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Preparation of Eu^{3+}-Y^{3+} co-doping red-emitting phosphors for white-light emitting diodes (W-LEDs) application and investigation of their optical characteristics

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Abstract Eu^{3+}-Y^{3+} co-doping $Ca_{0.54}Sr_{0.34-1.5x}Eu_{0.08}Y_x(MoO_4)_y(WO_4)_{1-y}$ ($x = 0.01$, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14, 0.16, 0.18, 0.20. $y = 0$, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0), have been prepared and their luminescent properties are investigated to seek a new red-emitting phosphor for ultraviolet-light emitting diodes chips. In absorption efficiency, luminescent intensity and chromaticity coordinates, $Ca_{0.54}Sr_{0.22}(MoO_4)_{0.2}(WO_4)_{0.8}$:$0.08Eu^{3+}$, $0.08Y^{3+}$ phosphor is better than commercial Y_2O_2S:Eu^{3+} phosphor excited by 390–405 nm light emitting diodes chip.

1 Introduction

Phosphors research are immensely important due to their applications in some fields such as lamp, plasma display panels (PDPs), field emission displays (FEDs) and solid-state lighting (SSL). White light based on light-emitting diodes (LEDs) already begin to replace traditional incandescent lamps and expected to replace fluorescent lamps in the near future. Now it is considered being a new generation of lighting owing to their high efficiency, reliability, pollution-free and low energy consumption [1, 2]. In 1998, the first white LED has been fabricated using blue LED with yellow phosphor YAG:Ce^{3+} [3].

In order to improve the efficiency of phosphors, crystal chemical substitutions have been carried out in the hosts lattice, such as YAG:Ce^{3+} ($(Y_{1-a}Gd_a)_3(Al_{1-b}Ga_b)_5O12$:$Ce^{3+}$). However, the spectral composition of the light created by the conventional two- band white LED (blue LED combined with yellow phosphor) differs from that of natural white light due to halo effect of blue/yellow color separation and poor color rendering index (CRI) caused by the lack of red emission [4].

The other approach to obtain white light is to combine UV-LED/laser diode with blue, green and red (BGR) phosphors [5]. High performance white LEDs have been fabricated by using NUV-LED with two or three kinds of blue, green, yellow, orange and red phosphors (BGYOR), which are based on SrS- and ZnS-based long wavelength phosphors [6]. Conventional red phosphors that are used for LED application are sulfide-based phosphors(CaS:Eu^{2+}, SrY_2S_4:Eu^{2+}, Y_2O_2S:Eu^{3+} and ZnCdS:Cu,Al), of which thermal/chemical stability is poor and decomposed compositions release bad smell under extended UV-irradiation. However, their emission efficiency, such as Y_2O_2S:Eu^{3+} red phosphor, is less than that of the green and blue phosphors. It is reported Eu^{3+}-substituted phosphors containing WO_4 and MoO_4 tetrahedra with scheelite-related structures [7, 8].

The efficiency of charge transfer (CT) band (due to MoO_4/WO_4 tetrahedra) is not good enough to give high emission intensity for near-UV excitation. So we have explored the possibility of Eu^{3+}-Sm^{3+}, Eu^{3+}-$Gd^{3+}$and Eu^{3+}-La^{3+} co-doped double hosts MoO_4–WO_4 tetrahedra structure as potential red-emitting-phosphor candidates for white LEDs [9–13]. It is found that the emission efficiency of phosphors are improved obviously. In order to improve

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the emission property of phosphors, in this paper, we shall synthesize Eu^{3+}-Y^{3+} co-activated double hosts MoO_4–WO_4 tetrahedra structure $Ca_{0.54}Sr_{0.34-1.5x}Eu_{0.08}Y_x(MoO_4)_y(WO_4)_{1-y}$ phosphor by solid-state reaction in air and investigate its luminescent properties.

