P-70: Photoluminescence of $SrO-Al_2O_3$ Doped with Eu and Ce Excited at near UV

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Abstract

The effect of excitation energy and various dopants(Eu and Ce) on the emission wavelength and intensity were investigated. According to PL spectra, $SrO-Al_2O_3$ phosphors had wide absorption band at nUV. By substituting Ce for Eu, the emission band and excitation wavelength were shifted to shorter wavelength. Ce doped $SrAl_2O_4$ and $Sr_4Al_{14}O_{25}$ showed greenish blue(475nm) and blue(400nm), respectively.

1. Introduction

In these years, the white LEDs organizing UV LED and RGB phosphors have been extensively investigated. Advantages of this LED are high efficiency and excellent CRI(Color Rendering Index). Furthermore, this LED is easy to control CCT(Correlated Color Temperature) by changing a ratio of RGB phosphor.[1,2]

But, some problems were remained. The most important property of RGB phosphor for UV LED is that the phosphors are excited at near UV. Many phosphors of commercial business have excitation wavelength about 250nm. So, development of new phosphors for nUV excitation has been demanded.

$SrO-Al_2O_3$ phosphors have various luminescent properties depending on dopants and mole ratios of raw materials. $SrAl_2O_4$:Eu and $Sr_4Al_{14}O_{25}$:Eu, Dy are known as long residual phosphor.[3-5] These phosphors are excited at above 350nm. So, they are one of promising phosphors to bring a solution above mentioned problem.

In this experiment, $SrAl_2O_4$ and $Sr_4Al_{14}O_{25}$ phosphor were synthesized by solid state reaction. The effect of dopants on the luminescent properties was investigated.

2. Experiment

$SrCO_3$ (Aldirich, 99.9%+), Eu_2O_3 (Aldrich, 99.99%), Dy_2O_3 (Aldirich, 99,99%), Ce_2O_3 (United International Inc., 99.99%), and H_3BO_3 (High Purity Chemical, 99.99%) were used as raw materials. SrO and Al_2O_3 was mixed at 1:1 and 4:7 mole ratio, respectively. As a flux, H_3BO_3 was added. The mixture was ball-milled for 24 hours and fired 5 hours at 1300℃ in N_2+vacuum atmosphere. N_2 gas was flowed at 5cc/min while firing.

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To investigated the dopant effects, $Sr_{1-x}Al_2O_4:Eu_x$ (x=0.001~0.01), $Sr_{1-x}Al_2O_4:Ce_x$ (x=0.03~0.08), $Sr_{4(1-x)}Al_{14}O_{25}:Eu_x$ (x=0.02~0.08), and $Sr_{4(1-x)}Al_{14}O_{25}:Ce_x$ (x=0.05~0.07) were synthesized. The crystalline of prepared powders were analyzed by XRD (X-ray diffractometer, SIEMENS D5005), and luminescence was measured by PL (Photoluminescence, PSI Darsa-5000) system.

3. Result & Discussion

3.1 Synthesis of $SrAl_2O_4$ and $Sr_4Al_{14}O_{25}$

Fig. 1 shows XRD patterns of $SrAl_2O_4$ with various contents of H_3BO_3 that was added as a flux. According to previous works,[3,5] a flux method has been introduced to synthesize $SrO-Al_2O_3$ powder. However, in these experimental conditions, a single phase $SrAl_2O_4$ could be obtained only without a flux, H_3BO_3.

