UV pumped three color phosphor blend White emitting LEDs

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Abstract

We have synthesized an Eu^{2+}-activated $Sr_3MgSi_2O_8$ blue phosphor and Ba_2SiO_4 green phosphor and Ba^{2+} co-doped Sr_3SiO_5 red phosphor investigated an attempt to develop white LEDs by combining it with a GaN blue LED chip($?_{em}$=405 nm). Three distinct emission bands from the GaN-based LED and the ($Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu) phosphor are clearly observed at 460nm, 520 nm and at around 600 nm, respectively. These three emission bands combine to give a spectrum that appears white to the naked eye. Our results show that GaN (405 nm chip)-based ($Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu) exhibits a better luminous efficiency than that of the industrially available product InGaN (460 nm chip)-based YAG:Ce.

1. Introduction

Remarkable progress can be observed in the development of white light-emitting diodes (LEDs) using GaN as well as InGaN chip [1,2]. Recently, especially, the white LEDs in which a blue LED is combined with a yellow YAG:Ce phosphor were investigated extensively due to their applications, such as back-lighting for liquid crystal displays (LCDs) and incandescent lamps. There have been some detailed studies on the integration of the blue LED and the yellow phosphor, as this creates white light from a combination of a blue LED emission (460 nm) and a broad-band yellow YAG phosphor [3]. Besides above-mentioned method, there are another approaches to generating white light from LEDs. White light emitting diodes (LEDs) can be fabricated by optical excitation of phosphor in the ultraviolet (UV) wavelength range. Kaufmann et al., [4]reported a white LED using a UV AlGaInN LED pump source and broad band red, green and blue emitting phosphors with individual luminescence peak near 610, 550 and 460 nm, respectively. The LED pump source emitted at 380 – 410 nm, that is, near the boundary between the visible and UV spectrum. The phosphor blend consisted of three phosphors emitting in the red, green and blue part of the spectrum. All components of the UV-pumped phosphor system must have high UV absorption, high quantum efficiency, and also, good photo- and temperature stability. New phosphors must be identified in the red, green and especially in the blue wavelength regimes, which satisfy these requirements. The phosphor conversion of LED light for white light strongly depends on the strong absorption of the blue LED emission wavelength. The strong absorption can be expected from dipole-allowed electron transitions in activated ions. The Ce^{3+} and Eu^{2+} ions are well known activated ions, which can be crystal field shifted in the spectral location of their absorption and emission lines. However, very few efficient new blue and yellow phosphors have actually been discovered, besides the YAG:Ce phosphor and the organic luminescent materials.

In the present work, we have synthesized an Eu^{2+}-activated $Sr_3MgSi_2O_8$ blue phosphor and Ba_2SiO_4 green phosphor and Ba^{2+} co-doped Sr_3SiO_5 red phosphor investigated in an attempt to

develop white LEDs through the integration of the GaN blue LED chip ($?_{em}$=405 nm) and the ($Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu) phosphor into a single package.

2. Experiments

Powder samples with the general formula $(Sr_{3-x}Eu_x)MgSi_2O_8$, $(Ba_{2-x}Eu_x)SiO_4$ and $(Sr_{3-x-y}Ba_xEu_y)SiO_5$ were prepared by solid-state reaction. The stating materials used in the preparation of this phosphor were powders greater than 99.9% pure of $SrCO_3$, SiO_2, MgO, $BaCO_3$, and Eu_2O_3. Preweighed powders were mixed thoroughly in acetone in an agate mortar and dried at 130°C for about 24 h to drive off the solvent and successively heat-treated at several conditions of temperature and duration time, followed by an additional grinding and firing in a reduction atmosphere. At this time the gas flow was adjusted to yield a mixture of 4 vol nitrogen to 1 vol hydrogen.

The excitation and emission spectra of the fired samples were measured with a Perkin-Elmer LS-50 luminescence spectrometer with a xenon flash lamp ($?\nu^{1/2}$ = 10μs). To investigate the white luminescent LEDs of Eu^{2+} - doped $Sr_3MgSi_2O_8$ + Ba_2SiO_4 + Ba^{2+} co-doped Sr_3SiO_5 phosphor, white luminescence conversion LEDs were fabricated. Based on standard LED technology, GaN-based $Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu white LEDs were encapsulated in a transparent epoxy resin. The emission spectra of a GaN-based $Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu under a forward bias of 20 mA were measured using a 50 cm single-grating monochrometer.

