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Color control of the mechanoluminescent material through a combination of color centers

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Abstract. We have synthesized the new organic mechanoluminescent material based on a 1,10-phenanthroline and an acetylacetone. The synthesized material shows both the photoluminescence and the mechanoluminescence with a green-color (main peak at 545 nm) by doping of a terbium (Tb). We have also investigated an effect of co-doping of Tb and europium (Eu) or dysprosium (Dy) on the luminescence property. Single doping gives a luminescence corresponding to each dopant with the main peak at 545, 612 or 573 nm for Tb, Eu or Dy, respectively, but the co-doping of Tb and Eu gives the luminescence corresponding to their doping amount ratio. As a result, the visual color can be controlled by the ratio. On the other hand, the co-doping of Tb and Dy keeps the luminescence corresponding to Tb single doping, but enhances its intensity. The results suggest that the electron transition process is different between the Tb-Eu and Tb-Dy co-doping. In the case of Tb/Eu co-doping, each dopant induced each own luminescence due to a significant difference in the electron energy state level between Tb and Eu. In centrally, the energy state of Dy becomes an extra electron supplier to Tb for the Tb/Dy co-doping. The results can expand application fields of the mechanoluminescence.

Keywords: Mechanoluminescence, Organic Materials, Co-Doping.

1 Introduction

Mechanoluminescence (ML) is a phenomenon of light emission originated from a mechanical action on a solid [1]. The ML is classified into fracto-, plastico- and elastico-MLs according to an excitation mode of the electrons. The typical example of fracto-ML is a light emission induced by the plate force during and prior to an earthquake [2-4]. The plastico-ML can be observed by peeling an adhesive tape in the vacuum [5]. Additionally, the elastico-ML resulted from a mechanical stress produces a piezo- electric field on the surface of crystals [6-8]. The electric field near the color center is high due to a change in the local structure. The change may reduce the carrier trap depth or effective band bending [9-11]. When the material structure is fractured, the electrons are excited to the higher energy levels followed by the relaxation process of electrons to lower energy levels[12,13]. The energy difference is released as a light emission with a different wavelength [14].

Many inorganic mechanoluminescent materials have been synthesized so far with various dopants [15-17]. Difficulty, however, to use the inorganic materials is that they are typically synthesized at high temperatures over 1000°C [18]. In order to realize a low temperature synthesis of the ML materials, we have succeeded to synthesize the europium doped dibenzoylmethide triethylammonium (EuD_4TEA) that has been well known an organic triboluminescence material [19]. The synthesis is completed at very low temperature of 70°C by a controlled slow cooling method. The synthesized material shows a very strong ML at 612 nm in the visible region. Furthermore, we have found that an addition of 1-ethenylpyrrolidin-2-one [(polyvinylpyrrolidone) (PVP) enhances the ML intensity of EuD4TEA through the modification of ligand frameworks [20].

In order to realize a light emission from terbium (Tb) color center for the organic ML material, we have newly synthesized a 1,10-phenanthroline and an acetyl acetone-based material. In this study we have described luminescence properties of the newly synthesized material and investigated an effect of the co-doping with europium (Eu) or dysprosium (Dy) for a color control of the ML. When each color center is doped separately, the synthesized material shows both the photoluminescence (PL) and the ML induced by each dopant whose main peak at 545 nm (Tb), 612 nm (Eu) or 573 nm (Dy). On the other hand, Co-doping of Tb and Eu leads to a change in the visible color of luminescence depending on an amount ratio of Tb/Eu, while a co-doping of Tb and Dy just enhance the luminescence intensity originated from the Tb color center.

2 Experimental

2.1 Synthesis

The synthesis of new organic ML material was followed by our previously reported procedures and methods [20,21]. All chemicals used were the reagent grades.

