

The luminescence properties of $\text{Sr}_3\text{Gd}(\text{BO}_3)_3:\text{Tb}^{3+}$ phosphors under vacuum ultraviolet excitation

ZHAO WenYu^{1,2}, GAO SongWei³, AN ShengLi^{2,3*}, FAN Bin¹ & LI SongBo¹

¹ School of Chemistry and Chemical Engineering, Inner Mongolia University of Science and Technology, Baotou 014010, China;

² School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China;

³ School of Material and Metallurgical Engineering, Inner Mongolia University of Science and Technology, Baotou 014010, China

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Tb^{3+} -activated $\text{Sr}_3\text{Gd}(\text{BO}_3)_3$ green phosphors were prepared by conventional solid-state reaction. The vacuum ultraviolet (VUV) excitation, photoluminescence (PL) and decay properties of the phosphors in the visible range were investigated. The excitation spectrum showed a strong broad band from 160 to 200 nm with a maximum at 183 nm which was adjacent to the VUV excitation light source of 172 nm. Under excitation at 172 nm, the optimum co-doping concentration of Tb^{3+} was 10 mol%, and the emission intensity of $\text{Sr}_3\text{Gd}_{0.9}(\text{BO}_3)_3:0.1\text{Tb}^{3+}$ was comparable to that of commercial $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$. The strongest emission peak of $\text{Sr}_3\text{Gd}_{0.9}(\text{BO}_3)_3:0.1\text{Tb}^{3+}$ was at 543 nm with chromaticity coordinates of (0.2626, 0.4922) and a lifetime of 2.32 ms. The optical properties of the green phosphor $\text{Sr}_3\text{Gd}(\text{BO}_3)_3:\text{Tb}^{3+}$ make it suitable for use in Hg-free fluorescent lamps and plasma display panels.

phosphor, vacuum ultraviolet, optical properties, photoluminescence

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Plasma display panels (PDPs) are a promising type of flat panel display that have attracted great interest because of advantages such as fast response, large screen size, good environment durability, low energy consumption, good color purity, wide viewing angle, and good temperature stability. Phosphors play an important role in the performance of PDPs. A commercial green vacuum ultraviolet (VUV) phosphor from Asa, $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ (ZSM), has high luminous efficiency and good color purity, but a long decay time (~4–23 ms), which causes a serious lag in image transformation [1]. It is necessary to overcome this shortcoming by improving existing phosphors and/or developing new green phosphors for PDPs.

Lanthanide-doped borate phosphors are good candidates for PDPs because of their high chemical stability, low synthesis temperature, short decay time, intense luminescence and high efficiency. Examples include the red phosphor $(\text{Y,Gd})\text{BO}_3:\text{Eu}$ and green phosphors $(\text{Y,Gd})\text{BO}_3:\text{Tb}$, and $\text{GdMgB}_5\text{O}_{10}:\text{Ce}$, Tb [2]. A number of rare earth-activated

$\text{M}_3\text{Ln}(\text{BO}_3)_3$ ($\text{M}=\text{Ba}$, Sr and $\text{Ln}=\text{La-Lu}$, Y , Sc) double borate materials have been developed, such as laser host materials $\text{Sr}_3\text{Tb}(\text{BO}_3)_3$ [3] and Yb^{3+} -doped $\text{Sr}_3\text{Gd}(\text{BO}_3)_3$ [4], nonlinear optical materials $\text{Ba}_3\text{R}(\text{BO}_3)_3$ ($\text{R}=\text{Y}$, Ho-Lu) [5], magneto-optical materials $\text{Sr}_3\text{Gd}(\text{BO}_3)_3$ and $\text{Sr}_3\text{Tb}_x\text{Gd}_{1-x}(\text{BO}_3)_3$ [6]. The photoluminescence (PL) properties of Tb^{3+} -doped $\text{Ba}_3\text{Ln}(\text{BO}_3)_3$ ($\text{Ln}=\text{Lu}$ and Gd) phosphors under VUV excitation have been studied [7]. However, the VUV-excited luminescence of $\text{Sr}_3\text{Tb}_x\text{Gd}_{1-x}(\text{BO}_3)_3$ has not been reported to date. Tb^{3+} ions as luminescence centers can not only emit green light, but also have a short decay time [8–10], their materials show potential for application as phosphors in PDPs. In this paper, Tb^{3+} -activated $\text{Sr}_3\text{Gd}(\text{BO}_3)_3$ green VUV phosphors are prepared and their PL properties investigated.

