

Methods to improve the fluorescence intensity of CaS:Eu²⁺ red-emitting phosphor for white LED

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Abstract

In order to improve the fluorescence intensity of red-emitting phosphor based on alkaline earth sulfide CaS:Eu²⁺ for white LED (light-emitting diode), many methods were used. When the flux is NH₄F, auxiliary activator is Er³⁺, intensity of phosphor CaS:Eu²⁺ has the strongest brightness. On the other hand, introduction of Sr could make the maximum excitation band shift to high energy, which make the phosphor match well with blue light GaN-based LED; Mg partly substitute for the alkaline earth Ca could make the intensity of red emitting phosphor increase greatly. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

White light-emitting diodes (LEDs), the so-called next generation solid-state lighting, have many advantages over the existing incandescent and halogen lamps in reliability, energy saving, maintenance and safety, and therefore are gaining lots of attentions. As the methods available for creating white light LED, the phosphor-converted (pc) emission method is the most common. For the way of phosphor conversion, a blue light GaN (gallium nitride) LED chip loaded with a yellow phosphor YAG ((Y_{1-a}Gd_a)₃(Al_{1-b}Ga_b)₅O₁₂:Ce³⁺) to obtain white light, which is now widely used as a conventional white LED. The phosphor YAG:Ce emits yellow light when excited by blue light; consequently, the yellow light could combined with the blue LED (~470 nm) to produce white light (as the eye sees it). However, because the yellow light emitting from the phosphor YAG:Ce lacks sufficient red emission, this white light has a low color rendering index Ra (CRI), in the 60–70 range. As may be expected, red enhanced YAG:Ce or combine a small amount of red phosphor with YAG:Ce could improve the CRI to the acceptable range (Ra > 80) and increased the light conversion [1–9].

As a promising white light generation way, many attentions have been paid to three primary color white LED. A blue LED is precoated with a green phosphor and a red phosphor, and the phosphors emit the green and red light when excited by the blue light from the blue GaN-based LED, respectively. Not all the blue light is absorbed by the phosphors, the rest blue light is mixed with the green and red emissions as a three-band white light. Three-band white LED maintains a very high color-rendering index (Ra > 90) [10]. However, the red light emitting phosphor for white LED is commercially still limited to divalent Eu ion activated alkaline earth binary sulfides. The conventional alkaline earth sulfides are known to be excellent and versatile phosphor materials. As members of alkaline earth sulfide families, especially Eu²⁺ doped SrS and CaS was considered to be the most promising candidates for red phosphor. However, the binary sulfide-based phosphors have low chemical stabilities and low luminescence. It is necessary to improve the stability and enhance luminance of sulfides. Our previous works have been carried out to improve the stability of binary sulfides-based phosphors by encapsued a layer of thin coating on their surfaces, and the coated sulfides-based phosphors show a good chemical stability [11,12].

The purpose of this work is to develop some methods to improve the luminance of red-emitting phosphor. Divalent europium (Eu²⁺) activated alkaline earth sulfides-based phosphor with high brightness have been prepared by the solid-state

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reaction technique at high temperature and reductive atmosphere. Effects from partial substitution of Ca by other alkaline earth elements Sr or Mg, fluxes and co-activators on the intensity of red phosphor were investigated.

2. Experimental

2.1. Sample preparation

Red-emitting phosphor samples were prepared by the solid-state reaction technique at high temperature and CO reductive atmosphere. Raw materials include CaCO_3 , SrCO_3 , $(\text{MgCO}_3)_4$, $\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, NH_4X ($\text{X} = \text{Cl}/\text{F}$), sulfur, $\text{Eu}(\text{NO}_3)_3$ and $\text{RE}(\text{NO}_3)_3$ (0.01 mol L^{-1}) solution, and all starting materials were analytical grade. For the molar doping concentration of dopant and codopant was focused on 1.0%. The mole rate of alkaline earth ions and sulfur was from 1:2 to 1:3. The starting compositions were intimately mixed in evaporator, dried at 60°C for several hours, then mixed again by an agate mortar and pestle. The mixture was placed in a small covered aluminum crucible, and this small crucible was put in a large aluminum crucible. The space between the two crucibles was filled with carbon, to reduce the Eu^{3+} into Eu^{2+} , and to avoid oxidation of the products and reactants in the heating process. The large crucible with its contents was placed in a muff furnace under ordinary atmospheres, and heated to 900°C for 2–3 h. It was then cooled to room temperature and crushed the products to fine powder.

