Synthesis, characterization and properties of Dy3+-activated single host borosilicate phosphors

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Abstract. New phosphors Sr3B2SiO8: Dy3+ have been successfully synthesized via solid-state reaction process. Emission/excitation spectra, photoluminescence decay behaviors were investigated in detail. Under the excitation of 351 nm, the emission spectrum consisting of the characteristic transitions of Dy 3+ which mainly peaking at 480, 487 nm and 574 nm corresponding to the 4F9/2 → 6H15/2 and 4F9/2 → 6H13/2, respectively, the intensity of the blue emission stronger than the yellow one which indicated that Dy 3+ ions take the site without inversion symmetry. The chromaticity coordinates of Sr3-xB2SiO8: x Dy3+ fixed in the white region. The results showed the kind of phosphor may be act potential applications in the fields of UV-excited white LEDs.

1. Introduction
White-light-emitting diodes (W-LEDs) have been paid more and more attention as the advantage of longer lifetime, higher rendering index, higher luminosity efficiency and lower energy consumption. Novel phosphor materials can be effectively excited by ultraviolet or blue light which can emit strong blue, green, red light, gain importance. Therefore, many efforts have been made to develop the single–phased white emitting phosphors for w-LEDs [1-3]. At present, there are many hosts that can be activated by Dy3+ ions, such as borates, phosphates, aluminates, silicates, etc [4-7]. Of all the hosts, borates due to their stable physical and chemical properties, excellent thermal stability and better absorption in UV region, therefore, it have attracted extensive attention. Recently, borosilicate host Sr3B2SiO8 has been investigated by the researchers [8-10], the materials emit intense visible light and are promising phosphors for practical application. However, the PL properties of the materials have not been investigated widely, this prompted us to study the fluorescence properties of rare earth ions in these borates. Dy3+ plays an important role in the production of white light luminescent materials. In general, Dy3+ exhibits two intense emission bands, one is the blue emission at about 470-500 nm corresponding to the 4F9/2 → 6H15/2 transition, the other is yellow emission at about 560-600 nm corresponding to the 4F9/2 → 6H13/2 transition. The yellow emission is an electric dipole transition, which is strongly influenced by the chemical environment surrounding Dy3+ ions. Consequently, Dy3+-activated luminescent materials attracted much attention as the result of the significant applications as
potential single phase for white phosphors. In this paper, we utilize the advantages of borosilicate and choose \( \text{Sr}_3\text{B}_2\text{SiO}_8 \) as substrate of luminescent material, and doped with trivalent rare earth \( \text{Dy}^{3+} \) to analyze the luminescence properties under ultraviolet excitation conditions. \( \text{Sr}_3\text{B}_2\text{SiO}_8: \text{Dy}^{3+} \) phosphors were synthesized successfully by the solid-state reaction, the corresponding structure and luminescent properties were investigated in detail, the CIE of phosphors were also calculated. The results suggest that \( \text{Sr}_3\text{B}_2\text{SiO}_8: \text{Dy}^{3+} \) may be used as potential single phase phosphors for UV-based w-LEDs.

2. Experimental

\( \text{Sr}_3\text{B}_2\text{SiO}_8: \text{Dy}^{3+} \) phosphors were prepared by a solid-state reaction technique. Analytical reagent grade (99.90%) \( \text{SrCO}_3 \), \( \text{H}_3\text{BO}_3 \), \( \text{SiO}_2 \), spectrographically pure (99.99%) \( \text{Dy}_2\text{O}_3 \) were employed as reactants. Reactant samples were first quantified by the stoichiometric ratio and then thoroughly mixed by grinding them in an agate mortar for 2 hours, then transferred samples into the corundum crucible and placed in a muff furnace at 600°C for 1h, then get out and grinding them in an agate mortar for 1 hour again, subsequently, firing at 1000°C for 3h finally, corundum crucibles were cooled to room temperature and the phosphor samples were obtained. The powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8-advance X-ray powder diffractometer with Cu Kα radiation (\( \lambda = 1.5406 \) Å), 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 \( 2\theta = 10-60^\circ \). The excitation and emission spectra were measured by a Spectrofluorophotometer RF-5301PC series equipped with a 150W 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

The phase purities and the crystal structures of the as-prepared powder samples were characterized by XRD at room temperature. The XRD patterns of \( \text{Sr}_{3-x}\text{B}_2\text{SiO}_8: x \text{Dy}^{3+} \) (\( x = 0.01-0.05 \)) phosphor samples with the \( \text{Dy}^{3+} \) concentrations are seen in Fig.1. All of the diffraction peaks are accord with \( \text{Sr}_3\text{B}_2\text{SiO}_8 \) (JCPDS card No.32-1224). All these samples are of single phase without any impurities. This indicates that doping of \( \text{Dy}^{3+} \) 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, space group is Pnma, lattice parameters of \( a = 12.355 \) (2), \( b = 3.916 \) (1), \( c = 5.405 \) (4), and \( V = 261.50 \) (56) Å\(^3\). The radii of \( \text{Dy}^{3+} \) ion (0.091 nm) are smaller than the radius of \( \text{Sr}^{2+} \) ion (0.126 nm), and the variety of the lattice constant and lattice volume decreases along with the different \( \text{Dy} \) containing adding, as presented in Table 1.

