Effect of added Polyvinylpyrrolidone on Mechanoluminescent Property of Europium-doped Dibenzoylmethide Triethylammonium

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(Received October 15, 2015)

Europium-doped dibenzoylmethide triethylammonium (EuD₄TEA) has been known as an organic mechanoluminescent (ML) material. In the present study the ML properties are investigated for the EuD₄TEA with an addition of polyvinylpyrrolidone (PVP). For the first time novel organic ML material has been successfully synthesized by controlled slow cooling method at very low temperature of 70 $^{\circ}$ C. The ML properties are characterized by using Hamamatsu Photonic Multichannel Analyzer (PMA). The ML spectrum corresponds to the europium D₀ to f_n transition. The results suggest that the addition of PVP enhances ML intensity of EuD₄TEA. Effect of the addition will be discussed in detail.

1. Introduction

Mechanoluminescence (ML) is a phenomenon of light emission resulting from mechanical action on a solid[1]. There are several forms of ML such as fracto-, plastico- and elastico-ML, among the ML forms the fracto-ML is well known because most inorganic materials emit the light when they fracture such as a result of plate force during and just before the earth quake[2, 3]. The ML also can be observed by peeling an adhesive tape in a vacuum. When the crystal bonds are broken along the planes with opposite charge and then re-connected, light is emitted as the charges pass through the gaps created from the fracture. When the material is fractured, electrons are excited to the higher energy levels followed by transition to the lower energy levels.

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Energy difference between corresponding levels is emitted as a light with different wavelengths [4]. So far, many inorganic machanoluminescent materials have been synthesized with various dopants[5]. Such as SrAl₂O₄: Eu, BaAl₂O₄: Eu, SrAl₂O₄: Eu, Dy and ZnS:Mn. However, the problem is that, they are usually synthesized at high temperatures over 1000 °C [6].

We are focused to synthesize the ML material at low temperature based on organic materials such as europium tetrakis dibenzoylmethide triethylammonium (EuD₄TEA)[7]. We have succeeded to synthesize the EuD₄TEA at very low temperature of 70 °C by using a controlled slow cooling method. This paper has discussed effect of an addition of polyvinylpyrrolidone (PVP) to the EuD₄TEA on the ML properties.

2. Experimental

First ethyl alcohol (99.9%, Wako) was heated till 70 $^{\circ}$ C and then 1, 3-diphenylpropane-1, 3-dione (99%, Wako) was added and stirred. After the solute was completely dissolved, europium nitrate hexahydrate (99.9%, Wako) was added into the solution. PVP (99%, Wako) and trimethylamine (99.8%) were added further and solution was kept at 70 $^{\circ}$ C for 20 min. Then the solution container was capped tightly and inserted in the thermos overnight. Controlled slow cooling in the thermos is effective to grow nice crystals. For comparison, the EuD₄TEA based material without PVP was also synthesized. Photoluminescence (PL) and ML properties were measured for both synthesized materials at the room temperature.

3. Results & discussion

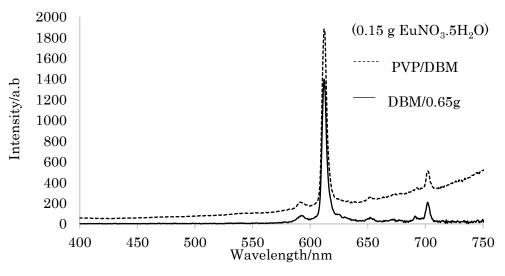


Fig.1 Mechanoluminescence intensity spectra of europium tetrakis dibenzoylmethidetriethylammonium synthesized adding and without adding PVP.

Figure 1 shows ML intensity comparison for samples before and after addition of PVP polymer. These spectra clearly show an increase of ML intensity after addition of PVP. Black curve corresponds to the ML intensity of the material with higher amount of europium nitrate hexahydrate. However, small amount of europium nitrate hexahydrate with addition of PVP results in much higher ML intensity (red curve). PVP polymer makes coordination bond with Eu⁺³ and it is the reason for the higher electron transition rate, hence more excitation.

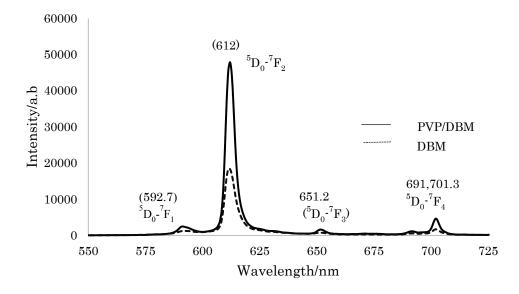


Fig. 2 Comparison of Photoluminescence intensity spectrum on ML material after and before adding PVP

Figure 2 corresponds to the PL spectra of synthesized ML material before and after addition of PVP polymer. The PL emission lines with 357.0 nm excitation are 592.7 nm, 612.0 nm, 651.2 nm and 701.3 nm. Those emission lines belongs to the $^5\text{D}0$ to $^7\text{F}_n$ (n= 1,2,3,4) electron transitions. After addition of PVP to the synthesized material, ML and PL emission intensity increased.

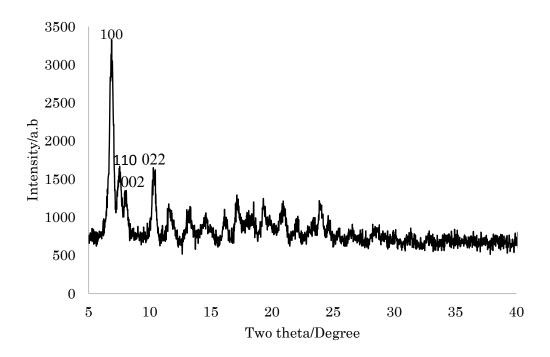


Fig. 3 XRD pattern of the ML material after addition of PVP

Figure 3 shows XRD pattern of EuD₄TEA with PVP. It is evidence for the crystallinity of the newly synthesized mechanoluminescent material. Low defect concentration in the crystalline material results in better electron transport properties, without trapping and recombination. Newly synthesized EuD₄TEA material with PVP addition has shown higher ML and PL intensity than without PVP.

4. Conclusions

We have successfully synthesized ML material at low temperature at 70°C without addition and with addition of PVP. ML and PL intensity are characterized by using Hamamatsu photonic multichannel analyzer. PL spectrum with 357 nm excitation consists of emission lines at 592.7 nm, 612.0 nm, 651.2 nm and 701.3 nm. Those emission wavelength belongs to electron transition between $^5\text{D}_0$ to $^7\text{F}_n$ (n=1,2,3,4) energy levels . Newly synthesized EuD₄TEA material with addition of PVP has much higher PL and ML intensity than without PVP.

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