



Structural characterizations of organic-based materials with extensive mechanoluminescence properties



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ABSTRACT

The organic mechanoluminescent (ML) material europium-doped dibenzoylmethide triethylammonium (EuD₄TEA) is known as a triboluminescent material. Our group has synthesized a novel ML material with the addition of 1-ethenylpyrrolidin-2-one [(polyvinylpyrrolidone) (PVP)], which changed the ligand of the mechanoluminescent material. This research investigated the ML material structure, molecular orbital electron distributions of the ligands, ML mechanism and enhancement in the photoluminescence (PL) intensity with PVP. For the first time, the ML material structure was characterized using nuclear magnetic resonance spectroscopy (NMR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Gaussian DFT/B3LYP/6-31G(d,p) software. The ML properties were characterized using a Hamamatsu Photonic Multichannel Analyzer (PMA). The material can be applied to the real-time visualization of the stress field near the tip of a crack, an ML light source, determination of laser and ultrasonic powers, secret message writing and earthquake detection sensors.

1. Introduction

Mechanoluminescence (ML) is a light-emission event that results from a mechanical action on a solid [1]. Fracto-, plastico- and elasto-ML are various forms of ML. Among the various ML forms, fracto-ML is well known because most inorganic materials emit light when they fracture as a result of the plate force during and prior to an earthquake [2–4]. Additionally, plastico-ML can be observed by peeling an adhesive tape in a vacuum [5,6]. When the crystal bonds are broken along oppositely charged planes and then reconnect, light is emitted as the charges pass through the gaps that were created from the fracture [7,8]. Once the material is fractured, the electrons are excited to higher energy levels and then transition to the lower energy levels [9,10]. The energy difference between the corresponding levels is emitted as a light with different wavelengths [11]. The third type of ML mechanism, elasto-ML, results from a mechanical stress that produces a piezoelectric field on the surface of crystals [12–14]. This electric field that is near the color center is high because of changes in the local structure. These changes may reduce the carrier trap depth or effect band bending [15–17]. After decreasing the carrier trap depth, the thermal de-trapping of the carriers may occur. Trapped charge carriers can tunnel to the conduction band because of the band bending. The electrons from the conduction band may be captured by the excited state of the

activator ions. This may cause a de-excitation of the color center and produce the emission [18]. When plastico-mechanoluminescent materials are plastically deformed, a movement of dislocation occurs. Similarly, an electric field generated by the charge dislocation causes a bending of the valence, conduction and dislocation bands. Trapped electrons tunnel to the conduction band and the recombination of electrons and holes enables the light emission characteristic of the color center. However, the conduction band electrons are trapped by the color center and a potential energy transfer occurs as a result of the de-excitation of the rare earth cation. Both functions occur and electron-hole recombination is greater than that caused by the impact excitation [19]. The mechanism of the fracto-ML material is believed to be different. In this case, when the material fractures, two newly created, oppositely charged surfaces are generated, which produce an electric field and cause a dielectric breakdown of the surrounding gasses and, in turn, may give rise to gaseous discharge ML. Additionally, the electric field that caused the dielectric breakdown of the crystals and the recombination of the free carriers may lead to recombination luminescence [20,21]. To date, many inorganic mechanoluminescent materials have been synthesized with various dopants [22–24], such as Eu, dialuminum strontium oxygen(2-)SrAl₂O₄: Eu [25], Eu, Barium(2+), oxido(oxo)aluminum BaAl₂O₄: Eu [26], Eu, Dy, dialuminum strontium oxygen(2-)SrAl₂O₄: Eu, Dy [27] and zinc sulfide, ZnS: Mn [28].

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However, the difficulty is that they are typically synthesized at high temperatures that are greater than 1000 °C [29].

Our study is focused on the structure of the synthesized material, the ML and the mechanism for the increase in PL intensity. We have determined the structure of this synthesized ML material using nuclear magnetic resonance spectroscopy (NMR), X-ray photoelectron spectroscopy (XPS) and the molecular orbital diagram of the ligands. This paper has reviewed the structure of the synthesized ML material, mechanism of the intensity enhancement and crystallinity of the ML material.

2. Experimental

The synthesis of the PVP-based dibenzoyl methide triethylammonium compound was based on the our previously reported procedures and methods [30].

First, 80 mL ethyl alcohol (99.9%, Wako) was heated to 70 °C and then 0.8 mmol 1, 3-diphenylpropane-1,3-dione (99%, Wako) (DBM) was added to the solution mixture and stirred. Next, the solute was completely dissolved and 0.3 mmol europium nitrate hexahydrate (99.9%, Wako) was added to the mixture. Then, 0.1 g PVP (99%, Wako) and 0.5 ml N,N-diethylethanamine, triethylamine (99.8%) (TEA) were added. After adding the compounds, the solution was maintained at 70 °C for 20 min. Then, the solution vessel was tightly capped and placed in a thermos overnight. The regulated slow cooling in the thermos was critical for optimal crystal formation. For comparison, a material that was based on EuD₄TEA without PVP was also synthesized. Photoluminescence (PL) and ML properties were measured for both of the synthesized materials at room temperature.

