Research Article

Synthesis and Luminescent Characteristics of Ce^{3+} -Activated Borosilicate Blue-Emitting Phosphors for LEDs

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The phosphors $\text{Sr}_3\text{B}_2\text{SiO}_8:\text{Ce}^{3+}$ have been successfully synthesized via solid-state reaction process. Emission/excitation spectra and photoluminescence decay behaviors were investigated in detail. Under the excitation of 340 nm, the emission spectrum presented an asymmetry emission band extended from 350 to 600 nm, which with the main peak at 425 nm can be fitted in two peaks (23940 cm^{-1} and 21934 cm^{-1}). The chromaticity coordinates of $\text{Sr}_{3-x}\text{B}_2\text{SiO}_8:x\text{Ce}^{3+}$ are fixed in the blue region; when the intensity of Ce^{3+} reached the maximum, the chromaticity coordinate is (0.154, 0.088) which is more close to the standard CIE of blue light (0.140, 0.080). The results showed the kind of phosphor may have potential applications in the fields of UV-excited white LEDs.

1. Introduction

White-light-emitting diodes (w-LEDs) attract more attention as the result of their advantages such as longer lifetime, higher rendering index, higher luminosity efficiency, and lower energy consumption [1, 2]. Commonly, we combine the blue light of GaN chips and the yellow emission of $\text{YAG}:\text{Ce}^{3+}$ to gain white light [3–5]; however, the type of white color varies with the input power and a poor color rendering index ($R_a < 80$). Researchers made efforts to overcome the disadvantages mentioned above; novel phosphors can be effectively excited by ultraviolet or blue light and emit strong blue, green, and red light [6–8]. Tricolor phosphors with higher stability and intense absorption in UV spectral region are just in demand to meet the optimum requirements of w-LEDs.

Ce^{3+} ions play a significant role in the rare earth ions; commonly, they act as the blue-emitting phosphors due to the parity allowed electric dipole transition of $4f \rightarrow 5d$. Ce^{3+} -activated phosphors commonly act as the blue-emitting phosphors as the result of their $4f^1$ configuration in solids shows efficient broad band luminescence which due to the $4f \rightarrow 5d$ parity allowed electric dipole transition. The $4f \rightarrow 5d$ transitions of the Ce^{3+} ion have been widely

investigated and doped in the hosts such as $\text{Gd}_3(\text{Ga},\text{Al})_5\text{O}_{12}$ [9], $\text{NaY}_{0.6-x}\text{Ce}_{0.1}\text{Gd}_{0.3}\text{Eu}_x\text{F}_4$ [10], and $\text{Sr}_3\text{Al}_2\text{O}_5\text{Cl}_2$ [11]; generally, the $5d \rightarrow 4f$ emissions of the Ce^{3+} ion shift slightly to longer wavelengths which depend on the host composition, the crystal structure, or the lattice symmetry. In all of the hosts, borates have attracted extensive attention attributed to their stable physical and chemical properties, excellent thermal stability, and better absorption in UV region, especially borosilicate host $\text{Sr}_3\text{B}_2\text{SiO}_8$ as one kind of borate hosts, due to the adding of the boric acid; it can reduce the synthesis temperature of preparation of silicate. Recently, borosilicate host $\text{Sr}_3\text{B}_2\text{SiO}_8$ has been investigated by the researchers [12–14]; it indicated that the materials could emit intense visible light and may act as promising phosphors for practical application. However, the PL properties of borosilicate host materials have not been investigated widely; this prompted us to study the fluorescence properties of rare earth ions in these borates.

In this paper, we utilize the advantages of borosilicate and choose $\text{Sr}_3\text{B}_2\text{SiO}_8$ as the substrate of luminescent material and doped trivalent rare earth Ce^{3+} to analyze the luminescence properties under ultraviolet excitation conditions. $\text{Sr}_3\text{B}_2\text{SiO}_8:\text{Ce}^{3+}$ phosphors were synthesized successfully by

TABLE 1: Crystal data of $\text{Sr}_{3-x}\text{B}_2\text{SiO}_8:x\text{Ce}^{3+}$ ($x = 0\sim 0.05$) phosphors.