1 Experimental

1.1 Synthesis of $\text{Sr}_3\text{Gd}(\text{BO}_3)_3:\text{Tb}^{3+}$

$\text{Sr}_3\text{Gd}_{1-x}(\text{BO}_3)_3: x\text{Tb}^{3+}$ ($0 \leq x \leq 1$) samples were prepared by conventional solid-state reaction. Using appropriate stoi-

*Corresponding author (email: san@imust.cn)

chiometric ratios, SrCO₃ (strontia, AR grade, Sinopharm Chemical Reagent Co. Ltd., China), H₃BO₃ (boric acid, AR grade, Sinopharm Chemical Reagent Co. Ltd.), Gd₂O₃ (gadolinia, 99.99%, Baotou Research Institute of Rare Earths, China) and/or Tb₄O₇ (terbia, 99.99%, Baotou Research Institute of Rare Earths) were thoroughly ground in an agate mortar; an 8 wt% excess of H₃BO₃ was used to compensate for its evaporation at high temperature. The mixture was heated at 800°C for 3 h in air. The mixture was reground and then reheated at 1000°C for 12 h in a reducing atmosphere (5% H₂/95% N₂) for the Tb³⁺-doped samples and Sr₃Tb(BO₃)₃ or in air for the undoped host compound. The final samples were obtained by cooling down to room temperature.

1.2 Characterization

X-ray power diffraction (XRD) patterns were recorded on a Rigaku D/max-III B diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu K α radiation ($\lambda = 0.15405$ nm) operating at 35 kV and 60 mA. VUV PL spectra were measured at the VUV spectroscopy experimental station on beam line U24 of the National Synchrotron Radiation Laboratory (Hefei, China). The electron energy of the storage ring and beam current was 800 MeV and about 150–250 mA, respectively. A Seya-Namioka monochromator (1200 g mm⁻¹, 100–400 nm) was used for the photons produced by synchrotron radiation excitation, an Acton-275 monochromator (1200 g mm⁻¹, 330–700 nm) was used for the emitted photons, and the signal was detected by a Hamamatsu H5920-01 photomultiplier. The resolution of the instruments was about 0.2 nm. The working pressure was maintained at about 1×10^{-3} Pa. The relative VUV excitation intensities of the samples were corrected by dividing the measured excitation intensities of the samples by the excitation intensities of sodium salicylate (*o*-C₆H₄OHCOONa) under the same excitation conditions. The luminescence decay curve was recorded with an Edinburgh FLS 920 combined fluorescence lifetime and steady-state spectrometer. The sample was excited by an nF900 nanosecond flash lamp with a pulse width of 1 ns and pulse repetition rate of 40–100 kHz. All measurements were recorded at room temperature.

2 Results and discussion

XRD patterns of Sr₃Gd(BO₃)₃, Sr₃Gd_{0.9}(BO₃)₃:0.1Tb³⁺ and Sr₃Tb(BO₃)₃ powder [3] are compared in Figure 1. The XRD patterns of the samples prepared in this work were consistent with that of Sr₃Tb(BO₃)₃, indicating that they are a single pure phase. The doped Tb³⁺ ions prefer to occupy the Gd³⁺ sites in the crystal structure of Sr₃Gd(BO₃)₃: Tb³⁺ because Tb³⁺ and Gd³⁺ ions possess similar ionic radii and the same valence [11]. Sr₃Gd(BO₃)₃ and Sr₃Tb(BO₃)₃ form

