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Red Mechanoluminescence and Photoluminescence from Novel Europium Complexes

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Abstract: Two new binuclear (europium and lanthanum) β-diketone complexes $Eu_{0.9}La_{0.1}(TTA)_3Phen$ and $Eu_{0.5}La_{0.5}(TTA)_3Phen$ in which Phen is 1,10-phenanthroline, TTA is an anion of thenoyltrifluoroacetone (HTTA) were synthesized for the first time. They showed intense photoluminescence (PL) and mechanoluminescence (ML), and had their maximum PL and ML spectra peaked at 613.5 nm with half bandwidth of 10 nm respectively. Their PL and ML intensity were obviously stronger than these from $Eu(TTA)_3Phen$. It is considered that binuclear (europium and lanthanum) β-diketones complexes are promising ML and PL materials.

Keywords: Europium β-diketone chelate, synthesis, mechanoluminescence (ML), photolumine-scence (PL).

Introduction

Mechanoluminescence (ML) is light emission caused by mechanical force such as grinding, cutting and so on. Although some of inorganic and organic molecular solids show ML, the ML mechanism has not been clearly elucidated yet [1-4]. The compound, which shows all of ML, photoluminescence (PL) and electroluminescence (EL) properties, has never been reported.

Recently, organic europium-complexes have attracted significant interest for the development of EL devices [5-9]. It is considered that europium complexes are one of the best red EL materials due to their good stability, high quantum efficiency and sharp emission. In this work, the design and syntheses of complexes $Eu_{0.9}La_{0.1}(TTA)_3Phen$ and $Eu_{0.5}La_{0.5}(TTA)_3Phen$ were reported. The ML and PL properties from these two chelates were characterized, and their ML mechanism was discussed. As both of the binuclear β-diketone complexes had excellent PL properties, it is expected that they would have EL properties. Their EL properties are under investigation.

Experimental

Chelating reagents such as 2-thenoyltrifluoroacetone (HTTA) and 1,10-phenanthroline (Phen) were obtained from the Third Reagent Plant of Shanghai, and purified with ethanol / water. Europium chloride and Lanthanum chloride were synthesized according

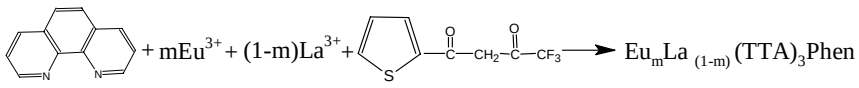
to literature 10.

The synthesis route of $Eu_{0.9}La_{0.1}(TTA)_3$ Phen was described in **Figure 1**. Europium chloride (0.9 mmol) and lanthanum chloride (0.1 mmol) were dissolved in 5 mL of pure water, then added into a solution of 3 mmol of HTTA in 30 mL of ethanol in a flask. The mixed solution was stirred, neutralized with 2 mol. L^{-1} sodium hydroxide and reacted for 0.5 hr at 50-60℃. After that, a solution of 1 mmol of Phen in 10 mL of ethanol was added into the above reactant and the granular precipitate was formed. The reaction mixture was continuously stirred for 2.5 hr and cooled to room temperature. The precipitate was filtered and washed with water and ethanol for several times, then recrystallized with acetone and ethanol. The pale yellow crystal was obtained with a yield of 72.5%, mp 253℃.

Similarly, $Eu_{0.5}La_{0.5}(TTA)_3$ Phen was synthesized. The pale yellow crystal was obtained with a yield 74.2%, mp 251℃.

The PL and ML spectra from solid $Eu_{0.9}La_{0.1}(TTA)_3$ Phen and $Eu_{0.5}La_{0.5}(TTA)_3$ Phen were measured with a fluorescence spectrophotometer (HITACHI-850).The ML spectra were measured in the condition of grinding the solid chelates with glass rod in a quartz cell

Figure 1. Scheme of preparation of $Eu_mLa_{(1-m)}(TTA)_3$ Phen



Phen **HTTA**

$Eu_mLa_{(1-m)}(TTA)_3$Phen

m=0.9 **1**

m=0.5 **2**

Results and Discussion

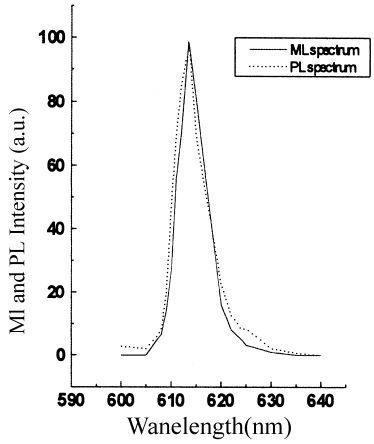
It was observed that the ML and PL spectra from solid $Eu_{0.9}La_{0.1}(TTA)_3$ Phen were almost identical to those from solid $Eu_{0.5}La_{0.5}(TTA)_3$ Phen. Therefore, only the PL and ML spectra from solid $Eu_{0.5}La_{0.5}(TTA)_3$ Phen were given in **Figure 2.** The PL spectrum from solid $Eu_{0.5}La_{0.5}(TTA)_3$ Phen was given for excitation at 538 nm. Its ML and PL spectra were very similar and had their maximum spectral peaks of 613.5 nm with the half bandwidth of 10 nm. This indicated that both of the two binuclear chelates could emit bright red light under mechanical force and light excitation.

The emission phenomena had not been found when the two chelates were heated. This showed that ML was not caused by thermal energy. It might be related to formation of charge and field when the chelate was being ground or cut. The separated charge could recombine and release the energy quickly. The energy transfer could take place from singlet state to triplet state of ligand (HTTA) in these two europium chelates. As the energy of the triplet state of ligand was well suitable to one of the exciting state of central ion (Eu^{3+}), the characteristic emission bands from this central ion (Eu^{3+}) were observed as a result of rapid intermolecular energy transfer.

The ML spectra from the two chelates were characteristic emission spectra of

europium ion caused by 4f electronic transfer from ^5D_o to $^7F_2$. Here lanthanum ion itself could not emit light, but it could make europium ion to emit stronger light due to "co-emissive effect".

Figure 2. The PL and ML spectra from $Eu_{0.5}La_{0.5}(TTA)_3Phen$



The ML intensity from the two chelates would decrease when the crystals of these chelates were split continuously. The chelates could emit stronger light when the applied stress was increased. It was curious that there was not ML phenomenon for the powder of the two chelates in the same condition. This indicated that ML intensity should depend on the volume of the crystals of these chelates and applied stress on them.

Conclusion

Two new binuclear (europium and lanthanum) β -diketone complexes were synthesized for the first time. They have intense ML and PL. Their maximum ML and PL spectra peaks located at 613.5 nm with half bandwidth of 10 nm. It is considered that binuclear (europium and lanthanum) β-diketone complexes are promising ML and PL materials.

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