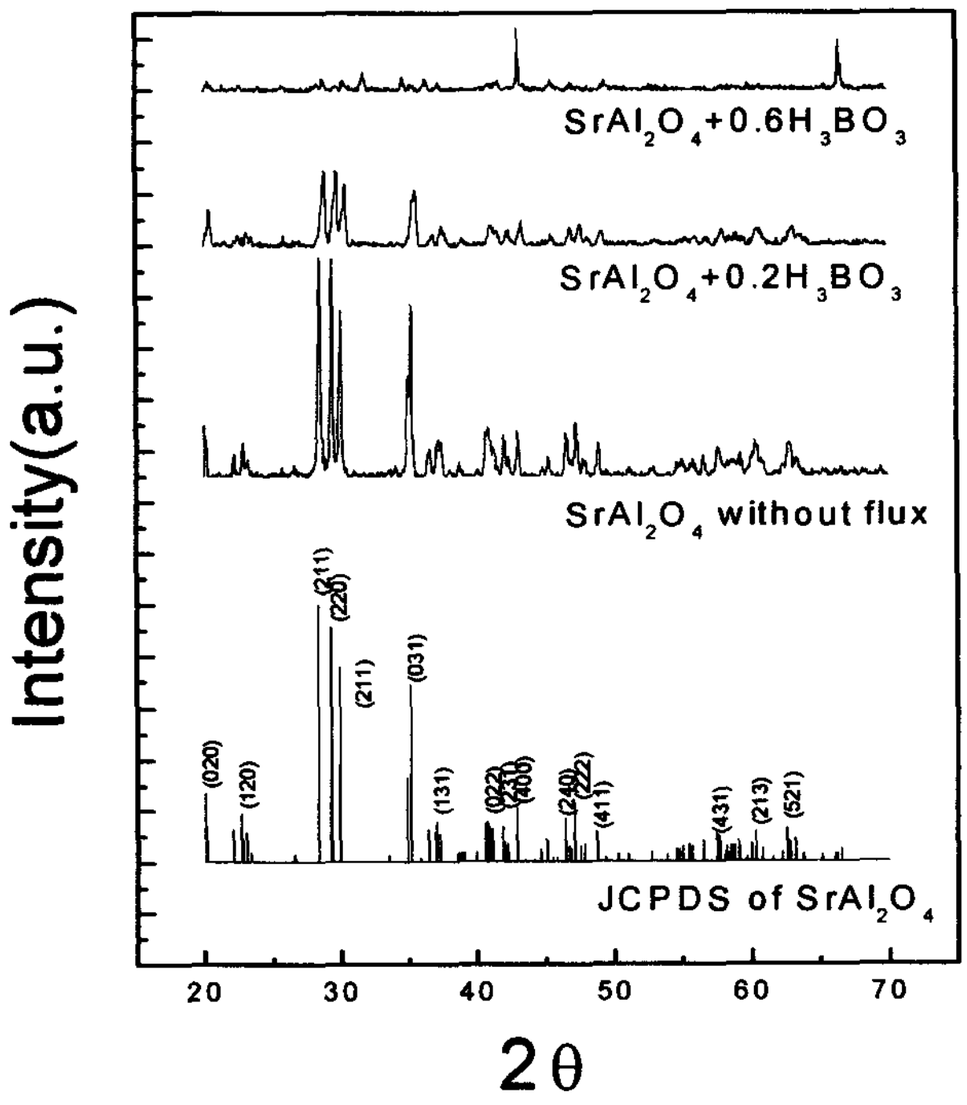

Fig. 1. XRD patterns of $SrAl_2O_4$ powders.