2 Experimental

2.1 Synthesis

The phosphors were prepared by using the solid-state reaction at high temperature, of which the reactants include CaO(A.R.grade), $SrCO_3$(A.R.grade), Eu_2O_3(99.99% purity), MoO_3(A.R.grade), Y_2O_3(A.R.grade) and WO_3 (A.R.grade). According to the nominal composition $Ca_{0.54}Sr_{0.34-1.5x}Eu_{0.08}Y_x(MoO4)_y(WO_4)_{1-y}$ $(x = 0.01, 0.02, 0.04, 0.06, 0.08, 0.12, 0.16, 0.20.\ y = 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0)$, the synthesized system may be as following:

$$0.46SrCO_3 + 0.54CaO + (1-y)\,WO_3 + yMoO_3 \rightarrow Ca_{0.54}Sr_{0.46}(MoO_4)_y(WO_4)_{1-y} \tag{1}$$

$$Ca_{0.54}Sr_{0.46}(MoO_4)_y(WO_4)_{1-y} + 0.04Eu_2O_3 \rightarrow Ca_{0.54}Sr_{0.34}Eu_{0.08}(MoO_4)_y(WO_4)_{1-y} + 0.12SrO \tag{2}$$

$$Ca_{0.54}Sr_{0.34}Eu_{0.08}(MoO_4)_y(WO_4)_{1-y} + 0.5xY_2O_3 \rightarrow Ca_{0.54}Sr_{0.34-1.5x}Eu_{0.08}Y_x(MoO_4)_y(WO_4)_{1-y} \tag{3}$$

The stoichiometric reactants were first ground and prefired at 500 °C for 2 h, and then heated at 600–1,100 °C in air for 3 h and the powders were obtained. Then the luminescence properties of the product were studied, NH_4Cl employed as flux.

2.2 X-ray powder diffraction and photoluminescence characterization

The structure of the product was recorded by X-ray powder diffraction (XRD) employing CuK_α radiation at 40 kv and 250 mA. A step size of 0.02°(2θ) was used with a scan speed of 4°/min. Excitation and emission spectra, excitation and emission slits set at 2.5 nm, were measured by using a Hitachi F-4600 spectrometer equipped with a 150 W-xenon lamp under a working voltage of 500 V. All the measurements were performed at room temperature.

3 Results and discussion

3.1 X-ray powder diffraction analysis

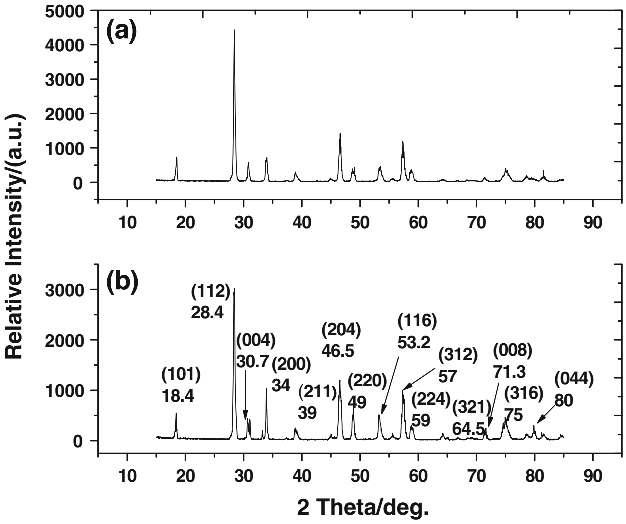

Fig. 1 The XRD patterns of $Ca_{0.54}Sr_{0.34}Eu_{0.08}(MoO_4)_{0.2}(WO_4)_{0.8}$ (**a**) and $Ca_{0.54}Sr_{0.46}MoO_4$ (**b**)

Figure 1a and b show XRD patterns of $Ca_{0.54}Sr_{0.34}Eu_{0.08}(MoO_4)_{0.2}(WO_4)_{0.8}$ and $Ca_{0.54}Sr_{0.46}MoO_4$, respectively. Both patterns are shown without unidentified diffraction peaks from impurity. The XRD patterns of $Ca_{0.54}Sr_{0.34}Eu_{0.08}(MoO_4)_{0.2}(WO_4)_{0.8}$ and $Ca_{0.54}Sr_{0.46}MoO_4$ are sheelite structures with space group $I4_1/a$ and similar unit cell parameters, $a = 0.5203$ nm, $c = 1.1330$ nm for the former and $a = 0.5352$ nm, $c = 1.1645$ nm for the latter. It is demonstrated that the cell unit of the latter increases a little because of W^{6+}(0.062 nm) substituting Mo^{6+}(0.062 nm) and Eu^{3+}(0.095 nm) substituting Sr^{2+}(0.113 nm). Figure 1b depicts the situation of main reflection peaks, which is investigated that the situation of main reflection peaks are consistent and their intensities increase with Eu^{3+} and W^{6+} ions introduced into the host lattice.

