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Spectral Characteristics of $LiSrBO_3$: Sm^{3+} Phosphor for White LED*

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Abstract: A novel red phosphor, $LiSrBO_3$: Sm^{3+}, is synthesized by solid state reaction method, and the spectral characteristics are investigated. The emission and excitation spectra indicate that $LiSrBO_3$: Sm^{3+} phosphor can be effectively excited by near ultraviolet (UV) (404 nm), and exhibits a satisfactory red performance (599 nm), nicely fitting in with the widely applied UV chips. The effect of Sm^{3+} concentration on the emission intensity is studied, and the results show that the intensities reach the peak value at 3 mol% Sm^{3+}. With doping Na^+ or K^+, the intensities are enhanced.

Key words: White LED; $LiSrBO_3$: Sm^{3+}; Spectral characteristics
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0 Introduction

Recently, remarkable progress can be observed in the development of white light emitting diodes (LEDs) using GaN as well as InGaN chip[1-2]. For example, a white LED device has been commendably realized using YAG: Ce as a broad band yellow phosphor coated on the blue LED chip[3]. However, there exist at least two drawbacks in this combination. Firstly, the overall efficiency decreases rapidly when lowering the correlated color temperature of the device. Secondly, a concern with this device is that the "white" output light has an undesirable color balance for a true color rendition; *viz.*, the output light is deficient in the region of the visible light (above 600 nm). Hence, a separate red light source may be used to compensate for the red deficiency of the output light[4-5]. Another promising possibility is the fabrication of white LEDs by employing red, green and blue emitting phosphors that are excited by UV or near UV LED chip. Presently, the red phosphors focus on the Eu^{3+} ion activating phosphor[6-7]. These phosphors can be effectively excited by the 4f-4f excitation wavelength of Eu^{3+} at 395 nm. However, at that wavelength the emission efficiency of GaN LED is not very high[8]. For example, at forward current I_f = 350 mA, θ_a = 25 ℃, the electro-optical characteristics show that the emission efficiency, at 400 nm, is fourfold that at 395 nm. Accordingly, the phosphors that can be effectively excited by 400 nm or >400 nm GaN LED chip have become the focus of research. Recently, our research results show that Sm^{3+} ion activating the alkali and alkaline-earth metals borate exhibit a satisfactory performance[9]. Therefore, in this work, $LiSrBO_3$: Sm^{3+} phosphor was synthesized, and the spectral characteristics were investigated. The all results are useful for the development of LEDs.

1 Experiment

$LiSrBO_3$: Sm^{3+} phosphors are synthesized by solid-state reaction. $SrCO_3$, H_3BO_3, Li_2CO_3, Na_2CO_3, K_2CO_3 and Sm_2O_3 (99.99% in mass) are used for the starting materials. After the individual materials are mixed in the requisite proportions sufficiently, the powders are calcined at 700 ℃ for 2 h, then $LiSrBO_3$: Sm^{3+} phosphors are obtained. The structure is checked with a powder *x*-ray diffractometer (XRD, D/max - rA, CuK_α, 40 kV, 100 mA, λ = 0.154 06 nm). The spectral characteristics are measured by a RF-540 fluorescence spectrophotometer. All the characteristics of the phosphors are investigated at room temperature.

2 Results and discussion

2.1 Structure of $LiSrBO_3$: Sm^{3+} phosphor

Fig. 1 shows the XRD pattern of $LiSrBO_3$: Sm^{3+} phosphor, and all patterns agree well with

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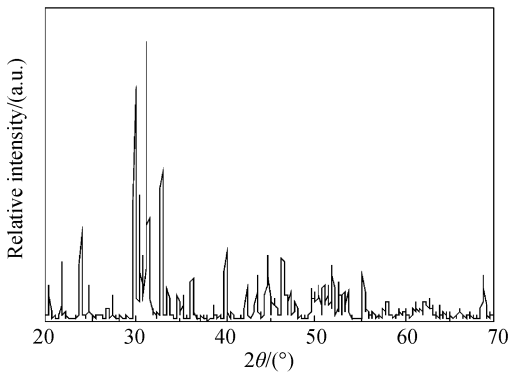

Fig. 1 XRD pattern of $LiSrBO_3$: Sm^{3+} phosphor

Ref. [10]. Hence, doping 1 mol% Sm^{3+} does not make any variation of XRD pattern. $LiSrBO_3$ has a monoclinic structure with $P2_1/n$ space group, and itslattice parameter is $a=0.647\ 6$ nm, $b=0.668\ 4$ nm, $c=0.684\ 3$ nm.