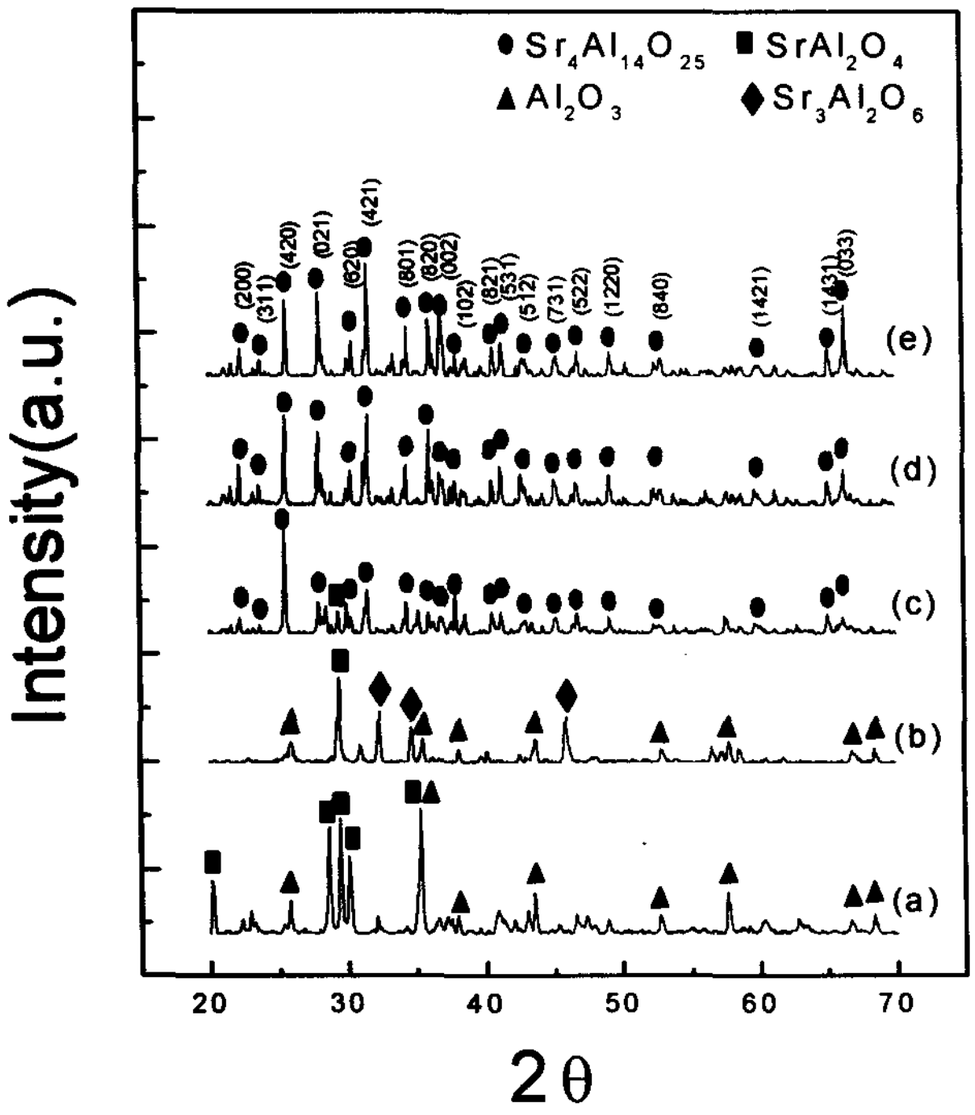

Fig. 2. XRD patterns of $Sr_4Al_{14}O_{25}$ powders.
(a) 0 mol H_3BO_3, (b) 0.2mol H_3BO_3, (c) 0.4mol H_3BO_3, (d) 0.6mol H_3BO_3, and (e) 0.8mol H_3BO_3

By adding H_3BO_3, other phases were appeared in XRD as shown in Fig. 1 (b) and (c). On the contrary, a single phase $Sr_4Al_{14}O_{25}$ could be obtained by adding a flux, H_3BO_3 as shown in Fig. 2 (d) and (e). When H_3BO_3 was not added, secondary phases such as Al_2O_3, $SrAl_2O_4$, and $Sr_3Al_2O_6$ were observed in Fig. 2 (a), (b), and (c). This indicated that H_3BO_3 was effective in synthesizing a single phase $Sr_4Al_{14}O_{25}$, but not for $SrAl_2O_4$.

3.2 Photoluminescence of $SrAl_2O_4$:Eu, Ce

Fig. 3 shows PL spectra of $SrAl_2O_4$ doped with 6 mol% of Ce and 0.3 mol% Eu, respectively. Emission wavelength of $SrAl_2O_4$:Ce and $SrAl_2O_4$:Eu arte 475 nm (excited at 360 nm) and 515 nm (excited at 390 nm), respectively. Doping concentrations were decided from Fig. 4, which shows the PL intensity of $SrAl_2O_4$ as a function of doping concentrations of Eu and Ce.

When doping 6 mol% of Ce and 0.3 mol% Eu, maximum intensities were observed, respectively. As shown in Fig. 3, PL spectra of $SrAl_2O_4$:Eu and $SrAl_2O_4$:Ce exhibited apparently different emission bands. It was known that the emission wavelength of $SrAl_2O_4$:Eu was about 510~520 nm. By substituting Ce for Eu, the emission wavelength shifted to the shorter one, about 475 nm that was greenish-blue. CIE of $SrAl_2O_4$:Ce was x=0.22 and y=0.31.