3.2 SEM patterns analysis

Rainho et al. [14] studied that the cell unit size had great effect on the dispersion of UV and mentioned the correlated formula. The dispersion coefficient s and the average grain size g has a relation as follows:

$$\ln s = \ln k - \ln g + 0.5\ \ln^2 \sigma \text{ or}$$
$$\log s = \log k - \log g + 1.15129\ \log^2 \sigma$$

where k is a constant and σ is broaden standard deviation of granulometric normal distribution. It can be indicated that, the less the phosphors grain size is, the bigger granulometric distribution width and distribution coefficient s are. In Fig. 2 shown the SEM patterns of $Ca_{0.54}Sr_{0.34}Eu_{0.08}(MoO_4)_{0.2}(WO_4)_{0.8}$ with different flux dosages, the SEM patterns indicate that the grains diameters are approximately 6–8 µm as the amount of NH_4Cl flux reaches 4 mol%. The luminescent system appears melting and agglomeration when the amount of NH_4Cl flux is

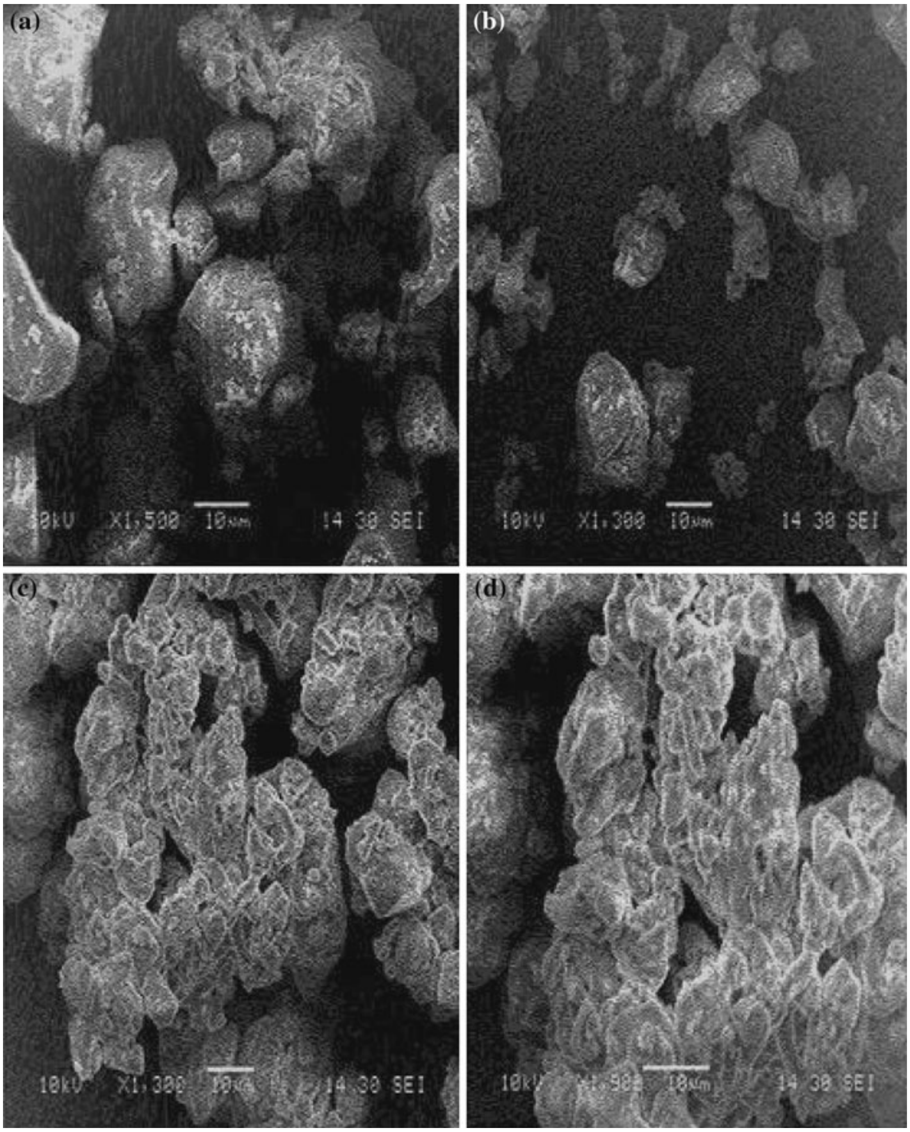

Fig. 2 The SEM patterns of $Ca_{0.54}Sr_{0.34}Eu_{0.08}(MoO_4)_{0.2}(WO_4)_{0.8}$ with **a** 0 mol% NH_4Cl, **b** 4 mol% NH_4Cl, **c** 8 mol% NH_4Cl, **d** 12 mol% NH_4Cl

8–12 mol%. The results show the appropriate dosage and category of flux can improve the grain size and crystal structures of luminescent system, of which can improve its luminescent properties.