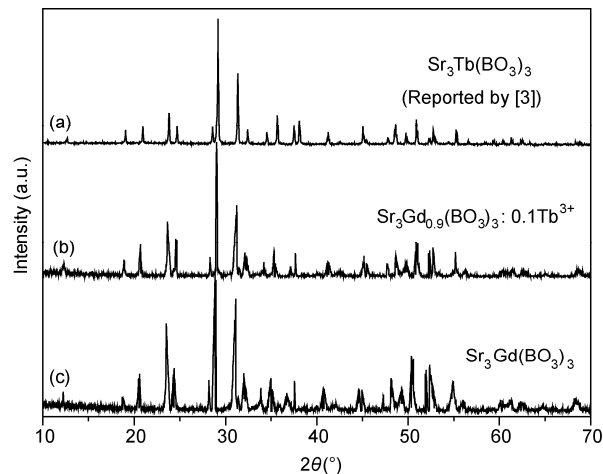


Figure 1 XRD patterns of Sr₃Gd(BO₃)₃, Sr₃Gd_{0.9}(BO₃)₃:0.1Tb³⁺ and Sr₃Tb(BO₃)₃ [3].

a complete solid solution because of their similar crystal structure. The diffraction peaks show shift to slightly higher angle when Gd³⁺ ions are substituted with Tb³⁺ ions because the radius of Gd³⁺ is a little larger than that of Tb³⁺. The relative intensity of the diffraction peaks varies slightly as the doping concentration of Tb³⁺ ions increases, which may be related to the preferential growth of microcrystal particles.

The change in luminescence intensity at 543 nm with the doping concentration x of Sr₃Gd_{1-x}(BO₃)₃:xTb³⁺ ($0 \leq x \leq 0.2$) is presented in Figure 2 ($\lambda_{\text{ex}} = 172$ nm). The luminescence intensity increases as x increases until it reaches a maximum at 10 mol%. As x continues to increase, the luminescence intensity begins to decrease. In general, a low dopant concentration results in weak luminescence, while a high dopant concentration causes luminescence quenching. For Tb³⁺, when x exceeds a critical value, the ⁵D₄→⁷F_J transitions of Tb³⁺ are quenched by non-radiative energy transfer between Tb³⁺ ions and cross-relaxation between the ⁵D₃→

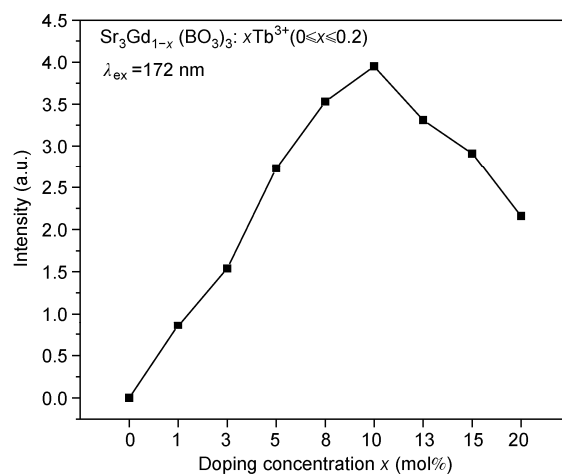


Figure 2 Change in luminescence intensity at 543 nm with doping concentration x ($\lambda_{\text{ex}} = 172$ nm).

5D_4 and $^7F_0 \rightarrow ^7F_6$ transitions [10]. These results show that the optimum co-doping concentration of Tb^{3+} for these systems is 10 mol%.

