

Control of Luminescence Intensity from Eu³⁺-doped Polyimide Nanoparticles by UV-irradiation and Thermal Treatment

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The control of luminescence intensity from Eu³⁺-doped polyimide (PI) nanoparticle film by UV-irradiation and thermal treatment was reported. In the system, it was observed that luminescence intensity assigned to rare earth ion increased with increase of the UV-irradiation time, whereas the intensity decreased with elevation of thermal treatment temperature and vanished at 200°C. It was estimated that the mechanism of the above phenomena is based on a reversible change in an energy transfer probability from PI to rare earth ion by the UV-irradiation and the thermal treatment. Luminescence intensity dependence on doped Eu³⁺ concentration was also investigated. Luminescence intensity increased with increase of Eu³⁺ concentration up to 5 wt%, and the concentration quenching of luminescence was observed above 5 wt%.

Key words: rare earth ion, polyimide, luminescence, energy transfer, optical memory

1. INTRODUCTION

The memory density in data storage has increased markedly. However, the memory density is still low because the binary recording system in one recording spot is used. The multinary recording system leads to high-density data storage and the materials for high-density recording medium using the multinary recording is reported. The persistent spectral hole burning in Eu³⁺ or Sm²⁺-doped glasses, i.e., some holes located at different wavelengths in a luminescence band are generated by the multiwavelength excitations, is one of the attractive phenomenon for high-density recording and has been studied extensively [1-4]. However, the recording system is complicated and expensive because the multiwavelength sources are required. Semiconductor nanocrystal surface-capped by tri-octylphosphine oxide is also promising material for the high-density recordable optical memory medium based on luminescence [5]. This material shows excitation-time dependent luminescence (ETDL) by irradiation of monowavelength excitation, i.e., luminescence intensity increase with increase of the excitation time. Therefore, the multinary recording is achieved by setting some thresholds in luminescence intensity. The material allows only once recording and cannot be reused.

We found that Eu³⁺-doped polyimide suits to the material for a high-density recordable and rewritable optical memory medium based on luminescence. Polymers have good properties such as a transparency, easy processability, low density and low cost and low fabrication energy. In particular, PI is one of the most promising high-performance polymer possessing highly thermal stability and good mechanical property. In this paper, we report the preparation of Eu³⁺-doped

polyimide and its luminescence properties.

2. EXPERIMENTAL

Polyamic acid (PAA) used as the precursor polymer of polyimide (PI) was produced by polyaddition reaction of 4,4'-oxydianiline (ODA) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) in *N*-methyl-2-pyrrolidinone (NMP), and the average molecular weight was ca. 120,000. All solvents and Eu(NO₃)₃·6H₂O were purchased from Wako Pure Chemical Industries, Ltd., and used without further purification. Eu³⁺-doped PAA nanoparticles were prepared by the conventional reprecipitation method [6-8]. Preparation method of non-doped PI particles has been already reported [9,10]. PAA and Eu(NO₃)₃·6H₂O were dissolved in NMP (good solvent). Weight ratio of PAA to NMP was 0.007 and Eu³⁺ to PAA was 0.01, 0.03, 0.05, 0.07, 0.10 and 0.20. This solution (100 μl) was rapidly injected using a microsyringe into 10 ml of cyclohexane (poor solvent) stirred vigorously. A small amount of the dispersing agent, Acrylic A-1380 (Dainippon Ink And Chemicals), was added into cyclohexane in order to suppress the aggregation of fine particles. Eu³⁺-doped PAA nanoparticles were immediately obtained after injection. Eu³⁺-doped PI nanoparticles could be obtained through the "two-steps imidization", i.e., the Eu³⁺-doped PAA nanoparticles were chemically imidized, thereafter thermally imidized up to quantitative conversion. Chemical imidization was performed by adding 500 μl of pyridine/acetic anhydride mixture (1:1) into the Eu³⁺-doped PAA nanoparticles dispersion liquid and keeping at room temperature for 3 h. Eu³⁺-doped PI nanoparticles in the resultant liquid were centrifuged at 12,000 rpm, washed with cyclohexane and redispersed into

cyclohexane. The nanoparticles were electro-deposited onto ITO substrates in the dispersion liquid, and the nanoparticle films obtained were further cured at 270°C for 1 hour. Scanning electron microscope (SEM) photographs were taken by a JSM-6700F (JEOL). UV-irradiation was performed by a battery operated UV lamp (Spectroline EF-160C/J, 254 nm, 6 W). Luminescence and excitation spectra were recorded on a Hitachi F-2500 fluorescence spectrometer.

