Development of $(La,Y)_3Si_6N_{11}:Ce^{3+}$ Nitride Yellow Phosphors for High-Power Excitation

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ABSTRACT

$(La,Y)_3Si_6N_{11}:Ce^{3+}$ (LSN) phosphor has been used for white LEDs in back light units (BLUs). We have succeeded in developing LSN phosphors with wide color variations and excellent luminescence properties. We expect that LSN phosphors will be used not only in BLUs but also in other lighting and laser devices.

1. INTRODUCTION

$(La,Y)_3Si_6N_{11}:Ce^{3+}$ (LSN) is a good candidate for yellow-emitting phosphor in white LEDs due to its wide and strong absorption in the UV to blue region and its efficient yellow luminescence [1][2][3]. Figure 1 shows the excitation and emission spectra of LSN as compared to those of $Y_3Al_5O_{12}:Ce^{3+}$ (YAG). The emission spectrum of LSN has a broad band consisting of a peak and a shoulder. Those are attributed to the Ce^{3+} emissions. It should be noted that the LSN exhibits strong emission in the green region, as seen in Fig. 1. As a result, LSN has been widely used for back light units (BLUs) because of its unique spectral property.

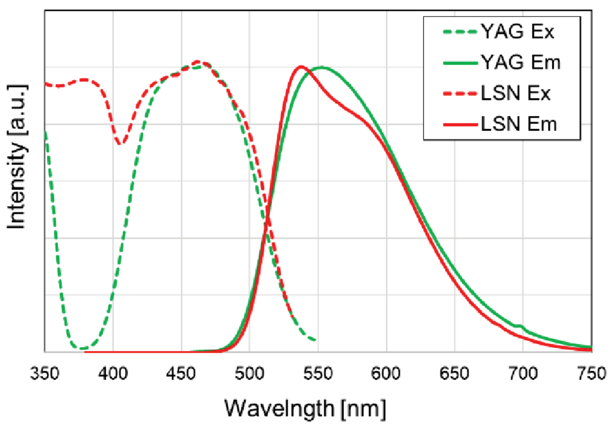


Fig. 1. PL emission and excitation spectra of LSN and YAG.

It is known that the emission peak wavelength is red shifted by substitution of yttrium to Lanthanum [4][5]. LSN has high luminescence efficiency and good thermal stability regardless of yttrium concentration. Because of these excellent characteristics, LSN is also expected to be used as a yellow phosphor in lighting devices instead of YAG.

Various high-power small-size LED packages are being developed these days. In such packages, –phosphors in LEDs must meet strict environment requirements: they must have excellent temperature stability and luminance saturation property, as well as high conversion efficiency.

In this work, we investigate whether LSN has a potential to meet these strict requirements.

2. EXPERIMENTAL PROCEDURE

A lanthanum silicide alloy, Si3N4, cerium, and yttrium sources were weighed and mixed. The Ce and Y concentrations were controlled according to the required emission color. The filling of raw powders was performed in a globe box to prevent raw materials from oxidizing. The crucibles containing raw materials were heated at 1600°C or lower in a flowing N_2-H_2 gas. After the sieving process, the fired sample was washed and ground.

Photoluminescence (PL) excitation and emission spectra at room temperature and thermal quenching properties were measured using a fluorescence spectrophotometer. Internal quantum efficiency (iQE) dependence on the excitation density of samples was measured using a blue laser diode, in which phosphor was dispersed in a resin.

3. RESULTS AND DISCUSSION

Figure 2 shows the PL emission spectra of LSN.

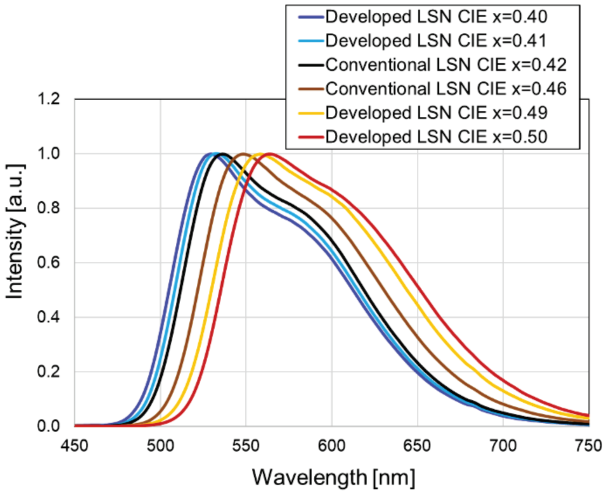


Fig. 2. PL emission spectra of conventional and developed LSN.

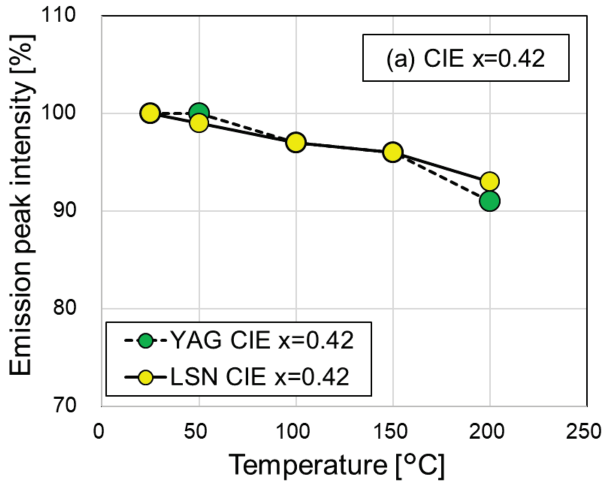
We succeeded to get LSN with a wider emission range than in conventional LSN by adjusting the Ce and Y ratio in the composition. The emission peak wavelength of the sample which had the shortest emission wavelength in this work was 531 nm, and the dominant wavelength of the sample was 565 nm. The CIE chromaticity coordinates of the shortest LSN was x=0.403 and y=0.566.