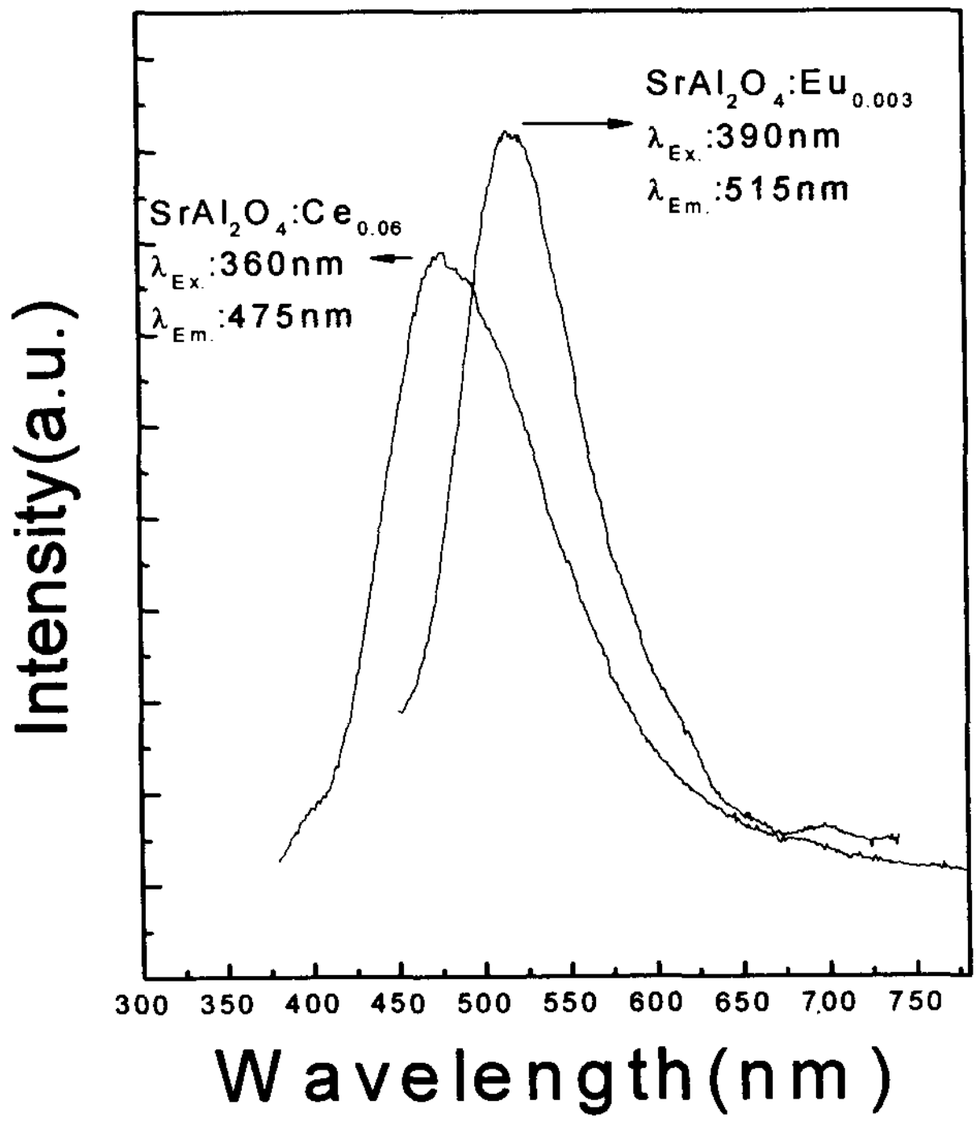

Fig. 3. PL spectra of $SrAl_2O_4$:Eu and $SrAl_2O_4$:Ce.

