Research Article

Rare Earth Doped Lanthanum Calcium Borate Polycrystalline Red Phosphors

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Received 19 March 2014; Accepted 15 July 2014; Published 5 August 2014

Academic Editor: Somchai Thongtem

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1. Introduction

White light emitting diodes (LEDs) are considered as the next generation solid-state lighting systems because of their excellent properties such as high efficiency, low power consumption, long lifetime, and lower toxicity [1–6]. The LED based solid-state lighting techniques have gained great achievements since the white LEDs became commercially available by Nichia Chemical Co. in 1997 [7–9]. There are three ways to produce white LEDs: (i) combining a blue LED with a yellow phosphor, for example, Y3Al5O12:Ce³⁺, (ii) mixing red, green, and blue emissions from three LEDs, and (iii) exciting red/green/blue tricolor phosphors with a near-UV LED (370–410 nm). The third is a flexible and convenient way to obtain high quality white LEDs due to the following advantages, generated white color by phosphors, that is, high tolerance to UV chips’ color variation and excellent color rendering index [10]. The main tricolor phosphors for near-UV InGaN-based LEDs are still under developing just as BaMgAl10O17:Eu²⁺ for blue, ZnS:Cu²⁺/Al³⁺ for green, and Y₂O₃:S:Eu³⁺ for red [11–13]. Among them, the red phosphor has received much attention due to the fact that it can improve color rendering index; therefore it is meaningful to develop numerous red phosphors with higher efficiency to improve the performance of white LEDs [13–17].

During the past decades, rare earth ions doped in various host materials have been widely studied due to their characteristic luminescence properties. Among the rare earth ions, Sm³⁺, Eu³⁺, Tb³⁺, and Dy³⁺ are important activator ions for producing visible light [18–25]. Sm³⁺ activated luminescent materials have received much attention at present [26, 27]. They show bright emissions in orange and red regions attributed to the transitions from the excited state 4G5/2 to the ground state 6H5/2 and the other state 6HJ (J = 7/2, 9/2, and 11/2), which can be used in high density optical storage, temperature sensors, under sea communication, various fluorescent devices, color display, and visible solid-state lasers [2, 28–30]. Luminescence of Eu³⁺ is especially useful to probe the local structure of luminescent centers in a host lattice because of its simple energy level structure, great sensitivity to ligand field, and similar lanthanide chemical properties to the other rare earth ions [31–33].

Single-phased Sm³⁺ doped lanthanum calcium borate (SmₓLa₂₋ₓCaB₁₀O₁₉, SLCB, x = 0.06) polycrystalline red phosphor was prepared by solid-state reaction method. The phosphor has two main excitation peaks located at 398.5 nm and 469.0 nm, which are nicely in accordance with the emitting wavelengths of commercial near-UV and blue light emitting diode chips. Under the excitation of 398.0 nm, the dominant red emission of Sm³⁺ in SLCB phosphor is centered at 598.0 nm corresponding to the transition of 4G5/2 → 6H7/2. The Eu³⁺ fluorescence in the red spectral region is applied as a spectroscopic probe to reveal the local site symmetry in the host lattice and, hence, Judd-Ofelt parameters Ω(t = 2, 4) of Eu³⁺ in the phosphor matrix are derived to be 3.62 × 10⁻²⁰ and 1.97 × 10⁻²⁰ cm², indicating a high asymmetrical and strong covalent environment around rare earth luminescence centers. Herein, the red phosphors are promising good candidates employed in white light emitting diodes (LEDs) illumination.
Growing interest recently has been focused on luminescence of trivalent rare earth ions in phosphates, tungstates, borates, molybdates, and alumimates, among which rare earth doped borates are especially attractive because of their wide UV transparency, exceptional optical damage thresholds, excellent chemical and thermal stability, and high luminescence efficiency [34–42]. Hence, a borate phosphor which efficiently emits red fluorescence under the UV and blue light excitation is of great significance to be synthesized for efficient excitation range matches the output wavelengths and bluish-green spectral regions. This suggests that the effective excitation range matches the output wavelengths of InGaN-based LED chips well; thus, the phosphors have potential application in the solid-state LED lighting.