First ethyl alcohol was heated till 70 °C and then desired dopant nitrate(s) ($Tb(NO_3)_3.5H_2O$, $Eu(NO_3)_3.6H_2O$ and/or $Dy(NO_3)_3.6H_2O$) was(were) added and stirred. After 1,10-phenanthroline (phen) and acetyl acetone (acac) were added in the solution, it became cloudy. Finally, trimethylamine (TEA) was added till the solute was completely dissolved. The solution container was capped tightly and inserted in the thermos for 24 h. Controlled slow cooling in the thermos is critical for optimal crystal formation. Formed crystal in the solution was collected through the filtration followed by natural drying. The synthesized materials are summarized in Tables 1, 2 and 3.

Table 1. Composition of single doped synthesized materials.

Comp. Specimen	Tb [mmol]	Eu [mmol]	Dy [mmol	acac [mmol]	phen [mlmol]	TEA [mmol]	ethanol [mL]
Tb Complex	1.0	-	-	3.0	1.0	3.0	40
Eu Complex	-	1.0	-	3.0	1.0	3.0	40
Dy Complex	-	-	1.0	3.0	1.0	3.0	40

Table 2. Composition of Tb-Eu co-doped synthesized materials.

Ratio Comp.	5:1	5:2	2:1	5:3	5:5
Tb (NO$_3$)$_3$ [mmol]	0.5	0.5	0.5	0.5	0.5
Eu (NO$_3$)$_3$ [mmol]	0.1	0.2	0.25	0.3	0.5
acac [mmol]	1.5	1.5	1.5	1.5	1.5
phen [mmol]	0.5	0.5	0.5	0.5	0.5
TEA [mmol]	1.5	1.5	1.5	1.5	1.5
ethanol [mL]	40	40	40	40	40

Table 3. Composition of Tb-Dy co-doped synthesized materials.

Ratio Comp.	5:1	5:2	5:3	5:4
Tb (NO$_3$)$_3$ [mmol]	0.5	1.0	0.5	0.5
Eu (NO$_3$)$_3$ [mmol]	0.1	0.4	0.3	0.4
acac [mmol]	1.5	3.0	1.5	1.5
phen [mmol]	0.5	1.0	0.5	0.5
TEA [mmol]	1.5	3.0	1.5	1.5
ethanol [mL]	40	50	40	40

2.2 Characterization

The mechanoluminescence and photoluminescence intensities were characterized by using the photonic multichannel analyzer (Hamamatsu Photonics, PMA-12). Results and discussion

3 Results and discussion

3.1 Luminescence property for the single doping

Both the photoluminescence and the mechanoluminescense correspond to the electron energy transitions of each single dopant for the single doped synthesized materials. Figure 1 shows the ML spectrum of Tb-doped material (Tb Complex). The result indicates the peaks at 488 nm, 545 nm, 584 nm and 620 nm corresponding to the electron energy transitions of terbium, from $^5D_4$ to ^7F_n (n = 3, 4, 5 and 6).

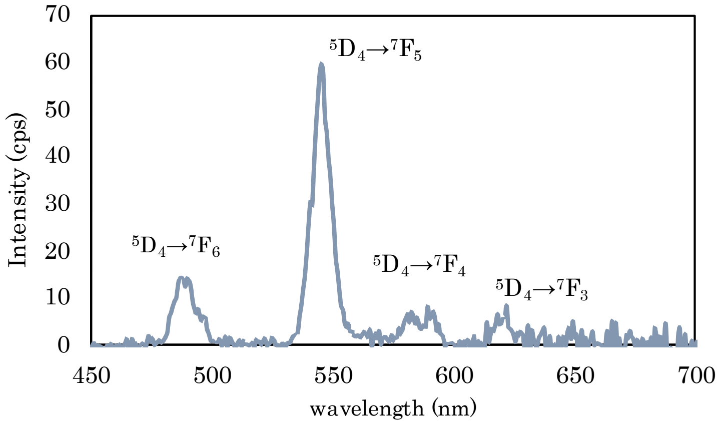

Fig. 1. Mechanoluminescence spectrum of the Tb-doped synthesized material.