$x\text{Ce}^{3+}$ (mol)	0	0.0025	0.005	0.01	0.03	0.05
Radiation type	Cu-K α	Cu-K α	Cu-K α	Cu-K α	Cu-K α	Cu-K α
Wavelength ($\text{\AA}$)	1.5406	1.5406	1.5406	1.5406	1.5406	1.5406
Profile range ($^\circ$)	10–60	10–60	10–60	10–60	10–60	10–60
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pnma	Pnma	Pnma	Pnma	Pnma	Pnma
Z	4	4	4	4	4	4
<i>a</i>	12.355 (2)	12.350 (2)	12.234 (1)	12.018 (3)	11.871 (0)	11.684 (1)
<i>b</i>	3.916 (1)	3.894 (4)	3.873 (1)	3.849 (0)	3.827 (2)	3.805 (2)
<i>c</i>	5.405 (4)	5.393 (3)	5.321 (0)	5.315 (0)	5.302 (2)	5.294 (3)
<i>V</i> ($\text{\AA}^3$)	261.50 (56)	259.35 (42)	252.12 (11)	245.85 (74)	240.87 (15)	235.35 (86)

the solid-state reaction; corresponding luminescent properties were investigated in detail; the CIE of phosphors were also calculated. The results suggest that $\text{Sr}_3\text{B}_2\text{SiO}_8:\text{Ce}^{3+}$ may be used as potential blue phosphors for UV-based w-LEDs.

2. Experimental Section

2.1. Synthesis of $\text{Sr}_{3-x}\text{B}_2\text{SiO}_8:x\text{Ce}^{3+}$ ($x = 0.0025 \sim 0.05$) Phosphors. $\text{Sr}_{3-x}\text{B}_2\text{SiO}_8:x\text{Ce}^{3+}$ ($x = 0.0025 \sim 0.05$) phosphors were prepared by a solid-state reaction technique [15]. Reactants SrCO_3 , H_3BO_3 , and SiO_2 are analytical reagent grade (99.90%), and CeO_2 is spectrographic grade (99.99%). Reactant samples were first quantified by the stoichiometric ratio and then thoroughly mixed by grinding them in an agate mortar for 2 hours; then, samples were transferred into the corundum crucible and placed in a muffle furnace at 600°C for 1 h; then, the samples were got out from the muffle furnace and ground for 1 h again, subsequently, firing at 1000°C for 3 h in the reducing atmosphere (95% N_2 + 5% H_2). Finally, corundum crucibles were cooled to room temperature and the phosphor samples were obtained.

2.2. Characterization of $\text{Sr}_{3-x}\text{B}_2\text{SiO}_8:x\text{Ce}^{3+}$ ($x = 0.0025 \sim 0.05$) Phosphors. The powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8-advance X-ray powder diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$); the operation voltage and current were maintained at 40 kV and 40 mA, respectively; a scan rate of $2^\circ/\text{min}$ was applied to record the patterns in the range of $2\theta = 10\sim 60^\circ$. The excitation and emission spectra were measured by a Spectrofluorophotometer RF-5301PC series equipped with a 150 W Xenon lamp. The luminescence decay curves were obtained from a Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz). All the experiments were performed at room temperature.

3. Result and Discussion

3.1. The Crystal Structures of the Samples. The phase purities of the as-prepared powder samples were characterized by XRD at room temperature. The XRD patterns of $\text{Sr}_{3-x}\text{B}_2\text{SiO}_8:x\text{Ce}^{3+}$ ($x = 0.0025 \sim 0.05$) phosphor samples with

FIGURE 1: Typical XRD patterns of $\text{Sr}_{3-x}\text{B}_2\text{SiO}_8:x\text{Ce}^{3+}$.

different Ce^{3+} concentrations are shown in Figure 1. All of the diffraction peaks are in accordance with $\text{Sr}_3\text{B}_2\text{SiO}_8$ (JCPDS card number 32-1224). All these samples are single phase without any impurities. This indicates that doping Ce^{3+} ions in $\text{Sr}_3\text{B}_2\text{SiO}_8$ host with such a small concentration has no other phase specific changes. The crystal system is Orthorhombic, the space group is Pnma, and lattice parameters of $a = 12.355$ (2), $b = 3.916$ (1), $c = 5.405$ (4), and $V = 261.50$ (56) $\text{\AA}^3$. When the replacement of Sr^{2+} by Ce^{3+} occurs, the lattice constant and lattice volume vary, the radii of Ce^{3+} ion (0.1143 nm) are smaller than the radius of Sr^{2+} ion (0.1260 nm), and the variety of the lattice constant and lattice volume decreases along with the different Ce-containing adding, as presented in Table 1 [16].