![Fig.1. Typical XRD patterns of \( \text{Sr}_{3-x}\text{B}_2\text{SiO}_8: x \text{Dy}^{3+} \) (\( x = 0.01-0.05 \)).](image-url)
Table 1 Crystal data of Sr_{3-x}B_{2}SiO_{8}: x Dy^{3+} (x = 0-0.09) phosphors

| xDy^{3+} (mol) | 0    | 0.01 | 0.03 | 0.05 | 0.07 | 0.09 |
|----------------|------|------|------|------|------|------|
| Crystal system | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic |
| Space group    | Pnma | Pnma | Pnma | Pnma | Pnma | Pnma |
| Z              | 4    | 4    | 4    | 4    | 4    | 4    |
| a              | 12.355(2) | 12.350(2) | 12.234(1) | 12.018(3) | 11.871(0) | 11.684(1) |
| b              | 3.916(1) | 3.894(4) | 3.873(1) | 3.849(0) | 3.827(2) | 3.805(2) |
| c              | 5.405(4) | 5.393(3) | 5.321(0) | 5.315(0) | 5.302(2) | 5.294(3) |
| V(Å³)          | 261.50(56) | 259.35(42) | 252.12(11) | 245.85(74) | 240.87(15) | 235.35(86) |

Fig. 2 depicted the PL excitation and emission spectra of Dy^{3+} doped Sr_{3}B_{2}SiO_{8} phosphor samples with 3mol% concentration. Fig. 2-a shows the excitation spectrum of the sample that monitored by the Dy^{3+}^{4}F_{9/2}→^{4}H_{13/2} transition at the emission of 574 nm which consists of a stronger excitation band from 280 to 420 nm with a maximum at 351 nm, we can see that in the fields of UV wavelength (350~410 nm), there were excitation peaks located at 326, 351, 366 and 388 nm, respectively. These excitation peaks are due to the f-f transitions of Dy^{3+} ions from ground state ^{6}H_{15/2} to the various excited states ^{4}F_{5/2}, ^{6}P_{5/2}, ^{6}P_{7/2}, ^{4}F_{7/2}, respectively. The strong excitation bands located in the wavelength of 350~410 nm imply that the kind of phosphor may be act potential applications in the fields of UV-excited or near UV-excited white LEDs.

Fig. 2. Photoluminescence excitation (a, λ_em = 574 nm) and emission (b, λ_ex = 351 nm) spectra of Sr_{2.97}B_{2}SiO_{8}: 0.03 Dy^{3+}.

Under the excitation of UV light (around 351 nm), the Sr_{3}B_{2}SiO_{8}:Dy^{3+} phosphors show the characteristic emissions of Dy^{3+}, as shown in Fig.2-b. Fig.2-b presents the emission spectrum of the sample excited by 351 nm which covers the region from 450 to 600 nm consisting of the characteristic transitions of Dy^{3+} which dominated by two main groups of lines in the blue region nm peaking at 480,
487 nm and the yellow-orange region peaking at 574 nm corresponding to the transition from \( ^4F_{9/2} \) to \( ^6H_{15/2} \) and \( ^4F_{9/2} \) to \( ^6H_{13/2} \), respectively. It can be seen that the emission intensity at 574 nm is stronger than the emission intensity at 480/487 nm, namely, the intensity of yellow emission is greater than that of the blue emission. It is well known that the hypersensitive transition is strongly influenced by the outside environment surrounding Dy\(^{3+}\), and the magnetic dipole transition is insensitive to the crystal field around the Dy\(^{3+}\) ions. When Dy\(^{3+}\) is located at a low symmetry site (without inversion symmetry), the yellow emission is dominant in the emission spectrum; when Dy\(^{3+}\) is at a high symmetry site (with inversion symmetry), the blue emission would be stronger than the yellow one. Thus, the stronger yellow emission indicates that Dy\(^{3+}\) ions take the site without inversion symmetry.