Since the main electron energy transitions of Eu and Dy are from $^5D_0$ to ^7F_i (i=1,2 and 3) and from $^4F_{9/2}$ to $^6H_{j/2}$ (j=11, 13 and 15), respectively, both the PL and ML spectra show the peaks at 591 nm, 612 nm and 652 nm for Eu Complex and at 482 nm, 573 nm and 660 nm for Dy Complex. It is noted, however, that the ML intensity is very weak for Dy Complex

We have succeeded for the first time to achieve a control of color emitted from the same ML material just by changing a dopant (color center). Energy diagrams of ligands, phen and acac which are discussed later are strong responsible for the success.

3.2 Luminescence property for the co-doping

In order to realize an mixed light emission based on two color centers for the ML material, we have doped two kinds of dopant simultaneously to the synthesized ML material. Figure 2 shows the ML spectra when Tb and Eu are co-doped with the different molar ratios of Tb/Eu (Tb/Eu Complex). As shown in Fig. 1, the peaks originated from Tb Complex disappear beyond the ratio of Tb:Eu=2:1. In contrast, the peaks originated from Eu Complex appear in conjunction with the co-doping. Property of the PL is also very similar for the Tb/Eu Comlex).

The results suggest that the co-doping ranging between Tb:Eu 5:2 and 2:1 might lead to a mixed visual light emission originated from two dopants, Tb and Eu. Actually, a chromaticity diagram for the PL of Tb/Eu Complex is obtained as shown in Fig. 3. The figure clearly indicates that the chromaticity of emitted light is changed by the amount ratio of Tb/Eu. The ML property also shows the same result.

On the other hand, the co-doping of Tb and Dy to the synthesized material (Tb/Dy Complex) shows no ML derived from the Dy dopant for any amount ratio of Tb/Dy but enhances intensities corresponding to Tb Complex up to Tb:Dy=5:3 as shown in Fig. 4. The PL property of Tb/Dy complex is also similar. Figure 5 shows a variation of the ML intensity detected at 545 nm in Fig. 4 with the amount ratio of Dy dopant. The maximum ML intensity is obtained by the Dy doping molar ratio of 29% to Tb dopant as shown in Fig. 5.

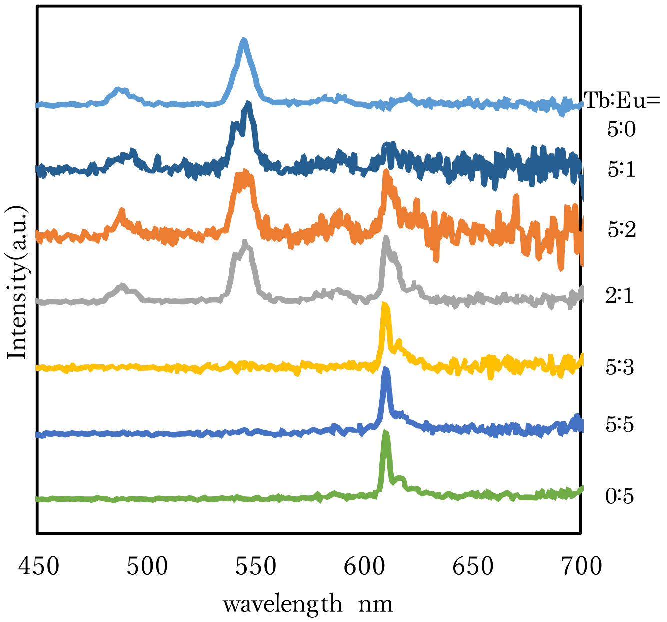

Fig. 2. Mechanoluminescence spectra of the Tb/Eu-co-doped synthesized material. The ratios indicated on right side are the molar ratios of Tb/Eu.