3.2. The PL Excitation and Emission Spectra of Ce^{3+} Doped $\text{Sr}_3\text{B}_2\text{SiO}_8$ Phosphor. Figure 2 shows the PL excitation and emission spectra of Ce^{3+} doped $\text{Sr}_3\text{B}_2\text{SiO}_8$ phosphor samples with 0.5 mol% concentration. It can be observed clearly that the excitation spectrum of Ce^{3+} covers the range from 220 to 400 nm that shows two absorption bands, one between 220 and 300 nm and one around 340 nm. Both bands are

FIGURE 2: Photoluminescence excitation ((a) $\lambda_{em} = 425$ nm) and emission ((b) $\lambda_{ex} = 340$ nm) spectra of $\text{Sr}_{2.995}\text{B}_2\text{SiO}_8:0.005\text{Ce}^{3+}$.

FIGURE 3: Photoluminescence emission spectra of $\text{Sr}_{3-x}\text{B}_2\text{SiO}_8:x\text{Ce}^{3+}$ with different Ce^{3+} concentration under the excitation of 340 nm.

due to optically allowed $5d^04f^1 \rightarrow 5d^14f^0$ transitions. The excitation band split two characteristic peaks that are influenced by the crystal field environment of Ce^{3+} ions and the strongest excitation peak centered at 340 nm. Under the excitation of 340 nm, the emission spectrum presents an asymmetry emission band with the main peak at 425 nm; it also can be fitted in two peaks (23940 cm^{-1} and 21934 cm^{-1}); the deviation of the peaks is 2006 cm^{-1} which is in accordance with the theoretical energy difference of $^2F_{5/2}$ and $^2F_{7/2}$ (about $2000\sim 2200\text{ cm}^{-1}$) of Ce^{3+} [17].

3.3. The Emission Spectra of Series Samples of $\text{Sr}_{3-x}\text{B}_2\text{SiO}_8:x\text{Ce}^{3+}$ ($x = 0.0025\sim 0.05$). Figure 3 shows the emission spectra of series samples of $\text{Sr}_{3-x}\text{B}_2\text{SiO}_8:x\text{Ce}^{3+}$ ($x = 0.0025\sim$

0.05) under the excitation of 340 nm. From Figure 3, it is shown that the emission intensities increase with the Ce^{3+} concentration adding and then gradually decrease above $0.5\text{ mol}\%$. The figure also shows that the emission maximum shifts slightly to longer wavelengths with the increase of Ce^{3+} concentration which attribute crystal field environment of Ce^{3+} ions. Emission intensity increases significantly as the Ce^{3+} concentration is increased and gradually decreases as the doping concentration becomes greater than $x = 0.005$. As a result, the distance between Ce^{3+} ions becomes smaller with the adding of Ce^{3+} ions, leading to high probability of energy transfer among the Ce^{3+} ions. The loss of energy causes the emission intensity to be reduced, then leading to concentration quenching. Therefore, the optimum doping concentration of Ce^{3+} is fixed at $0.5\text{ mol}\%$.

3.4. The Critical Distance of Energy Transfer between Ce^{3+} Ions. With the concentration of Ce^{3+} ions increasing, the average distance between Ce^{3+} ions gradually decreased; then, the concentration quenching occurred; the concentration quenching may be induced by cross-relaxation processes in close $\text{Ce}^{3+} \rightarrow \text{Ce}^{3+}$. Namely, as the Ce^{3+} concentration increases, the possibility of energy transfer increases. According to the report of Blasse, we can roughly estimate the critical distance of energy transfer (R_c) and calculate it as follows [18]:

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

Here V is the unit cell volume, X_c is the critical concentration of dopant ions, and N is the number of host cations in the ions in a unit cell. For $\text{Sr}_3\text{B}_2\text{SiO}_8$ host, $V = 252.12(11)\text{ \AA}^3$, $N = 4$, and the critical concentration X_c is about 0.005 in our system.

The R_c value is about $28.8\text{ \AA}$ by using (1). The R_c value obtained above indicates the possibility of exchange interaction of ions. In general, there are three mechanisms for nonradiate energy transfer including exchange interaction, radiation reabsorption, and electric multipolar interactions. The exchange interaction is only for $5\text{ \AA}$, and the radiation reabsorption needs the emission and excitation spectra has widely overlapping; therefore, it can be inferred that electric multipolar interactions would be the energy transfer mechanism between Ce^{3+} and Ce^{3+} in the system.