Figure 3 is the emission spectrum of SLCB phosphor excited by 398.0 nm. The characteristic emissions of SLCB phosphor consist of five emission bands, which are attributed to the transitions from $^4\text{G}_{5/2}$ state to $^6\text{H}_j$ ($j = 5/2, 7/2, 9/2, 11/2,$ and 13/2) states of Sm$^{3+}$. Among these, the strongest emission peak located at 598.0 nm originates from the typical transition $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ and the other peaks at 562.0, 646.5, 706.0, and 735.0 nm are attributed to the transitions of $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$, $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$, $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{11/2}$, and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{13/2}$, respectively [50–54]. Among these emission peaks, the transition emission $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ (598.0 nm, orangish red) with $\Delta J = \pm 1$ is a magnetic dipole (MD) allowed one, but it is also electric dipole (ED) dominated one and the other transition $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{11/2}$ does not appreciably depend on the chemical surroundings of the luminescence center and its symmetry; however, the ED

2. Experiments

SLCB phosphor was synthesized by a solid-state reaction route at high temperature using the following chemical reaction:

$$x\text{Sm}_3\text{O}_3 + (2 - x) \text{La}_3\text{O}_3 + 2\text{CaCO}_3 + 20\text{H}_3\text{BO}_3 \rightarrow 2\text{Sm}_2\text{La}_{2-x}\text{CaB}_{10}\text{O}_{19} + 2\text{CO}_2 \uparrow + 30\text{H}_2\text{O} \uparrow \quad (1)$$

Here, the $x$ value of SLCB sample is the molar replacement of La$^{3+}$ by Sm$^{3+}$, which is adopted to be 0.06 to maintain the brightness of phosphors and avoid the fluorescence quenching because of high concentration doping. Reagents La$_3$O$_3$ (99.99%), CaCO$_3$ (99.99%), H$_3$BO$_3$ (99.9%), and Sm$_2$O$_3$ (99.99%) were used as raw materials. They were weighed according to the stoichiometric proportion, except for H$_3$BO$_3$ with an excess of 6.5 wt% to compensate for the volatilization of B$_2$O$_3$ at high temperature. After being ground and mixed thoroughly in an agate mortar, the mixture was placed into an electric furnace and preheated at 500°C for 10 h. Being cooled and ground again, the mixture was sintered at 930°C for 24 h twice with the intermediate grinding.

The crystallographic structure of SLCB powders was characterized by X-ray powder diffraction analysis using a D/Max-3B X-ray diffractometer with 40 kV, 20 mA. The excitation and emission spectra were recorded on a Jobin Yvon FluoroLog-3 spectrophotometer with a R928 photomultiplier tube (PMT) detector, and a commercial CW Xe-lamp was used as pump source. A JSM-6460LV scanning electron microscopy was used for the observation of particle morphology. The photographs of the samples were taken by a Sony a200 digital camera. ELCB phosphor was prepared by the same way except that Eu$_2$O$_3$ was used instead of Sm$_2$O$_3$ and the measurements were carried out at the same condition as SLCB phosphor.

3. Results and Discussion

3.1. X-Ray Diffraction Analysis. To check the phase purity and the structure of the sample, the powder X-ray diffraction (XRD) measurement for the sample was carried out. Figure 1 presents a comparison between the experimental result for SLCB phosphor and JCPDS card 54-0033 (La$_3$CaB$_{10}$O$_{19}$). The observed peaks are in good agreement with the JCPDS data indicating that the main phase of the prepared phosphor is LCB. Because of lanthanide contraction, rare earth ions have similar radius, coordination environment, and physical-chemical properties. When La$^{3+}$ in the lattice is replaced by Sm$^{3+}$, the crystal structure does not change dramatically. The doped product crystallizes as monoclinic structure with a space group of C2 and lattice parameters values $a = 1.1028$ nm, $b = 0.6556$ nm, $c = 0.9114$ nm, and $\beta = 91.431^\circ$ [43, 44]. The effect of Sm$^{3+}$ doping in LCB host is seductive to be developed as a red phosphor for solid-state LED lighting.

Herein, Sm$^{3+}$ activated lanthanum calcium borate phosphor (Sm$_{3-x}$La$_{2-x}$CaB$_{10}$O$_{19}$, SLCB) was prepared by the solid-state reaction technique, and an attempt was made to investigate its luminescence characteristics. Eu$^{3+}$ was adopted as a probe in ELCB (Eu$_{3-x}$La$_{2-x}$CaB$_{10}$O$_{19}$, ELCB) phosphor through the calculation of $J$-$O$ parameters to reflect the local microenvironment around the rare earth ions in the compounds. The bright red fluorescence obtained from SLCB phosphor suggests that the as-prepared phosphor is a promising red luminescent material for white LEDs.