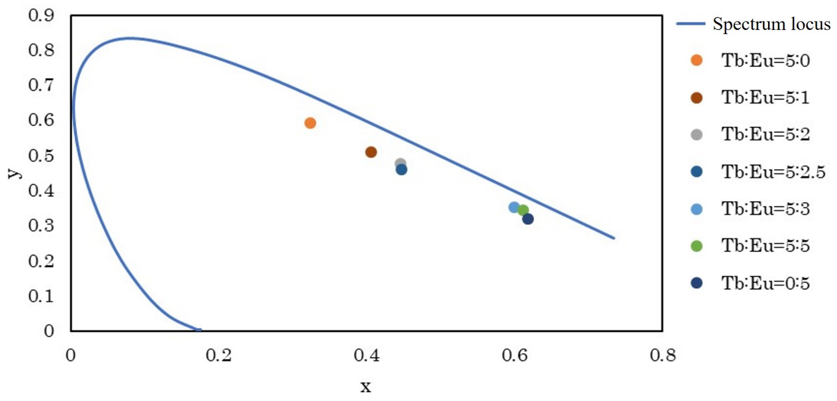

Fig. 3. Chromaticity diagram for the PL of Tb/Eu-co-doped synthesized material. The ratios indicated on right side are the molar ratios of Tb/Eu.

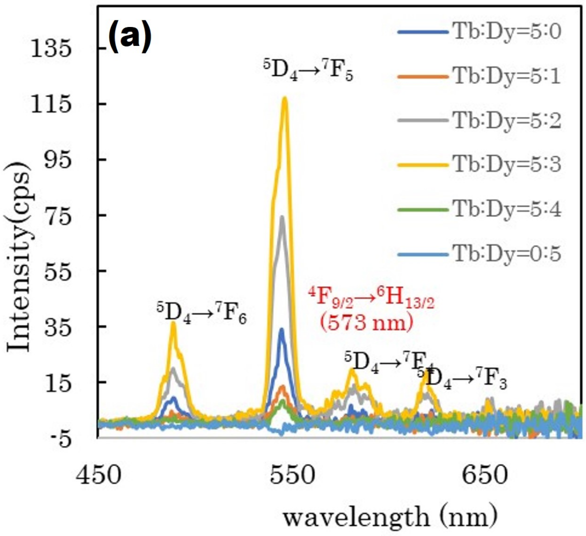

Fig. 4. Mechanoluminescence spectra of the Tb/Dy-co-doped synthesized material. The ratios inserted in the graph are the molar ratios of Tb/Dy.

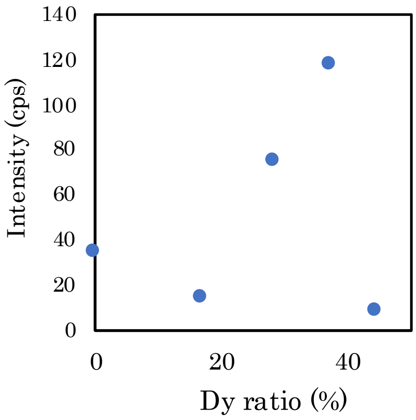

Fig. 5. Variation of the ML Intensity of the main peak at 545 m in fig. 4 with the amount ratio of Dy dopant.

Difference in the effect of co-doping between the Tb/Eu Complex and the Tb/Dy Complex should be related to the difference in energy diagram of the co-doped synthesized materials as shown in Figs. 6 and 7. S and T in the figures denote the excited singlet states and the excited triplet states for the ligands, phenanthroline (phen) and acetyl acetone (acac).

