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Letter

Blue-emitting phosphor $M_2B_5O_9Cl$: Eu^{2+} (M=Sr, Ca) for white LEDs

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ABSTRACT

Eu^{2+} doped $M_2B_5O_9Cl$ (M=Ca, Sr) phosphors were prepared by a solid-state reaction method. Luminescent properties of as-synthesized phosphors were investigated under the excitation of near-ultraviolet (n-UV) light. Photoluminescence (PL) spectra revealed a blue emission band, and the emission band shifted to a longer wavelength region as Ca^{2+} substituted Sr^{2+}. The photoluminescence excitation (PLE) spectra of $M_2B_5O_9Cl$: Eu^{2+} (M=Ca, Sr) showed broadband absorptions in the n-UV region. Moreover, the as-prepared phosphors were also compared with commercial $BaMgAl_{10}O_{17}$: Eu^{2+} (BAM) blue phosphor. The present phosphors showed a narrower full width at half-maximum and higher PL intensity than the reference BAM under the n-UV light excitation.

1. Introduction

In response to the ever-decreasing fossil energy resource and the growing threat of climate change, many governments have put a tremendous emphasis on developing new energy source and the saving-energy technologies. Solid-state lighting (SSL) is an energy-efficient lighting technology, which offers advantages such as low power consumption, long lifetime (>100,000 h), and environmental friendliness. It is estimated that even if only 50% SSL were to be achieved and displaced current white-lighting technologies, the electricity used for lighting would be cut by 62% [1,2]. However, commercial white light emitting diodes (w-LEDs) produced by combining a blue LED chip with yellow-emitting phosphor cannot meet the requirement of general illumination due to their poor color rendering index (<75) and unsatisfactory high color temperature (>4500 K) because of weak red emission [3,4]. One of the feasibilities to overcome these problems and to obtain the w-LEDs with high performance is using near-ultraviolet LEDs (n-UV LEDs) pumping red, green and blue tricolor phosphors, which provides an excellent color rendering index and the tunable color temperature [5].

Presently, the emission bands of LEDs are close to the n-UV range around 400 nm, which offers a high efficient solid-state lighting, thus it is estimated that the w-LEDs produced through exciting multiphosphors by a n-UV LED chip will dominate the market products in the near future [6]. Due to tricolor phosphors playing the special roles in the n-UV white light-emitting diodes, much attention has recently been paid to the development of new phosphors with good luminescence properties that can be excited with the longer UV range (350–420 nm). Because the red and green phosphors can share the absorption in blue range, the blue phosphor should exhibit higher efficiency. Currently, $BaMgAl_{10}O_{17}$: Eu^{2+} (BAM: Eu^{2+}) has been regarded as the preferred blue-emitting phosphor for w-LEDs based on the n-UV LED, but BAM shows a poor absorption band around near-UV range, which is not well suitable for current available commercial n-UV emitting InGaN chips [7]. In addition, the synthesis of BAM: Eu^{2+} is usually at temperature as high as 1300–1600 °C for several hours, which leads to the increase of w-LEDs cost [8]. Thus, it is necessary to search for new blue phosphors those can be efficiently excited in the n-UV range, especially near 400 nm to enhance the luminous efficiency.

The phosphors of Eu^{2+} ions doped alkaline earth haloborates $M_2B_5O_9R$ (M=Ca, Sr, Ba; R=Cl, Br) have gained special attention because of possible applications as storage phosphors for X-ray imaging and thermalneutron detection. Eu^{3+} is easy to reduce to Eu^{2+} in this system, and these phosphors show strong absorption in n-UV region and strong blue emitting [9–11]. In addition, these phosphors were usually synthesized below 1000 °C, whose poten-

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tial low-cost synthesis is in favor of the popularization of W-LEDs devices. However, there are few reports on Eu^{2+} doped $M_2B_5O_9R$ used as blue-emitting phosphors in solid-state lighting [12]. In this paper, we report the luminescence properties of Eu^{2+} doped $M_2B_5O_9Cl$ (M=Ca, Sr) as a potential blue emitting phosphor for w-LEDs based on the n-UV LED chips.

