Spectral Variations of Eu^{2+} Emission in Sr- or Ba-Silicate, Borate and Borosilicate Hosts

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Abstract

Depending on host environments, Eu^{2+} emission can be spectrally tuned by manipulating the energy levels between allowed 4f↔5d transition. Spectral variations of Eu^{2+} emission from narrow green emission to broad yellow emission band were achieved by varying the host lattices such as Sr- or Ba-silicate, borate, and borosilicate.

1. Introduction

Recently, white LEDs (light emitting diodes) for the application to illumination and backlighting sources have been highlighted due to high brightness, high power efficiency, low applied voltage, and long lasting life [1,2]. At present, white LEDs composed of blue InGaN LEDs and Ce-doped yttrium aluminum garnet (YAG :Ce) yellow phosphor at epoxy is commercialized. However, this structure has a critical disadvantage of a low CRI (color rendering index) [2,3]. To improve color rendering properties, white LEDs composed of red, green, and blue (RGB) phosphors and near-UV LEDs are proposed instead of YAG :Ce-based white LEDs. In order to ensure required white LED characteristics, depending on their targeted applications, the spectral properties of phosphors should be manipulated by varying activators and/or host lattices. In our study, Eu^{2+} ion (4f↔5d transition) was doped into various host environments, i.e., Sr- or Ba-silicate, borosilicate and borate to achieve the tunability of emission color.

2. Experimental

The phosphor samples of Eu^{2+} ion-doped Sr- or Ba-silicate, borate, and borosilicate were synthesized by a conventional solid-state reaction method. The starting materials used in the preparation of the phosphors were pure powders greater than 99.9% of $SrCO_3$, $BaCO_3$, SiO_2, B_2O_3, Eu_2O_3 and $Sr(NO_3)_2$, $Ba(NO_3)_2$, $Eu(NO_3)_3$, and H_3BO_3. These materials were mixed in ethanol and DI water, respectively. A mixed solution was dried at 100°C in an oven, and grinded. The resulting powders were annealed in a tube furnace at 1200–1400°C for 4hr in a reducing atmosphere. At this time, the gas flow was adjusted to yield a mixture of four volumes of nitrogen to one volume of hydrogen.

3. Results and discussion

PL excitation and emission spectra of $Sr_2SiO_4:Eu^{2+}$ and $Ba_2SiO_4:Eu^{2+}$ phosphors are shown in Fig. 1(a) and (b), respectively, and the SEM images for their particle morphologies are also presented in the inset of each figure. In Fig. 1(a), the luminescent spectrum of $Sr_{1.93}SiO_4:Eu_{0.07}$ phosphor shows a broad yellow band emission, peaking at 545 nm. As shown in PL spectrum of $Ba_{1.93}SiO_4:Eu_{0.07}$ phosphors in Fig. 1(b), a narrower green band emission, peaking at 510 nm with the full-width half-maximum (FWHM) about 64 nm, is observed. Asymmetric spectral shape indicates that two cation sites for Eu^{2+} doping exist in both Sr_2SiO_4 and Ba_2SiO_4 phosphor hosts [4,5]. The broadness of the emission band indicates an interaction between the host and the activator, implying that the degrees of host-activator interaction are different between $Sr_2SiO_4:Eu^{2+}$ and $Ba_2SiO_4:Eu^{2+}$ phosphors.

In addition to silicate-based phosphor systems, borosilicate hosts were selected for Eu^{2+} doping. The PL excitation and emission spectra of Ba-borosilicate phosphors with different host compositions and a fixed Eu concentration of 0.07 mole are shown in Fig. 2, presenting the their dependency on host composition. While the $Ba_{1.93}B_2SiO_7:Eu_{0.07}$ and $Ba_{1.93}B_2Si_3O_{11}:Eu_{0.07}$ exhibited a limited excitation band, $Ba_{1.93}B_2Si_2O_9:Eu_{0.07}$ exhibited a quite extended excitation maximum up to 450 nm. The emissions of

two former phosphors are in the green region peaking at 505–510 nm while that of the latter phosphor is in the green-yellowish region peaking at 525–530 nm. With respect to their applicability to white LEDs,

