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Author(s)
MIYAZAKI Hidetoshi / Kato Wataru / Yamada Katsumi

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Dysprosium hydroxide nanoparticle-embedded photoluminescent composite films

Hidetoshi Miyazaki, Wataru Kato, Katsumi Yamada

Graduate School of Natural Science Technology, Shimane University, 1060, Nishikawatsu, Matsue, Shimane 690-8504, Japan

miya@riko.shimane-u.ac.jp

Abstract

$Dy(NO_3)_3$ was dissolved in water–ethanol complex solvent, and the obtained solution was used to fabricate composite films wherein Dy compound particles were embedded in a transparent urethane resin. All the resulting composite films exhibited photoluminescence properties attributed to the Dy-based compounds. When the composite films were prepared by varying the water/ethanol ratio of the raw material solution, the PL intensity was stronger when the water content of the composites was higher. Further ultraviolet irradiation of the resulting films caused the disappearance of the Dy–OH bonds and decrease in the PL intensity of the films. The increase in the PL intensity with increasing water content was attributed to the presence of Dy–OH bonds in the films. In addition, we investigated the presence and PL properties of Dy–OH bonds in Dy-based particle composite films.

Keywords: Composite, Dysprosium, Photoluminescence

1. Introduction

Rare-earth-based materials have been widely studied and used in high-performance light-emitting devices because of their 4f electron-induced luminescence properties [1-5]. Several fluorescent materials use rare-earth elements, among which the yellow phosphor YAG:Ce [4] and long afterglow $SrAl_2O_4$:Eu,Dy [5] are applied. Generally, rare-earth-doped materials and glass/composite materials embedded with various rare-earth oxide nanoparticles have been studied [1-6] and mainly used owing to their own fluorescence; however, they are also used to adjust the color temperature.

The photoluminescence (PL) properties of Dy-based phosphors have been widely studied by doping Dy^{3+} into matrix phases such as crystals or glasses [7-10]. Investigations on the PL properties by forming nanoparticles or nanorods have also been reported [11-13]. We previously reported the PL properties of composite materials comprising Sm_2O_3 and Pr_2O_3 nanoparticles embedded in urethane resin [14, 15]. Urethane resin was used as the matrix because it shows transparency in the visible to near-infrared (IR) region and is easy to handle during material fabrication. Based on these studies, composite materials with PL properties can be fabricated by embedding Dy-based nanoparticles in urethane resin.

In this study, Dy compound-based composites exhibiting PL properties were fabricated using $Dy(NO_3)_3$ and transparent urethane resin. Furthermore, the relationship between the water content of the Dy-based composites and their PL properties was clarified.

2. Experimental procedure

$Dy(NO_3)_3$ (Fujifilm Wako Pure Chemical Corp., Japan) was dissolved in 2.0 mL of a solvent mixture of ethanol and ion-exchanged water (ethanol: 1.0–2.0 mL, ion-exchanged water: 0–1.0 mL) at a concentration of 4.0 M. The prepared precursor solution (1.0 mL) was mixed with 3.0 g of liquid urethane resin (M-40; AsahiKasei Chemicals Corp., Japan). The urethane resin comprised 55–70% unsaturated urethane prepolymer, 25–35% methacrylate derivatives, less than 5% additives, and 1% 2,6-di-tertbutyl-4-methylphenol. The urethane resin can be cured by ultraviolet-visible (UV-vis) light irradiation. The mixture was homogenized for 10 min to obtain a precursor slurry. Subsequently, the precursor slurry was degassed at 1 kPa for 20 min to remove dissolved air and placed into a mold made of glass plates to obtain a film with a thickness of 1.0 mm. The precursor films were irradiated with UV light for 10 min to cure the urethane resin matrix and the resulting composite was removed from the glass plates. Where, we used a Hg lamp with 100W though this investigation. The PL properties and microstructures of the as-prepared composites were evaluated. The composite films were re-irradiated with UV-vis light for 20 min to confirm the structural changes in the Dy-derived particles in the composite. To summarize these UV irradiation operations: the urethane resin was cured by a first UV irradiation, and then a subsequent UV irradiation resulted in the migration and clustering of dysprosium ions in the urethane matrix.

