Synthesis and Photoluminescence Studies of Eu^{3+} Activated Borosilicate Phosphor $(Gd_{1-x}Eu_x)_3BSi_2O_{10}$ for White Light Emitting Diodes

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Certain silicate materials with different crystal structures show excellent luminescence properties. Furthermore, these silicate compounds have high chemical and thermal stability and considered as an excellent phosphor host materials. In this study, we report $(Gd_{1-x}Eu_x)_3BSi_2O_{10}$ as a novel ultraviolet (UV) excited white phosphors prepared under solid state reaction and their luminescence properties at 393 nm excitation were investigated in detail. The as prepared $(Gd_{1-x}Eu_x)_3BSi_2O_{10}$ phosphors showed red emission with UV (around 580–630 nm) and near-UV light (around 250–410 nm). The chromaticity coordinates (0.60, 0.34) of the prepared borosilicate phosphor were very close to the NTSC standard value (0.67, 0.33) and its emission intensity was almost similar to commercial red phosphor $Y_2O_2S{:}0.05Eu^{3+}$. Further, as prepared $(Gd_{1-x}Eu_x)_3BSi_2O_{10}$ material is considered to be an efficient red-emitting phosphor for UV based light emitting diodes (LED).
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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 $Y_3Al_5O_{12}{:}Ce^{3+}$ (YAG:Ce^{3+}) phosphor dispersed in the epoxy resin on a blue LED chip.[1] But, YAG:Ce^{3+} 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) is combined with tri-color (red, green, blue) phosphors.[2,3] However, this approach exhibits high color rendering index. Unfortunately, the chemical stability and efficiency of present commercial red phosphor $Y_2O_2S{:}Eu^{3+}$ is much lower than other phosphors, such as $SrAl_2O_4{:}Eu^{2+}$ green phosphor and $BaMgAl_{10}O_{17}{:}Eu^{2+}$ blue phosphor.[4] Therefore, there is a need to synthesize new phosphors for alternative tri-color based white LEDs that absorb in the near-UV light and emit in the red region. A search for physically and chemically stable inorganic rare-earth –based red silicate phosphor with higher photoluminescence efficiency and better color purity under near UV light excitation is an attractive and challenging task.

Recently, some borosilicate based phosphor materials have been discovered with unconventional properties for use in white-light LEDs.[5–7] Among these phosphors, Gadolinium borosilicate ($Gd_3BSi_2O_{10}$) shows a wide range of applications because of its steady crystalline structure[8] (Figure 1). It belongs to the orthorhombic structure with a space group of *Pbca*. The crystallographic parameters are a = 0.9630 nm, b = 0.6959 nm, c = 2.2792 nm. In this structure SiO_4 occupies tetrahedral and BO_3 occupies triangle structure with a vertex in common. There are three different Gd sites and the coordination of the Gd^{3+} are slightly irregular eight- (Gd1), nine- (Gd2, Gd3) folds. Furthermore, each Gd sites of this compound have different coordination number and Gd-O coordinate bond distance (0.229 nm < Gd-O < 0.293 nm) with Gd sites comparable with two-dimension arrangement. Also, it prevents the concentration quenching of luminescence, because Eu^{3+} is separated by [SiO_4] tetrahedral and [BO_3] triangle polyhedral.

