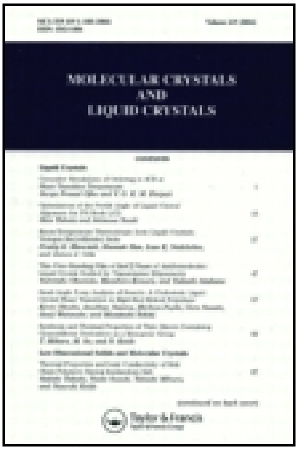

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Transient Behavior of Mechanoluminescence from Europium Complex in Powder and in Polymer-Dispersed Film

Noriyuki Takada [a] , Shigeru Hieda [b] , Jun-Ichi Sugiyama [a] , Ryuzi Katoh [a] & Nobutsugu Minami [a]

[a] National Institute of Materials and Chemical Research, AIST, Tsukuba, Ibaraki, 305, JAPAN

[b] Futaba Corporation, R & D Center, Chousei, Chiba, 299-43, JAPAN

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Transient Behavior of Mechanoluminescence from Europium Complex in Powder and in Polymer-Dispersed Film

NORIYUKI TAKADA[a], SHIGERU HIEDA[b], JUN-ICHI SUGIYAMA[a], RYUZI KATOH[a], and NOBUTSUGU MINAMI[a]
[a]National Institute of Materials and Chemical Research, AIST, Tsukuba, Ibaraki 305, JAPAN; [b]Futaba Corporation, R&D Center, Chousei, Chiba 299-43, JAPAN

Transient properties of mechanoluminescence (ML) from europium complex in powder and in polymer-dispersed film were investigated. In polymer-dispersed film, its decay curve was found to be composed of two components corresponding to the emission from ambient nitrogen molecules and europium ion. On the other hand, the decay curve of powder was composed of a single component corresponding to the emission from europium ion. From these results and supplemental experiments, the difference in ML excitation mechanism between polymer-dispersed film and powder is discussed.

Keywords: mechanoluminescence; europium complex; transient behavior; frictional electrification; excitation mechanism

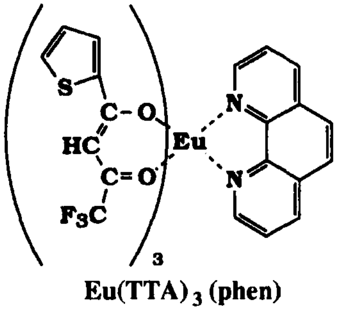
INTRODUCTION

Mechanoluminescence (ML)[1] is the emission of light caused by mechanical stimuli (rubbing, crushing etc.) to a material. A large number of inorganic salts[2] and organic molecular solids[1] show ML. While complexes of rare earth metals such as Eu are considered particularly useful luminescent materials because of their characteristic features such as intense and spectrally sharp light emission, only few works have been done about their mechanoluminescent properties. For example, among numerous Eu complexes, only those of dibenzoylmethide have been known to possess ML activities[3].

We found that Eu complexes with tris(thenoyltrifluoroacetone) and phenanthroline ligands, whose ML functions have never been investigated before, showed ML in powder[4]. We could also observe ML from Eu complexes dispersed in polymer films[5], which must have important implications for technological applications.

In this paper, we describe the ML properties (spectral and transient behavior) of Eu complex in powder and in polymer-dispersed film, and the difference in ML excitation mechanism between them is discussed.

EXPERIMENTAL



Eu(TTA)$_3$ (phen)

FIGURE 1 Molecular structure and abbreviation of Eu complex.

The molecular structure and abbreviation of the Eu complex used in this study is shown in Fig.1[4].

For the measurements of ML properties (spectra, transient properties etc.), powder and polymer-dispersed film of the Eu complex were used. Polymer-dispersed film was prepared by casting methylene chloride solution containing 10wt% Eu complex and 90wt% polycarbonate on glass substrate. After dried in vacuum, film was peeled from the substrate and then put on them again, where film could be fixed by electrostatic force. This procedure was necessary for the occurrence of ML from polymer-dispersed film.

