

Luminescence properties and chemical structure of red fluorescent material using europium(III)-doped benzoguanamine

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Europium (Eu) has been extensively studied as a red-emitting material. However, conventional Eu-containing complexes are typically synthesized in small amounts due to difficulties in controlling the complexation reaction and the difficulty of synthesis on a large (gram) scale [1]. Moreover, they also have the issue of low solubility in organic solvents, making it difficult to apply to devices through wet-process. To solve this issue, we fabricated Eu-doped benzoguanamine using europium chloride hexahydrate, which shows red luminescence with high color purity and good dispersibility in several solutions [2]. In addition, we investigated the annealing condition and Eu-doping condition to maximize its photoluminescence (PL) intensity. In this research, we varied the preparation conditions of the samples in detail to identify the conditions that maximize PL quantum yield (PLQY) and studied their chemical structures using X-ray photoelectron spectroscopy (XPS).

A total of 25 samples were prepared under five different Eu-doping conditions (1, 5, 10, 15, and 20 wt%) and five different annealing temperatures (220, 240, 260, 280, and 300°C). These were made by mixing europium hexahydrate and benzoguanamine, grinding them in a crucible, and annealing them in an electric furnace. Figure 1 shows PLQY values of the 25 samples. The PLQY tends to be higher in samples with synthesis temperatures above 260°C. This is most likely caused by melting of benzoguanamine above its melting point (228°C), which improved the reactivity of the raw material and facilitated the uniform dispersion of Eu(III) ions. This is believed to have optimized energy transfer and increased PLQY. For samples with synthesis temperatures above 260°C, PLQY tended to flatten when the addition concentration exceeded 10 wt%. This is due to concentration quenching caused by the excess Eu-doping.

Figure 2 shows the results of XPS observation. The Eu 3d spectra in Fig.(a) show peaks at 1125 and 1135 eV attributed to $\text{Eu}_{3d_{5/2}}$. This is consistent with Eu(III) ions in the Eu_2O_3 form, suggesting that the added Eu(III) ions are trivalent. From the N 1s spectra in Fig.(b), peaks attributed to the amino group of benzoguanamine were observed around 398 eV. In addition, the peak shifted to the higher energy side and the peak intensity decreased with increasing Eu doping concentration. These results clearly indicate that the Eu(III) ion and benzoguanamine are coordinately bonded via an amino group ($-\text{NH}_2$). Therefore, the peak shift and intensity decrease observed in Fig.(b) are due to the decrease in electron density caused by the attraction of the positive charge of the Eu(III) ion to the nitrogen side via this bonding. From these results, we concluded that the Eu(III) ion is most likely to form a complex with benzoguanamine.

At the conference, we will discuss in more detail with XRD, FT-IR, and PL lifetime results.

References

- [1] S. Miyazaki, et al., *Chem. Sci.*, **14**, 6867 (2023).
- [2] T. Niimi, H. Takemura, N. Ohtani, *Jpn. J. Appl. Phys.*, **63**, 02SP17 (2024).

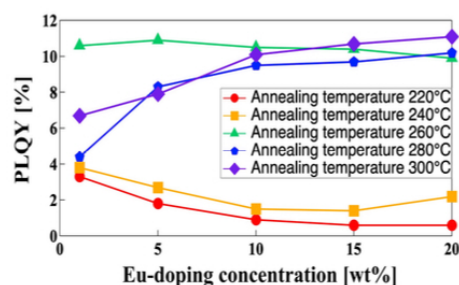


Fig. 1. PLQY values of 25 samples.

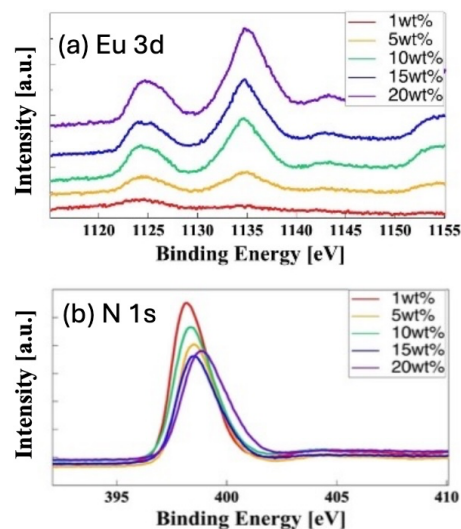


Fig. 2. Eu-doping concentration dependence of XPS of five samples annealed at 260°C: (a) Eu 3d and (b) N 1s spectra.