Excitation spectra measured for $Sr_3Gd_{0.9}(BO_3)_3:0.1Tb^{3+}$, $Sr_3Tb(BO_3)_3$ and $Sr_3Gd(BO_3)_3$ are depicted in Figure 3. For $Sr_3Gd_{0.9}(BO_3)_3:0.1Tb^{3+}$, the sharp peaks at about 273 and 312 nm are attributed to the $^8S_{7/2} \rightarrow ^6I_1$ and $^8S_{7/2} \rightarrow ^6P_1$ transitions of Gd^{3+} ions, respectively. This indicates that energy transfer occurs from Gd^{3+} to Tb^{3+} in $Sr_3Gd_{0.9}(BO_3)_3:0.1Tb^{3+}$. By comparison with the spectra for $Sr_3Tb(BO_3)_3$ and $Sr_3Gd(BO_3)_3$, the two broad bands located at 232 and 183 nm can be assigned to the $f-d$ transition of Tb^{3+} ions and a host-related absorption, respectively [7]. In addition, the $f-f$ transition of Tb^{3+} and Gd^{3+} ions may also appear in the region of 130–280 nm [12].

When an electron is promoted from the $4f^8$ ground state to the $4f^75d^1$ excited level within Tb^{3+} ions, it can give rise to two groups of $4f-5d$ transitions: spin-allowed (SA) transitions that are stronger and appear at higher energy, and spin-forbidden (SF) transitions that are weaker and appear at lower energy [13]. In the spectrum for $Sr_3Gd(BO_3)_3$, the broad excitation bands located at 232 and 273 nm are from the SA and SF transitions of Tb^{3+} ions, respectively. Therefore, for $Sr_3Gd(BO_3)_3:Tb^{3+}$, the transition from the $^8S_{7/2}$ energy level to the 6I_1 levels of Gd^{3+} with a maximum at about 273 nm overlaps with the $4f-5d$ transition of Tb^{3+} . This provides further evidence for efficient energy transfer from Gd^{3+} to Tb^{3+} in $Sr_3Gd(BO_3)_3:Tb^{3+}$.

Emission spectra obtained for $Sr_3Gd(BO_3)_3:Tb^{3+}$, $Sr_3Gd(BO_3)_3$, $Sr_3Gd(BO_3)_3:Y^{3+}$ and commercial phosphor ZSM upon excitation at 172 nm are compared in Figure 4. For $Sr_3Gd(BO_3)_3:Tb^{3+}$, the emission peaks at 380–460 nm and 480–650 nm are assigned to the $^5D_3 \rightarrow ^7F_J$ and $^5D_4 \rightarrow ^7F_J$ transitions of Tb^{3+} , respectively. The main emission peak at 543 nm corresponds to the $^5D_4 \rightarrow ^7F_5$ transition of Tb^{3+} . On the basis of this data and that in [14], the Commission Internationale de l'Eclairage (CIE) chromaticity coordinates for the emission from $Sr_3Gd(BO_3)_3:Tb^{3+}$ are $x = 0.2626$ and

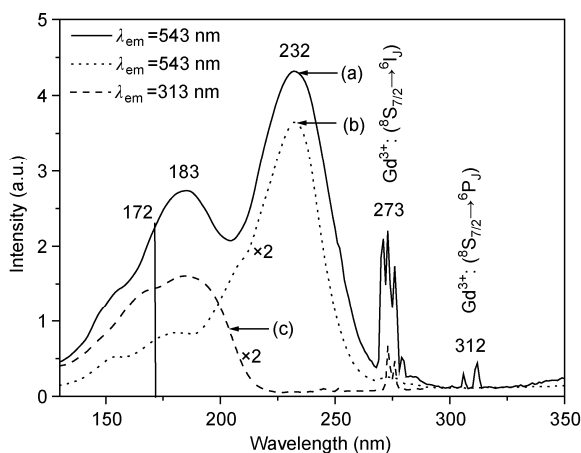


Figure 3 Excitation spectra obtained for $Sr_3Gd_{0.9}(BO_3)_3:0.1Tb^{3+}$ (a), $Sr_3Tb(BO_3)_3$ (b) and $Sr_3Gd(BO_3)_3$ (c).