2. Experimental

All of the powder samples $M_2B_5O_9Cl$ (M=Ca, Sr) were synthesized by a high temperature solid-state reaction technique under a CO reducing atmosphere. Stoichiometric amount of raw materials, analytical grade, $SrCO_3$ or $CaCO_3$, $SrCl_2 \cdot 6H_2O$ or $CaCl_2$ (5% excess), H_3BO_3 (10% excess), Eu_2O_3 (99.99%) were mixed homogeneously and placed in a small covered corundum crucible. Then the small crucible was contained in a large outer crucible and buried in carbon sticks. Afterwards, the large crucible with its contents was placed in a muffle furnace under ambient atmospheres and fired at 900 °C for 4 h. The excess of H_3BO_3 or the corresponding alkaline earth chlorides was used for the compensation of evaporation at high temperature. And the excess of $SrCl_2$ or $CaCl_2$ was also served as flux in the above process [13,14]. In addition, their emission intensities were compared with commercial blue emitting phosphor BAM: Eu^{2+}. The commercial three primary color phosphors red phosphor Y_2O_3: Eu^{3+}, green phosphor $LaPO_4$: Ce^{3+}, Tb^{3+}, and blue phosphor BAM: Eu^{2+} were all purchased from NICHIA Corporation (Japan).

The structure and phase purity of sintered samples were identified by powder X-ray diffraction (XRD) analysis using a X'Pert PRO advanced automatic diffractometer with Cu-Kα radiation operated at 40 kV and 40 mA. The measurements of photoluminescence (PL) and photoluminescence excitation (PLE) spectra were carried out using a JASCO FP-6500 fluorescence spectrophotometer equipped with a 150 W Xenon lamp as the excitation light source. To eliminate the second-order emission of the source radiation, a cutoff filter was used in the measurements. PL spectra of all samples were tested three times to reduce the error and all measurements were performed at room temperature.

3. Results and discussions

The powder XRD patterns of as-prepared phosphors are similar, thus only the patterns of $Sr_{1.92}Eu_{0.08}B_5O_9Cl$ and $Ca_{1.92}Eu_{0.08}B_5O_9Cl$ phosphors annealed at 900 °C for 4 h are exhibited in Fig. 1 as representative samples. In addition, the standard JCPDS profiles of $Sr_2B_5O_9Cl$ (25-0890) and $Ca_2B_5O_9Cl$ (23-0859) are also shown in Fig. 1a and d, respectively. By careful comparison with the given XRD patterns, all of the diffraction peaks are in good agreement with the standard files and no diffraction peaks from the raw materials or other impurities are found. It indicates that the dopants Eu^{2+} do not significantly influence the structure of the host in our experimental range, and the single-phased phosphors with formula $M_2B_5O_9Cl$: Eu^{2+} (M=Ca, Sr) can be obtained successfully in our experimental conditions. The synthesis temperature is 400 °C lower than that of the commercial blue emitting phosphor BAM: Eu^{2+}.

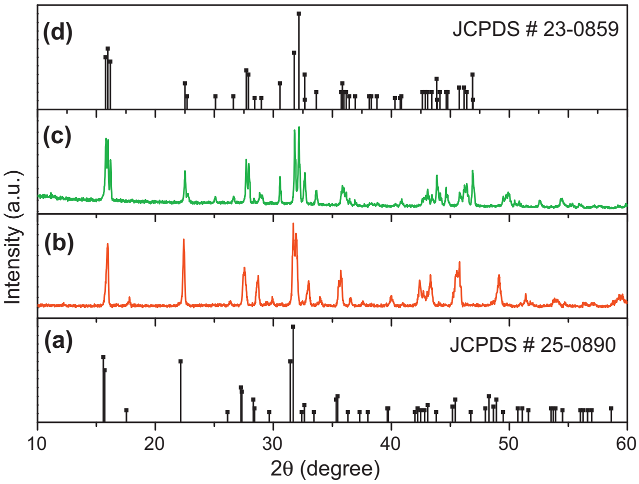

Fig. 1. XRD patterns of the standard $Sr_2B_5O_9Cl$ (a), $Ca_2B_5O_9Cl$ (d) and samples $Sr_{1.92}Eu_{0.08}B_5O_9Cl$ (b), $Ca_{1.92}Eu_{0.08}B_5O_9Cl$ (c).