3. RESULTS AND DISCUSSION

Figure 1 shows SEM photographs of Eu^{3+} -doped PI nanoparticles with controlled size. The average size of Eu^{3+} -doped PI nanoparticles investigated by SEM photographs was ca. 300 nm. Luminescence spectra of Eu^{3+} -doped (5 wt%) PI nanoparticle film after the

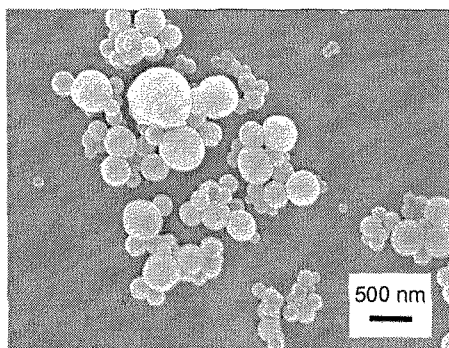


Fig. 1 SEM photograph of Eu^{3+} -doped PI particles.

UV-irradiation for various times is shown in Fig. 2. Typical luminescence bands ascribed to Eu^{3+} were observed at 579 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_0$), 593 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), 616 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$), 653 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_3$) and 700 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_4$). Luminescence intensity increased with increase of UV-irradiation time, i.e., UV-induced luminescence enhancement was observed. The luminescence enhancement saturated with UV-irradiation for about 12 h. Its intensity was kept for several months in darkness and room temperature. In general, luminescence quenching occurred under high concentration of an activator. Therefore, the dependence of activator, Eu^{3+} , concentration on luminescence intensity was investigated. Figure 3

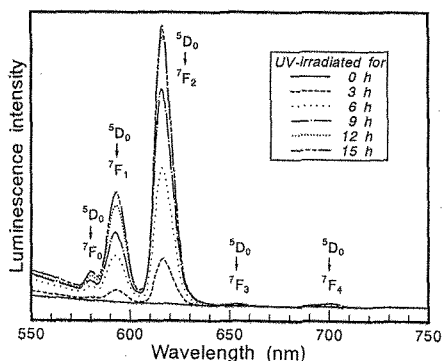


Fig. 2 Luminescence spectra of Eu^{3+} -doped PI nanoparticle film after UV-irradiation for various times. Excitation wavelength was 280 nm.

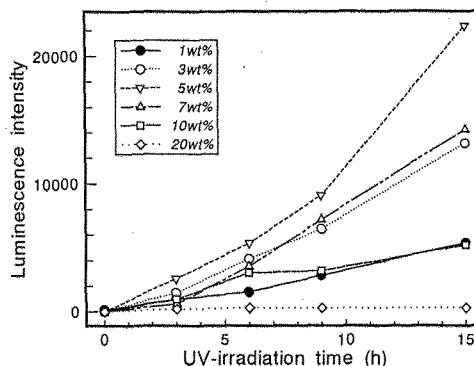


Fig. 3 Luminescence spectra of Eu^{3+} -doped (1, 3, 5, 7, 10, 20 wt%) PI nanoparticle films after UV-irradiation for various times. Excitation wavelength was 280 nm. Monitored wavelength was 616 nm.

shows luminescence spectra of Eu^{3+} (1~20 wt%) -doped PI particle films UV-irradiated for various times. All sample showed UV-induced luminescence enhancement. Luminescence intensity increased with increase of Eu^{3+} concentration up to 5 wt% and, luminescence quenching was observed beyond 5 wt% concentration. Rare earth ion-doped glasses usually show luminescence quenching at the concentration of ca. 1 wt%. It is suggested that the dispersity of Eu^{3+} in PI was good. Fig. 4 shows luminescence intensity of Eu^{3+} -doped PI nanoparticle film heat-treated at various temperatures for 30 minutes after UV-irradiation for 15 h at room temperature. Luminescence intensity measurement was performed at room temperature. Excitation wavelength was 280 nm and monitored wavelength was 618 nm. Luminescence intensity decreased with elevation of treatment temperature and disappeared at about 200°C. Figure 5 shows

