Improvement of Photoluminescent Characteristics by Post Annealing in O_3 atmosphere for $Y_4Si_2O_7N_2:Eu^{3+}$ Phosphors

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ABSTRACT

A low-temperature post-annealing in O_3 atmosphere has been attempted to enhance the Eu^{3+} activation for $Y_4Si_2O_7N_2:Eu^{3+}$ red phosphor, which were prepared by the solid-state reaction in NH_3. By the annealing, the photoluminescence excitation band due to the Eu^{3+} charge transfer state increases by about 40%, compared to the unannealed samples.

1 INTRODUCTION

Recently, the video format of "Rec. ITU-R BT.2020 (and BT.2100)" has been proposed, and a development of RGB phosphors covering a wide color gamut is desired. As a next generation red phosphor, a narrow emission band is required. In addition, to achieve a high luminous efficiency, the red phosphor should be excited by a blue LED light. We have been searching Eu^{3+} activated oxynitride phosphors for white LED applications. One of candidate phosphor is $Y_4Si_2O_7N_2:Eu^{3+}$. Nakamoto et al. reported that Eu^{3+}-activated $Y_4Si_2O_7N_2$ could be obtained by post annealing in air for both Eu^{2+} and Eu^{3+} containing $Y_4Si_2O_7N_2$ powder. The charge transfer state (CTS) energy of $Y_4Si_2O_7N_2:Eu^{3+}$ was estimated to be 3.61 eV lower than that of $La_2O_2S:Eu^{3+}$ (3.58 eV) [1]. However, the luminescent intensity was insufficient. In this paper, we attempt a low-temperature annealing in O_3 atmosphere, which has a much high oxidizability than O_2. Therefore, the O_3 annealing is expected to enhance Eu^{3+} activation by oxidizing Eu^{2+}, which is formed during the firing in reductive NH_3 atmosphere. A low-temperature oxidization process in O_3 is used for the ceramic synthesis [2].

2 EXPERIMENTAL

Phosphor samples were prepared by the solid state reaction method. Source materials of Y_2O_3, SiO_2, Si_3N_4, and Eu_2O_3 were mixed with the stoichiometric ratio. The Eu concentration was 1 mol% for all samples. The mixture was firstly fired at 1350℃ for 3h in NH_3 atmosphere [1]. After that, the post-annealing in O_3 atmosphere was performed for 5h at several temperatures between 385 - 485℃. Figure 1 shows the schematic diagram of the post-annealing system. A commercially supplied ozone generator having a generation performance of 20 g/h and an electric furnace are serially connected. The flow rate into the furnace was controlled by a valve. The photoluminescence (PL) and PL excitation (PLE) spectra were measured by using a fluorescence spectrometer (JASCO FP-6500). For the PL temperature measurements, the optional unit of the PMU-183 (JASCO) the HPC-503 (JASCO) were also used for the lower (90 ~ 290 K) and higher temperature (270 ~ 520 K) measurements, respectively.

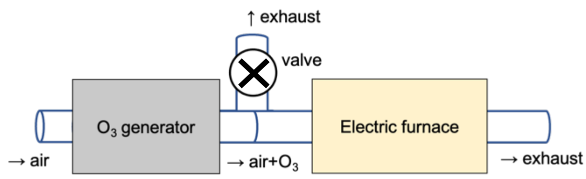

Fig.1 Schematic diagram of post-annealing system in O_3 atmosphere.

3 RESULTS AND DISCUSSION

In this study, we found that the optimum annealing temperature was 435℃ from the optical properties of obtained phosphor powders. In this section, the all results of the samples annealed at 435℃ are described.

Figure 2 shows the diffuse reflectance (DR) spectra of $Y_4Si_2O_7N_2:Eu^{3+}$ annealed at 435℃ in air or O_3 atmospheres. The result of the unannealed sample is also shown for reference. For the unannealed sample, a broad large absorption is observed in the spectral region from 300 to 550 nm. The absorption consists mainly of the $4f^7$–$5d4f^6$ transition in Eu^{2+} centers. The f-d absorption is reduced by the annealing, and weak absorption remains from 300 to 400 nm, in which is thought to be the Eu^{3+} CTS excitation band. Taking the variation of reflectance into account, one can conclude that the Eu^{2+} ions are oxidized into Eu^{3+} ions by the annealing, and that the O_3-annealing is more effective to obtain much more Eu^{3+} ions than the air-annealing.

