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A novel red-emitting phosphors $K_2Ba\ (MoO_4)_2$: Eu^{3+}, Sm^{3+} and improvement of luminescent properties for light emitting diodes

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ABSTRACT

The novel red-emitting phosphors $K_2Ba(MoO_4)_2$: Eu^{3+}, Sm^{3+} were prepared by solid-state reaction and their crystal structures, photo luminescent characteristics were investigated. The results show that all samples can be excited efficiently by UV (397 nm) and blue (466 nm) light, which are coupled well with the characteristic emission from UVLED and blue LED, respectively. A small amount of Sm^{3+}, acting as a sensitizer, increased the energy absorption around 400 nm. In the Eu^{3+}–Sm^{3+} co-doped system, both Eu^{3+} and Sm^{3+} f–f transition absorptions are observed in the excitation spectra, the intensities of the main emission line ($^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} at 616 nm) are strengthened because of the energy transition from Sm^{3+} to Eu^{3+}. The doping concentration of Eu^{3+}–Sm^{3+} was optimized. The approach to charge compensation was used: $Ba^{2+} \rightarrow Eu^{3+}/Sm^{3+} + X^-$ (X = F, Cl, and Br), and the influence of charge compensation on the luminescent intensity of phosphors is investigated.

1. Introduction

Currently, phosphor-converted (pc) white LEDs are attracting significant attention. The phosphors are pumped by UV-InGaN chips (~400 nm) or blue GaN chips (~460 nm) and generate white light [1,2]. However, the efficiency of the Y_2O_2S: Eu^{3+} is instable due to the release of sulfide gas, and is much lower than that of the blue and green phosphors [3]. Based on blue LED plus yellow phosphor, there exists at least two drawbacks, such as lower color-rendering index, lower luminous efficiency [4]. So that red-emitting phosphor is introduced to improve the CRI and increase the light conversion efficiency [5]. Hence, in order to improve the efficiency of the phosphor, it is urgent to research and develop new families of red-emitting phosphors with high absorption in the UV or blue wavelengths of GaN-based LED chips [6].

To find novel efficient red-emitting LED phosphors, europium has been the focus of attention as an activator in red phosphors because of its strong red emission. Especially, Eu^{3+} doped phosphors as red phosphors can be effectively excited by near-UV and blue light, and then emit stronger red fluorescence attributable to the $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 3) transitions.

Kang and co-workers investigated the luminescence properties of Eu^{3+} and Sm^{3+} doped K_2WO_4 phosphors [7]. He et al. reported the phosphor $K_2Bi(PO_4)(MO_4)$: Eu^{3+} (M = Mo, W) red-emitting phosphor, which can be excited by UV light and near-UV range (370–400 nm), and perform pure red luminescence (615 nm) from the Eu^{3+} transition of $^5D_0 \rightarrow {}^7F_2$ [8]. Ren and Chen et al. studied the luminescent properties of Eu^{3+}-activated $(La, Gd)_2(MoO_4)_3$ [9]. The phosphors of $BaGd_{1.2}Eu_{0.8}(WO_4)_{0.4}(MoO_4)_{3.6}$ and Eu^{3+} activated $MLa_2(MoO_4)_4$ based (M = Ba, Sr and Ca) were prepared and studied [10,11]. Besides, it is well known that Sm^{3+} ions acting as a sensitizer exhibit strong absorption at about 395/405 nm in many host lattices [12,13], which is close to the emission wavelength of near UV InGaN-based chips. For Eu^{3+}/Sm^{3+} system, the excitation wavelength range for Eu^{3+} emission is broadened due to the energy transfer from Sm^{3+} to Eu^{3+} [14–17].

In this study, novel red-emitting phosphor $K_2Ba(MoO_4)_2$: Eu^{3+}/Sm^{3+} has been successfully synthesized by a solid-state reaction. Under near-UV and blue light excitation, $K_2Ba(MoO_4)_2$: Eu^{3+}/Sm^{3+} phosphors emitted an intense red light. Characterizations of the powders were carried out by using Powder X-ray diffraction (XRD) and luminescence spectrophotometer. To the best of our knowledge, no paper has been published on the preparation of Eu^{3+}/Sm^{3+} ions doped $K_2Ba(MoO_4)_2$. Based on these considerations, in this paper, we reported the preparation of $K_2Ba(MoO_4)_2$: Eu^{3+}/Sm^{3+} phosphors and the photoluminescence properties.