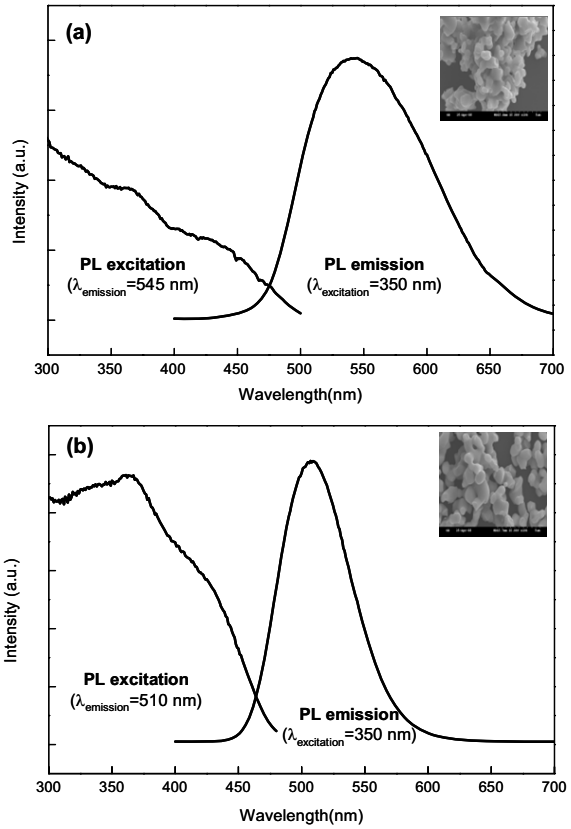

Fig. 1. PL excitation and emission spectra of (a) Sr_2SiO_4:Eu and (b) Ba_2SiO_4:Eu phosphor.

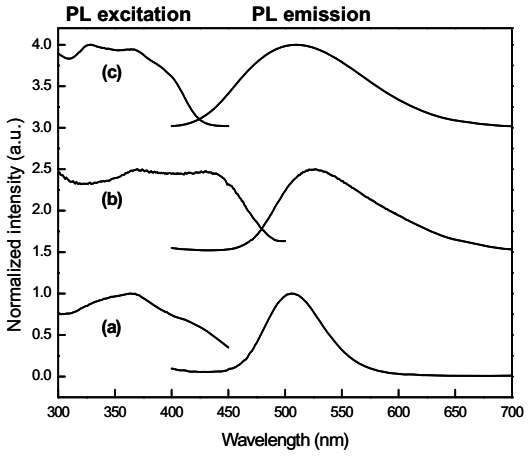

Fig. 2. PL excitation and emission spectra of (a) $Ba_{1.93}B_2SiO_7$:$Eu_{0.07}$, (b) $Ba_{1.93}B_2Si_2O_9$:$Eu_{0.07}$ and (c) $Ba_{1.93}B_2Si_3O_{11}$:$Eu_{0.07}$ phosphors.

the suitable excitation band of yellow-emitting $Ba_{1.93}B_2Si_2O_9$:$Eu_{0.07}$ phosphor can make it useful for the fabrication of both near UV and blue LED chip-based white LEDs.

As another new host candidate, Sr-borate phosphors were tested for Eu doping. PL excitation and emission spectra of $Sr_{1.93}B_2O_5$:$Eu_{0.07}$ phosphors are presented in Fig. 3. Broad excitation wavelengths up to ~450 nm make these phosphors applicable to white LEDs using blue or near UV LEDs. From the viewpoint of white light illumination, a wider band emission of phosphor leads to a higher CRI value of white LEDs. The band emission of $Sr_{1.93}B_2O_5$:$Eu_{0.07}$ phosphor displayed a slightly wider full-width-at-half-maximum (FWHM) of 126 nm as compared to that (119 nm) of YAG:Ce phosphor. Therefore, with respect to CRI value, use of this phosphor for white LEDs is expected to generate a white light comparable or superior to that of YAG:Ce-based white LEDs.

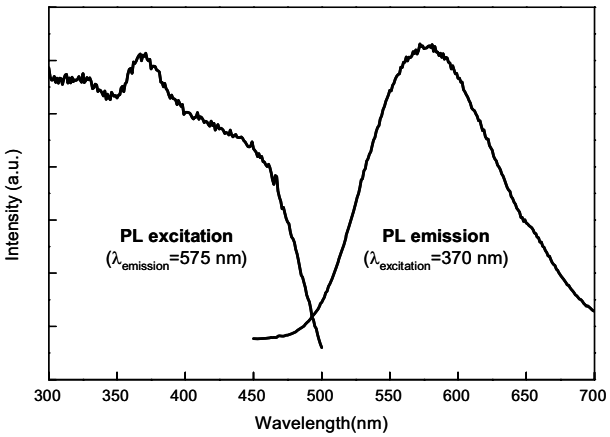

Fig. 3. PL excitation and emission spectra of $Sr_2B_2O_5$:Eu phosphor.

The PL emission intensity of $Sr_{1.93}B_2O_5$:$Eu_{0.07}$ phosphor increased with an increasing firing temperature up to 1300°C due to an improved crystallinity as shown in Fig. 4. However, higher firing temperatures than 1300°C produced a melted glassy phase that could not be collected as a powder form. PL emission of 1300°C-annealed $Sr_{2-x}B_2O_5$:Eu_x phosphors was not spectrally affected by Eu concentration while a higher activator concentration was reported to induce a red-shifted emission in Sr_2SiO_4:Eu^{2+} or Sr_3SiO_5:Ce^{3+} phosphors. Its intensity increased with an increasing Eu concentration up to x=0.07, and then decreased at x=0.1 due to the concentration quenching as shown in Fig. 5.