2.2 Emission and excitation spectra of $LiSrBO_3$: Sm^{3+} phosphor

Fig. 2 shows the emission and excitation spectra of $LiSrBO_3$: Sm^{3+} phosphor with 1 mol% Sm^{3+}. The emission spectrum exhibits three emission bands at 563, 599 and 647 nm, which correspond to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$ and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ typical transitions of Sm^{3+}, respectively. The strongest one appears at 599 nm. The three typical emission peaks are split in different ways. The energy level transition $^4G_{5/2} \rightarrow {}^6H_{5/2}$ is split into 563 and 569 nm emission peaks; $^4G_{5/2} \rightarrow {}^6H_{7/2}$ is split into 599, 606 and 610 nm emission peaks, and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ is split into 647 and 651 nm emission peaks. These splits were resulted in the crystal field effects, and their extents are related to the structure characteristic of $LiSrBO_3$ crystal field[11].

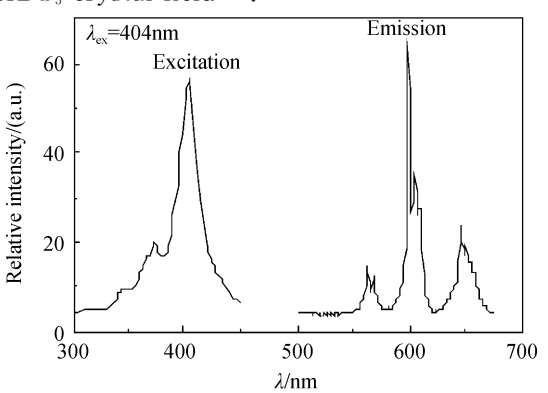

Fig. 2 Emission and excitation spectra of $LiSrBO_3$: Sm^{3+} phosphor

Monitored at 599 nm, the excitation spectrum has several bands at 346, 373 and 404 nm, corresponding to the characteristic f-f transitions of Sm^{3+}, respectively. The strongest one is at 404 nm, which is attributed to the $^6H_{5/2} \rightarrow {}^4L_{13/2}$ transition of Sm^{3+}. The spectral characteristics indicate that this phosphor can be excited effectively by UV LED, and emit red light, and the CIE chromaticity is ($x=0.635$, $y=0.357$), moreover, the main excitation peak (404 nm) is higher than 400 nm. Therefore, $LiSrBO_3$: Sm^{3+} phosphor is a promising red phosphor for white LED.

2.3 Effect of Sm^{3+} concentration on emission intensity of $LiSrBO_3$: Sm^{3+} phosphor

The emission intensity of $LiSrBO_3$: Sm^{3+} phosphor with different Sm^{3+} concentration is shown in Fig. 3. And the Sm^{3+} concentration is from 1 mol% to 6 mol%. Fig. 3 shows that the intensities initially increase with increasing Sm^{3+} concentration, and reach a maximum at 3 mol% Sm^{3+}. A decrease in the intensity is observed as the Sm^{3+} concentration increases, and this shows the occurrence of energy migration between Sm^{3+} in different sites in the lattice, resulting in concentration quenching. A nonradiative energy transfer from one Sm^{3+} to another Sm^{3+} takes place. According to Ref. [11], the probability of energy transfer among Sm^{3+} ions increases when the Sm^{3+} concentration increases. Nonradiative energy transfer from one Sm^{3+} to another Sm^{3+} usually may occur by exchange interaction, radiation reabsorption or mutipole-multipole interaction. In the case of the Sm^{3+} ion, the exchange interaction is responsible for energy transfer for forbidden transitions with a typical critical distance, which is about 0.5 nm[11].

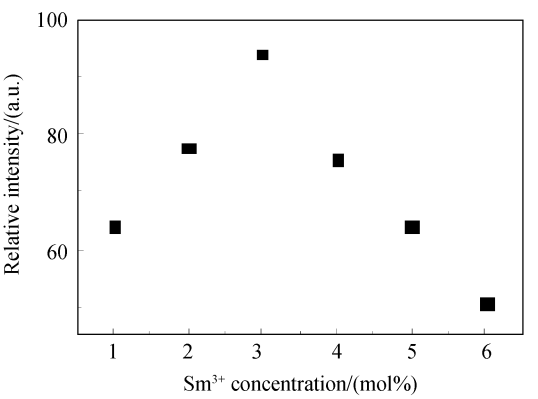

Fig. 3 Emission intensity of $LiSrBO_3$: Sm^{3+} phosphor as function of Sm^{3+} concentration

