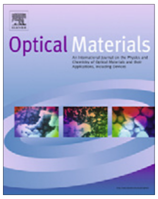
Optical Materials 33 (2011) 1262–1265

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat



$Ca_3Al_2(SiO_4)_{3-\delta}Cl_{4\delta}$:$Eu^{2+}$, Mn^{2+}: A potential phosphor with energy transfer for near-UV pumped white-LEDs

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ARTICLE INFO

Article history:
Received 29 December 2010
Received in revised form 18 February 2011
Accepted 21 February 2011
Available online 22 March 2011

Keywords:
Phosphors
Energy transfers
Light emitting diodes

ABSTRACT

A series of Eu^{2+} and Mn^{2+} coactivated $Ca_3Al_2(SiO_4)_{3-\delta}Cl_{4\delta}$ phosphors have been synthesized by solid state reactions and their luminescence properties have been investigated by means of powder diffuse reflection, photoluminescence excitation and emission spectra, and lifetimes. The phosphor $Ca_3Al_2(SiO_4)_{3-\delta}Cl_{4\delta}$:$Eu^{2+}$, Mn^{2+} exhibits two dominating bands situated at 460 and 550 nm, originate from the allowed 5d → 4f transition of the Eu^{2+} ion and the $^4T_{1g}(4G) \rightarrow {}^6A_{1g}(6S)$ transition of the Mn^{2+} ion, respectively. We have discovered that energy transfers from Eu^{2+} to Mn^{2+} by directly observing significant overlap of the excitation spectrum of Mn^{2+} and the emission spectrum of Eu^{2+} as well as the decline of lifetimes of Eu^{2+}. By utilizing the principle of energy transfer, we have demonstrated that with appropriate tuning of activator content $Ca_3Al_2(SiO_4)_{3-\delta}Cl_{4\delta}$:$Eu^{2+}$, Mn^{2+} phosphors exhibit potential to act as a phosphor for near ultraviolet light-emitting diodes.

1. Introduction

White light-emitting diodes (white-LEDs) have attracted much attention in recent years, in which white light can be generated by a blue-emitting InGaN chip and yellow-emitting phosphor $Y_3Al_5O_{12}$:Ce^{3+} garnet (YAG:Ce^{3+}) [1]. However, this method has the following problems: white emitting color changes with input power, low color-rendering index due to two color mixing and low reproducibility due to strong dependence of white color quality on an amount of phosphor. From this point of view, single-composition phosphors for ultraviolet (UV) or near ultraviolet (NUV) excitations have drawn many attentions for solid state lighting. As compared to the InGaN-based blue LED chip combined with YAG:Ce^{3+} phosphor, a white-LED fabricated using a phosphor blend of single-composition emission tunable phosphor pumped with UV/NUV chips has advantages of high tolerance to UV chip color variation and excellent color-rendering index [2–6]. One of the strategies for generating single-phased emission-tunable phosphor is by co-doping sensitizer and activator into the same host, which is based on the mechanism of energy transfer from sensitizer to activator. The phosphors with energy transfer mechanism of sensitizer/activator, such as Eu^{2+}/Mn^{2+}, have been synthesized and investigated in many hosts [7–11]. Although there were sweeping studies on the above fields in the past years, Eu^{2+}/Mn^{2+}-coactivated calcium aluminate silicate chloride were rarely reported.

In this work, We have demonstrated a single-composition emission-tunable $Ca_3Al_2(SiO_4)_{3-\delta}Cl_{4\delta}$:$Eu_x^{2+}$, Mn_y^{2+} phosphor by energy transfer mechanism between the luminescence centers Eu^{2+} and Mn^{2+}, the color can be tuned from blue to yellow. We have also proven that a near-white light can be achieved by increasing the dopant contents of Mn^{2+}. The $Ca_3Al_2(SiO_4)_{3-\delta}Cl_{4\delta}$:$Eu^{2+}$, Mn^{2+} phosphor exhibits great potential for use in white NUV-LED applications.

2. Experimental

$Ca_{3-x-y}Al_2(SiO_4)_{3-\delta}Cl_{4\delta}$:$Eu_x^{2+}$, Mn_y^{2+} $(0.8 \leqslant \delta \leqslant 1.5)$ phosphors were synthesized by a high-temperature solid-state reaction. The starting materials, $CaCO_3$, Al_2O_3, SiO_2 and $CaCl_2$ of reagent grade, were mixed together. A small amount of high-purity Eu_2O_3 and $MnCO_3$ was added into the mixture. The well-mixed reactants were placed in a crucible closed with a lid. The reactants were calcined at 1000 °C in 10% H_2/90% N_2 for 4 h.