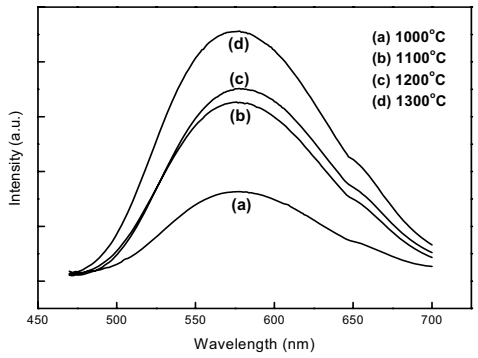

Fig. 4. PL emission spectra excited at 370nm of $Sr_2B_2O_5$:Eu phosphors as a function of annealing temperature.

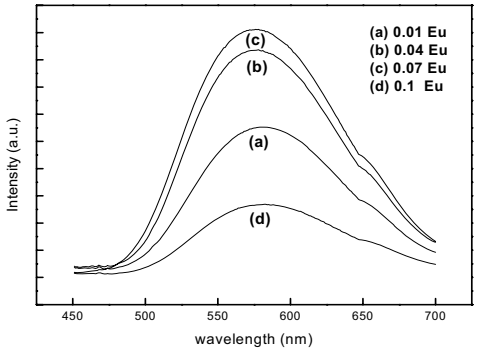

Fig. 5. Eu^{2+} concentration dependence of emission spectra of the $Sr_2B_2O_5$ system under the 370 nm excitation wavelength.

We applied $Sr_2B_2O_5$:Eu phosphors on a 450 nm blue LED chip. The $Sr_2B_2O_5$:Eu phosphor-epoxy mixture was dispensed on the LED chip and thermally cured at 100℃ for several hours. The resulting InGaN-pumped, $Sr_2B_2O_5$:Eu-converted white LED and its luminescence spectra under various forward currents are presented in Fig. 5. The luminescence spectra consist of two bands; blue emission by an LED chip and yellow emission by $Sr_{1.93}B_2O_5$:$Eu_{0.07}$ phosphor excited by blue excitation. Due to the partial spectral overlapping of 450 nm blue emission and broad yellow emission, the doublet feature is seen in the first blue region. These two emission bands combine to give a spectrum that appears warm white to the naked eye. The fabricated white LEDs displayed CIE chromaticity coordinates of (x=0.340–0.372, y=0.287–0.314) and color temperatures of 3664–4905 K under the applied currents of 5–60 mA. Better CRI value of 75–77 was measured from $Sr_{1.93}B_2O_5$:$Eu_{0.07}$-based white LED than that (~71) of commercialized YAG:Ce-based white LEDs.

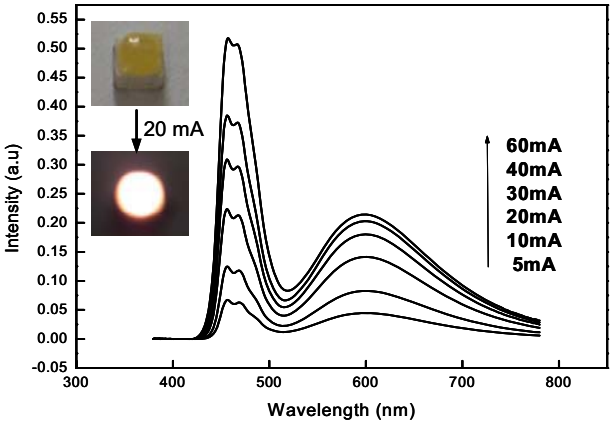

Fig. 6. EL spectra of an InGaN LED-pumped white LED using $Sr_2B_2O_5$:Eu phosphor under various forward currents. The photographs of a white LED operating under a forward current of 20 mA are shown in the inset of figure.

4. Summary

In present work, spectral variations of Eu^{2+} emission in Sr- or Ba-silicate, borosilicate, and borate hosts were investigated. Among those phosphors, Eu^{2+}-doped $Ba_{1.93}B_2Si_2O_9$:$Eu_{0.07}$ and $Sr_{1.93}B_2O_5$:$Eu_{0.07}$ can be regarded as novel yellow phosphors that can be applicable to near UV- or blue-pumped white LEDs due to their suitable excitation band and broad emission band. The yellow phosphor-converted white LEDs were successfully fabricated by pre-coating $Sr_{1.93}B_2O_5$:$Eu_{0.07}$ phosphors on 460 nm InGaN chips, and higher CRI values of 75–77 versus YAG:Ce-based white LED could be obtained from those white LEDs.

5. Acknowledgment

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6. References

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