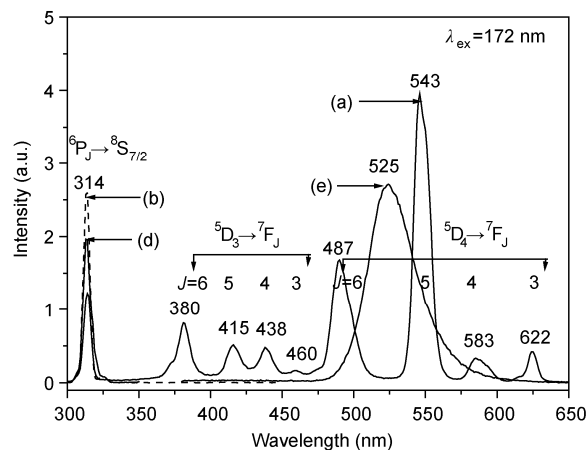


Figure 4 Emission spectra determined for $Sr_3Gd_{0.9}(BO_3)_3:0.1Tb^{3+}$ (a), $Sr_3Gd(BO_3)_3$ (b), $Sr_3Gd_{0.9}(BO_3)_3:0.1Y^{3+}$ (d) and ZSM (e).

$y = 0.4922$, indicating it is green phosphor. According to the approximate formula ($T = -437n^3 + 3601n^2 - 6861n + 5514.31$, $n = (x - 0.3320)/(y - 0.1858)$) [15,16], the relative color temperature of $Sr_3Gd_{0.9}(BO_3)_3:0.1Tb^{3+}$ is 7258.1550 K. In addition, as is shown in Figure 4, the luminescent intensity of Gd^{3+} at 314 nm weakens when substituted by non-luminous Y^{3+} . In contrast, when Gd^{3+} is replaced by Tb^{3+} at the same concentration, the luminescent intensity at 314 nm decreases greatly. This indicates that part of the energy is transferred to Tb^{3+} . Thus, compared with the spectrum for $Sr_3Gd(BO_3)_3$, the decrease of emission at 314 nm for $Sr_3Gd_{0.9}(BO_3)_3:0.1Tb^{3+}$ is generated not only from energy transfer from Gd^{3+} to Tb^{3+} , but also from the decrease in the concentration of Gd^{3+} . Comparing the spectra for $Sr_3Gd_{0.9}(BO_3)_3:0.1Tb^{3+}$ and ZSM, the emission intensity of $Sr_3Gd_{0.9}(BO_3)_3:0.1Tb^{3+}$ at 543 nm is about 145% that of ZSM at 525 nm upon excitation at 172 nm. The light intensity for the range 380–650 nm of $Sr_3Gd_{0.9}(BO_3)_3:0.1Tb^{3+}$ is about 98% that of ZSM. For PL, the radiant efficiency (η) is defined as the ratio of emitted luminescent power and the power absorption of the material from the exciting radiation [17]. The luminous efficiency (L) is defined as the ratio of the luminous flux $\Phi(\nu)$ emitted by the material and the absorbed power [17]. In general, $\Phi(\nu)$ is given by the folding or weighting of the spectral power distribution $\Phi(\lambda)$ with the normalized photopic response curve $V(\lambda)$ and the constant factor K_m [18]. $\Phi(\lambda)$ is directly proportional to the intensity of PL emission. Therefore, η and L can be also determined roughly from the PL emission peak areas and the weighting of PL emission intensity with the normalized photopic response curve $V(\lambda)$, respectively. According to the experimental data, the emission peak area of the $Sr_3Gd_{0.9}(BO_3)_3:0.1Tb^{3+}$ phosphor is similar to that of ZSM. The weighting of the PL emission intensity with $V(\lambda)$ of $Sr_3Gd_{0.9}(BO_3)_3:0.1Tb^{3+}$ is higher than that of ZSM. Therefore, η of $Sr_3Gd_{0.9}(BO_3)_3:0.1Tb^{3+}$ might be similar to that of ZSM, and L of $Sr_3Gd_{0.9}(BO_3)_3:0.1Tb^{3+}$ might be higher than that of ZSM.