The structure of sintered samples was identified by an X-ray powder diffractometer (Rigaku D/MAX-2500 V), using Cu Kα radiation (λ = 1.54056 Å). A step size of 0.02°(2θ) was used with a scanning speed of 4°/min. The measurements of photoluminescence (PL) and photoluminescence excitation (PLE) spectra were performed by using a Hitachi F4500 spectrometer equipped with a 150 W xenon lamp under a working voltage of 700 V. The

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doi:10.1016/j.optmat.2011.02.025

excitation and emission slits were both set at 2.5 nm. The diffuse reflectance measurements are performed using the same spectrometer with $BaSO_4$ powder as a reflectance standard. In fluorescence lifetime measurements, the third harmonic (355 nm) of an Nd-doped yttrium aluminum garnet pulsed laser (Spectra-Physics, GCR 130) was used as an excitation source, and the signals were detected with a Tektronix digital oscilloscope (TDS 3052).

3. Results and discussion

Fig. 1 shows the powder XRD pattern of $Ca_3Al_2(SiO_4)_{3-\delta}Cl_{4\delta}$ ($0.8 \leqslant \delta \leqslant 1.5$) phosphor with different δ contents. It can be seen that the $Ca_3Al_2(SiO_4)_3Cl_4$ (JCPDS No. 50-1543) are hardly obtained in single-phase form with small amounts of secondary phase. Xia reported that the phosphors they synthesized with the given chemical composition of $Ca_3Al_2(SiO_4)_3Cl_4$ matrix did not match any data in the JCPDS base after careful comparison with the reported calcium aluminate silicate chloride compounds [12]. However, as increase δ content in our work, the second phase reduces and a single phase of $Ca_{3-x-y}Al_2(SiO_4)_{3-\delta}Cl_{4\delta}$(JCPDS No. 50-1542) can be obtained.

XRD patterns of $Ca_{3-x-y}Al_2(SiO_4)_{3-\delta}Cl_{4\delta}(\delta = 1.3)$:$Eu_x^{2+}$, Mn_y^{2+} with varying Eu^{2+} and Mn^{2+} concentrations are shown in Fig. 2. All phases purity of the prepared phosphors were analyzed with JCPDS No. 50-1542 as a reference, indicating that the doped Eu^{2+} ions or co-doped Eu^{2+}/Mn^{2+} ions have not caused any observable change in the $Ca_{3-x-y}Al_2(SiO_4)_{1.7}Cl_{5.2}$ (CASC) host structure.

Fig. 3 shows the powder diffuse reflection spectra of the CASC host, Eu^{2+} singly doped, and Eu^{2+} and Mn^{2+} co-doped samples. It is obvious that the host CASC shows a platform of high reflection in the wavelength range of 300–600 nm and then starts to decrease from 200 to 300 nm, due to the host absorption. We speculate that the strong absorption in the region from 200 to 230 nm might be come from the band-to-band transitions, while the weaker broad absorption over 230–300 nm might be attributed to the tightly bound Frankel excitions, which were usually observed at the place close to the bandgap in large bandgap crystals. When the Eu^{2+} ion is singly doped into the host, two broad bands appear between 250 and 400 nm, which are derived from the 4f–5d electronic dipole allowed transitions of Eu^{2+} ion. For CASC:Eu^{2+}, Mn^{2+}, a similar spectrum is observed, except for the enhanced absorption intensity. Mn^{2+} ions may also contribute to the increased absorption intensity in the wavelength range from 250 to 450 nm by means of the metal–ligand charge transfer band of Mn^{2+}–O^{2-} and 3d–3d forbidden transitions of Mn^{2+} ion with the electronic configuration of $3d^5$.

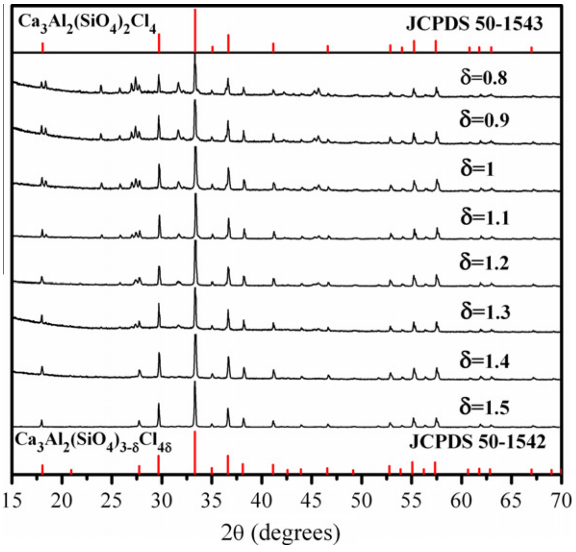

Fig. 1. The powder XRD patterns of $Ca_3Al_2(SiO_4)_{3-\delta}Cl_{4\delta}$ ($0.8 \leqslant \delta \leqslant 1.5$) phosphors with different δ contents.

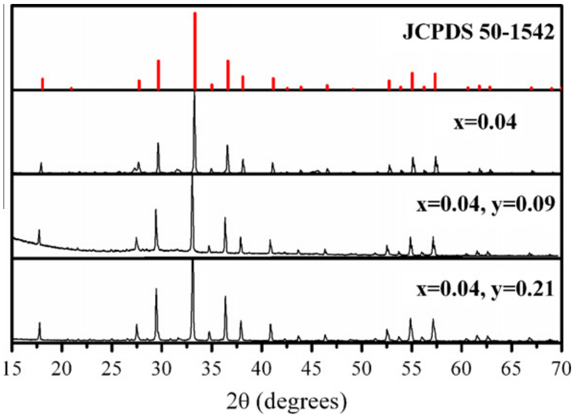

Fig. 2. XRD patterns of CASC:Eu_x^{2+}, Mn_y^{2+} with varying Eu^{2+} and Mn^{2+} concentrations.

