Synthesis and Photoluminescence Studies of Eu³⁺ Activated Borosilicate Phosphor (Gd₁₋ₓEux)₃BSi₂O₁₀ for White Light Emitting Diodes

Tadashi Ishigaki,a,d Puttaswamy Madhusudan,b Michiyto Inoue,b Shinnosuke Kamei,b Kazuyoshi Uematsuc, Kenji Todaa,b,c and Mineo Satod,e

aCenter for Transdisciplinary Research, bGraduate School of Science and Technology and cDepartment of Chemistry and Chemical Engineering, Niigata University, Niigata 950-2181, Japan

dElectronic address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).

Since the discovery of LEDs many efforts have been made to develop white light emitting diodes toward a more suitable technological process allowing a facile and low-cost scale-up production. Furthermore, LEDs are considered to be promising light sources, which have the merits of long lifetime, high efficiency, excellent reliability, and good resistance to vibration. In recent years, LED’s are used as an alternative to traditional incandescent and fluorescent lamps. The most common commercial white LEDs use a blue-emitting LED that excites a yellow-emitting Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce³⁺) phosphor dispersed in the epoxy resin on a blue LED chip.1 But, YAG:Ce³⁺ shows greenish yellow light, so these white LEDs exhibit low color rendering index. To overcome this problem, a near-UV LED (around 370–410 nm) has been discovered with unconventional properties for use in white-light LEDs. 5–9 Among these phosphors, Gadolinium borosilicate (Gd₃BSi₂O₁₀) shows a wide range of applications because of its steady photoluminescence efficiency and better color purity under near UV light LEDs. 10–12 Between these phosphors, Eu³⁺ ions exhibit strong absorption at about 395 nm in many host lattices9–11 and which is close to the emission wavelength (around 390–410 nm) of near UV- InGaN based LED chips. The activated Eu³⁺ ions are assumed to substitute Gd sites and Eu³⁺ doped Gd₃BSi₂O₁₀ are considered to be a promising red-emitting phosphor for near-UV based white LED lighting.

Experimental

The phosphors were synthesized by conventional solid-state reaction method. The raw materials, Gd₂O₃ (purity 99.99%; Shinetsu Chemical Co. Inc.), H₃BO₃ (purity 99.99%; Kojundo Chemical Co. Inc.), SiO₂ (purity 99.9%; Wako Pure Chemical Industries Ltd.), Eu₂O₃ (purity 99.99%; Shinetsu Chemical Co.) were used as received without any further processing. Briefly, an appropriate stoichiometric amount of (Gd₁₋ₓEux)₃BSi₂O₁₀ mixture were wet ground by using an agate mortar and pestle. A small amount of ethanol was added during the grinding in order to obtain homogeneous mixtures. The samples were pre-heated in an alumina boat at 827 K for 3 h in air and further heated in a muffle furnace at 1373 K for 12 h in air. Finally, the samples were ground into powder for further characterization.

The phase purity of as prepared powders were identified by X-ray powder diffractometer (MX-Labo; Mac Science Ltd.) operating at 40 kV and 25 mA using CuKα radiation. The data was collected at a step-scanning mode in the 2θ range of 20–100 degrees with a 0.02 degree scan speed. The excitation and emission spectra of the powder samples were measured using a spectrophotometer with Xe lamp light source. (FP-6500/6600; Jasco Inc.). Temperature-dependent measurements were performed at 297–423 K using spectrophotometer with a heat controller (HPC-503, Jasco Inc.).

Identification of synthesized samples.— Figure 2 shows the X-ray diffraction (XRD) pattern of (Gd₁₋ₓEux)₃BSi₂O₁₀ phosphor and all the diffraction peaks can be indexed as an orthorhombic phase of Gd₃BSi₂O₁₀ and match very well with the reported data (Inorganic crystal structure database card No. 86150) indicating single phase. Furthermore, all diffraction peaks are sharp and intense, signifying


**JSS SPECIAL ISSUE ON LUMINESCENT MATERIALS FOR SOLID STATE LIGHTING**

*E-mail: tishigaki@eng.niigata-u.ac.jp*
highly crystalline nature of the as-prepared phosphor material. Since Gd$^{3+}$ and Eu$^{3+}$ have almost the same ionic radii (Gd$^{3+}$: 0.1193 nm, Eu$^{3+}$: 0.1206 nm) and tri-valent oxidation state, (Gd$_{1-x}$Eu$_x$)$_3$BSi$_2$O$_{10}$ was able to substitute Gd for Eu. Furthermore, Eu$_3$BSi$_2$O$_{10}$ has the isotypic structure of Gd$_3$BSi$_2$O$_{10}$ has reported by Chi et al.\textsuperscript{12}