2. Experimental

A series of red-emitting phosphors were obtained by solid-state reaction. The starting materials obtained from Sinopharm Chemical Reagent Co., Ltd. were $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (A.R.), $BaCO_3$ (A.R.), K_2CO_3 (A.R.), Eu_2O_3 (4N), Sm_2O_3 (4N), NH_4F (A.R.), NH_4Cl (A.R.), NH_4Br (A.R.), PEG (polyethylene glycol) with an average molecular weight of M_r: 3500–4500 (A.R.), CH_3CH_2OH (A.R.). Assuming a complete

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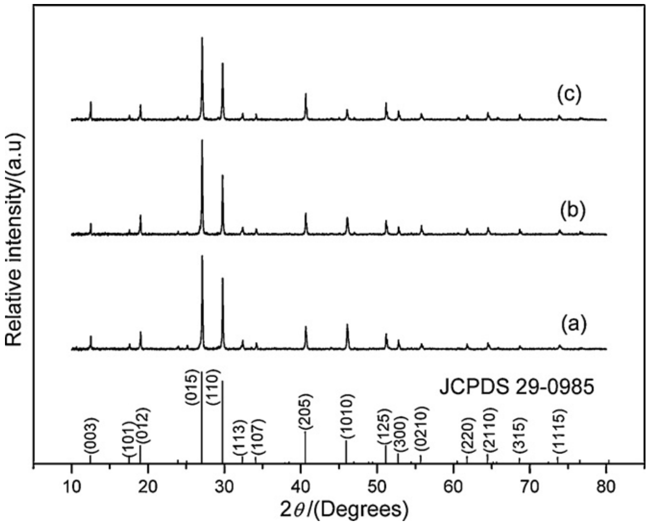

Fig. 1. X-ray diffraction patterns of (a) $K_2Ba(MoO_4)_2$: $0.015Sm^{3+}$, (b) $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$ and (c) $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, $0.015Sm^{3+}$ phosphors.

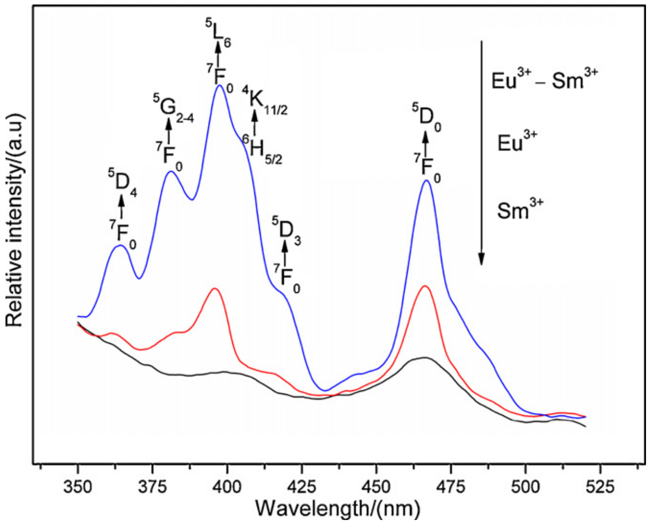

Fig. 2. The excitation (λ_{em} = 616 nm) spectra of $K_2Ba(MoO_4)_2$: $0.015Sm^{3+}$, $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$ and $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, $0.015Sm^{3+}$ phosphors.

reaction and in accordance with stoichiometric ratio, the materials were weighted and mixed along with appropriate ethanol as a solvent and PEG as a dispersing agent, sufficiently ground until the mixture became homogeneous and viscous precursor. Then, the samples were calcined at 800 °C for 5 h. Finally, they were grinded slightly to obtain the phosphor powder.

The synthesized powders were identified by X-ray powder diffraction (XRD; Bruker D8, Germany), operating at 40 kV and 40 mA and using Cu Kα radiation (λ = 1.5406 Å). The XRD patterns were collected in the range of $10° \leq 2\theta \leq 80°$. The excitation and emission measurements were measured on a PerkinElmer LS-55 (PerkinElmer Corporation, USA) luminescence spectrophotometer equipped with a xenon discharge lamp as an excitation source.