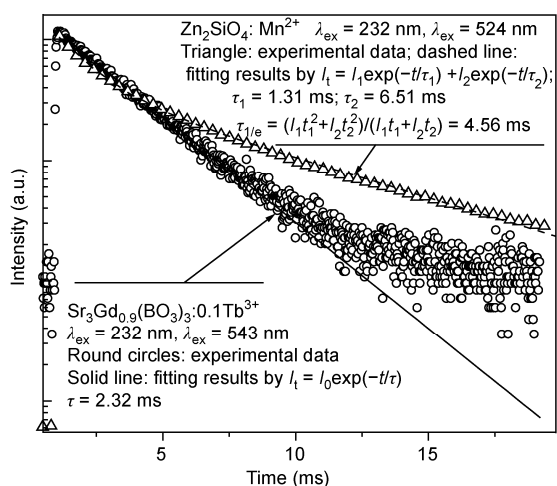


Figure 5 PL decay curves determined for $\text{Sr}_3\text{Gd}_{0.9}(\text{BO}_3)_3:0.1\text{Tb}^{3+}$ and commercial phosphor ZSM ($\lambda_{\text{ex}}=232$ nm).

PL decay curves measured for $\text{Sr}_3\text{Gd}_{0.9}(\text{BO}_3)_3:0.1\text{Tb}^{3+}$ and commercial phosphor ZSM upon excitation at 232 nm are presented in Figure 5. The decay curve for $\text{Sr}_3\text{Gd}_{0.9}(\text{BO}_3)_3:0.1\text{Tb}^{3+}$ can be fitted to the single exponential equation $I = I_0 \exp(-t/\tau)$, in which I_0 is the initial intensity at $t = 0$ and τ is the decay lifetime. Using this equation, the excited state lifetime for $\text{Sr}_3\text{Gd}_{0.9}(\text{BO}_3)_3:0.1\text{Tb}^{3+}$ was determined to be 2.32 ms (the time to decay $1/e$ of the original intensity). According to [20], $\tau_{1/e}$ of commercial phosphor ZSM is 4.56 ms, so $\text{Sr}_3\text{Gd}_{0.9}(\text{BO}_3)_3:0.1\text{Tb}^{3+}$ has a shorter decay time. Although the above results were obtained following excitation at 232 nm, it is believed that the activator decay under VUV excitation will be around this value in the present case.

3 Conclusions

$\text{Sr}_3\text{Gd}(\text{BO}_3)_3:\text{Tb}^{3+}$ phosphors were prepared by solid-state reaction. XRD revealed that Tb^{3+} ions act as luminescent centers, inhabiting the sites of Gd^{3+} ions. Upon excitation at 172 nm, the emission intensity of $\text{Sr}_3\text{Gd}_{0.9}(\text{BO}_3)_3:0.1\text{Tb}^{3+}$ is the strongest of the investigated dopant concentrations. A strong excitation band located at 183 nm is caused by host-related absorption. For $\text{Sr}_3\text{Gd}(\text{BO}_3)_3:\text{Tb}^{3+}$, SA and SF $f-d$ transitions were located at 232 and 273 nm, respectively. The excitation peaks at about 273 and 312 nm were attributed to $^8\text{S}_{7/2} \rightarrow ^6\text{I}_1$ and $^8\text{S}_{7/2} \rightarrow ^6\text{P}_1$ transitions of Gd^{3+} ions, respectively. Energy transfer from Gd^{3+} to Tb^{3+} was observed. The emission intensity of $\text{Sr}_3\text{Gd}_{0.9}(\text{BO}_3)_3:0.1\text{Tb}^{3+}$ at 543 nm was about 145% that of commercial phosphor ZSM

at 525 nm. The light intensity for the range 380–650 nm of $\text{Sr}_3\text{Gd}_{0.9}(\text{BO}_3)_3:0.1\text{Tb}^{3+}$ was similar to that of ZSM upon excitation at 172 nm. The lifetime of $\text{Sr}_3\text{Gd}(\text{BO}_3)_3:\text{Tb}^{3+}$ was 2.32 ms, so it is considered promising as a green phosphor for use in PDPs, Hg-free lamps or LCD backlights.

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