3. Result and Discussions

3.1 $Sr_3MgSi_2O_8$:Eu blue phosphor

Fig.1 shows the fluorescence spectra of $Sr_3MgSi_2O_8$:Eu samples with different Eu^{2+} content. As seen from this figure, the emission spectra shows a broad-band character, and the broadness of the emission band indicates an interaction between the host and the activator, which can be attributed to the presence of an excited electron in an outer shell of the Eu^{2+} ion[5]. The emission band at about 455 nm shifts to a longer wavelength with an increase in Eu^{2+} concentration. This may be attributed to some increases of the probability of an energy transfer among Eu^{2+} ions as the Eu^{2+} concentration increases[6]. A non-radiative energy transfer from one Eu^{2+} ion to another Eu^{2+} ion usually occurs as a result of an exchange interaction, radiation reabsorption or a multipole-multipole interaction. In the case of the Eu^{2+} ion, the $4f^7 \rightarrow 4f^6 5d^1$ transition is allowed, while the exchange interaction is responsible for the energy transfer of forbidden transitions and typical critical distance, which is about 5Å[7]. It is indicated that the exchange interaction plays no role in the energy transfer between Eu^{2+} ions. Since the 4f→5d transition of Eu^{2+} is allowed, the energy transfer in the present case will occur only as a result of an electric multipolar interaction. As an increased of Eu^{2+} concentration, the distance between Eu^{2+} ions becomes less, and the probability of energy transfer among Eu^{2+} ions increases. In other words, the probability of Eu^{2+} ions at higher levels of 5d which make an energy transfer to the lower 5d levels of Eu^{2+} ions, increases with an increase of Eu^{2+} concentration[6]. It makes it possible to shift of emission peak to the longer wavelength with an increase of Eu^{2+} concentration.

3.2 Ba_2SiO_4:Eu green phosphor

Fluorescence spectra of Ba_2SiO_4:Eu^{2+} phosphor with different Eu^{2+} concentrations are shown in Fig. 2. As can be seen from this figure, the emission spectra show the broad- band character and the fluorescence intensity increases with Eu^{2+} concentration and reaches a maximum at 0.1mol Eu^{2+}. The broadness of the emission band indicates an interaction between the host and the activator which can be attributed to the presence of an excited electron in an outer shell of the Eu^{2+} ion [8]. The emission band at about 504nm shifts slightly to the longer wavelength with the increase of Eu^{2+} concentration. It may be attributed to some changes of the crystal field around Eu^{2+} as the Eu^{2+} concentration increased. Although the 4f electrons of Eu^{2+} are not sensitive to lattice environment due to the shielding function of the electrons in the outer shell, the 5d

electrons will be split by the crystal field, which may lead to the shift of the emission peak.

3.3 Ba^{2+} co-doped Sr_3SiO_5:Eu red phosphor

The fluorescence spectra of $(Sr_{2.93-y}Ba_y)SiO_5:Eu_{0.07}$ samples with different Ba^{2+} contents are shown in Fig. 3. When the amount of Ba^{2+} is increased in the composition of $(Sr_{2.93-y}Ba_y)SiO_5:Eu_{0.07}$ the emission band shift gradually to longer wavelength. In orthorhombic form of Sr_3SiO_5, the alkaline earth ions form chains along the c-axis. It is indicated that a Eu^{2+} ion in these chains experiences positive charges due to cation neighbors in the chain direction, in addition to the negative charges of the nearest anion neighbors. The positive charges can orient one d-orbital preferentially. In other words, as the length of the c-axis increases by replacing part of the Sr^{2+} by Ba^{2+} ions, the effect of preferential orientation of a d-orbital in the chain direction decreases, so that the Eu^{2+} emission shifts to longer wavelength.