The film thickness was measured using a Vernier micrometer. The microstructures and particles in the composite films were characterized using transmission electron microscopy (TEM, EM-002B; Topcon Corp., Japan). The Dy-based particles in the composites were characterized using IR spectroscopy (Jasco FTIR 4600, Jasco, Japan). The transmittance of the films was measured using a UV-vis spectrophotometer (UV-1600; Shimadzu Corp., Japan) at a wavelength range of 200–1100 nm. The PL properties were evaluated using a spectrophotometer (RF-5300 PC; Shimadzu Corp., Japan), and a 430 nm optical filter was used to remove the duplicated light resulting from the Xe light source.

3. Results and discussion

The composite films were fabricated by varying water content (0, 0.2, 0.5, and 1.0

mL) in an ethanol–water solvent mixture (2 mL). The samples are denoted as S1 (no water), S2 (0.2 mL water), S3 (0.5 mL water), and S4 (1.0 mL water).

Figure 1 shows the UV-vis transmission and PL spectra of the composite films. The transmission spectra of the composite films in Figure 1 (a) exhibit absorption bands at 388, 451, 756, 806, and 910 nm; these absorption bands were attributed to the transitions of Dy^{3+} from $^6H_{15/2}$ to $^4I_{13/2}$, $^4I_{15/2}$, $^6F_{3/2}$, $^6F_{5/2}$, and $^6F_{7/2}$, respectively [9, 10]. The composite films S3 and S4 were cloudy; therefore, their transmittances were low. These results were attributed to the presence of water fractions in the urethane matrix because of the high-water content of the composites. Based on the absorption bands obtained from the transmission spectra and previous studies, it was assumed that excitation at 451 nm results in emission at approximately 570 nm [9, 10]. Therefore, we evaluated the PL properties of the composite films under excitation at 451 nm (Figure. 1(b)). All films exhibited PL with a peak at 570 nm. Moreover, a broad PL shoulder at approximately 550 nm was observed in the urethane matrix. The PL intensity of S1 was low and that at 570 nm increased with increasing amount of water in the composite films. S3 and S4 exhibited low transmittance over the entire visible-light range owing to cloudiness (Figure. 1(a)); thus, at the excitation wavelength (451 nm) the light also had low transmission. However, strong PL intensities were observed for S3 and S4. The

Dy-derived particles close to the film surface were considered to exhibit sufficient fluorescence intensity. We discuss later the effect of water on the formation of the Dy-based compounds and their PL properties.

Figure 2 presents the bright-field TEM images of the composite films of S1, S2, S3, and S4. The Dy-based compounds particles were dark (having contrast) relative to the urethane resin matrix because of the high electron density of dysprosium. The mean particle sizes of S1, S2, S3, and S4 were 4.2, 4.1, 4.4, and 3.9 nm, respectively. Similar to the PL properties of Sm- and Pr-based composite films reported previously [14, 15], the PL properties of Dy-based compounds are attributed to their small particle size.

In previous studies, we fabricated composite films embedding Sm or Pr complex mixtures and evaluated their PL properties [14, 15]. In these studies, the Sm- and Pr-based compounds migrated through the films upon further long-term UV irradiation, causing the growth of the Sm- or Pr-based compound particles. In this study, we also further UV irradiated the Dy-based composite films to evaluate their particle compositions, microstructures, and PL properties. Thus, in the present study, we subsequently performed UV irradiation of S3, which is a typical Dy-based composite film, and evaluated the PL properties of the resulting composites.

Figure 3 depicts the PL spectra of the S3 composite film before and after 20 min of