On the other hand, the longest emission wavelength and the dominant wavelength were 565 nm and 578 nm, respectively. The CIE chromaticity coordinates of the longest LSN was x=0.504 and y=0.494. These emission color ranges of the samples are much wider than in previous reports [4][5].

We evaluated thermal stability and luminescence saturation characteristics of LSN. We chose three LSN samples which have different luminescent color, CIE x=0.42, 0.46, and 0.49. For comparison, commercial YAG with the same emission color was also evaluated. However, there was no commercial YAG sample with the CIE x=0.49. Figure 3 shows thermal quenching of the PL intensity of LSN as compared with YAG. The LSN and YAG exhibit similar thermal quenching when CIE x = 0.42, as shown in Fig. 3(a). However, the emission peak intensity of YAG drastically decreases when CIE x =0.46 and LSN shows a slight decrease when CIE x=0.46 and 0.49, as shown in Fig. 3(b).

The iQE dependence on the excitation density of LSN and YAG with under blue laser excitation are shown in Fig. 4. The LSN and YAG show similar maintenance of iQE when CIE x=0.42, as demonstrated in Fig. 4(a). However, the YAG exhibits a drastic decrease when CIE x=0.46 and LSN show slight decrease when CIE x=0.46 and 0.49, as shown in Fig. 4(b).

These results indicate that YAG has lower emission efficiency at higher temperatures and higher excitation densities when the emission wavelength becomes longer. On the other hand, LSN has excellent thermal stability and low excitation density dependence regardless of the emission color range.



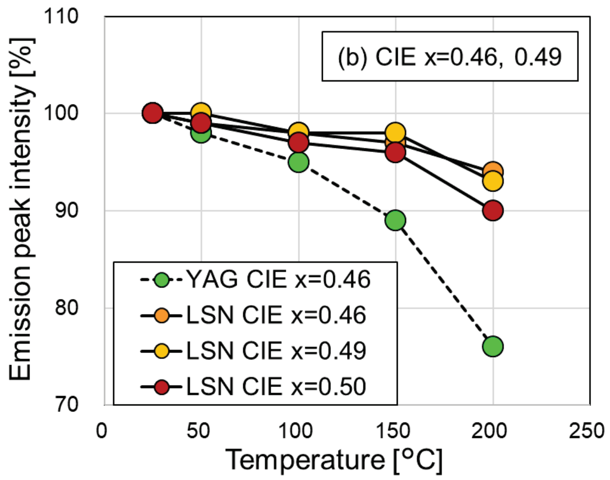


Fig. 3. Dependence of PL intensity of LSN and YAG on temperature, (a) CIE x=0.42, (b) CIE x=0.46 and 0.49.

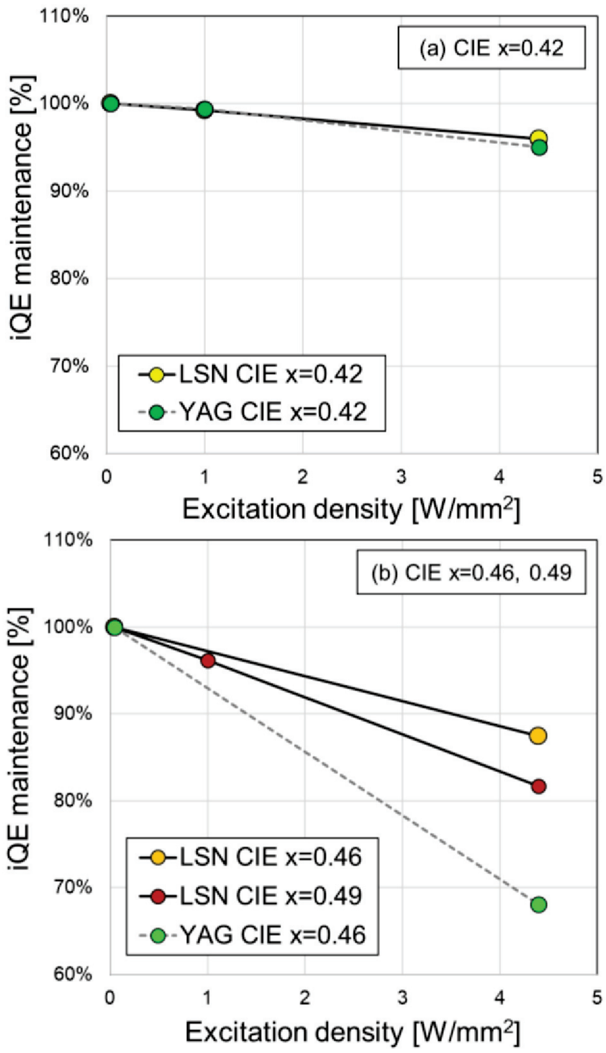


Fig. 4. Dependence of iQE of LSN and YAG on excitation density, (a) CIE x=0.42, (b) CIE x=0.46 and 0.49.

4. CONCLUSION

We succeeded in expanding the luminescent color range of LSN by adjusting the composition. LSN with its longer emission wavelength has excellent thermal stability and luminescence saturation characteristics compared to YAG, which has the same emission color. These results indicate that LSN can replace YAG as a yellow-orange phosphor in applications requiring high excitation density such as high-power LEDs or laser diode devices.

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