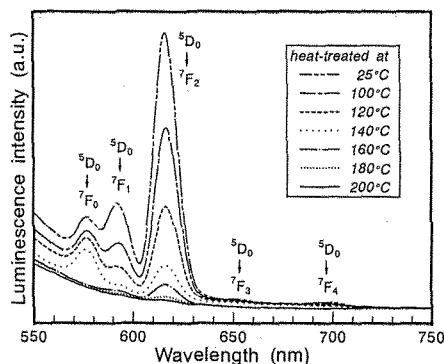


Fig. 4 Luminescence spectra of Eu^{3+} -doped PI particle films after UV-irradiation for 15 h and then thermal treatment at various temperatures.

luminescence intensity UV-irradiated for various times again after the thermal elimination of luminescence. Luminescence intensity increased with increase of UV-irradiation time again and finally recovered to the intensity UV-irradiated for 15 h before thermally erased. Thus, luminescence intensity of rare earth ion-doped PI particles could be controlled by UV-irradiation and thermal treatment. Figure 6 shows excitation spectra of Eu^{3+} -doped PI particle film, obtained by the luminescence at 618 nm, after the

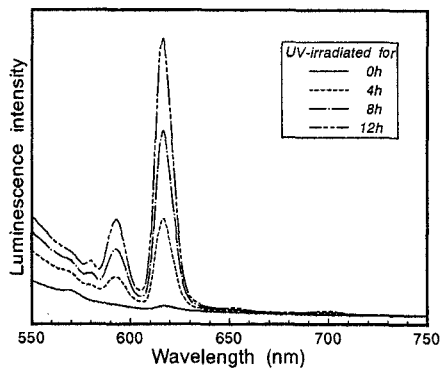


Fig. 5 Luminescence spectra of Eu^{3+} -doped PI nanoparticle film UV-irradiated for various times after thermal elimination. Excitation wavelength was 280 nm.

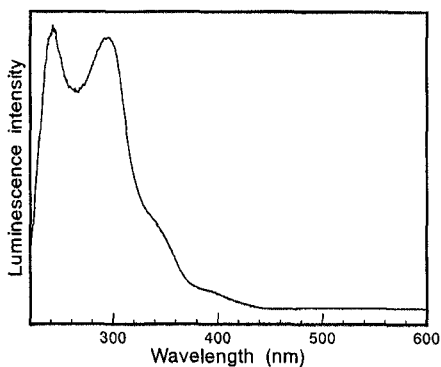


Fig. 6 Excitation spectra of Eu^{3+} -doped (5 wt%) PI nanoparticle film after UV-irradiation for 15 h. Monitored wavelength was 280 nm.

UV-irradiation for 15 hours. Two broad bands at 240 nm and 296 nm and a shoulder around 346 nm ascribed to PI were observed. Therefore, an energy transfer from PI to Eu^{3+} was suggested.

Although there is no report of these phenomena in regard to rare earth ion doped inorganic crystal, glass, polymer and rare earth complex, there were several reports about the luminescence enhancement of semiconductor particles in organic matrices by UV-irradiation [5,11]. The mechanisms were explained as reduction of trap sites, which acted as luminescence killer centers, in polymers or semiconductor particle surfaces, or decrease in quenching at trap sites. However, no one has reported that the trap sites act as killer centers for luminescence of rare earth ion. The oxidation of rare earth ions (Eu^{2+} , Tb^{3+} , Sm^{2+}) by UV-irradiation with existing of trap sites and the reduction of oxidized rare earth ions (Eu^{3+} , Tb^{4+} , Sm^{3+}) through a release of the trapped electron by a thermal energy are also known [12,13]. The change of charge number is often examined by an EPR measurement [14]. Eu^{3+} -doped PI particles were investigated by the EPR measurement. As a result, there was no change in EPR signals indicating that the oxidation-reduction of Eu ion occurred. Therefore, it was estimated that an energy transfer probability from PI to Eu^{3+} was changed reversibly by the UV-irradiation and the thermal treatment. Further

analysis such as the estimation of the lifetime must be performed to clarify the detailed mechanism.

4. CONCLUSION

Size-controlled Eu^{3+} -doped PI particles by the reprecipitation method were prepared. Eu^{3+} -doped PI particles showed the interesting luminescence properties: luminescence intensity assigned to Eu^{3+} increased with increase of the UV-irradiation time. The intensity decreased with elevation of treatment temperature, and vanished at 200°C. After the erase of luminescence, the intensity increased under the UV-irradiation again. UV-induced enhancement, thermal elimination and UV-reinduced enhancement after elimination of luminescence of Eu^{3+} have never been reported. Eu^{3+} -doped PI particles may be the promising material for the high-density rewritable memory medium.

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