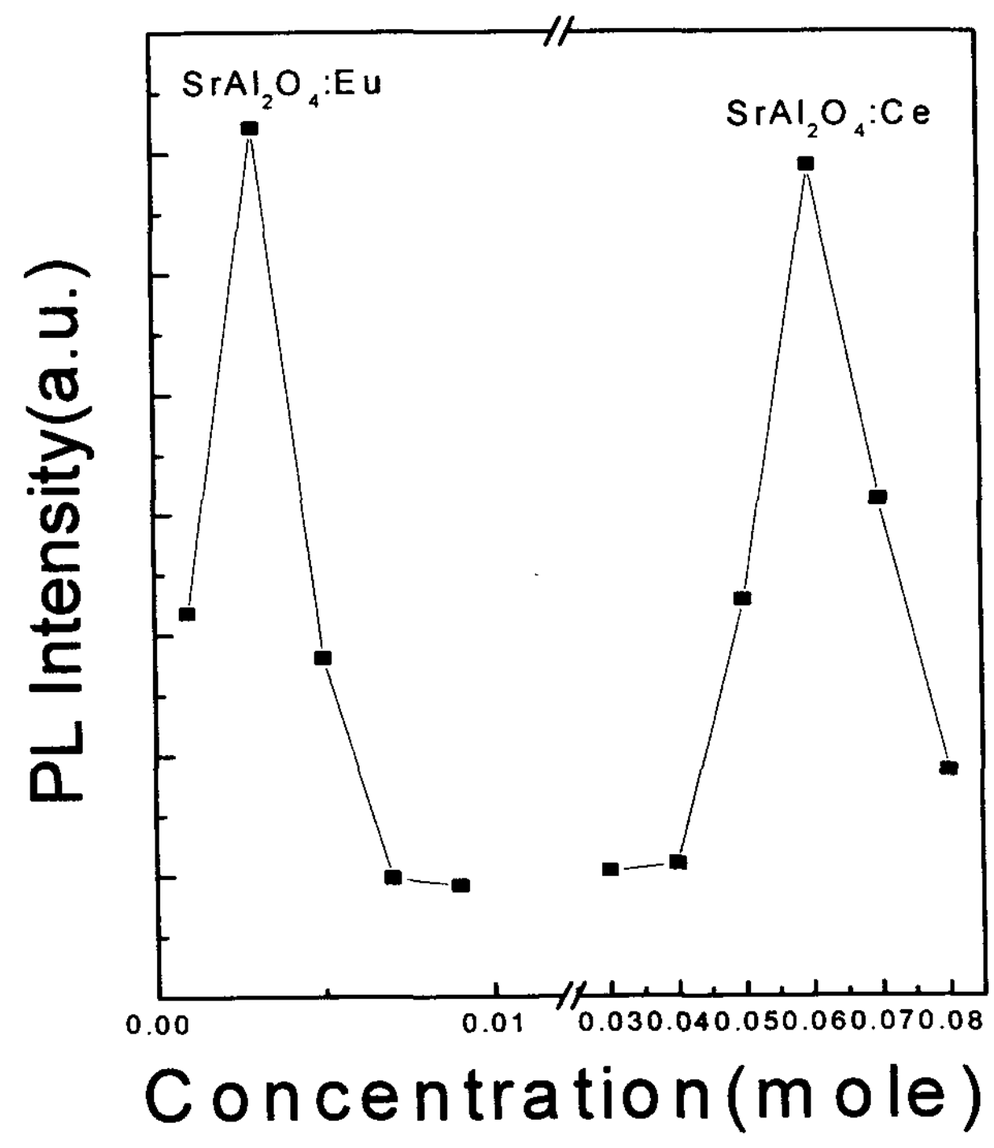

Fig. 4. PL intensity of $SrAl_2O_4$ as a function of doping concentrations of Eu and Ce.