2.1. Characterization

The mechanoluminescence and photoluminescence intensities were characterized using a photonic multichannel analyzer. The absolute values of higher occupied molecular orbital (HOMO) and lower unoccupied molecular orbital (LUMO) energy levels of each chemical were characterized using Gaussian DFT/B3LYP/6–31G(d,p) software. Scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM) and field emission scanning electron microscopy (FESEM) were conducted on a JEM-2100F electron microscope. X-ray diffraction (XRD) images were collected using a Rigaku RINT-Ultima III diffractometer. XPS measurements were performed using a KRATOS AXIS Ultra spectrometer.

3. Results and discussion

3.1. Mechanoluminescence and photoluminescence study

Fig. 1 shows an ML intensity comparison for specimens before and after the addition of the PVP polymer. These spectra clearly show an increase in the ML intensity after the addition of PVP. The solid curve corresponds to the ML enhancement of the material with a larger quantity of europium nitrate hexahydrate. However, europium nitrate hexahydrate with the addition of PVP resulted in a higher ML intensity (red curve). The PVP polymer bonded with Eu⁺³ and facilitated a higher electron-transition rate and hence a greater excitation. Additionally, the results suggest that the local environment surrounding the Eu⁺³ ion was more disordered. Hence, the degree of polarization for europium-doped dibenzoylmethide triethylammonium was higher when PVP was infused into the ML material. This led to a higher probability for electric dipole-allowed transitions. Fig. 2 shows the spectra of the PL intensity of the formed ML material before and after the addition of the PVP polymer. The corresponding PL emission wavelengths are 592.7 nm, 612.0 nm, 651.2 nm and 701.3 nm. All the

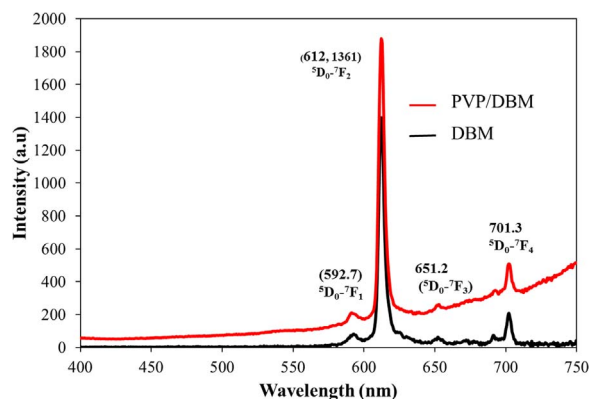


Fig. 1. Mechanoluminescent intensity spectra of europium tetrakis dibenzoylmethide triethylammonium synthesized with and without PVP. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

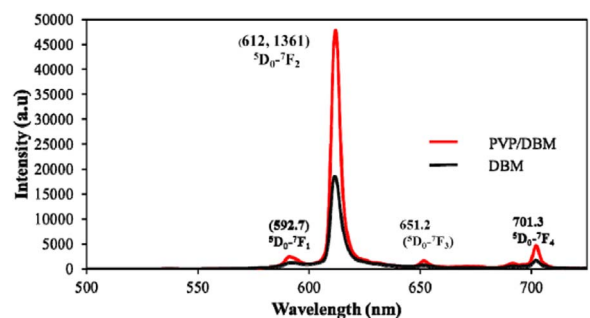


Fig. 2. Comparison of the photoluminescence intensity spectra of the ML material with and without PVP.

emission lines belong to the europium ⁵D₀ to ⁷F_n (n = 1, 2, 3 and 4) electron energy transitions. However, after PVP addition in the synthesized materials, the ML and PL emission intensities increased.

3.2. Crystallography and structural studies

Figs. 3 and 4 show the X-ray diffraction patterns for EuD₄TEA without and with PVP, respectively. The XRD characterization carried out for 2θ values from 5° to 40°, and the prominent XRD peaks were observed in the range of 5° to 10°. In Fig. 3, the 2θ values at 6.68, 6.87, 7.00 and 7.60 correspond to the (100), (200), (110) and (011) Millar planes, respectively, and in good agreement with JCPDS card no: 96-711-8092. The XRD measurements confirmed that the crystal structure similar to the europium, 2,2'-bipyridine 5,5'-dicarboxylic acid (C₃₆Eu₂N₆O₁₇) compound and the crystal system is monoclinic. The Millar planes (100), (200) reveal that the structure has grown along the vertical c plane and when other two planes, (110) and (011), are considered it can be concluded that the material has a rod-like structure. Corresponding TEM and SEM images, as shown in Figs. 5(a) and (c), further confirm that material has a rod-like formation. Refined XRD data for the compound prepared without PVP added material has provided in Supporting data file. Fig. 4 depicts that the XRD profile for the synthesized ML material with PVP and the 2θ values at 6.79, 6.88 and 7.41 correspond to the (100), (200), (110) Millar planes, respectively. This is related to the JCPDS card number 96-711-8093. Corresponding Millar planes reveal that structure steadily grows parallel to the vertical c plane and TEM and SEM images, illustrated in Fig. 6(a) and (c), also verify that ML material has rod-like structure. The crystal system is monoclinic and comparable to europium, 2,2'-bipyridine 5,5-

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