3. Results and discussion

Fig. 1 presents the XRD patterns of $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, $K_2Ba(MoO_4)_2$: $0.015Sm^{3+}$ and $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, $0.015Sm^{3+}$ phosphors. From the XRD patterns, it can be seen that no impurities are observed in the resulting product. All diffraction peaks index well to the phase structure of $K_2Ba(MoO_4)_2$ (Contrast JCPDS date file No. 29-0985) with lattice parameters $Z = 3$, $a = 6.0051$ Å and V(unit cell volume) = 216.55 Å^3, which belongs to space group R-3m(166). It indicates that codoping limited Eu^{3+} and Sm^{3+} ions do not cause any significant change to the crystal phases of the products.

The excitation spectra of $K_2Ba(MoO_4)_2$: $0.015Sm^{3+}$, $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$ and $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, $0.015Sm^{3+}$ phosphors are shown in Fig. 2. From Fig. 2, it can be seen that some strong sharp lines are in the 350–500 nm longer wavelength range. We can observe that the excitation spectra of $K_2Ba(MoO_4)_2$: $0.015Sm^{3+}$ phosphor show the absorption peaks at ∼404 and ∼466 nm. In the excitation spectrum of $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$ sample, the intrinsic excitation bands of Eu^{3+} are observed, including the peak at ∼364 nm attributed to $^7F_0 \rightarrow {}^5D_4$, the peaks at ∼381 nm attributed to $^7F_0 \rightarrow {}^5G_{2-4}$, the peak at ∼397 nm attributed to $^7F_0 \rightarrow {}^5L_6$, the peak at ∼466 nm attributed to $^7F_0 \rightarrow {}^5D_2$, respectively. Compared with that of Eu^{3+} single-doped sample, the excitation spectrum of $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, $0.015Sm^{3+}$ could be adjusted by adding a small amount of Sm^{3+}. The intensities of the spectra are enhanced and the excitation peaks at ∼397 and ∼466 nm are broadened, which are attributed to $^6H_{5/2} \rightarrow {}^4K_{11/2}$ and $^6H_{5/2} \rightarrow {}^4I_{13/2}$ of Sm^{3+}, respectively. Two of the major absorptions are at 397 and 466 nm, which are nicely in agreement with the UV or blue output wavelengths of GaN-based LED chips, respectively.

Fig. 3 displays the emission spectra $K_2Ba(MoO_4)_2$: $0.015Sm^{3+}$, $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$ and $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, $0.015Sm^{3+}$ phosphors excited at 397 nm, and the inset shows the emission intensity of samples excited at 466 nm. Under the excitation of UV light (∼397 nm) and blue-light irradiation (∼466 nm), the emission spectrum is described by the well-known $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2,. . .) emission lines of the Eu^{3+} ions with a strong emission for $J = 2$ at ∼616 nm. From Fig. 3, it can be found that the peaks located near 592 and 616 nm originate from the transitions of Eu^{3+} ion from $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ levels, respectively. As seen from Fig. 3, the intensity of emission spectra of $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, $0.015Sm^{3+}$ is about 2.18 times as strong as that of $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, while the intensity of emission spectra of $K_2Ba(MoO_4)_2$: $0.015Sm^{3+}$ is very weak.

When excited by 397 and 466 nm, the emission intensity (616 nm, $^5D_0 \rightarrow {}^7F_2$) of the phosphor versus the doping concentration of Eu^{3+} is shown in Fig. 4, respectively. It was found that the relative emission intensity increase when Eu^{3+} concentrations x increases, the maximum intensity was observed for $x = 0.10$, and then decreases with further increases in the doping concentration. This indicates a concentration quenching effect of the luminescence in the host, which results in the energy transfer and ultimately quenches the emission from the $^5D_0$ level of the Eu^{3+} ion [18,19].

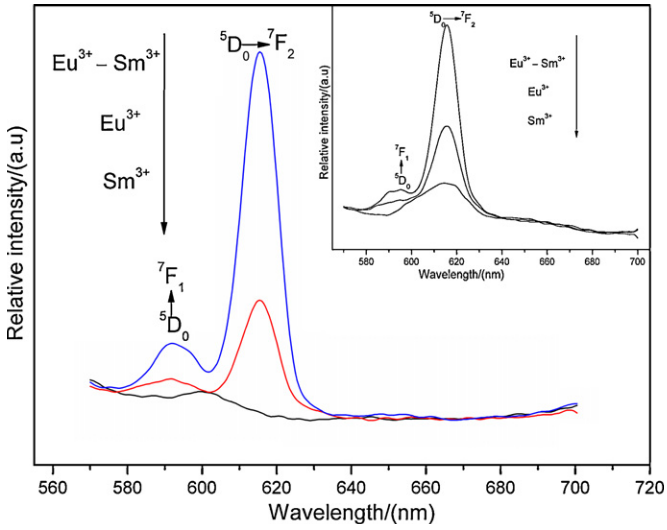

Fig. 3. The emission (λ_{ex} = 397 nm) spectra of $K_2Ba(MoO_4)_2$: $0.015Sm^{3+}$, $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$ and $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, $0.015Sm^{3+}$ phosphors, and the inset shows the emission intensity of samples excited at 466 nm.