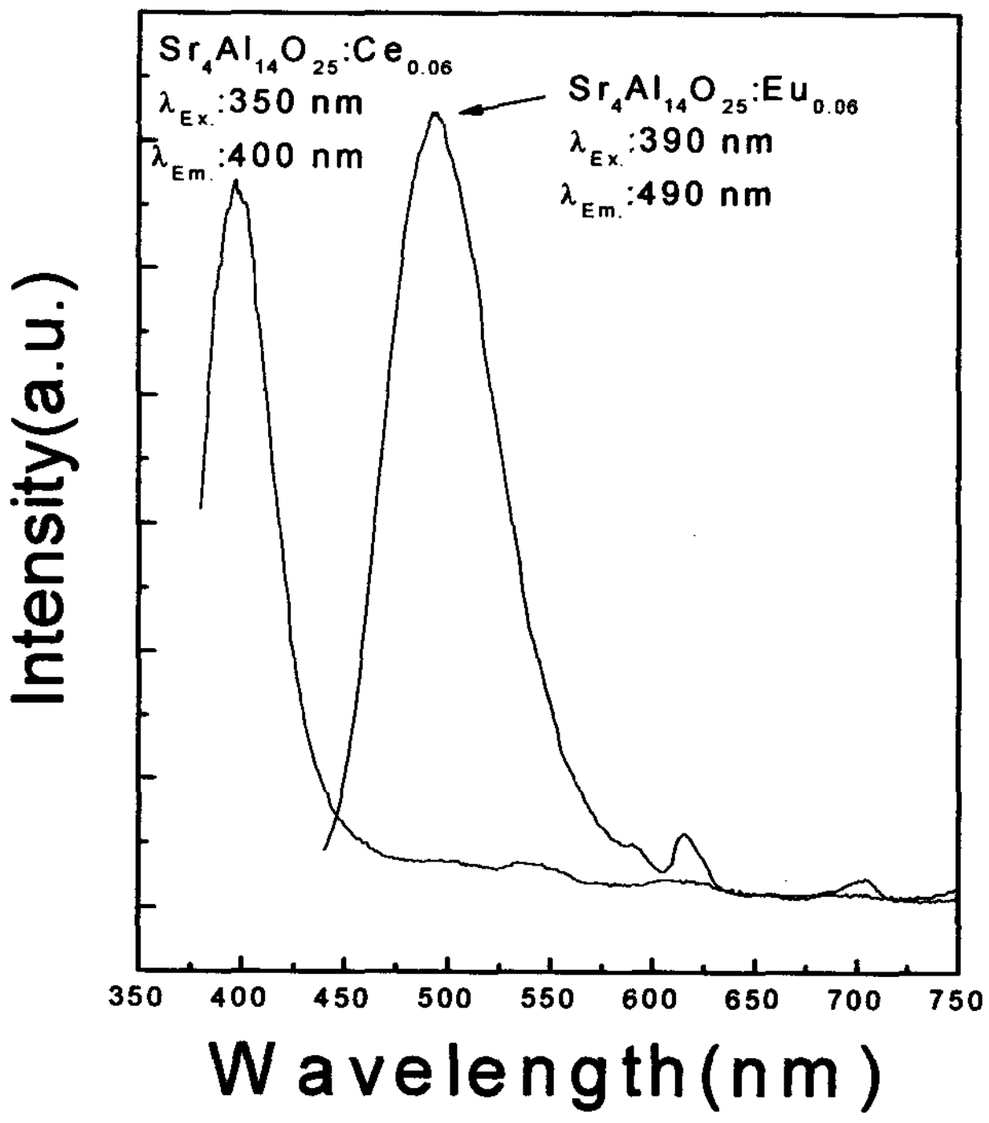

Fig. 5. PL spectra of $Sr_4Al_{14}O_{25}$:Eu and $Sr_4Al_{14}O_{25}$:Ce.