SLCB phosphor was synthesized by a solid-state reaction route at high temperature using the following chemical reaction:

$$x\text{Sm}_3\text{O}_3 + (2 - x) \text{La}_3\text{O}_3 + 2\text{CaCO}_3 + 20\text{H}_3\text{BO}_3 \rightarrow 2\text{Sm}_2\text{La}_{2-x}\text{CaB}_{10}\text{O}_{19} + 2\text{CO}_2 \uparrow + 30\text{H}_2\text{O} \uparrow \quad (1)$$

Here, the $x$ value of SLCB sample is the molar replacement of La$^{3+}$ by Sm$^{3+}$, which is adopted to be 0.06 to maintain the brightness of phosphors and avoid the fluorescence quenching because of high concentration doping. Reagents La$_3$O$_3$ (99.99%), CaCO$_3$ (99.99%), H$_3$BO$_3$ (99.9%), and Sm$_2$O$_3$ (99.99%) were used as raw materials. They were weighed according to the stoichiometric proportion, except for H$_3$BO$_3$ with an excess of 6.5 wt% to compensate for the volatilization of B$_2$O$_3$ at high temperature. After being ground and mixed thoroughly in an agate mortar, the mixture was placed into an electric furnace and preheated at 500°C for 10 h. Being cooled and ground again, the mixture was sintered at 930°C for 24 h twice with the intermediate grinding.

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transition belongs to hypersensitive transitions. Generally, the intensity ratio of ED to MD transitions has been used to evaluate the symmetry of the local environment of the trivalent $4f$ ions. The greater the intensity of the ED transition, the more the asymmetry nature [55]. In this work, the emission due to $^4G_{5/2} \rightarrow ^6H_{9/2}$ (ED) transition of Sm$^{3+}$ is more intense than $^4G_{5/2} \rightarrow ^6H_{5/2}$, specifying the asymmetric nature of host matrix. And the three main emission peaks of SLCB phosphor always split just similarly to the reports of LiBaBO$_3$:Sm$^{3+}$ [56], Gd$_2$MoO$_6$:Sm$^{3+}$ [57], and GdVO$_4$:Sm$^{3+}$ [58]. Those splits result from the crystal field effects, and the split extents are related to the structure characteristic of the crystal field.

### 3.3. Intensity Parameters of the Spectroscopic Probe Eu$^{3+}$ in ELCB Phosphor

Figure 4 presents the emission spectrum of ELCB phosphor excited at 391.0 nm in the wavelength of 560–720 nm. There are several typical emission bands around 560–720 nm assigned to the $^5D_0 \rightarrow ^7F_J$ ($J = 0–4$) transitions of Eu$^{3+}$ [59–63], of which the red emission band at 617 nm is the most intense one due to the electric dipole transition $^5D_0 \rightarrow ^7F_2$.

Luminescence of Eu$^{3+}$ is especially useful to probe the local symmetry and bonding characteristics of luminescent...
centers in a host lattice on account of its unsplit $^7\text{F}_0$ ground state and relatively simple energy level scheme. The symmetry of the crystal site in which Eu$^{3+}$ is located can be determined by the intensity ratio between $^5\text{D}_0 \rightarrow ^7\text{F}_3$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition emissions in ELCB [64–67]. Here, the ratio is 1.9076 in ELCB phosphor from Figure 4, indicating that $^5\text{D}_0 \rightarrow ^7\text{F}_2$ electric dipole transition is dominated and Eu$^{3+}$ is in an inversion asymmetrical site.

Moreover, in order to further identify the asymmetry of Eu$^{3+}$ in ELCB phosphor, the intensity parameters are calculated. Generally, J-O intensity parameters are derived from absorption spectra; however, in consideration of the special energy level structure of Eu$^{3+}$, they should be calculated from the emission spectra because the recorded absorption peaks are not enough to get accurate results [68–70]. The transitions of Eu$^{3+}$ from $^5\text{D}_0$ to $^7\text{F}_j (j = 2, 4, \text{and} 6)$ are electronic dipole allowed ones and hypersensitive to the local environment around Eu$^{3+}$. The spontaneous emission probability $A_{\text{sp}}$ from $|\psi\rangle$ to $|\psi'\rangle$ is given by the following expression:

$$ A_{\text{sp}} = \frac{64\pi^4 e^2 \nu^3}{3h (2J + 1)} \frac{n(n^2 + 2)^2}{9} \Omega_j \langle \psi | U(t) | \psi' \rangle^2, $$