2.2. Sample characterization

The XRD patterns of the phosphor samples were obtained using a D/max-III A (Rigaku, Japan) diffract-meter with $\text{Cu K}\alpha$ ($\lambda = 1.54065 \text{ \AA}$) radiation at 35 kV and 25 mA. Photoluminescent excitation and emission measurements were carried out using a hitachi model F-4500 fluorescence spectrophotometer at room temperature. All samples were tested three times to reduce the error. The TL emission spectra were measured using a linear heater and optical multi-channel analyzer with a temperature control system, and powder samples were irradiated by 1000LX D_{65} standard lamp for 5 min.

3. Results and discussion

3.1. Effect of different fluxes on the intensity of sulfide-based phosphor

Flux is usually added to the raw material mixture to help crystal growth. For the preparation of alkaline earth binary sulfide phosphors, typical fluxes are alkaline carbonate Li_2CO_3 , Na_2CO_3 and NH_4Cl . Fig. 1a–d shows the relative fluorescence intensity of $\text{CaS}:\text{Eu}^{2+}$, Er^{3+} with Na_2CO_3 , Li_2CO_3 , NH_4Cl and NH_4F as flux, respectively. Flux was about 2–5% of raw materials by weight. The relatively fluorescence intensity of sample containing Na_2CO_3 flux is lower than that of sample with Li_2CO_3 as flux, which indicates that lithium compounds are particularly effective in promoting crystal growth and dif-

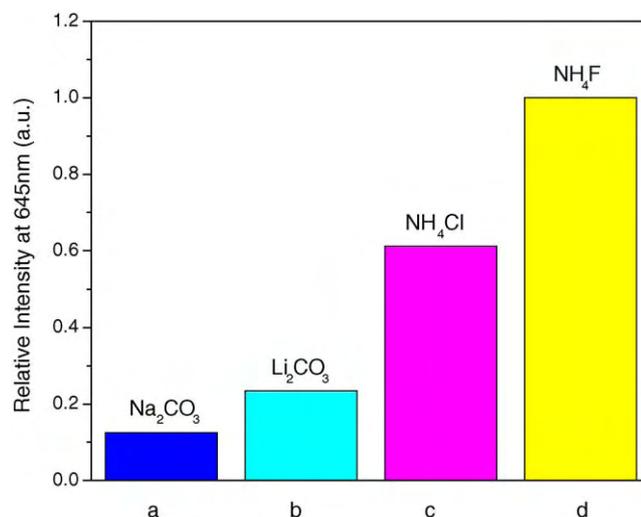


Fig. 1. Effect of different flux on the relative fluorescence intensity at 645 nm in $\text{CaS}:\text{Eu}^{2+}$, Er^{3+} samples: (a) containing Na_2CO_3 , (b) containing Li_2CO_3 , (c) containing NH_4Cl and (d) containing NH_4F .

fusion of activator ions into the sulfides lattice. This probably because Li^+ , which has a small ionic radius ($R_{\text{Li}} = 0.06 \text{ nm}$, $R_{\text{Na}} = 0.095 \text{ nm}$, $R_{\text{K}^+} = 0.133 \text{ nm}$) [13], enters interstitial sites and generate cation vacancies; ionic diffusion is accelerated through these means [14]. Alkali carbonate fluxes that promote crystal growth and ion diffusion effects remarkably, but they also have a side effect to degrade luminescence efficiency, because the constituent ions of the fluxes are likely remain in the phosphor lattice as impurities. So the products have to be washed by cold deionized water to remove the rest fluxes, which would lead to the PL intensity decreasing of phosphor and the loss of the yield. However, the products need not be washed, as the flux is NH_4Cl . So the relative intensity of sample prepared with NH_4Cl as flux is higher than those of samples with alkali carbonate fluxes.