We can estimate roughly of the critical distance of energy transfer (R_c), the distance at which the probability of transfer is equal to the probability of radiative emission, can be made using the relation by Blasse to calculate R_c between activator ions of the kind doped in a host lattice

$R_c \approx 2(\frac{3V}{4\pi x_c N})^{1/3}$, Where V is the volume of the unit cell, x_c is the critical concentration of the activator ion, andNis the number of host cations in the unit cell[12]. The lattice parameter of $LiSrBO_3$: Sm^{3+} is $a=0.647\ 6$ nm, $b=0.668\ 4$ nm, $c=0.684\ 3$ nm,so the unit cell volume of $LiSrBO_3$ is $0.296\ 2$ nm^3. Since the emission spectra of $LiSrBO_3$: Sm^{3+} [$x=0.01-0.06$] show maximum intensity for $x=0.03$, this value is used as the critical concentration x_c. The number of formula units per unit cell in $LiSrBO_3$ is 3. Using these values, the obtained R_c value is ≈ 1.85 nm. Therefore, the energy transfer in the present case will occur only by electric multipolar in interaction.

Dexter proposed that the interaction type between sensitizers or between sensitizer and activator can be determined by $\lg(I/x)=c-(\theta/3)\lg x$[13]. Among the concentration quenching mechanism caused by the electric multipole interaction, the dipole-dipole (d-d), dipole-quadripole (d-q) and quadripole-quadripole (q-q) interactions correspond to $\theta=6$, 8 and 10, respectively. Iis the emission intensity of the phosphor, and x is the activator concentration. According to this method, the emission intensities of $LiSrBO_3$: Sm^{3+} phosphors are measured with Sm^{3+} concentrations of 3, 4, 5 and 6 mol%, and the concentration dependence curves ($\lg(I/x)\sim\lg x$) are shown in Fig. 4. According to the linear slope, $\theta=5.64\approx 6$. Hence, the concentration quenching mechanism of Sm^{3+} in $LiSrBO_3$ is the d-d interaction.

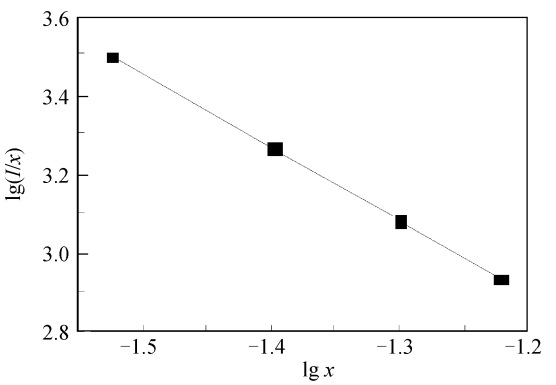

Fig. 4　Relation between the $\lg(I/x)$ and $\lg x$ of Sm^{3+}

2.4　Effect of Na^+ or K^+ on emission spectrum of $LiSrBO_3$: Sm^{3+} phosphor

When a trivalent metallic ion, such as Sm^{3+}, is incorporated into a host lattice and substitutes for a divalent metallic ion, the charge balancing is necessarily required. For $LiSrBO_3$: Sm^{3+}, Sr^{2+} is substituted by Sm^{3+}, and should produce positive univalent charge surplus; when Sr^{2+} is substituted by Na^+, or K^+, and should produce negative charge univalent surplus, the whole presents electricity neutrality due to the attraction of particles with opposite charges. Consequently, we introduce Na^+, or K^+ to full with $LiSrBO_3$: Sm^{3+}, and investigated its effect on the emission intensity of $LiSrBO_3$: Sm^{3+} phosphor. Na^+ or K^+ concentration are all from 1 mol% to 6 mol%, and the Sm^{3+} concentration is 3 mol% in this research. Under the condition of doping Na^+, the influence of Na^+ concentrations on the emission spectrum of $LiNaSrBO_3$: Sm^{3+} phosphor is studied, and the result is shown in Fig. 5. The results show that the emission intensity increases with increasing Na^+ concentration, then decreases, and reaches the maximum value at 4 mol% Na^+.