3.5. Fluorescence Lifetime of Phosphors. The experiment tests the fluorescence lifetime of different concentrations of Ce^{3+} in $\text{Sr}_3\text{B}_2\text{SiO}_8$ system. Figure 4 presented the fluorescence decay curves and simple orbit transition of Ce^{3+} ; after fitting, the values can be well fitted by a single exponential function:

$$I = I_0 \exp\left(-\frac{t}{\tau}\right) + A, \quad (2)$$

where I and I_0 are the luminescence intensities at times t and 0 , t is the time, τ is the luminescence lifetime, and A is the value for different fittings. For $\text{Sr}_{3-x}\text{B}_2\text{SiO}_8:x\text{Ce}^{3+}$ ($x = 0.0025\sim 0.05$) samples, based on the decay curves and the

TABLE 2: Corresponding variations of CIE chromaticity coordinate for $\text{Sr}_{3-x}\text{B}_2\text{SiO}_8:x\text{Ce}^{3+}$ ($x = 0.0025\sim 0.05$) phosphor.

White LEDs site	CIE coordinates (x, y)	λ_{ex} range (nm)	λ_{em} (nm)
1	0.175, 0.099	220–400	422
2	0.154, 0.088	220–400	425
3	0.194, 0.116	220–400	430
4	0.210, 0.135	220–400	439
5	0.223, 0.155	220–400	442
Standard CIE of blue light	0.140, 0.080	—	—

FIGURE 4: Photoluminescence decay curves of Ce^{3+} in $\text{Sr}_{3-x}\text{B}_2\text{SiO}_8:x\text{Ce}^{3+}$ ($x = 0.0025\sim 0.05$) phosphors.

above-mentioned equation (2), the luminescence lifetime of Ce^{3+} is 39.98, 40.03, 38.77, 36.95, and 35.80 ns.

3.6. The Chromaticity Coordinates of $\text{Sr}_{3-x}\text{B}_2\text{SiO}_8:x\text{Ce}^{3+}$. Figure 5 presented the chromaticity coordinates of different molar (0.0025~0.05 mol) of Ce^{3+} -activated $\text{Sr}_3\text{B}_2\text{SiO}_8$ phosphors. It can be observed that, with the Ce^{3+} ions added (0.0025~0.05 mol), the color moved to the blue region, and the chromaticity coordinates of $\text{Sr}_3\text{B}_2\text{SiO}_8:\text{Ce}^{3+}$ are (1) (0.175, 0.099), (2) (0.154, 0.088), (3) (0.194, 0.116), (4) (0.210, 0.135), and (5) (0.223, 0.155), respectively, as shown in Table 2. When the intensity of Ce^{3+} reaches the maximum, it is more close to the standard CIE of blue light (0.140, 0.080) and the CIE of the commercial blue phosphor $\text{BaMgAl}_{10}\text{O}_7:\text{Eu}^{2+}$ is (0.147, 0.067); from the CIE chromaticity diagram of $\text{Sr}_3\text{B}_2\text{SiO}_8:\text{Ce}^{3+}$, it is obviously seen that we have realized that the blue light emission could be excited by UV in $\text{Sr}_3\text{B}_2\text{SiO}_8:\text{Ce}^{3+}$ phosphors, which may be promising for white LEDs under UV excitation.

FIGURE 5: Chromaticity coordinates of $\text{Sr}_{3-x}\text{B}_2\text{SiO}_8:x\text{Ce}^{3+}$.

4. Conclusions

In summary, a series of $\text{Sr}_3\text{B}_2\text{SiO}_8:\text{Ce}^{3+}$ phosphors have been synthesized by traditional high temperature solid-state reaction. The phosphors $\text{Sr}_3\text{B}_2\text{SiO}_8:\text{Ce}^{3+}$ can be excited under the UV region and show blue-emitting light extended from 350 to 600 nm. When the concentration of Ce^{3+} is 0.5% mol, the chromaticity coordinates of $\text{Sr}_{2.995}\text{B}_2\text{SiO}_8:0.005\text{Ce}^{3+}$ are (0.154, 0.088) which are more close to the standard CIE of blue light (0.140, 0.080). The results showed that $\text{Sr}_3\text{B}_2\text{SiO}_8:\text{Ce}^{3+}$ phosphors may act as a blue component for white LEDs.

Conflict of Interests

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

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