As the phosphor $\text{CaS}:\text{Eu}^{2+}$, Er^{3+} using NH_4F as flux, its relative intensity is the highest. It was observed that the particle size grows and the stability enhances due to the addition of NH_4F , which have been intensively investigated in our previous work [15], and this results also have been reported by Murata et al. [16] that addition of CaF_2 make the particle size of their phosphor grows and a 10% increase in fluorescence intensity. In our work, NH_4F play the same role as CaF_2 , because HF (from decomposition of NH_4F) reacts with raw materials CaCO_3 and produced CaF_2 .

3.2. Effect of auxiliary activator RE^{3+} on the fluorescence intensity of sulfide phosphor

The RE^{3+} codopants were usually used to enhance the persistent luminescence and fluorescence intensity in Eu^{2+} doped phosphor [17–19], here, our purpose is to investigate the effect of rare earth ions on the fluorescence intensity of $\text{CaS}:\text{Eu}^{2+}$ phosphor. XRD patterns of obtained CaS -based phosphor doped with various rare earth ions were used to check the phase and structural purity of samples. No changes in the XRD peaks of the

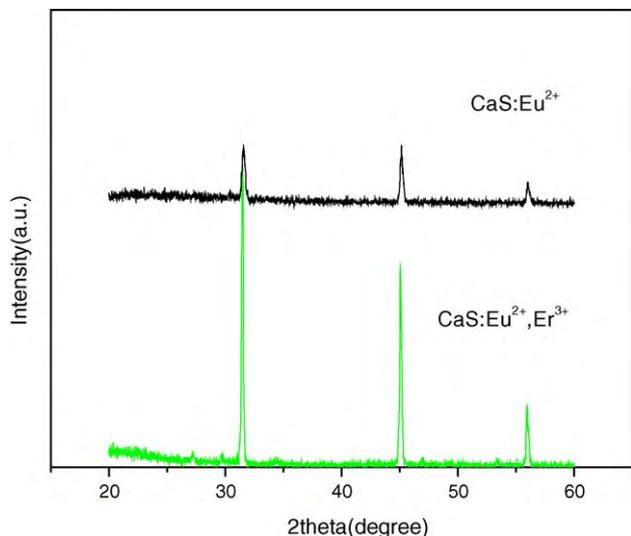


Fig. 2. X-ray diffraction curve of with and without auxiliary activator Er phosphor.

prepared CaS:Eu²⁺, RE³⁺ phosphors were observed by adding other RE³⁺ ions. For example, Fig. 2 shows the XRD patterns of CaS:Eu³⁺ and CaS:Eu²⁺, Er³⁺ phosphors, all of the peaks can be indexed to the phase of CaS (JCPDS No. 25-134), indicating that the doping ions did not form any new phases in the synthesis process.

Fig. 3 shows the relative intensity of CaS:Eu²⁺, RE³⁺ phosphor ($\lambda_{ex} = 470$ nm). To reduce the error, the relative intensity of emission spectra measurement was repeated three times. It can be seen that only introduction of rare earth ions Pr, Tb and Er could make photo-luminescent intensity of phosphor increase remarkably from Fig. 3. Among phosphors codoped with Pr, Tb and Er, the intensity of CaS:Eu²⁺, Er³⁺ phosphor is the highest. Zhang et al. [20] and Jung et al. [21] have also found this phenomenon in phosphor BAM:Eu²⁺, that the codopant Er³⁺ did improve the intensity of BAM:Eu³⁺, but the believable reason is not at all understood and detailed investigations are still lacking. Inset of Fig. 3 gives the emission spectra of CaS:Eu²⁺, CaS:Eu²⁺,