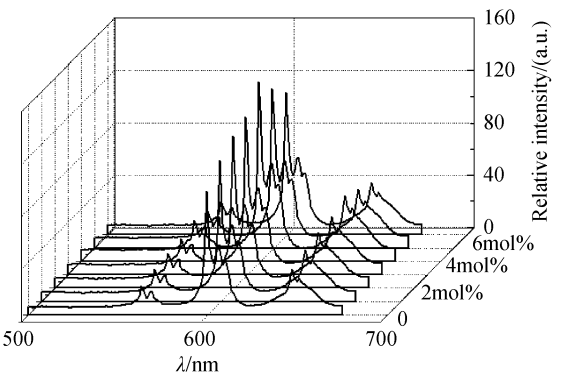

Fig. 5　Emission spectra of $LiNaSrBo_3$: Sm^{3+} phosphor as function of Na^+ concentration

Under the condition that K^+ is introduced, the emission intensity of $LiKSrBO_3$: Sm^{3+} is enhanced, too. However, the maximal emission intensity corresponding to the charge compensator concentration is different, and the concentration is 3 mol%. Fig. 6 exhibits the maximum with doping Na^+ and K^+, respectively. The results show that

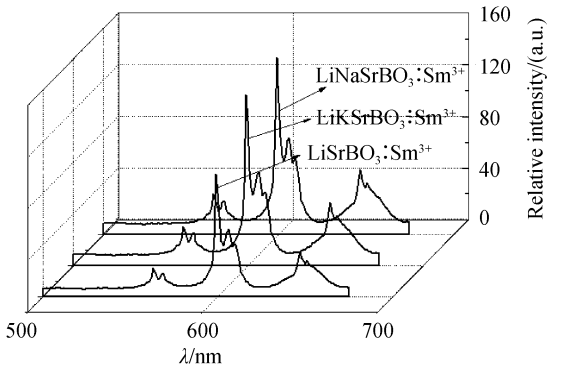

Fig. 6　Effect of Na^+ and K^+ on emission spectra of $LiSrBO_3$: Sm^{3+} phosphor

the maximum of doping Na^+ is higher than that of K^+, the results agree well with the Ref. [14].

The above results can be explained by the following reason. The aberration is brought in the crystal lattice when the charge compensator is incorporated into the host lattice, which induces the probability of transition emission. So the emission intensity of $LiSrBO_3 : Sm^{3+}$ phosphor is enhanced. However, the emission intensity does not increase all along with the increasing charge compensator, which means that only portion charge compensator is incorporated into the host lattice, when the doping concentration is higher than the Sm^{3+} concentration, the excrescent negative charge will engender and lead to the emission intensity decrease[15].

The difference of ionic radius can explain that the charge compensator concentration corresponding to the maximal emission intensity is different with different charges. The radius of Sr^{2+} in the host lattice is 0.118 nm, and the radii of Na^+ and K^+ are 0.116 and 0.133 nm, respectively. Compared Na^+ to K^+, the smaller ion is easy incorporated into the host lattice, so the doping concentration is higher than K^+, and is 4 mol%.

3 Conclusions

In summary, $LiSrBO_3 : Sm^{3+}$ phosphor is synthesized by solid state reaction method. The emission and excitation spectra of $LiSrBO_3 : Sm^{3+}$ phosphor exhibit that this phosphor can be efficiently excited by UV chip, and emit red light, the CIE chromaticity is ($x = 0.635$, $y = 0.357$). The concentration quenching mechanism of Sm^{3+} in $LiSrBO_3$ is the d-d interaction. The emission intensity of $LiSrBO_3 : Sm^{3+}$ phosphor was enhanced by doping Na^+ or K^+. The results illuminate that $LiSrBO_3 : Sm^{3+}$ phosphor is a promising red phosphor for white LEDs.

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白光 LED 用 $LiSrBO_3:Sm^{3+}$ 材料的光谱特性

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摘　要:采用固相法制备了一种新型的白光 LED 用 $LiSrBO_3:Sm^{3+}$ 红色发光材料,并研究了材料的光谱特性.材料的激发与发射光谱显示其能够被 404 nm 近紫外光激发,发射 599 nm 红光,很好的符合近紫外光激发下白光 LED 的需要.研究了 Sm^{3+} 浓度对材料发射强度的影响,发现 Sm^{3+} 浓度为 3 mol% 时,强度最大.添加 Na^+ 或 K^+ 也可提高 $LiSrBO_3:Sm^{3+}$ 材料的发射强度.

关键词:白光发光二极管;$LiSrBO_3:Sm^{3+}$;光谱特性

WANG Zhi-jun　was born in 1979. She is currently an instructor, and her research interests focus on plasma and luminescent phosphor.