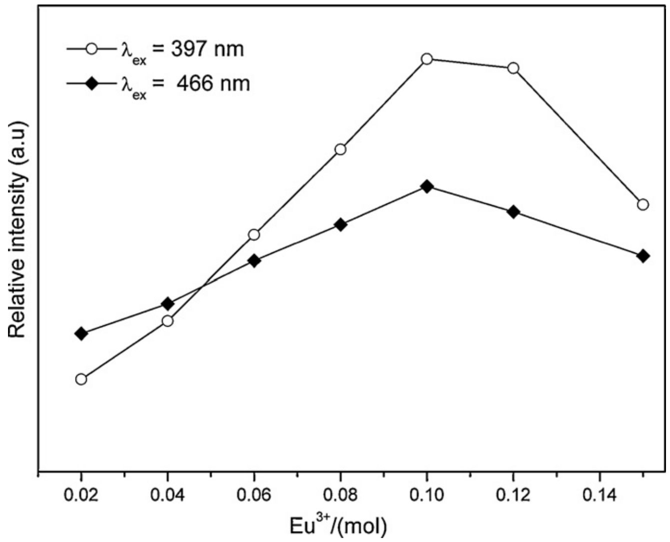

Fig. 4. Emission intensity (616 nm, $^5D_0 \rightarrow {}^7F_2$) of $K_2Ba(MoO_4)_2$: Eu^{3+} ($0.02 \le x \le 0.15$) powders vs. the doping concentration of Eu^{3+}.

The excitation and emission spectra of $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, ySm^{3+} ($0.00 \le y \le 0.03$) are shown in Figs. 5 and 6, respectively. Sm^{3+} ion can be used as an efficient sensitizer to enhance the light emission of Eu^{3+}-activated phosphors [20,21]. It can be found that the intensities of the excitation and emission spectra of the Eu^{3+}–Sm^{3+} co-doped system are enhanced as compared to the Eu^{3+}-doped system alone. The intensity of spectra increases when Sm^{3+} concentrations y increases, the maximum intensity was observed for $y = 0.015$. However, the intensity of spectra decreases with further increases in the doping concentration, which is due to the concentration quenching effects as y value is larger than 0.015.

The excitation spectra of Eu^{3+}–Sm^{3+} co-dope sample are remarkably different from that of the single Eu^{3+} doped sample. The excitation peak at ∼404 nm can be obviously detected, which is from the $^6H_{5/2} \rightarrow {}^4K_{11/2}$ transition of Sm^{3+} ions [21]. The 404 nm excitation peak of Sm^{3+} ions overlaps with that of Eu^{3+} ions at 397 nm and can induce the broadening of excitation band around 400 nm compared with the $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$ phosphor without Sm^{3+} doping. The excitation peaks around 466 nm are also broadened with the introduction of Sm^{3+} ions. These results indicate that the introduction of Sm^{3+} ions can broaden the excitation bands of $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$ phosphors, therefore, can enhance their energy absorption and emission intensity under near-UV or blue light irradiation.

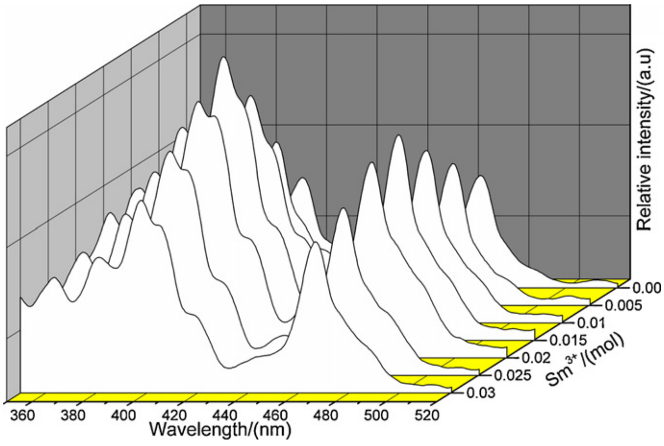

Fig. 5. The excitation ($\lambda_{em} = 616$ nm) spectra of $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, ySm^{3+} ($0.00 \le y \le 0.03$) phosphors.