Here, in this paper we report the synthesis and luminescence properties of novel red emitting borosilicate phosphor. Further, it is well known that Eu^{3+} ions exhibit strong absorption at about 395 nm in many host lattices[9–11] and which is close to the emission wavelength of near UV- InGaN based LED chips. The activated Eu^{3+} ions are assumed to substitute Gd sites and Eu^{3+} doped $Gd_3BSi_2O_{10}$ 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, Gd_2O_3 (purity 99.99%; Shinetsu Chemical Co. Inc.), H_3BO_3 (purity 99.99%; Kojundo Chemical Co. Inc.), SiO_2 (purity 99.9%; Wako Pure Chemical Industries Ltd.), Eu_2O_3 (purity 99.99%; Shinetsu Chemical Co.) were used as received without any further processing. Briefly, an appropriate stoichiometric amount of $(Gd_{1-x}Eu_x)_3BSi_2O_{10}$ 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 10–70 degrees with a 0.02 degree scan speed. The excitation and emission spectra of the powder samples were measured using a spectrofluorometer with Xe lamp light source. (FP-6500/6600; Jasco Inc.). Temperature-dependent measurements were performed at 297–423 K using spectrofluorometer with a heat controller (HPC-503, Jasco Inc.). The emission color chromaticities of samples were measured by Photonic Multi-channel Analyzer (C7473-36, Hamamatsu photonics).

Result and Discussion

Identification of synthesized samples.— Figure 2 shows the X-ray diffraction (XRD) pattern of $(Gd_{1-x}Eu_x)_3BSi_2O_{10}$ phosphor and all the diffraction peaks can be indexed as a orthorhombic phase of $Gd_3BSi_2O_{10}$ 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

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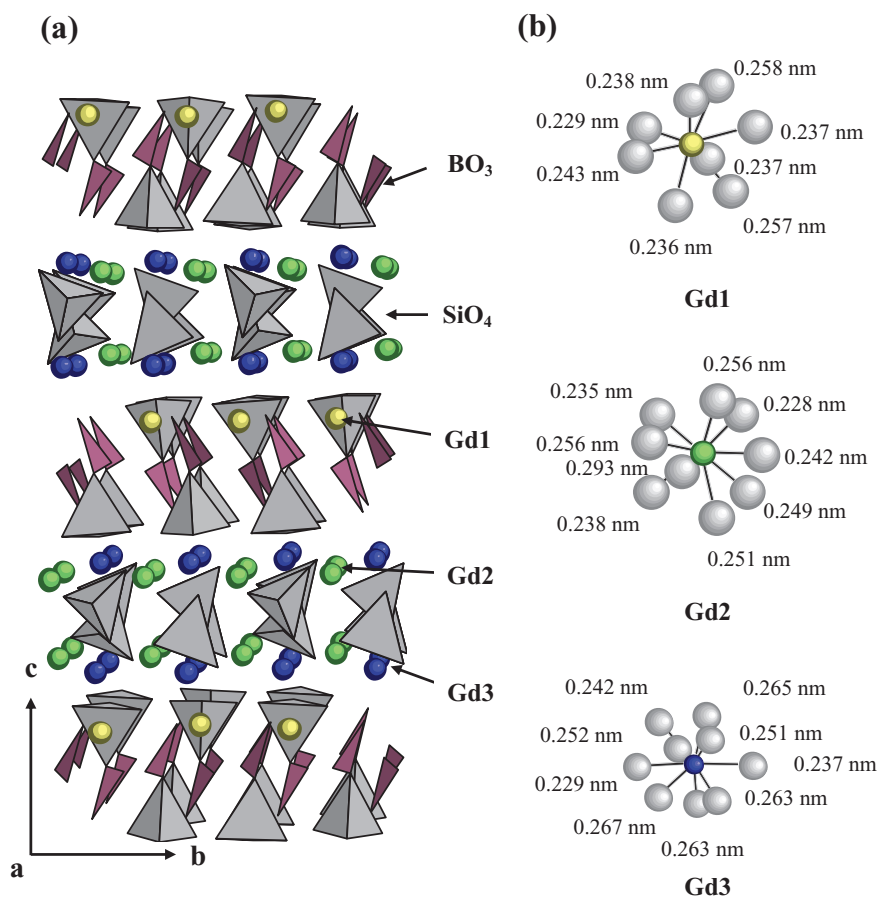[z]E-mail: tishigaki@eng.niigata-u.ac.jp

(a)

(b)

Gd1

Gd2

Gd3

Figure 1. (a) Shows $Gd_3BSi_2O_{10}$ orthorhombic crystal structure with SiO_4 tetrahedral and BO_3 triangle polyhedral structural arrangements. (b) shows th e coordinate environment of three Gd sites. These numerical values show the bond distances of Gd-O.