where $e$ is the electron charge, $\nu$ is the emission peak wavenumber, $h$ is the Planck constant, $n$ is the refractive index, $2J + 1$ is the degeneracy of the excited state, and $\langle \psi | U(t) | \psi' \rangle^2$ is the square of the reduced matrix elements of the tensor operator, which connects the initial state $|\psi\rangle$ with the final state $|\psi'\rangle$ and is considered to be independent of host matrix. The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition of Eu$^{3+}$ is magnetic-dipole allowed one and insensitive to the host matrix. The spontaneous emission probability of it ($A_{\text{md}}$) is given by

$$ A_{\text{md}} = \frac{64\pi^4 e^2 \nu^3}{3h (2J + 1)} n^3 S_{\text{md}}, $$

where the magnetic dipole line strength $S_{\text{md}}$ is constant and independent of the matrix, so the value of $A_{\text{md}}$ can be estimated by the value of fluoride glass ($A'_{\text{md}} = 60.3 \text{ s}^{-1}$). The relationship is

$$ A_{\text{md}} = \left( \frac{n}{n'} \right)^3 A'_{\text{md}}, \quad (4) $$

where $n (= 1.679)$ and $n' (= 1.522)$ are the refractive indices of ELCB crystal [71] and fluoride glass [72], respectively.

Based on the calculated $A_{\text{rad}}$, the selection rules, and the characteristic of transition intensities of Eu$^{3+}$, each of the $\Omega_j \langle \psi | U(t) | \psi' \rangle^2$ parameters decides the intensities of transitions because the remaining two are zero. Thus, the $\Omega_j$ can be estimated from the intensity ratios of $^5\text{D}_0 \rightarrow ^7\text{F}_{2,4}$ transitions to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition as

$$ \frac{\int I (\nu) d\nu}{\int I_{\text{md}} (\nu) d\nu} = \frac{A_j}{A_{\text{md}}} = \frac{64\pi^4 e^2 \nu^3}{3h (2J + 1)} \frac{n(n^2 + 2)^2}{9A_{\text{md}}} \Omega_j \langle \psi | U(t) | \psi' \rangle^2. \quad (5) $$

The calculated $\Omega_j$ ($t = 2$ and 4) values of Eu$^{3+}$ in ELCB phosphor are $3.62 \times 10^{-20}$ and $1.97 \times 10^{-20}$ cm$^3$, respectively. This result confirms a high inversion symmetric and strong covalent environment of Eu$^{3+}$ in the phosphor. The value of $\Omega_6$ cannot be given since the $^5\text{D}_0 \rightarrow ^7\text{F}_6$ emission is unable to be experimentally detected in this work.

Figure 5 presents the SEM pictures of the as-prepared SLCB and ELCB phosphors. The two samples have similar morphology and particle size distribution. Also, they have good dispersion and relatively narrow size distribution with the average size of about 0.5–6 μm. However, the particles have no regular and uniform shape, and some of them are agglomerated. The main reasons are that the primary nanocrystals with high energy would assemble to minimize the surface energy and they would be sintered in the heat treatment process.
4. Conclusion

A red emitting phosphor SLCB (Sm\(_{2-x}\)La\(_x\)CaB\(_{10}\)O\(_{19}\)) was prepared by solid-state reaction method in the air. XRD analysis indicates that the crystal belongs to a monoclinic system with unit cell parameters \(a = 1.1028\) nm, \(b = 0.6556\) nm, \(c = 0.9114\) nm, and \(\beta = 91.431^\circ\). The excitation spectrum shows that the phosphor can be efficiently excited by the commercial near-UV and blue light emitting diodes. Under the excitation of 398.0 nm, the phosphor presented red luminescence with efficient emissions at 562.0, 598.0, 646.5, 706.0, and 735.0 nm, corresponding to \(E_x^{2\rightarrow6}\) (\(J = 5/2,7/2,9/2,11/2,\) and 13/2) transitions, respectively. Eu\(^{3+}\) is used as a spectroscopic probe for the microstructure of ELCB (Eu\(_x\)La\(_{2-x}\)CaB\(_{10}\)O\(_{19}\)) phosphor and, thus, Judd-Olfet parameters \(\Omega_t (t = 2,4)\) in ELCB phosphor are derived to be \(3.62 \times 10^{-20}\) cm\(^2\) and \(1.97 \times 10^{-20}\) cm\(^2\), indicating a high asymmetrical and covalent environment around rare earth luminescence centers in the host lattice. The red fluorescence suggests that the two phosphors are potential candidates for light emitting diode applications.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant no. 61275057) and the Undergraduate Training Programs for Innovation and Entrepreneurship of Dalian Polytechnic University (Grant no. 2013013).

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