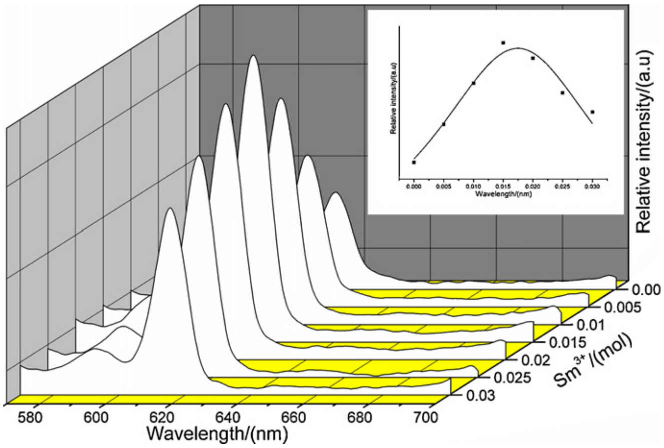

Fig. 6. The emission ($\lambda_{ex} = 397$ nm) spectra of $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, ySm^{3+} ($0.00 \le y \le 0.03$) phosphors, and the inset shows the emission intensity of samples excited at 466 nm.

In addition, in the emission spectra, the typical Sm^{3+} f–f transitions are not observed, including the main peaks at ∼602 and ∼647 nm corresponding to the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transitions, respectively. Based on the fact, it can be concluded that the Sm^{3+} ions act as a sensitizer in $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$ phosphors. This is due to the fact that some of the excited ions in $^4G_{5/2}$ levels of Sm^{3+} ion transferred their excitation energy to unexcited Eu^{3+} ions exciting them to the $^5D_0$ level. When the co-doped sample was excited at 397 nm photons, only the Eu^{3+} emission features appeared, and the spectrum was practically indistinguishable from the luminescence of Eu-singly doped powder. It implies that the absorbed energy of Sm^{3+} ions can be efficiently transferred to the Eu^{3+} ions. In a word, all results show that the energy transfer exists between Eu^{3+} and Sm^{3+}. The possible emission mechanism in $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, $0.015Sm^{3+}$ red-emitting phosphor is shown in Fig. 7. But there is no energy transfer fromEu^{3+} to Sm^{3+}, the reason of that has to result from the fact that the $^4G_{5/2}$ level of Sm^{3+} is located about 600 nm higher than the $^5D_0$ level of Eu^{3+},which makes the Eu-to-Sm energy transfer improbable rather, since simultaneously a significant portion of energy coming from

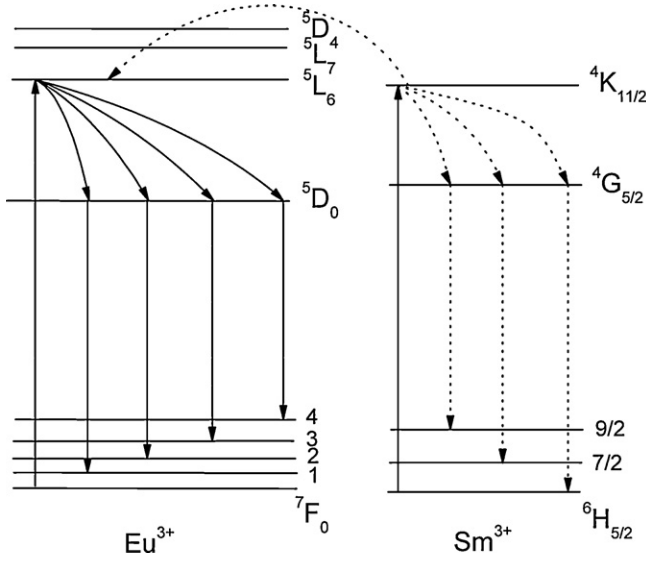

Fig. 7. Emission mechanism in $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, $0.015Sm^{3+}$ red-emitting phosphor.