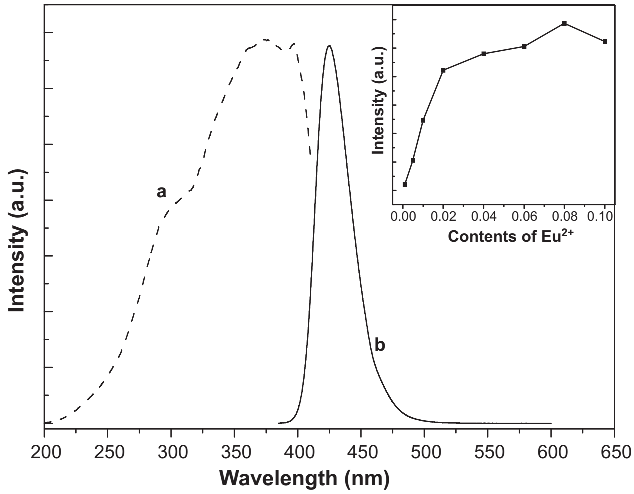

Fig. 2. PLE (a, λ_{em} = 425 nm) and PL (b, λ_{ex} = 365 nm) spectra of phosphor $Sr_{1.92}Eu_{0.08}B_5O_9Cl$. Inset: dependence of phosphor intensity on the contents of Eu^{2+}.

Structurally, haloborates $Ca_2B_5O_9Cl$ belongs to orthorhombic system, with the Pnn2 space group, and Ca^{2+} ions occupy two slightly different C_1 crystallographic sites in the structure [15]; whereas, $Sr_2B_5O_9Cl$ was considered to adopt a tetragonal structure with the $P4_22_12$ space group in early literature [16].

The PLE spectrum of $Sr_{1.92}Eu_{0.08}B_5O_9Cl$ phosphor is shown in Fig. 2a, monitored with an emission wavelength of 425 nm. The PLE spectrum shows a broad band between 250 and 410 nm, which corresponds to the 4f–5d transition of Eu^{2+}. Fig. 2b shows the PL spectrum of $Sr_{1.92}Eu_{0.08}B_5O_9Cl$ phosphor with 365 nm excitation. The PL spectrum presents a broad blue emission band centered at around 425 nm, which is attributed to the well-known $4f^65d^1(t_{2g}) \to 4f^7(^8S_{7/2})$ transition of Eu^{2+}. No other characteristic emission peaks from Eu^{3+} are observed in the PL spectra, indicating that Eu^{3+} ions have been reduced to Eu^{2+} completely in our experiments. No remarkable changes are found in the PL spectra under the excitation of n-UV light with different wavelength except for relative intensity.

It is generally accepted that the Eu^{2+} concentration plays an important role in the searching of optimal composition of phosphor. Therefore, the variations of PL intensity with different Eu^{2+} concentrations for $Sr_{2-x}Eu_xB_5O_9Cl$ have been investigated in this paper. The inset of Fig. 2 shows the dependence of the PL intensities of $Sr_{2-x}Eu_xB_5O_9Cl$ on the concentration of Eu^{2+} (x) with the excitation of 365 nm, here, the PL intensity is defined as the integrated area intensities in the range of 380–500 nm. It is observed that the PL intensity increases with the increasing of Eu^{2+} content until reaches a maximum at $x = 0.08$, then it falls steadily as the content of Eu^{2+} further increases due to concentration quenching, which is mainly caused by the non-radiative energy transfer among the identical Eu^{2+} ions. The probability of energy transfer between two activators is inversely proportional to the nth power of the distance of the activator ions. When the concentration of Eu^{2+} increases, the distance between Eu^{2+} ions becomes small, thus the probability of energy transfer increases. The concentration quenching phenomena will not occur if the average distance between the identical Eu^{2+} ions is so large that the energy migration is hampered, thus the critical distance is an important parameter which can be estimated according to the following formula [17]:

$$R_c \approx 2\left(\frac{3V}{4\pi x_c N}\right)^{1/3}$$

where V is the volume of the unit cell (in Å^3), x_c is the atom fraction of activator at which the quenching occurs, the so-called optimum