UV irradiation. Figure 4 shows the IR spectra of the source $Dy(NO_3)_3$ and the S3 composite film before and after 20 min of UV irradiation, and Figure 5 presents the TEM image of the S3 composite film after 20 min of UV irradiation. The PL intensity of the composite film decreased with the additional UV irradiation, and a low intensity peak at 570 nm appeared after 20 min of UV irradiation. The IR spectroscopy measurements revealed the presence of Dy–OH bonding (842 and 867 cm^{-1}) in the as-fabricated S3 sample [16], but no Dy–OH bonding was revealed in the sample after 20 min of UV irradiation. The spectrum of $Dy(NO_3)_3$ was similar to that reported previously [17], and it was observed in the composite spectra before and after UV irradiation. According to the TEM images, the mean particle size was 4.4 nm for the sample before UV irradiation, which increased to 10.6 nm after UV irradiation. From these IR and TEM results, we speculate the following: 1. Dy–OH-based particles (We speculated that Dy-based fine particles were formed by compounds with Dy-OH bonds, such as $Dy(OH)_3$ or DyO(OH).) with a diameter of approximately 4 nm were present in the as-fabricated composite films. 2. Additional UV irradiation caused the migration of Dy–OH-based particles in the matrix. 3. Accompanying this phenomenon, the OH groups bounded to Dy were removed, and Dy-based compound particles without OH groups grown. Figure 6 describes the process of Dy ion source in the composite growing into DyOH base particles by UV irradiation. Although the PL properties of the particles with Dy–OH bonds have been rarely reported, Dy-based compound nanoparticles with Dy–OH bonds exhibit strong PL properties. In a previous study on the PL properties of Dy_2O_3-based particles [13], it was reported that the smaller the particle size of Dy_2O_3, the higher the PL strength. In this study, the size of the Dy-based particles in the composite film after UV irradiation was approximately 10 nm, which is significantly small. However, the PL intensity of the composite after UV irradiation was considerably lower than that of the composite containing the Dy–OH-based particles (as-fabricated S3 composite). The particle size before UV irradiation (approximately 4 nm) was not significantly different after irradiation (approximately 10 nm), and the Dy–OH bonding was considered a major contributor to the PL of the Dy-based particles. According to the IR spectroscopy results, the raw material, $Dy(NO_3)_3$, remained in the fabricated composites. Thus, we assumed that the PL efficiency of the composites could be further improved by effectively converting the source $Dy(NO_3)_3$ to $Dy(OH)_3$.

4. Conclusion

Dy-based particle-embedded composite films were fabricated using $Dy(NO_3)_3$ and a urethane resin matrix by varying water content. All the resulting composite films exhibited PL properties originating from the transition of Dy from $^4F_{9/2}$ to $^6H_{13/2}$. With increasing water content in the composite, the composite became opaque; however, the PL intensity increased. The size of the Dy-based particles in the composite was of approximately 4 nm, regardless of the water content. Additional UV irradiation to the composite films with higher water content and stronger PL intensities resulted in the disappearance of the Dy–OH bonds and a decrease in the PL intensities. In summary, we demonstrated that the PL properties of Dy-based composites can be controlled by the Dy–OH bond presence in the particles of the films.

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Figure captions

Fig. 1. UV-Vis transmission spectra and PL spectra of the composite films of S1, S2, S3, and S4.

Fig. 2. Bright-field TEM images of the composite films of S1, S2, S3, and S4. Particles are within the dotted circle.

Fig. 3. PL spectra of the composite films of S3 before and after UV irradiation.

Fig. 4. IR transmission spectra of the source $Dy(NO_3)_3$ powder and the S3 samples before and after UV irradiation.

Fig. 5. Bright-field TEM images of the S3 samples before and after UV irradiation.

Fig. 6. A schematic illustration of the process of Dy ion source in the composite growing into DyOH base particles by UV irradiation.