3.3 Photoluminescence analysis

Shown in Fig. 3 are the excitation spectra monitored at 616 nm and emission spectra under 394, 465 and 535 nm, respectively, of $Ca_{0.54}Sr_{0.22}Eu_{0.08}Y_{0.08}(MoO_4)_{0.2}(WO_4)_{0.8}$. The excitation spectrum for monitoring $^5D_0 \rightarrow {}^7F_2$ emission of Eu^{3+} can be divided into two regions, the broad excitation band from ~210 nm extending up to 355 nm, its band edge located at 311 nm, attributed to the charge transfer transition of Eu–O, W–O and Mo–O group, and the narrow peaks located at wavelengths longer than 355 nm assigned to the f-f transitions of Eu^{3+}. The f-f transitions of Eu^{3+} in excitation spectrum include sharp lines $^7F_0 \rightarrow {}^5L_6$ at 394 nm, $^7F_0 \rightarrow {}^5D_2$ at 465 nm, and $^7F_0 \rightarrow {}^5D_1$ at 535 nm. For the Eu^{3+} doped phosphors, the intensity of charge transfer band is weaker than that of f-f transitions in the excitation spectrum. In the emission spectra of luminescent system, The typical emission spectra of $Ca_{0.54}Sr_{0.22}Eu_{0.08}Y_{0.08}(MoO_4)_{02}(WO_4)_{0.8}$ is composed of groups of several sharp lines, which belong to the intrinsic emission of trivalent Eu ion. The main emission line around 616 nm is assigned to the Eu^{3+} electric dipole transition of $^5D_0 \rightarrow {}^7F_2$, which is sensitive to the site symmetry. The domain emission peak at 616 nm indicates that the Eu^{3+} is located at the site lack of inversion

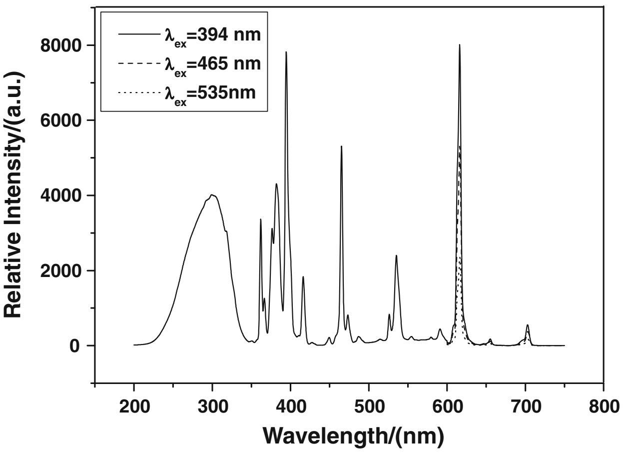

Fig. 3 The excitation spectra monitored at 616 nm and emission spectra under 394, 465 and 535 nm

symmetry, breaking the parity-selection rules. The emission spectra excited upon 394 and 465 nm have the same profile as that excited upon 535 nm. Obviously, this phosphor can be excited upon f-f transition from the excitation spectra. It is a good sign that this novel phosphor can strongly absorb ultraviolet (394 nm) and visible blue light (465 nm), and transfer the excitation energy to the red radiation. The wavelengths at 394 and 465 nm are nicely in agreement with the widely applied UV or blue output wavelengths of GaN-based LED chips.

Shown in Fig. 4 is the emission intensity of $Ca_{0.54}Sr_{0.22}Eu_{0.08}Y_{0.08}(MoO_4)_x(WO_4)_{1-x}$ ($x = 0, 0.1, 0.2, 0. 4, 0. 6, 0. 8, 1.0$) with different Mo^{6+} content under 394, 465 and 535 nm excitation, respectively. When the Mo^{6+} concentration is 0–20 mol%, with Mo^{6+} concentration increasing, the emission intensity of the samples strengthens obviously and reaches a maximum value, 20 mol%. Then, with Mo^{6+} concentration increasing, the emission intensity of samples can decrease in a certain extent when Mo^{6+} concentration is beyond 20 mol%. It is indicated that W^{6+} concentration and Mo^{6+} content may reach an optimum status in energy transfer, which can improve the crystal structures and luminescent properties of the phosphors.

