesized EuD₄TEA was combined and then sifted by a succession of U.S. standard mesh sieves. This method produced a total of five samples where the EuD₄TEA crystallites were all about the same size. Results here indicate that the normalized TL yield appears to be directly proportional to the square of the average grain size. However, the average effective surface area for the crystallites in each sample should be proportional to the square of the effective grain size. This result suggests the normalized triboluminescent yield for EuD₄TEA should be proportional to the effective surface area of the crystallites. This result represents the first step to fully understand the relationship between normalized TL yield and crystallite surface area. Finally, the prompt fluorescence decay times were measured for all of the acetone-synthesized EuD₄TEA samples. Results show that increasing the volume of acetone used during synthesis does not change the triboluminescent decay time for EuD₄TEA. Over all drops, the average measured triboluminescent decay time for EuD₄TEA was found to be 534.5 ± 7.3 μs, which is consistent with earlier published data. Using different

volumes of the acetone carrier solvent during synthesis does not change the emission properties of EuD₄TEA. Additional research is being carried out to fully understand this phenomenon.

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