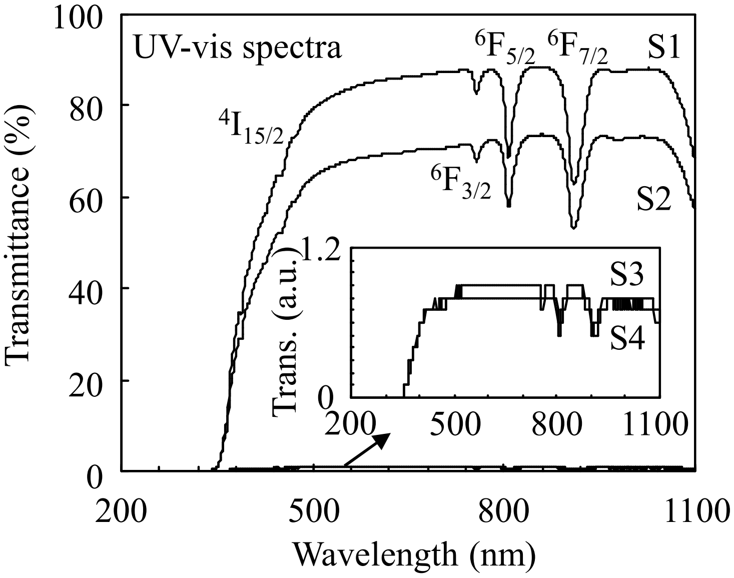

Fig. 1. (UV)
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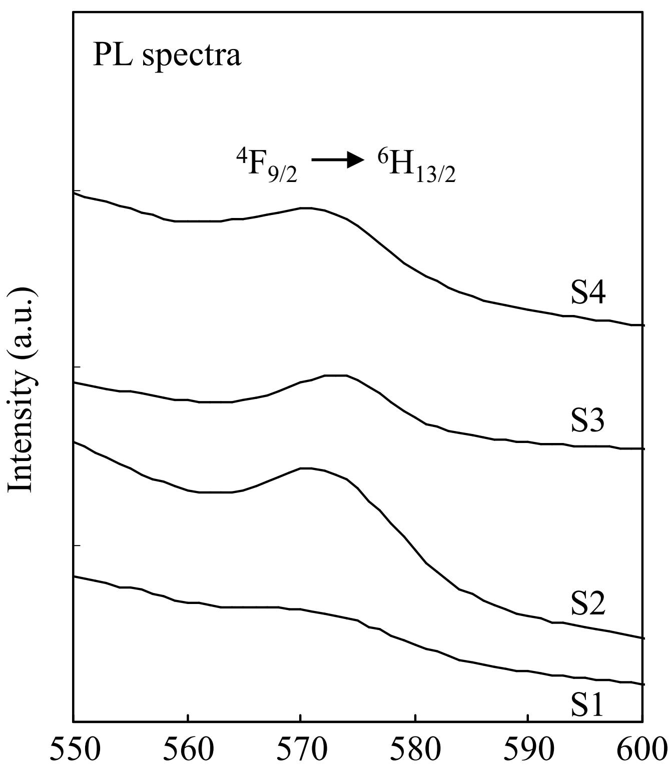