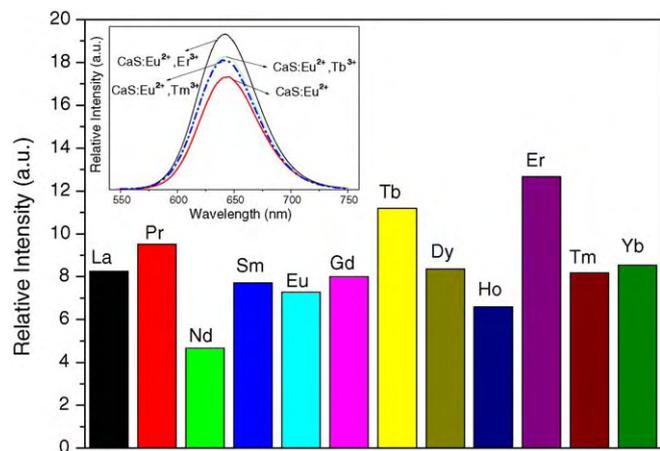


Fig. 3. Effect of codoping rare earths ions on the relative intensity at 645 nm in CaS:Eu²⁺, RE³⁺ phosphor. (Inset of the left: emission spectra of CaS:Eu²⁺, CaS:Eu²⁺, Tb³⁺; CaS:Eu²⁺, Tm³⁺; CaS:Eu²⁺, Er³⁺ and $\lambda_{ex} = 470$ nm.)

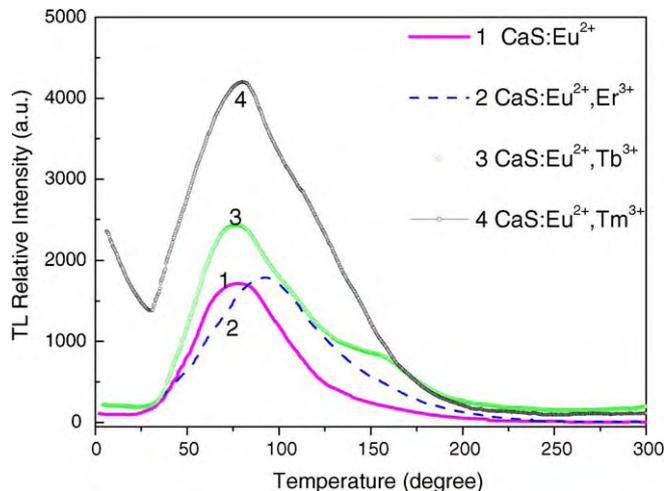


Fig. 4. Thermo-luminescence glow curves of phosphor CaS:Eu²⁺ and CaS:Eu²⁺, RE³⁺ (RE = Er, Tm, and Tb).

Tm³⁺, CaS:Eu²⁺, Tb³⁺ and CaS:Eu²⁺, Er³⁺ ($\lambda_{ex} = 470$ nm), a wide spectrum with a peak at about 645 nm, which is due to the typical 5d–4f transition emission of Eu²⁺, was observed for all samples. The doping of other rare earth ions did not shift the peak position, and special emission peaks from RE³⁺ did not present, which illustrated that the co-doped rare earth elements had little effect on the crystallographic environment of Eu²⁺ ion in the CaS host.

According to our previous research, the codoping rare earth ions RE³⁺ were used to act as traps or to modify the existing trap depths and densities, in order to get phosphor with long afterglow. However, our aim was to get red-emitting phosphor with higher luminescence intensity and shorter afterglow. We found the phosphor has a long afterglow as Pr³⁺, Sm³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Tm³⁺, Yb³⁺ were introduction, and could not see the afterglow with naked eyes as the co-dopant is La³⁺, Nd³⁺ or Er³⁺. It is well known that trapping centers play an essential role for photoenergy storage in persistent, photostimulable, and thermostimulable phosphors. And thermo-luminescence (TL) spectrum was a major technique for revealing trapping center [22]. The TL spectra of CaS:Eu²⁺, CaS:Eu²⁺, Er³⁺, CaS:Eu²⁺, Tb³⁺ and CaS:Eu²⁺, Tm³⁺ were shown in Fig. 4. At least one new TL peak appears in CaS:Eu²⁺, Tb³⁺ and CaS:Eu²⁺, Tm³⁺ phosphor, which indicated that new defects or traps were introduced. The intensity of their maximum TL glow peaks improving also shows the densities of the trapped carriers increasing [23]. Comparison with CaS:Eu²⁺, no remarkable changes were found in the TL glow spectrum of CaS:Eu²⁺, Er³⁺, therefore, the afterglow of CaS:Eu²⁺, Er³⁺ was not enhanced. As mentioned above, the luminescence intensity of red-emitting alkaline earth-based sulfide phosphor was improved but afterglow was not enhanced when Er³⁺ was introduced as auxiliary activator.