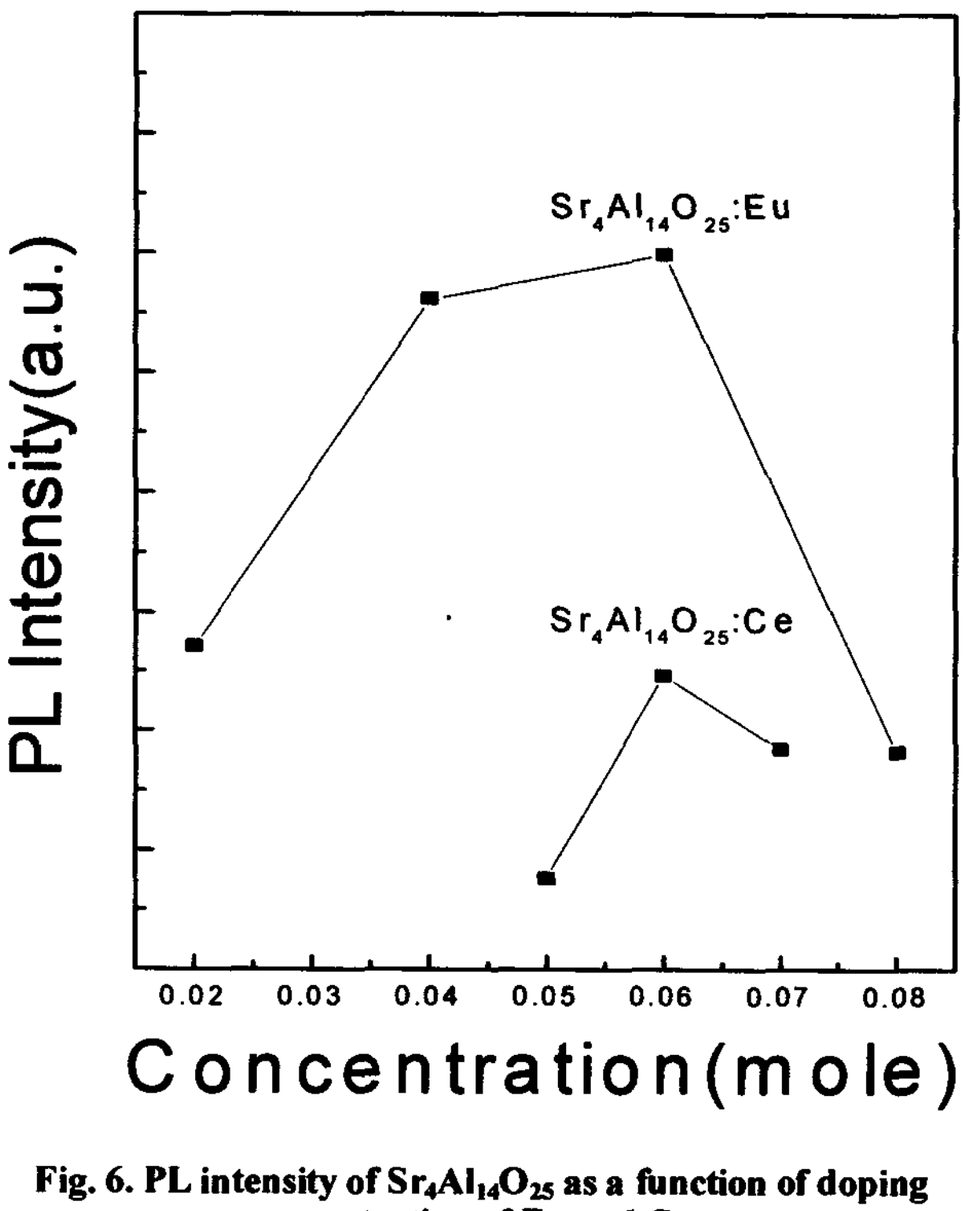

Fig. 6. PL intensity of $Sr_4Al_{14}O_{25}$ as a function of doping concentration of Eu and Ce.

3.3 Photoluminescence of $Sr_4Al_{14}O_{25}$:Eu, Ce

$Sr_4Al_{14}O_{25}$:Eu+Dy phosphors have been well known as long residual phosphors. They have a long decay time because of trap levels in band due to Dy.[6,7] However, Dy contributed to the weakening of the luminescent intensity. Therefore, a single dopant Eu is effective for the application to white LEDs.

Fig. 5 shows PL spectra of $Sr_4Al_{14}O_{25}$:Ce and $Sr_4Al_{14}O_{25}$:Eu. Both doping concentrations of Ce and Eu are 6 mol%, which was determined from the results of PL intensity as a function of doping concentrations of Eu and Ce as shown in Fig. 6. The emission wavelength of $Sr_4Al_{14}O_{25}$:Eu was 490 nm, while that of $Sr_4Al_{14}O_{25}$:Ce was 400 nm. By substituting Ce for Eu, the emission band drastically shifted to the short wavelength. The reasons are not clear at now. However, following possibility can be assumed. As shown in Fig. 5, PL spectra of $Sr_4Al_{14}O_{25}$:Ce excited at 350 nm exhibit 400 nm emission that is near UV. So it can be used as nUV source.

4. Conclusion

Ce dopant was substituted for Eu in SrO-Al_2O_3 phosphors, and the luminescent properties were compared with each other. Ce contributed to the shift of emission band to the shorter wavelength both in $SrAl_2O_4$ and $Sr_4Al_{14}O_{25}$ phosphors. $SrAl_2O_4$:Ce and $Sr_4Al_{14}O_{25}$:Ce exhibited the emission band at 475 nm and 400 nm, respectively.

5. Acknowledgements

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6. References

[1] Y. Narukawa, S. Saijou, Y. Kawakami, S. Fujita, T. Mukai, and S. Nakamura, Appl. Phys. Lett., **74** 558 (1999).
[2] E. Radkov, Conference Record of Light Emitting Diode 2003, Session 4, Technology Update:Phosphor, p.5 (Sandiego, October 2003).
[3] A. Nag and T.R.N. Kutty, J. Alloys and Compounds, **354** 221 (2003).
[4] Y. Lin, Z. Tang, and Z. Zhang, Mater. Lett., **51** 14 (2001)
[5] M. Kamada, J. Murakami, and N. Ohno, J. Luminescence, **87-89** 1042 (2000).
[6] M. Peng, Z. Pei, G. Hong, and Q. Su, Chem. Phys. Lett., **317** 1 (2003).
[7] T. Katsumata, S. Toyomane, A. Tonegawa, Y. Kanai, U. Kaneyama, K. Shakuno, R. Sakai, S. Komura, and T. Morikawa, J. Crystal Growth, **237-239** 361 (2002)