Figure 5 shows the emission spectra of $Ca_{0.54}Sr_{0.34-1.5x}Eu_{0.08}Y_x(MoO_4)_{0.2}(WO_4)_{0.8}$ ($x = 0.01, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14, 0.16, 0.20$) under 394 and 465 nm excitation respectively, with different Y^{3+} content. Y^{3+}-Eu^{3+} co-doped this system can improve its luminescent properties, when Y^{3+} concentration is 8 mol%, the emission intensity of luminescent system reaches the maximum value. Furthermore, a ratio between the integrated intensity of the two transitions, I_{0-J}/I_{0-J}, is used in lanthanide-based systems as a probe of the cation local surroundings [15]. As shown in Fig. 5, the transition $^5D_0 \rightarrow {}^7F_2$ (616 nm) is much stronger than the transition $^5D_0 \rightarrow {}^7F_3$ (655 nm) and $^5D_0 \rightarrow {}^7F_4$(702.8 nm), and the ratio of I_{0-2}/I_{0-3} and I_{0-2}/I_{0-4} are about 45.44, 14.43 (394 nm), 43.73 nm and 14.12(465 nm) respectively, which suggests that Eu^{3+} is located in a distorted cation environment. That is also favorable to improve the color purity of the red phosphors.

3.4 Red-emitting phosphors employment

To explore the highly efficient red-emitting phosphors for LED, two red-emitting LEDs were fabricated by

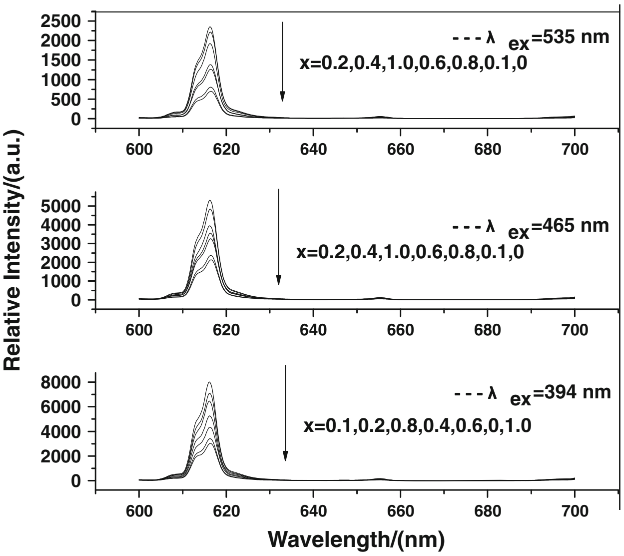

Fig. 4 The emission intensity of $Ca_{0.54}Sr_{0.22}Eu_{0.08}Y_{0.08}(MoO_4)_x(WO_4)_{1-x}$ ($x = 0, 0.1, 0.2, 0. 4, 0. 6, 0. 8, 1.0$) with different Mo^{6+} content under 394 nm, 465 nm or 535 nm excitation

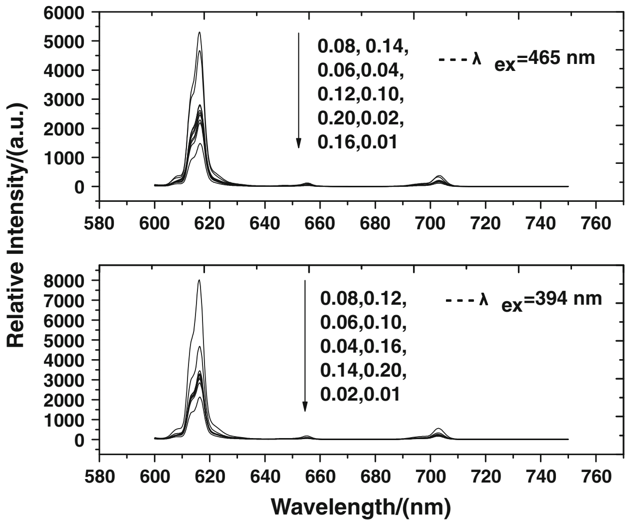

Fig. 5 The emission spectra of $Ca_{0.54}Sr_{0.34-1.5x}Eu_{0.08}Y_x(MoO_4)_{0.2}(WO_4)_{0.8}$ ($x = 0.01, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14, 0.16, 0.20$)under 394 or 465 nm excitation with different Y^{3+} content