The emission spectra of \( Sr_3B_2SiO_8: Dy^{3+} \) phosphors with various Dy\(^{3+}\) concentrations excited by 351 nm is shown in Fig.3, it can be seen that the emission peaks show roughly the same location, except for the intensity. With the concentration of Dy\(^{3+}\) ions increasing, the intensities of yellow and blue bands increased, and reach the maximum at 3 mol\%, then decrease with adding the concentration of Dy\(^{3+}\) ions. We can observe that the optimum doping concentration of Dy\(^{3+}\) is fixed at 3 mol\% from Fig.3.

![Photoluminescence emission spectra of \( Sr_3-xB_2SiO_8: xDy^{3+} \) with different Dy\(^{3+}\) concentration under the excitation of 351 nm.](image)

**Fig.3.** Photoluminescence emission spectra of \( Sr_3-xB_2SiO_8: xDy^{3+} \) with different Dy\(^{3+}\) concentration under the excitation of 351 nm.

Experiment tests the fluorescence lifetime of different concentrations of Dy\(^{3+}\) in \( SrB_2SiO_8 \) system. Fig.4 show the fluorescence decay curves and simple orbit transition of Dy\(^{3+}\), after fitting, the values can be well fitted by a single exponential function:

\[
I = I_0 \exp(-t/\tau) + A
\]

Here \( I \) and \( I_0 \) are the luminescence intensities at times \( t \) and 0, \( t \) is the time, \( \tau \) is the luminescence lifetime, and \( A \) is the value for different fittings. The luminescence lifetime of Dy\(^{3+}\) (0.01-0.09mol) in this host is 0.75, 0.82, 0.69, 0.60, 0.56 ms, respectively. The inset figure in Fig.4 confirmed the characteristic emission energy levels of Dy\(^{3+}\). Under the excitation of 351 nm, Dy\(^{3+}\) ions absorbed energy from the ground state \( ^6H_{15/2} \) to the various excited states \( ^4F_{5/2} \), \( ^4P_{3/2} \), \( ^4P_{1/2} \), \( ^4F_{7/2} \), the energy of \( ^4P_{3/2} \) energy level of Dy\(^{3+}\) ions to the \( ^4F_{9/2} \) energy level of Dy\(^{3+}\) ions by nonradiative relaxation, then the energy of \( ^4F_{9/2} \) energy level transfer to \( ^6H_{15/2} \) and \( ^6H_{13/2} \) energy level, leading to the characteristic emission of Dy\(^{3+}\) ions.
**Fig. 4.** Photoluminescence decay curves of Dy$^{3+}$ in Sr$_3$B$_2$SiO$_8$: x Dy$^{3+}$ (y = 0.01, 0.03, 0.05, 0.07, 0.09) phosphors; and characteristic emission energy levels of Dy$^{3+}$.

The chromaticity coordinates of different molar (0.01-0.09mol) of Dy$^{3+}$-activated Sr$_3$B$_2$SiO$_8$ are presented in Fig. 5. From Fig. 5, we can observed that with the Dy$^{3+}$ ions added (0.01–0.09 mol), the color moved to the white region, the chromaticity coordinates of Sr$_3$B$_2$SiO$_8$: Dy$^{3+}$ are 1: (0.320, 0.356), 2: (0.342, 0.361), 3: (0.351, 0.372), 4: (0.367, 0.380) and 5: (0.392, 0.383), respectively. When the intensity of Dy$^{3+}$ reach to the maximum, it more close to the standard CIE of white light (0.330, 0.330), from the CIE chromaticity diagram of Sr$_3$B$_2$SiO$_8$: Dy$^{3+}$, it is obviously seen that we have realized white light emission in a single host phosphor excited by UV in Sr$_3$B$_2$SiO$_8$: Dy$^{3+}$ phosphors, which is promising for W-LEDs under UV excitation.

**Fig. 5.** Chromaticity coordinates of Sr$_3$B$_2$SiO$_8$: x Dy$^{3+}$: 1:(0.320,0.356); 2:(0.342,0.361); 3:(0.351,0.372); 4:(0.367,0.380); 5:(0.392,0.383)
4. Conclusion
In summary, a series of Sr₂B₂SiO₈: Dy³⁺ phosphors have been synthesized by traditional high temperature solid state reaction. The phosphors Sr₂B₂SiO₈: Dy³⁺ excited under the UV region and show white emitting light extended from 450 to 680 nm. In addition, the mechanism of energy transfer between Dy³⁺ ions is d-d interaction, according to the study results based on Dexter’s formula and Reisfeld’s approximation. The CIE coordinate of Sr₂:0.03Dy³⁺ was calculate to be (x = 0.340, y = 0.360), which close to the standard CIE of white light (0.330, 0.330). The results showed that Sr₂B₂SiO₈: Dy³⁺ phosphors may be promising phosphor candidate in UV white LEDs.

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