Figure 3 shows the PL and PLE spectra of the same samples. All samples show sharp emission lines due to the $4f^6$-$4f^6$ transition of Eu^{3+} centers. In the PLE spectra, two broad excitation bands peaking at about 250 nm and 330 nm are observed. The former band is due to the host excitation, and the latter one is due to the CTS excitation, which are observed in DR spectra, respectively. A sharp excitation peak due to direct 4f-4f excitation is also observed at 460 nm. The spectral shapes are almost similar for all samples, thus the Eu^{3+} centers are located in the same sites in $Y_4Si_2O_7N_2$ crystals, and they are not changed by the annealing. All excitation bands are remarkably increased by annealing. Compared to the unannealed sample, the PLE intensities of the CTS band are approximately 1.4 and 2.6 times stronger for the air-annealing and O_3-annealing, respectively.

Figure 4 shows the PL temperature dependences of the same samples. The measurements were carried out under the UV irradiation at 335 nm which coincides with the CTS band. For the unannealed sample, the PL intensity below 250 K is almost saturated, however slight decrease is found below and above 200 K, which might be attributed to the thermally-assisted cross relaxation in the Eu^{3+} centers. Neglecting this deviation and assuming a single activation energy from CTS to 4f ground state, curve fitting based on Arrhenius equation is performed above 250 K region. The activation energy is estimated to be 0.21 eV, which is similar but slightly smaller than the previous value [3]. For the air-annealed and O_3-annealed samples, a similar temperature quenching is observed in the high temperature region above 250 K, and the corresponding estimated activation energy is 0.22 eV and 0.25 eV, respectively. Contrary, both annealed samples show gradual increase in the lower temperature range. This fact implies the existence of shallow defects, which might be considered to be formed with the Eu^{3+} oxidization by the low temperature annealing near the surface of the powder particles. Further improvements of reducing defects and/or stable Eu^{3+} activation are required to achieve a high luminescence.

4 CONCLUSIONS

The low-temperature post-annealing in O_3 atmosphere was attempted to enhance the Eu^{3+} activation for $Y_4Si_2O_7N_2:Eu^{3+}$ red phosphor. By the annealing, the intensity of the Eu^{3+} CTS excitation band is increased by about 40%, compared to the unannealed sample. This annealing technique is expected to be effective to activate Eu^{3+} centers, especially for high-covalent other oxynitride host materials.

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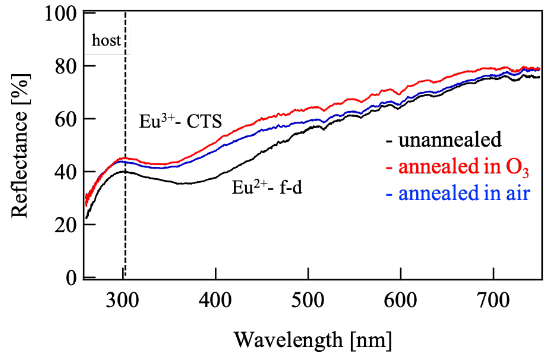

Fig.2 Diffuse reflectance spectra.

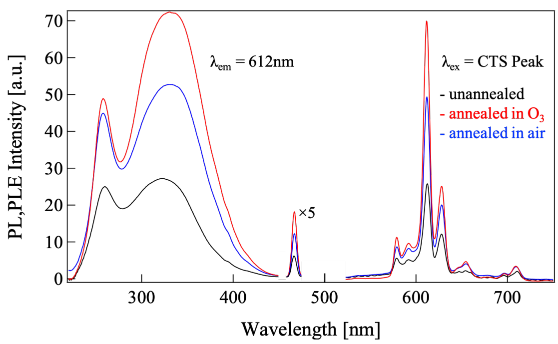

Fig.3 PL and PLE spectra.

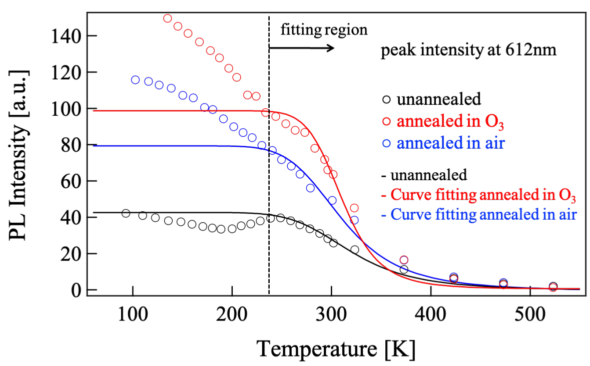

Fig.4 Temperature dependences of PL intensity.