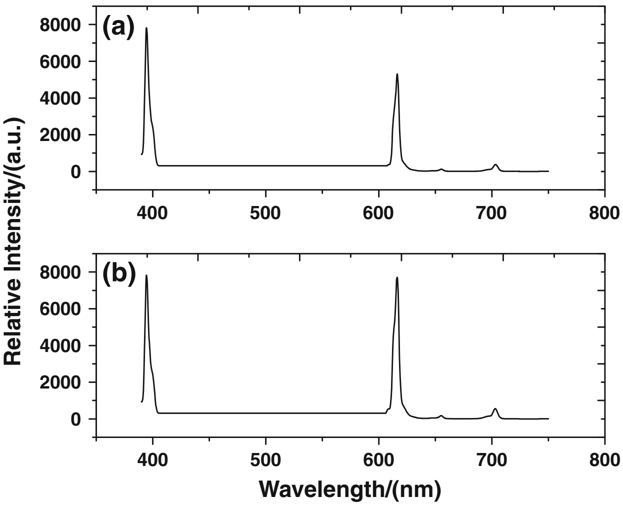

Fig. 6 Excitation spectra of the 394 nm bands in $Ca_{0.54}Sr_{0.12}(MoO_4)_{0.2}(WO_4)_{0.8}$:$0.08Eu^{3+}$, $0.08Y^{3+}$ phosphor (**b**) or Y_2O_2S:Eu^{3+} (**a**) and red LED emission spectrum excited by 390–405 nm LED chip

combining $Ca_{0.54}Sr_{0.22}Eu_{0.08}Y_{0.08}(MoO_4)_{0.2}(WO_4)_{0.8}$:0.08 Eu^{3+}, $0.08Y^{3+}$ (b) or commercial available Y_2O_2S:Eu^{3+}(a) with 390–405 nm LED chip. Shown in Fig. 6, the band at ~394 nm attributed to the LED chip and the sharp peaks at 616 nm due to the emissions of $Ca_{0.54}Sr_{0.22}Eu_{0.08}Y_{0.08}(MoO_4)_{0.2}(WO_4)_{0.8}$:$0.08Eu^{3+}$, $0.08Y^{3+}$ (b) or Y_2O_2S:Eu^{3+}(a). The CIE chromaticity coordinates of the phosphor $Ca_{0.54}Sr_{0.22}Eu_{0.08}Y_{0.08}(MoO_4)_{0.2}(WO_4)_{0.8}$ are calculated to be $x = 0.64$, $y = 0.36$ (394 nm) and Y_2O_2S:Eu^{3+} being $x = 0.63$, $y = 0.37$ (465 nm). The former is close to the standard of NTSC ($x = 0.67$, $y = 0.33$).

The intensive emission of LED chip at ~400 nm can be observed in Fig. 6, which is benefitable to obtain a white-light LED by combining this phosphor with appropriate blue and green phosphors. From the application angle, one good mono-color LED phosphor with luminescent property should own three characteristics. Above all, the phosphor must have efficient absorption at ~400 nm. Secondly, the phosphor exhibits high luminous intensity under ~400 nm excitation. Last but not least, the chromaticity coordinates of the phosphor is close to the NSTC standard values.

In a word, it is investigated that the luminescent property of $Ca_{0.54}Sr_{0.22}(MoO_4)_{0.2}(WO_4)_{0.8}$:$0.08Eu^{3+}$, $0.08Y^{3+}$ phosphor is better than that of commercial available Y_2O_2S:Eu^{3+} phosphor in the above three facets.

4 Conclusions

Through pre-heat, changing Y^{3+} concentration and $Mo^{6+}(W^{6+})$ content and adding appropriate NH_4Cl content(employed as flux), the luminescent properties of phosphors can be improved. $Ca_{0.54}Sr_{0.22}(MoO_4)_{0.2}(WO_4)_{0.8}$:$0.08Eu^{3+}$, $0.08Y^{3+}$ phosphor is better than commercial available Y_2O_2S:Eu^{3+} phosphor with 390–405 nm LED chip in absorption efficiency, luminescent intensity and the chromaticity coordinates. it is investigated that the red phosphors, Eu^{3+}-Y^{3+} co-doped $Ca_{0.54}Sr_{0.22}Eu_{0.08}Y_{0.08}(MoO_4)_{0.2}(WO_4)_{0.8}$ is an excellent red-emitting phosphors for LED.

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