3.3. Effect of Sr or Mg substitution on the fluorescence intensity of CaS:Eu²⁺, Er³⁺

Fig. 5 illustrates the excitation and emission spectra of Ca_{1-x}Sr_xS:Eu²⁺, Er³⁺ (0 ≤ x ≤ 1, CaS and SrS are completely

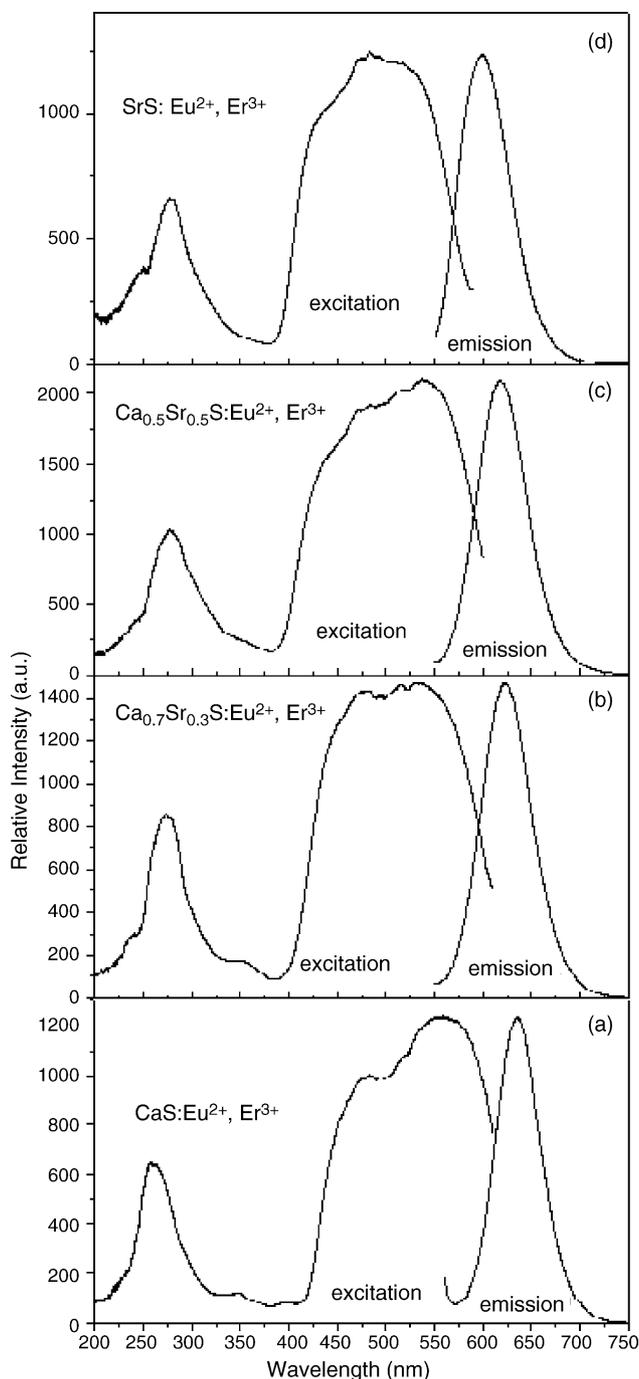


Fig. 5. The excitation and the emission ($\lambda_{ex}=470\text{ nm}$) spectra of $\text{Ca}_{1-x}\text{BSr}_x\text{BBS}:\text{Eu}^{2+}, \text{Er}^{3+}$ ($0 \leq x \leq 1$): (a) $x=0$, (b) $x=0.3$, (c) $x=0.5$ and (d) $x=1$.