ML and photoluminescence (PL) spectra were measured with a polychromator-ICCD multichannel spectrophotometer system (Princeton Instrument Inc.) through a plastic optical fiber. For ML experiments, the samples were rubbed with a tip of a glass tube into which the fiber was inserted and sealed. This system made it possible to efficiently collect light emission exactly from the rubbed spot of the samples. The transient properties of ML were monitored by a photomultiplier connected to a storage oscilloscope (HP 54542A), where emitted light was passed through a slit (1mm). The time resolution of the detection system was 20μs. To compare with ML, lifetime of PL from polymer-dispersed films was measured by a streak scope (HAMAMATSU PHOTONICS K.K.) in combination with a nitrogen laser (337nm, FWHM 1ns) as an excitation source. All experiments were done at room temperature in air unless otherwise specified.

RESULTS AND DISCUSSION

ML spectra of powder and polymer-dispersed film

Figure 2 shows the ML spectra of Eu(TTA)$_3$(phen) in powder (A) and in polymer-dispersed film (B) together with their PL spectra. Here, these spectra were normalized at the peak wavelength (611nm). ML and PL spectra are almost identical. Since PL of Eu-complex is known to originate from Eu ion[6], the similarity between ML and PL spectra indicates that ML is also attributable to the emission from Eu ion.

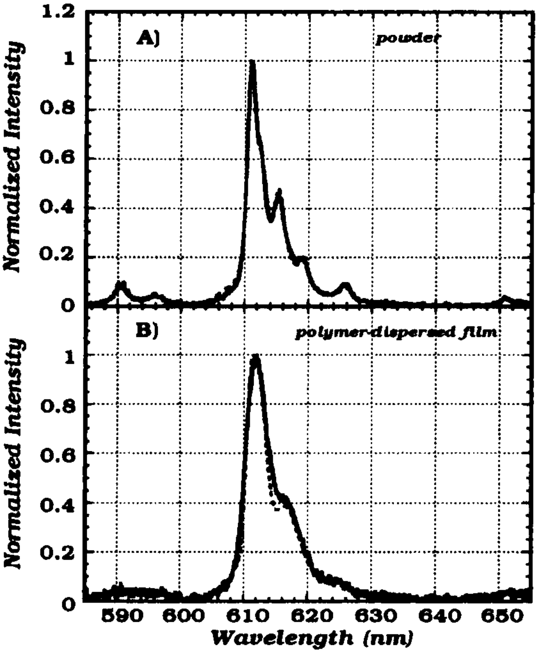


FIGURE 2 ML and PL spectra of Eu-complex in powder (A) and polymer-dispersed film (B).
(solid line : ML, broken line : PL)

Transient properties of ML in powder and in polymer-dispersed film

To obtain insight into the ML excitation mechanism, we studied its transient properties. Figure 3 shows emission relaxation curves of ML from powder and the polymer-dispersed film of Eu(TTA)$_3$(phen).

In the polymer-dispersed film, ML transient curve is composed of two decay components. The fast component decays within the resolution of the detection system (20μs). The slow component can be fit by a single exponential curve and the decay time is estimated to be about 600μs. We found that the spectral distribution was different for the two components; this was shown by inserting UV (280-380nm) or Vis (>520nm) passing filters in front of the photomultiplier. The former filter resulted in the fast component only, while the latter gave the slow one alone. For comparison, we measured the decay time of PL from Eu(TTA)$_3$(phen) dispersed in polymer film. The lifetime of PL obtained was almost the same as that of the slow component of ML, demonstrating that this component represents the emission from Eu ion. On the other hand, we attribute the fast component of ML to the discharge of nitrogen gas existing around the samples, because N_2 molecule is known to have many emission lines between 280 and 440nm and they decay within about a few ns.