3.4 GaN-based White emitting LEDs

The relative emission spectra of the white emitting InGaN (460 nm chip)-based YAG:Ce LED and ($Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu) LED are shown in Fig. 4. In the case of the InGaN-based YAG:Ce LED, two distinct emission bands from the InGaN-based LED and the YAG:Ce phosphor are clearly resolved at 460 nm and at around 560 nm, respectively. Likewise the GaN-based ($Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu) LED shows three wavelengths at 460 nm, 520nm and 600 nm. The 405 nm emission band is due to a radiative recombination from a GaN active layer. This UV(405nm) emission was used as an optical transition of the $Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu phosphor. The luminance of GaN-based $Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu LED measured from these results is about 210 cd/m^2, which is higher than that of the industrially available InGaN-based YAG:Ce (in this case, 200 cd/m^2).

The CIE chromaticity of GaN-based LED with different amounts of ($Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu) phosphor concentration are shown in Fig. 5. As the concentration of $Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu increases, the color shifts from blue to white. In addition, the chromaticity coordinates are close to the straight lines interconnecting the points of the blue pump and white. The correlated color temperature (CCT) of a GaN-based $Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu white LED packaged in a standard epoxy lamp configuration with a reflecting cup with a CIE chromaticity (x=0.32, y=0.33) is 6017 K. On the other hand, industrially available InGaN-based YAG:Ce was shown 6609 K with a CIE chromaticity (x=0.31, y=0.31).

4. Conclusions

This UV(405nm) emission was used as an optical transition of the $Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu phosphor. The luminance of GaN-based $Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu LED measured from these results is about 210 cd/m^2, which is higher than that of the industrially available InGaN-based YAG:Ce (in this case, 200 cd/m^2). The white GaN-based $Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu developed in this work showed a higher luminance compared with the industrially available InGaN-based YAG:Ce.

5. References

[1] P. Schlotter, J. Baur, Ch. Hielscher, M. Kunzer, H. Obloh, R. Schmidt, and J. Schneider: Mater. Sci. Eng, Vol. B59, 339 (1999).

[2] T. Tamura, T. Setomoto, and T. Taguchi: J. Lumin, Vol. 87-89 1180 (2000).

[3] P. Schlotter, J. Baur, Ch. Hielscher, M. Kunzer, H. Obloh, R. Schmidt, and J. Schneider: J. Mater. Sci. Eng Vol. B59 390 (1999).

[4] U. Kaufmann et al., Phys. Stat. Sol., (a) 188, 143 (2001).

[5] F. C. Palilla, A. K. Levine, and M. R. Tomkus, J. Electrochem. Soc., 115, 642 (1968).

[6] J. Qui, K. Miura, N. Sugimoto, and K. Hirao, J. Non-Crystall. Solids., 213 & 214, 266 (1997).

[7] D. C. Dexter, J. Chem. Phys., 21, 836 (1953).

[8] F. C. Palilla, A. K. Levine, and M. R. Tomkus, J. Electrochem. Soc. **115,** 642(1968).

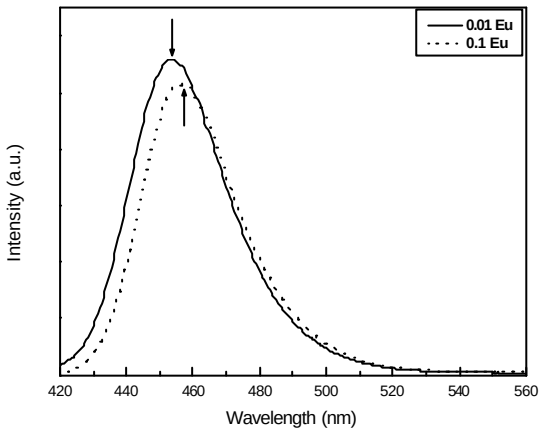

Fig. 1. The photoluminescence emission spectra of the Eu^{2+} in the $Sr_3MgSi_2O_8$ system by the Eu^{2+} concentration under the 405 nm excitation wavelength.