**Luminescence properties.**—The excitation and emission spectra of (Gd$_{1-x}$Eu$_x$)$_3$BSi$_2$O$_{10}$ are illustrated in Figure 3. The excitation spectrum of (Gd$_{1-x}$Eu$_x$)$_3$BSi$_2$O$_{10}$ phosphor (Figure 3a) contains sharp peaks such as $^7F_0 \rightarrow ^5L_6$ line with a maximum at 395 nm due to the f-f transitions and $^7F_0 \rightarrow ^5D_2$ band at around 467 nm, which are coupled well with the characteristic emission from UV-LED and blue LED, respectively. On the other hand, a broad excitation band in 200–350 nm range can be attributed to the charge transfer transition band from O$^{2-}$ to Eu$^{3+}$.\textsuperscript{4} Further, this charge transfer transition is spotted weak in Gd$_3$BSi$_2$O$_{10}$:Eu$^{3+}$. The emission bands at 588 and 614 nm are $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions respectively. Furthermore, it is known that $^5D_0 \rightarrow ^7F_2$ transitions are sensitive in symmetric properties of crystal field.\textsuperscript{4} In case of commercial Y$_2$O$_2$S:Eu$^{3+}$ red phosphor, it does not have an inversion symmetry, the emission spectra shows appreciable peak at 614 nm for $^5D_0 \rightarrow ^7F_2$ transitions.\textsuperscript{13} On the contrary, as prepared novel borosilicate phosphor, Gd$_3$BSi$_2$O$_{10}$ host material belongs to the space group of Pnma with inversion symmetry. Hence, weak $^5D_0 \rightarrow ^7F_2$ transitions were observed in Gd$_3$BSi$_2$O$_{10}$:Eu$^{3+}$ phosphor compared with that of emission spectrum of Y$_2$O$_2$S:Eu$^{3+}$. The emission intensity of (Gd$_{1-x}$Eu$_x$)$_3$BSi$_2$O$_{10}$ ($x = 0.01 \sim 0.70$) increases with increasing Eu$^{3+}$ concentration (Figure 4). The optimum concentration of Eu$^{3+}$ is 70 mol% and at higher concentration Gd$^{3+}$ was able to substitute to Eu$^{3+}$. The Eu$^{3+}$ ions were stacked layer by layer arrangement in Gd$_3$BSi$_2$O$_{10}$ such as in Gd$_{1-x}$Eu$_x$Ta$_3$O$_9$,\textsuperscript{14} La$_{1-x}$Eu$_x$Ta$_5$O$_{19}$,\textsuperscript{15} CaLa$_{1-x}$Eu$_x$GaO$_4$.\textsuperscript{16} Furthermore, it is difficult to
ensue concentration quenching between Eu\(^{3+}\) ions that are separated by [SiO\(_4\)] tetrahedral and [BO\(_3\)] triangle in Gd\(_3\)BSi\(_2\)O\(_{10}\):Eu\(^{3+}\). When the Eu\(^{3+}\) concentration was increased above x = 0.7, the emission intensity decreases.

There are three different Gd sites in borosilicate phosphor, the Gd1 sites (Gd-O: 0.229 – 0.258 nm) are separated by [SiO\(_4\)] tetrahedral and [BO\(_3\)] triangle (Figure 1a). Hence, emission intensity of (Gd\(_{0.7-x}\)Eu\(_x\))\(_3\)BSi\(_2\)O\(_{10}\) phosphor increases at lower Eu\(^{3+}\) concentration when Gd1 site is substituted by Eu\(^{3+}\) ion. Whereas Gd2 sites (Gd-O: 0.228 – 0.293 nm) have greater tendency for substitution of Eu\(^{3+}\) ions than Gd3 sites (Gd-O: 0.229 – 0.267 nm) because Gd2 sites have distorted coordination environment. The energy transmission between Gd1 and Gd2 is difficult because these Gd sites are isolated by [SiO\(_4\)] tetrahedral. On the other hand Gd2 and Gd3 are neighboring sites (Figure 1b) and when Eu\(^{3+}\) concentration is high, the concentration quenching occurred and substituted in Gd2 and Gd3 sites. Even though the concentration quenching was observed, the host material Gd\(_3\)BSi\(_2\)O\(_{10}\) is capable to substitute Gd\(^{3+}\) with Eu\(^{3+}\) at higher concentration.