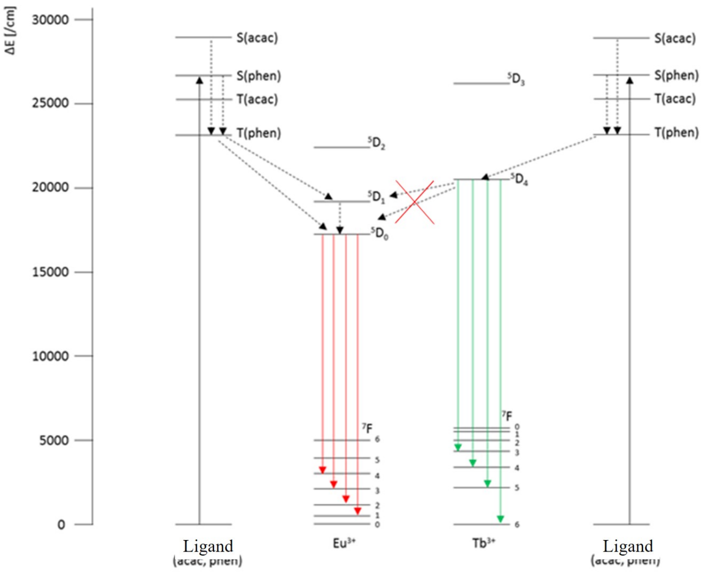

Fig. 6. Energy diagram of the Tb/Eu-co-doped synthesized material.

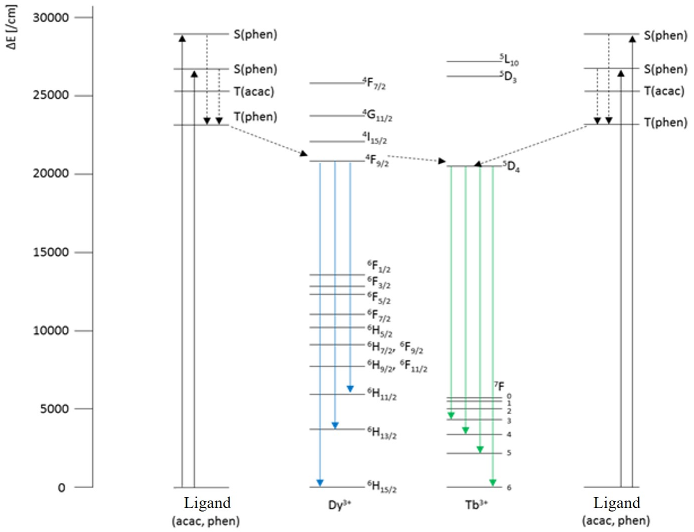

Fig. 7. Energy diagram of the Tb/Dy-co-doped synthesized material.

Figure 6 depicts that in the case of Tb/Eu Complex, mechanical stresses on the material excite the electrons to S(acac) and S(phen) followed by the transitions to T(acac) and T(phen) through an intersystem crossing. Collected electrons in the triplet states can transit to $^5D_4$ of Tb^{3+} and $^5D_0$ of Eu^{3+} followed by the transitions to ^7F_n (n = 3, 4, 5 and 6) of Tb^{3+} and ^7F_i (i=1,2 and 3) of Eu^{3+}, respectively because the energy difference between two states is significantly large. There is no communication between $^5D_4$ of Tb^{3+} and $^5D_0$ of Eu^{3+}. Thus, the luminescence from Tb/Eu Complex is changed by the amount ratio of Tb and Eu. On the other hand, since the energy of $^4F_{9/2}$ of Dy^{3+} is very close to that of $^5D_4$ of Tb^{3+} for the Tb/Dy Complex as shown in Fig.7, the collected electrons in $^4F_{9/2}$ of Dy^{3+} prefer the transition to $^5D_4$ of Tb^{3+} to that to $^6H_{j/2}$ (j=11, 13 and 15). Thus, the electron transitions within the Tb dopant are enhanced by an increase in the amount ratio of Dy dopant. Excess amount ratio of the Dy dopant, however, induces the electron transitions within the Dy^{3+} electron energy states as well resulting in a decrease in the transitions within the Tb dopant.

4 Conclusion

We have newly synthesized the 1,10-phenanthroline and the acetyl acetone-based organic ML material to realize a light emission induced by the Tb color center. It is found that the synthesized material also shows a scalability to accept the different color centers such as Eu and Dy, and emits the ML induced by the different single dopant. Additionally, the material has a capability to control a chromaticity of the ML by changing an amount ratio of the co-doped Tb/Eu and to enhance the ML intensity induced by Tb through a co-doping with Dy. The results might expand the application fields of ML not only to the stress sensings but also to displays.

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