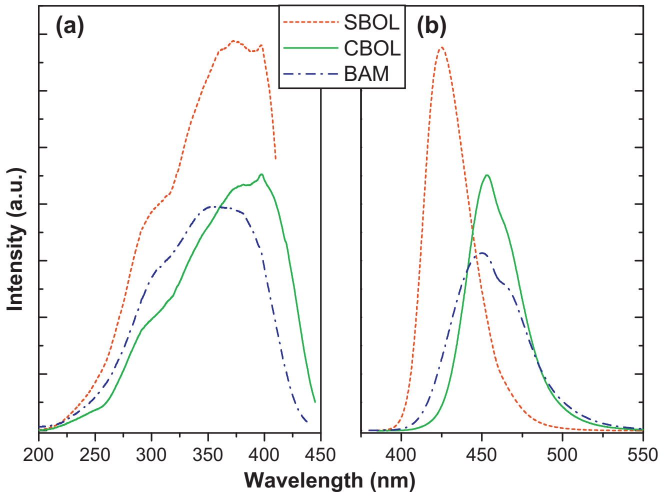

Fig. 3. PLE (a) and PL (b, $\lambda_{ex} = 397$ nm) of samples $Sr_{1.92}Eu_{0.08}B_5O_9Cl$, $Ca_{1.92}Eu_{0.08}B_5O_9Cl$, and the commercial products BAM: Eu^{2+}.

concentration, and N is the number of cations in the unit cell. According to the above experimental results and the crystal structure of the compound $Sr_2B_5O_9Cl$ [16], the values of V, N, and x_c are 837.35 Å^3, 4 and 0.08, respectively. The critical distance R_c of Eu^{2+} in $Sr_{2-x}Eu_xB_5O_9Cl$ phosphor is calculated to be about 17.1 Å.

Generally speaking, Eu^{2+} emission can vary from UV to red region depending on the host lattice, the size of the cation, and the strength of the crystal field [18]. In the present system, if Sr^{2+} ions are completely substituted by Ca^{2+} ions, the emission of Eu^{2+} will shift to a long wavelength side. Because the crystal field strength will be larger for Eu^{2+} in $Ca_2B_5O_9Cl$ than in $Sr_2B_5O_9Cl$ for the radius of Sr^{2+} (1.13 Å) is larger than that of Ca^{2+} (0.99 Å), which results in the longer wavelength emission band of Eu^{2+} in $Ca_2B_5O_9Cl$ than in $Sr_2B_5O_9Cl$ host lattice. As expected, the PL spectra of $Ca_{1.92}Eu_{0.08}B_5O_9Cl$ centered at 452 nm, which is longer than 425 nm of $Sr_{1.92}Eu_{0.08}B_5O_9Cl$ (as shown in Fig. 3b). In order to compare with commercial phosphor $BaMgAl_{10}O_{17}$: Eu^{2+} (BAM: Eu^{2+}), Fig. 3 gives the PLE and PL spectra of $M_{1.92}Eu_{0.08}B_5O_9Cl$ (M=Ca, Sr) phosphors with optimal composition and the commercial BAM: Eu^{2+} that is currently used as the blue emitting phosphor for w-LED based on n-UV InGaN chip. Fig. 3a shows the PLE spectra monitored at maximum emission peaks. It is comparatively seen that the as-synthesized samples $M_{1.92}Eu_{0.08}B_5O_9Cl$ (M=Ca, Sr) exhibit the stronger absorption bands in the region of 360–410 nm than that of BAM, especially the sample $Sr_{1.92}Eu_{0.08}B_5O_9Cl$. Fig. 3b presents the PL spectra of samples excited at 397 nm, the integrated emission intensity of $Sr_{1.92}Eu_{0.08}B_5O_9Cl$ and $Ca_{1.92}Eu_{0.08}B_5O_9Cl$ is 1.58 and 1.06 times higher than that of the reference BAM. Moreover, the full width at half maximum (FWHM) of samples $Sr_{1.92}Eu_{0.08}B_5O_9Cl$, $Ca_{1.92}Eu_{0.08}B_5O_9Cl$ and commercial BAM: Eu^{2+} blue phosphor is about 32, 37 and 52 nm, respectively, which indicates that $M_{1.92}Eu_{0.08}B_5O_9Cl$ (M=Sr, Ca) phosphor shows a purer color than the commercial blue phosphor [19]. The above results show that the as-prepared samples $M_{1.92}Eu_{0.08}B_5O_9Cl$ (M=Ca, Sr) are excellent candidates of blue emitting phosphor for w-LEDs based on n-UV InGaN chip.