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, $(Gd_{1-x}Eu_x)_3BSi_2O_{10}$ was able to substitute Gd for Eu. Furthermore, $Eu_3BSi_2O_{10}$ has the isotypic structure of $Gd_3BSi_2O_{10}$ has reported by Chi et al.[12]

Luminescence properties.— The excitation and emission spectra of $(Gd_{1-x}Eu_x)_3BSi_2O_{10}$ are illustrated in Figure 3. The excitation spectrum of $(Gd_{0.3}Eu_{0.7})_3BSi_2O_{10}$ 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+}.[4] Further, this charge transfer transition is spotted weak in $Gd_3BSi_2O_{10}$: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.[4] In case of commercial Y_2O_2S: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.[13] On the contrary, as prepared novel borosilicate phosphor, $Gd_3BSi_2O_{10}$ host material belongs to the space group of *Pbca* with inversion symmetry. Hence, weak $^5D_0 \rightarrow ^7F_2$ transitions were observed in $Gd_3BSi_2O_{10}$:Eu^{3+} phosphor compared with that of emission spectrum of Y_2O_2S:Eu^{3+}.

The emission intensity of $(Gd_{1-x}Eu_x)_3BSi_2O_{10}$ ($x = 0.01 \sim 0.70$) 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 $Gd_3BSi_2O_{10}$ such as in $Gd_{1-x}Eu_xTa_3O_9$,[14] $La_{1-x}Eu_xTa_7O_{19}$,[15] $CaLa_{1-x}Eu_xGaO_4$.[16] Furthermore, it is difficult to
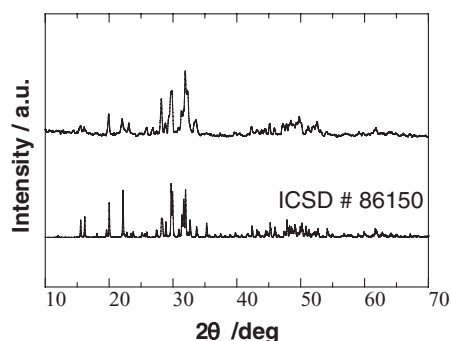
Figure 2. XRD patterns of $(Gd_{0.3}Eu_{0.7})_3BSi_2O_{10}$ phosphor material compared with standard ICSD $Gd_3BSi_2O_{10}$ data.

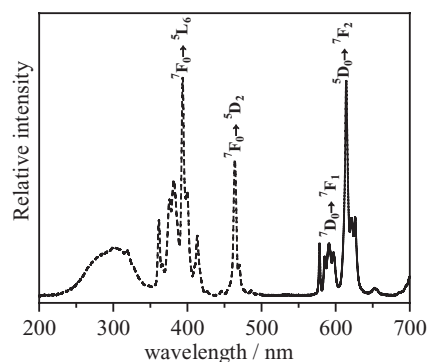**Figure 3.** Excitation and emission spectra of $(Gd_{0.3}Eu_{0.7})_3BSi_2O_{10}$ phosphor excited at 395 nm. The broken line shows excitation spectrum, and the solid line shows emission spectrum.
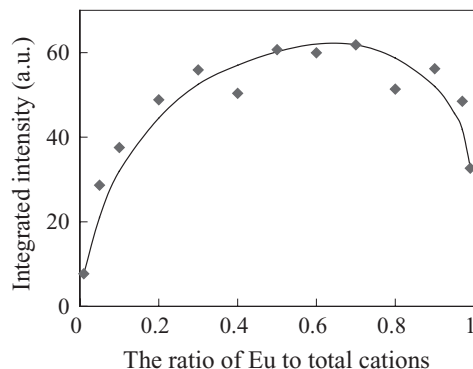
Figure 4. The relationship between Eu^{3+} ion concentration and 614 nm emission intensity of the phosphor under 395 nm excitation compared with that of $Y_2O_2S:Eu^{3+}$.