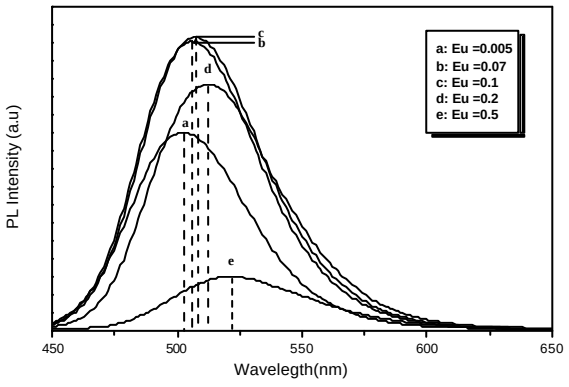

Fig. 2. The emission spectra of Ba_2SiO_4: Eu^{2+} prepared by varying Eu^{2+} concentrations.

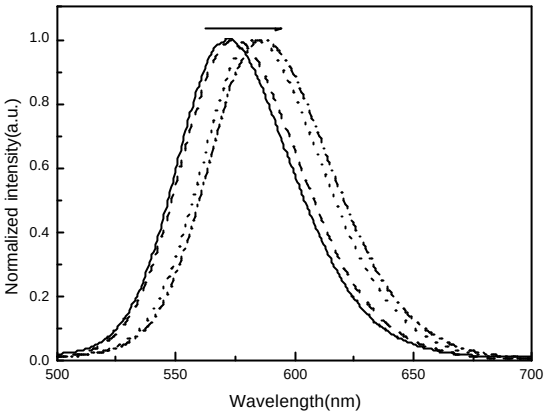

Fig. 3. Photoluminescence emission spectra of the Ba^{2+} in the $(Sr_{2.93-y}Ba_y)SiO_5:Eu_{0.07}$ system by varying the Ba^{2+} concentration under the 405 nm excitation wavelength. Solid line (0 mol Ba^{2+}), dashed line (0.1 mol Ba^{2+}), dotted line (0.3 mol Ba^{2+}), and dashed-dotted line (0.5 mol Ba^{2+}).

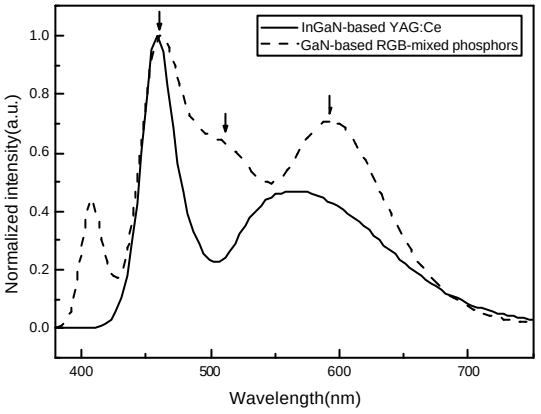

Fig. 3. Relative emission spectra of a white light-emitting InGaN-based YAG:Ce LED and GaN-based ($Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu) LED under a 20 mA drive current. Spectra were measured with a 50 cm single-grating monochrometer under a forward bias of 20 mA.

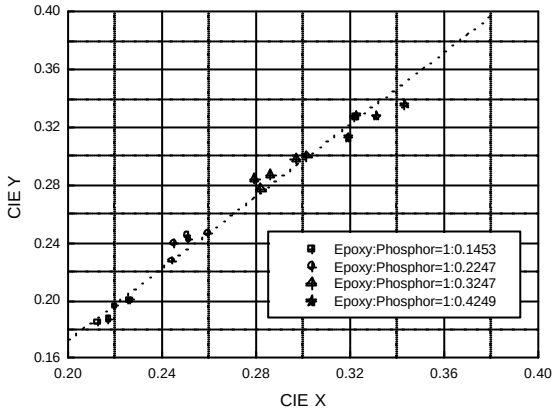

Fig. 4. CIE chromaticity points of GaN-based ($Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu) LED. The chromaticity points of GaN-based ($Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu) LED, produced by varying the ($Sr_3MgSi_2O_8$:Eu + Ba_2SiO_4:Eu + Ba^{2+} co-doped Sr_3SiO_5:Eu) concentration, are on the straight line connecting the chromaticity point of GaN LED (marked by a closed circle).