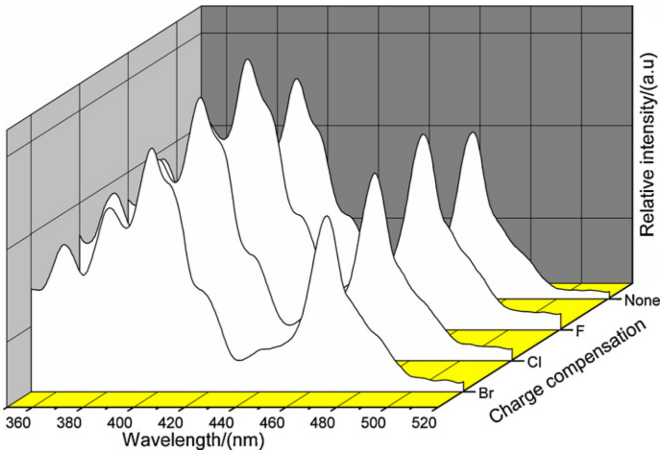

Fig. 8. Excitation spectra of $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, $0.015Sm^{3+}$ samples with different charge compensators monitored at 616 nm.

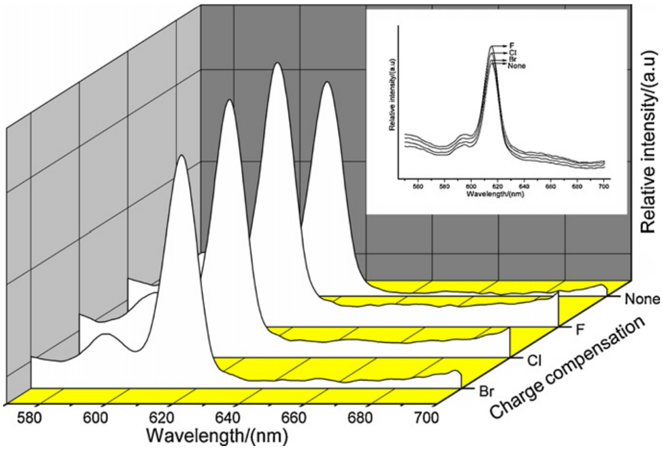

Fig. 9. Emission (λ_{ex} = 397 nm) spectra of $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, $0.015Sm^{3+}$ samples with different charge compensations, and the inset shows the emission intensity of samples excited at 466 nm.

phonons would have to be intercepted by Sm^{3+} too [22]. Besides, the low concentration of Sm^{3+} additionally hinders such transfer of energy. The above conclusions suggest that excitation into other Sm^{3+} states should also lead to mostly Eu^{3+} luminescence.

As the molar concentration of charge compensation is 0.115, the influence of charge compensations on the luminescent intensity of $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, $0.015Sm^{3+}$ is investigated. The way of charge compensation was employed. $Ba^{2+} \rightarrow Eu^{3+}/Sm^{3+} + X^-$, where X^- is a monovalent anion like F^-, Cl^-, and Br^-. The relative excitation intensities of $K_2Ba(MoO_4)_2$: $0.10Eu^{3+}$, $0.015Sm^{3+}$ phosphors with different charge compensators are given in Fig. 8. Shown in Fig. 9 is relative emission intensities of $^5D_0$–$^7F_2$ transition with 0.115 mol NH_4X (X = F, Cl, Br) employed as a charge compensator excited at 397 nm, and the inset shows the emission intensity of samples excited at 466 nm. From Figs. 8 and 9, it can be found that the intensities of the spectra of the Eu^{3+}/Sm^{3+}–X^- co-doped system are enhanced as compared to the Eu^{3+}/Sm^{3+}-doped system. It may be that the completely luminous system is electropositive and a monovalent anion (F^-, Cl^-, and Br^-) can neutralize the superfluous positive charge of the luminous system, which can better improve the luminous properties of the system. Compared with other samples, F^- is the optimum charge compensation for the luminescent system $K_2Ba(MoO_4)_2$: Eu^{3+}. The detailed mechanism will be further clarified and subsequently addressed elsewhere. The distinctions in the luminescent intensities for the samples doped with various halogen elements maybe due to the differences in their ionic radii and electro negativities.

4. Conclusions

In conclusion, the red phosphors of Eu^{3+}/Sm^{3+} doped $K_2Ba(MoO_4)_2$ were synthesized by solid-state reaction. These phosphors can be excited by 397 and 466 nm, which cover the available range of commercial n-UV LED and blue LED chips. The introduction of Sm^{3+} ions can broaden the excitation bands of the phosphors and strengthened emission intensity at 616 nm. Besides, the optimum Eu^{3+} and Sm^{3+} doping concentration are 0.10 and 0.015, respectively. F^- is the optimum charge compensation, which can better improve the luminous properties of the phosphors.

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