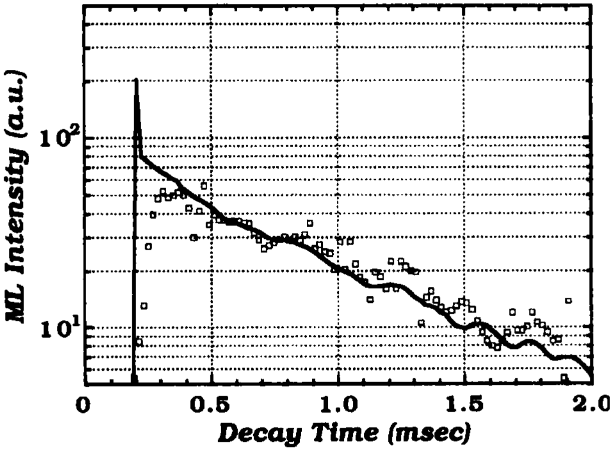


FIGURE 3 ML transient properties of powder (square) and polymer-dispersed film (solid line).

For the powder, we found that the ML transient curve was composed of a single decay component, which was almost the same as the slow component of polymer-dispersed film. The fast component corresponding to the nitrogen discharge was not observed.

From these results and supplementary experiments, we can discuss the difference in the ML excitation mechanism between polymer-dispersed film and powder.

Excitation mechanism of ML in polymer-dispersed film and in powder

When polymer-dispersed film adhering to the glass substrate is rubbed by the rod, frictional electrification occurs and momentary electric field is formed between the polymer film and glass substrate, which can be strong enough to induce discharge of air. Therefore the fast component corresponding to emission from nitrogen molecules was observed. The slow component of ML corresponding to the emission from $Eu(TTA)_3(phen)$ can be explained by two possible excitation mechanisms of the Eu complex; by the reabsorption of the emission light from nitrogen and by electron impact. In the latter mechanism, electrons emitted and accelerated by the strong electric field are supposed to directly hit the Eu complex existing at the counter surface. To study the mechanism more closely, we measured ML from a polymer-dispersed film under high vacuum (10^{-6}Torr), where nitrogen discharge could be precluded. The results showed that the emission corresponding to Eu ion was stronger than that in air, while no emission due to nitrogen was observed. These facts demonstrated that ML from Eu complex dispersed in polymer film is predominantly excited by electron impact.

For the powder, the most plausible mechanism would be also excitation by electrification, which is similar to the case of polymer-dispersed film. However, there are at least three possible routes to the formation of an electrical potential difference: frictional electrification caused by rubbing two dissimilar materials together, piezoelectrification caused by the deformation of noncentrosymmetric crystal and internal electrification caused by cracking in crystal.

First, the importance of frictional electrification was probed by using four different materials for rubbing: rods made of steel, glass, plastic and wood, which should give different extent of frictional electrification. In practice, however, no difference was found among the four. Next, we tried to observe ML from the powder in different environments; under high vacuum (10^{-6}Torr) and in liquid. For the latter, the powder was put into water or hexane, in which the complex is insoluble. If frictional electrification is of primary importance, ML intensity will be changed by the environment. In either case, ML intensity was almost the same as that in air. These observations indicate that, for the Eu complex powder, frictional electrification is not an important factor for the occurrence ML; a situation different from that of polymer-dispersed film. On the other hand, it would not be easy to assess the contribution of internal electrification and piezoelectrification. That Eu(TTA)$_3$(phen) belongs to noncentrosymmetric space group suggests the importance of the latter mechanism. The quantitative treatments of ML intensity, the analysis of the dependence of ML on crystal size, the observation of ML by mechanical stimuli in microscopic scale and so on are important to elucidate the detail of the mechanism.

CONCLUSION

We measured the transient properties of ML from Eu complex in powder and in polymer-dispersed film. For the polymer-dispersed film, its decay curve was found to be composed of two components corresponding to the emission from nitrogen molecules and from Eu ion. The ML excitation can be explained by discharge of air and electron impact both caused by frictional electrification. For the powder, ML excitation of Eu complex is caused not by frictional electrification, but by piezoelectrification and/or internal electrification in crystal.

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