From the corresponding PL spectra upon 397 nm excitation, the commission International de l'Eclairage chromaticity coordination of the phosphors $M_{1.92}Eu_{0.08}B_5O_9Cl$ (M=Sr, Ca) have been calculated to be (0.162, 0.015) and (0.143, 0.048) for M=Sr or Ca, respectively, which are depicted in the CIE 1931 chromaticity diagram (as shown in Fig. 4) and fall into the blue region. The chromaticity coordinates of commercial red phosphor Y_2O_3: Eu^{3+} (0.658, 0.341), green phosphor $LaPO_4$: Ce^{3+}, Tb^{3+} (0.335, 0.588) and the blue phosphor BAM: Eu^{2+} (0.146, 0.057) are also calculated according to their PL spectra and presented in Fig. 4. The CIE coordinates of $Ca_{1.92}Eu_{0.08}B_5O_9Cl$ are more closer to that of the commercial blue emitting phosphor BAM. The above characteristic indexes of the samples show that the $M_{1.92}Eu_{0.08}B_5O_9Cl$ (M=Sr, Ca) phosphors have intense blue emission under the excitation of n-UV light, thus the as-prepared phosphors have a great potential to replace the current blue emitting phosphor BAM in w-LEDs based on n-UV InGaN chip.

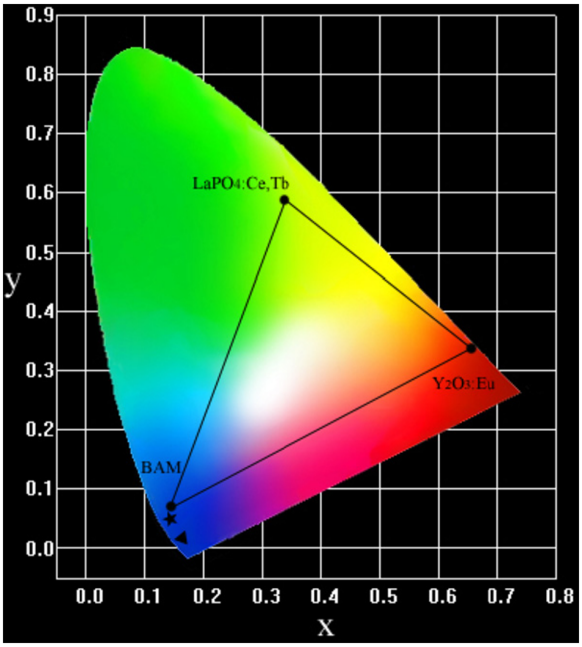

Fig. 4. The CIE coordinates of phosphors $Sr_{1.92}Eu_{0.08}B_5O_9Cl$ (marked with ▽) and $Ca_{1.92}Eu_{0.08}B_5O_9Cl$ (marked as star).

4. Conclusions

In summary, blue emitting phosphors $M_2B_5O_9Cl$: xEu^{2+} (M=Ca, Sr) were synthesized by a conventional solid-state reaction method. As the concentration of Eu^{2+} is 0.08, the phosphors $M_2B_5O_9Cl$: Eu^{2+} (M=Ca, Sr) show the highest PL intensity. The PLE spectra of the present phosphors show the intense broadband absorptions in n-UV 360–410 nm region, which match well with the emission of n-UV chip. The PL spectra of $M_{1.92}Eu_{0.08}B_5O_9Cl$ (M=Sr, Ca) phosphors exhibit broadband emission in the blue region, and show a purer color than the commercial blue phosphor BAM: Eu^{2+}. PL peaks of $Sr_{1.92}Eu_{0.08}B_5O_9Cl$ and $Ca_{1.92}Eu_{0.08}B_5O_9Cl$ locate at 425 and 452 nm, whose PL intensity is about 1.58 and 1.06 times higher than that of the reference BAM, respectively. Moreover, the reaction temperature of the present phosphors is at least lower about 400 °C than that of the BAM. Therefore, the as-prepared phosphors $M_{1.92}Eu_{0.08}B_5O_9Cl$ (M=Sr, Ca) have a great potential to replace the current BAM: Eu^{2+} used as blue emitting phosphor for the solid state lighting based on n-UV LED chip.

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