Gd\(_3\)BSi\(_2\)O\(_{10}\):Eu\(^{3+}\) phosphor shows similar excitation and emission spectrum as CaEu\(_3\)Si\(_3\)O\(_{13}\). Furthermore, Gd\(_3\)BSi\(_2\)O\(_{10}\):Eu\(^{3+}\) shows 1.37 times higher luminescence intensity than [SiO\(_4\)] tetrahedral. In case of CaEu\(_3\)Si\(_3\)O\(_{13}\) phosphor all [SiO\(_4\)] tetrahedral are isolated in the crystal structure.

The temperature of LED is even more than 373 K in poor heat radiation and in the case of using phosphor that is weak against heat, the emission spectrum of white LED changes with temperature.\(^{18}\) Therefore, the phosphors for a white LED are required to show high emission intensity at higher temperature. Figure 5 shows the temperature dependence luminescence relative intensity spectra of (Gd\(_{0.7}\)Eu\(_{0.3}\))\(_3\)BSi\(_2\)O\(_{10}\) and YAG:Ce\(^{3+}\) (P46-Y3) respectively. The luminescence intensity of Gd\(_3\)BSi\(_2\)O\(_{10}\):Eu\(^{3+}\) phosphor decreased gradually with increasing temperature. Gd\(_3\)BSi\(_2\)O\(_{10}\):Eu\(^{3+}\) phosphor maintained a luminescence intensity of 80% at 373 K and 71% at 423 K at 293 K. On the contrary, the luminescence intensity of commercially available YAG:Ce\(^{3+}\) (P46-Y3) phosphor is measured to be 87% at 373 K and 72% at 423 K. In contrast, Gd\(_3\)BSi\(_2\)O\(_{10}\) phosphor shows a similar thermal characterization of YAG:Ce\(^{3+}\) (P46-Y3) phosphor.

The CIE chromaticity color coordinates (0.60, 0.34) of (Gd\(_{0.7}\)Eu\(_{0.3}\))\(_3\)BSi\(_2\)O\(_{10}\) phosphor indicates orange-tinged red equivalent to Y\(_2\)O\(_2\)S:0.05Eu\(^{3+}\) (0.63, 0.35).\(^{18}\) This is due to the appreciable two main emission peaks at 588 nm for 5D\(_0\) → 7F\(_2\) and 614 nm for 5D\(_0\) → 7F\(_2\) transitions, respectively. This result shows that an ideal white color was achieved in (Gd\(_{0.7}\)Eu\(_{0.3}\))\(_3\)BSi\(_2\)O\(_{10}\) phosphor under 395 nm LED excitation by controlling Eu\(^{3+}\) dopant concentration. Furthermore, (Gd\(_{0.7}\)Eu\(_{0.3}\))\(_3\)BSi\(_2\)O\(_{10}\) phosphor is ideal to red phosphor for a white LED, lighting system in broad emission spectrum.

Conclusions

In conclusion, we synthesized the novel red-emitted gadolinium borosilicate phosphor, Gd\(_3\)BSi\(_2\)O\(_{10}\):Eu\(^{3+}\) for white LED application using the solid-state reaction method. Gd\(_3\)BSi\(_2\)O\(_{10}\) is able to substitute Gd\(^{3+}\) with Eu\(^{3+}\) at higher 70 mol% concentration. These red phosphor materials have the main excitation band located at 395 nm, and dominant emission peak at 588 and 614 nm respectively. Further, Gd\(_3\)BSi\(_2\)O\(_{10}\):Eu\(^{3+}\) phosphors can be excited by the near-UV LED, centered at 390 nm. The luminescent intensity reached the maximum when the concentration of Eu\(^{3+}\) ion was 70 mol%. Gd\(_3\)BSi\(_2\)O\(_{10}\):Eu\(^{3+}\) shows good thermal stability and expected to be an ideal candidate for tri-color phosphors based white LED.

Acknowledgment

This work was supported by a project from the Center for Transdisciplinary Research, Niigata University.

References


Figure 4. The relationship between Eu\(^{3+}\) ion concentration and 614 nm emission intensity of the phosphor under 395 nm excitation compared with that of Y\(_2\)O\(_2\)S:Eu\(^{3+}\).

Figure 5. The temperature dependence luminescence relative intensity spectra of (Gd\(_{0.7}\)Eu\(_{0.3}\))\(_3\)BSi\(_2\)O\(_{10}\) and YAG:Ce\(^{3+}\) (P46-Y3).