Fig. 1. (PL)
H. Miyazaki

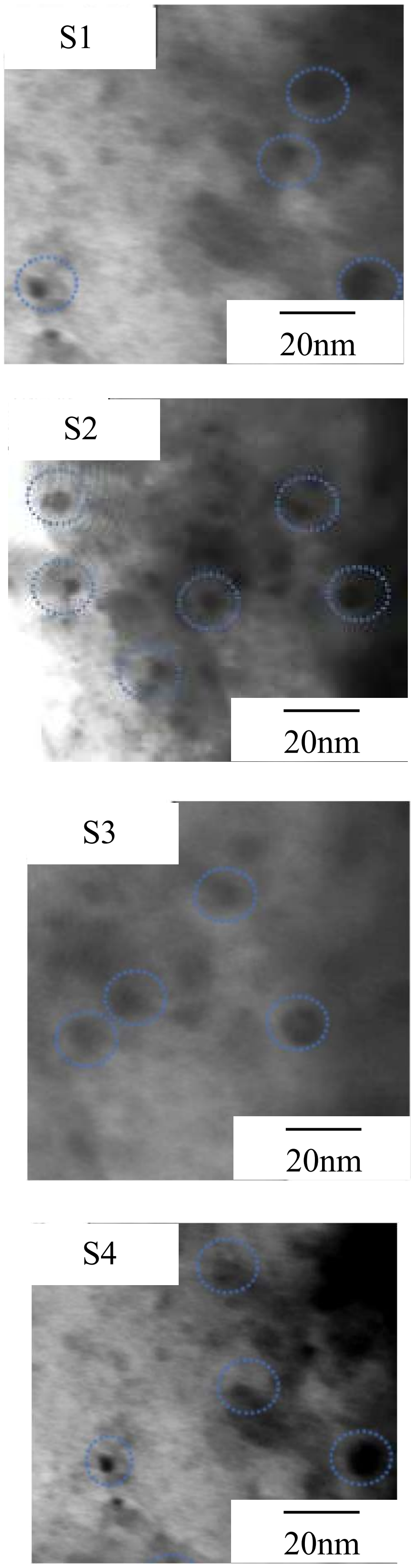

Fig. 2.
H. Miyazaki

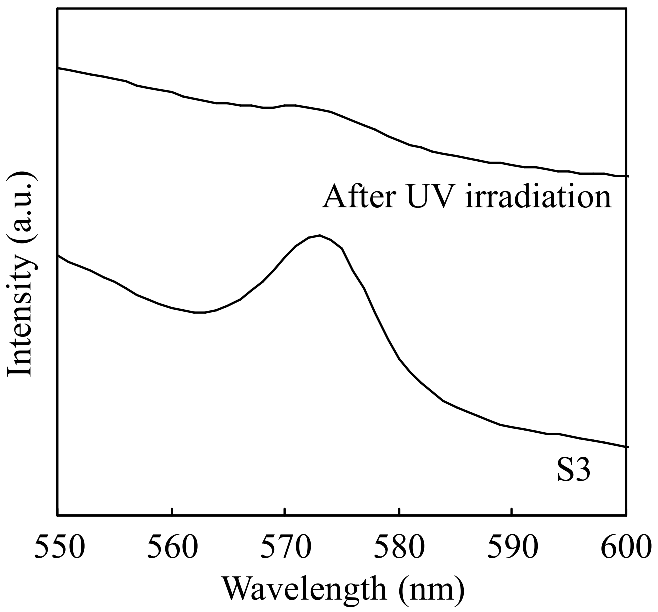

Fig. 3.
H. Miyazaki

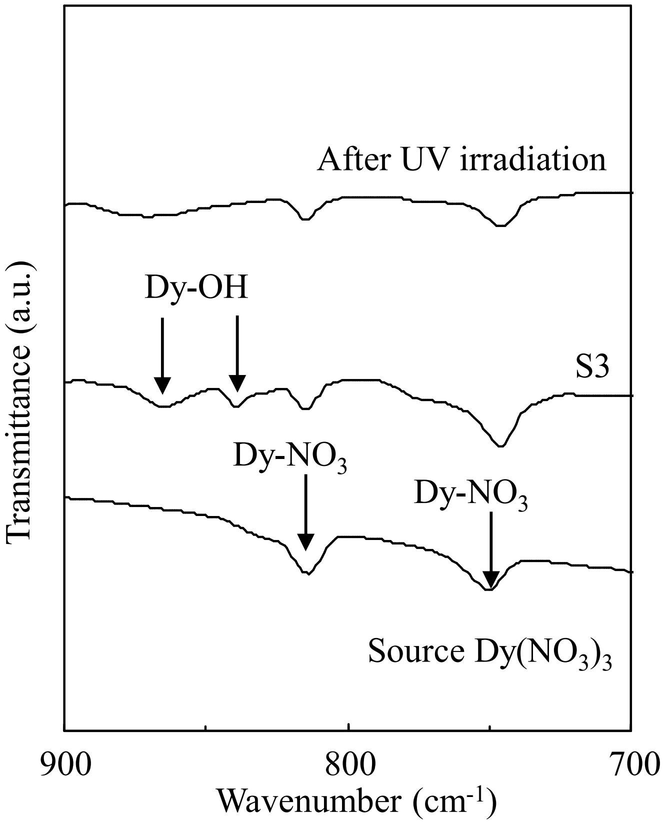

Fig. 4.
H. Miyazaki

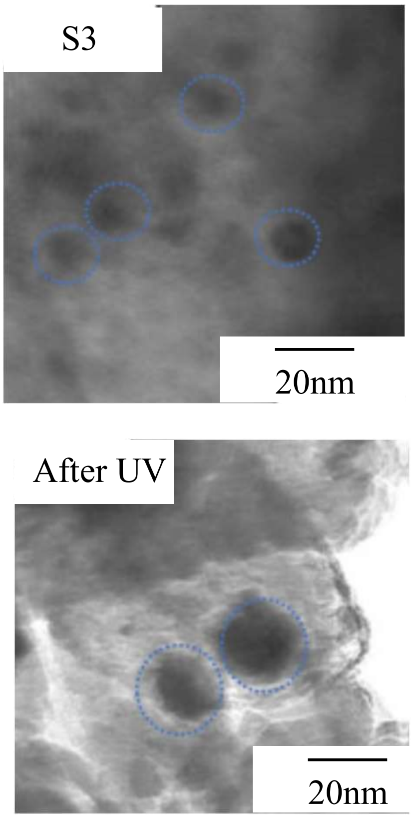

Fig. 5.
H. Miyazaki