miscible [24] phosphors with different Sr concentration x , respectively. The excitation spectra of the phosphors conclude two broad bands, at around 260 and 400–600 nm. These phosphors have strong absorption from 400–600 nm, which were attributed to 4f–5d transitions of Eu^{2+} . These phosphors can be well excited by blue light (460–470 nm) from GaN LED chip. Four changes have been found with the Sr concentration x from 0 to 1 in Fig. 5, as follows: (1) the excitation band at around 260 nm shift from 258 nm ($x=0$) to 278 nm ($x=1$), the reason may attributed to band-gap energy become smaller and

smaller; (2) the strongest excitation band have a blue shift, the strongest absorption move from 550 nm in $\text{CaS}:\text{Eu}^{2+}, \text{Er}^{3+}$ to 470 nm in $\text{SrS}:\text{Eu}^{2+}, \text{Er}^{3+}$, which make it match better with blue GaN LED chip; (3) the emission of the phosphor shift from 645 to 615 nm, which results from the fact that the radius of Ca^{2+} (0.99 Å) is smaller than that of Sr^{2+} (1.13 Å), and the band-gap energy become smaller from CaS to SrS, and lead to the change of the crystal field and energy gap; (4) the emission intensity have a little increase with increasing of the x value, and achieve to the maximum with $x=0.5$, then begin to decrease with the increase of x value. According to these results, the strongest excitation band has shift to 470 nm and the intensity of emission has a little increase and achieve the maximum when $x=0.5$,