ensue concentration quenching between Eu^{3+} ions that are separated by $[SiO_4]$ tetrahedral and $[BO_3]$ triangle in $Gd_3BSi_2O_{10}:Eu^{3+}$. 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 $(Gd_{1-x}Eu_x)_3BSi_2O_{10}$ 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 co-ordination 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 $Gd_3BSi_2O_{10}$ is capable to substitute Gd^{3+} with Eu^{3+} at higher concentration.

$Gd_3BSi_2O_{10}:Eu^{3+}$ phosphor shows similar excitation and emission spectrum as $CaEu_4Si_3O_{13}$.[17] Furthermore, $Gd_3BSi_2O_{10}:Eu^{3+}$ shows 1.37 times higher luminescence intensity than $CaEu_4Si_3O_{13}$. In case of $CaEu_4Si_3O_{13}$ 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] There-
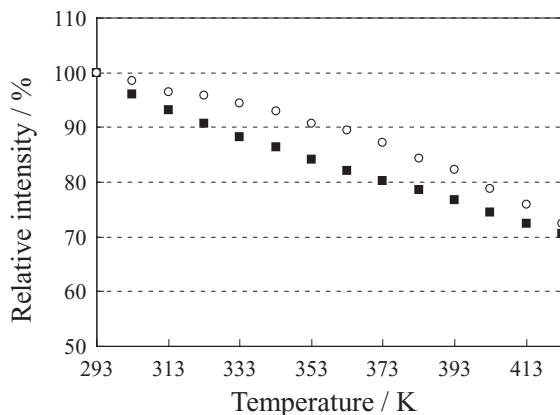
fore, the phosphors for a white LED are required to show high emission intensity at higher temperature. Figure 5 shows the temperature dependence luminescence relative intensity spectra of $(Gd_{0.3}Eu_{0.7})_3BSi_2O_{10}$ and YAG:Ce^{3+} (P46-Y3) respectively. The luminescence intensity of $Gd_3BSi_2O_{10}:Eu^{3+}$ phosphor decreased gradually with increasing temperature. $Gd_3BSi_2O_{10}:Eu^{3+}$ 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, $Gd_3BSi_2O_{10}$ phosphor show a similar thermal characterization of YAG:Ce^{3+} (P46-Y3) phosphor.

The CIE chromaticity color coordinates (0.60, 0.34) of $(Gd_{0.3}Eu_{0.7})_3BSi_2O_{10}$ phosphor indicates orange-tinged red equivalent to $Y_2O_2S:0.05Eu^{3+}$ (0.63, 0.35).[19] This is due to the appreciable two main emission peaks at 588 nm for $^5D_0 \rightarrow {}^7F_1$ and 614 nm for $^5D_0 \rightarrow {}^7F_2$ transitions, respectively. This result shows that an ideal white color was achieved in $(Gd_{0.3}Eu_{0.7})_3BSi_2O_{10}$ phosphor under 395 nm LED excitation by controlling Eu^{3+} dopant concentration. Furthermore, $(Gd_{0.3}Eu_{0.7})_3BSi_2O_{10}$ 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, $Gd_3BSi_2O_{10}:Eu^{3+}$ for white LED application using the solid-state reaction method. $Gd_3BSi_2O_{10}$ 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, $Gd_3BSi_2O_{10}:Eu^{3+}$ 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%. $Gd_3BSi_2O_{10}:Eu^{3+}$ shows good thermal stability and expected to be an ideal candidate for tri-color phosphors based white LED.

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Figure 5. The temperature dependence luminescence relative intensity spectra of $(Gd_{0.3}Eu_{0.7})_3BSi_2O_{10}$ (■) and YAG:Ce^{3+} (P46-Y3) (○).