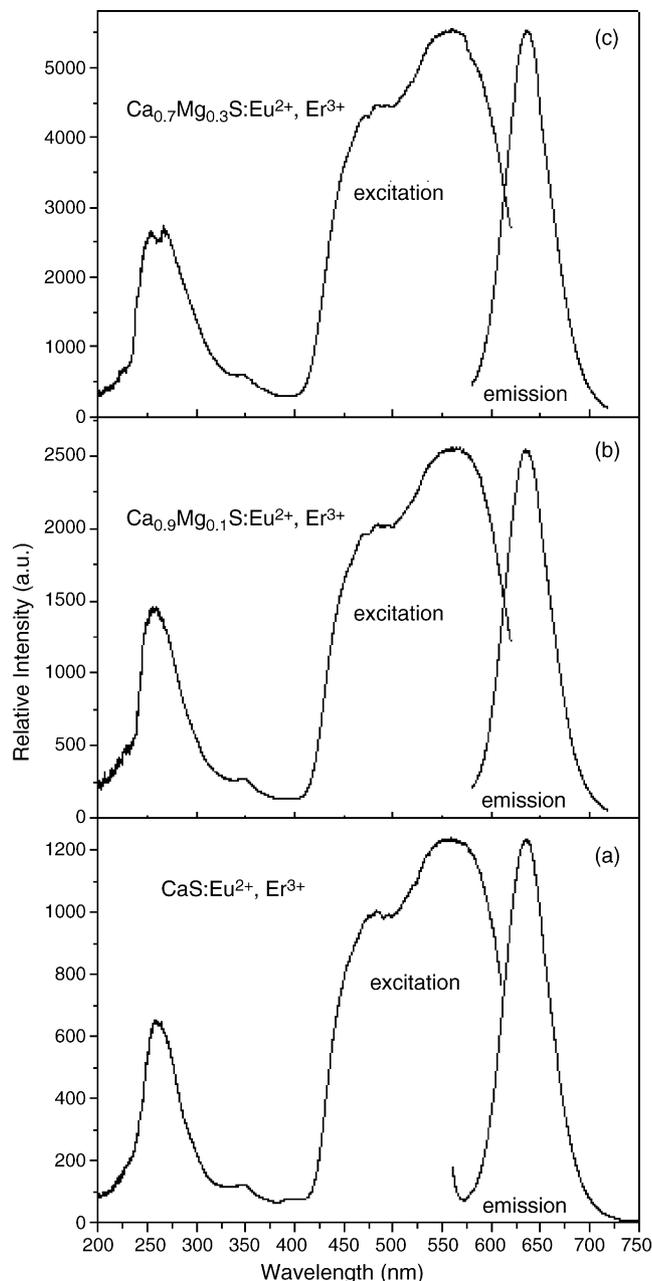


Fig. 6. The emission and excitation spectra of $\text{Ca}_{1-x}\text{Mg}_x\text{S}:\text{Eu}^{2+}, \text{Er}^{3+}$ ($0 \leq x \leq 0.3$): (a) $x=0$, (b) $x=0.1$ and (c) $x=0.3$.

which could match well with blue light GaN-based LED chip. Our red phosphor $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{S}:\text{Eu}^{2+}, \text{Er}^{3+}$ and green phosphor $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ have been used in a InGaN-based blue LED chip to fabricate a three-band white LED, its luminous efficacy is about 15 lm/W and the CIE chromaticity coordinate, the color temperature T_c , and the color rendering index Ra were (0.3236, 0.3242), 5937 K, and 92.2, respectively. These results indicate that such a three-band white LED is more optically perfect than the conventional YAG:Ce white LED [10]. Fig. 6 shows the emission and excitation spectra of $\text{Ca}_{1-x}\text{Mg}_x\text{S}:\text{Eu}^{2+}, \text{Er}^{3+}$ phosphor ($0 \leq x \leq 0.3$, CaS and MgS are partially miscible in our experimental condition [24]), their shapes of emission and excitation spectra are similar to $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}^{2+}, \text{Er}^{3+}$. However, we found that the relative intensity of phosphor $\text{Ca}_{1-x}\text{Mg}_x\text{S}:\text{Eu}^{2+}, \text{Er}^{3+}$ emission and excitation band increased with increasing of x and achieve the maximum at $x=0.3$; on the other hand, the strongest excitation broad-band has a small red shift, which is not beneficial for application in the blue light GaN LED, but this defect is not important compare with its improvement in luminescence intensity; the wavelength of the emission bands have no remarkable changes, which are in agreement with previous report [25]. Considering the effects of Mg and Sr on luminescent properties of $\text{CaS}:\text{Eu}^{2+}, \text{Er}^{3+}$ phosphors, we conclude that a suitable substitution of Ca by Sr or Mg is beneficial to enhance the intensity of red phosphor $\text{CaS}:\text{Eu}^{2+}, \text{Er}^{3+}$.

4. Conclusions

The red-emitting phosphors based on $\text{CaS}:\text{Eu}^{2+}, \text{Er}^{3+}$ used in blue GaN LED were synthesized by solid-state reaction at high temperature in CO reductive atmosphere. Many methods for improving the intensity of this red-emitting phosphor were found, as follows:

- (1) Different fluxes have a great effect on the intensity of the phosphor, among $\text{Na}_2\text{CO}_3, \text{Li}_2\text{CO}_3, \text{NH}_4\text{Cl}$ and NH_4F flux, the intensities of these phosphors were found in the order $I_{\text{Na}_2\text{CO}_3} < I_{\text{Li}_2\text{CO}_3} < I_{\text{NH}_4\text{Cl}} < I_{\text{NH}_4\text{F}}$, that is to say, NH_4F is the best flux in this phosphor.
- (2) Auxiliary activator Er^{3+} could improve the intensity of alkaline earth sulfides-based phosphor but not enhance their afterglow.
- (3) Addition of Sr could make the excitation band of $\text{CaS}:\text{Eu}^{2+}, \text{Er}^{3+}$ shift to low energy, which could match well with the blue light GaN-based LED; introduction of suitable molar Mg or Sr in $\text{CaS}:\text{Eu}^{2+}, \text{Er}^{3+}$ phosphor could improve its intensity greatly.

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