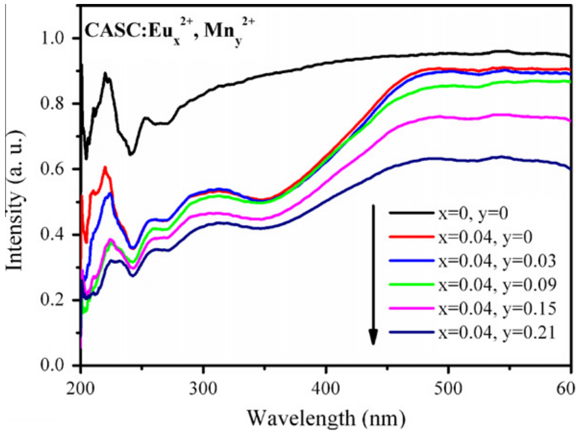

Fig. 3. The powder diffuse reflection spectra of the CASC host, Eu^{2+} singly doped, and Eu^{2+} and Mn^{2+} co-doped samples.

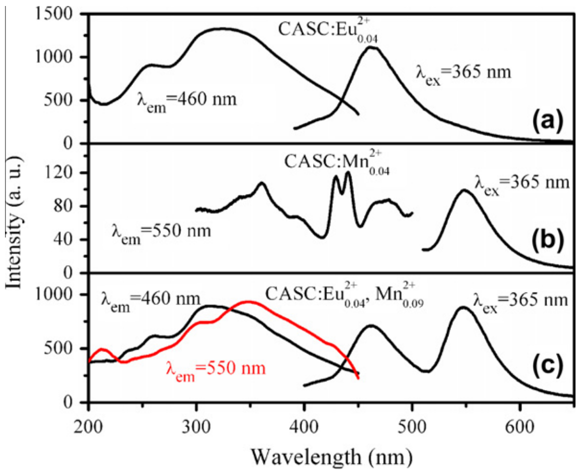

Fig. 4. The excitation and emission spectra of the CASC:$Eu_{0.04}^{2+}$ (a) and CASC:$Mn_{0.04}^{2+}$ (b) and CASC:$Eu_{0.04}^{2+}$, $Mn_{0.09}^{2+}$ (c) phosphors.

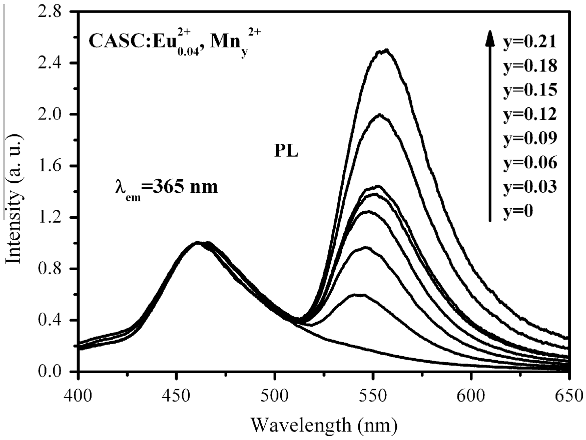

Fig. 5. The normalized emission spectra of Eu^{2+}, Mn^{2+} co-doped CASC various Mn^{2+} concentrations.

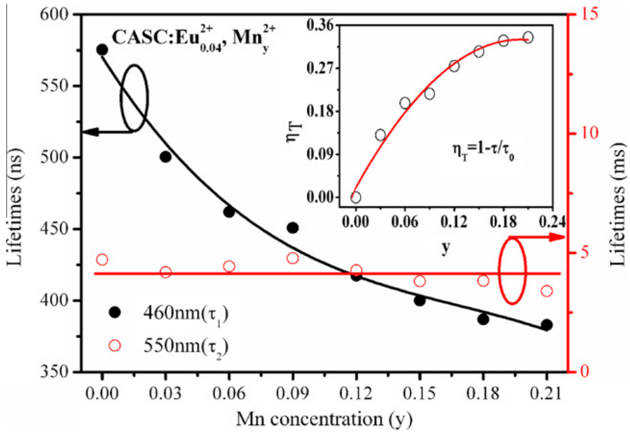

Fig. 6. The fluorescence lifetimes of Eu^{2+} (τ_1) and Mn^{2+} (τ_2). The inset is the fluorescence decay curves of CASC:$Eu^{2+}_{0.04}$, Mn^{2+}_{y} excited by 355 nm pulsed laser. Inset: the dependence of the energy transfer efficiency η_T in CASC:$Eu^{2+}_{0.04}$, Mn^{2+}_{y} on Mn^{2+} content y.

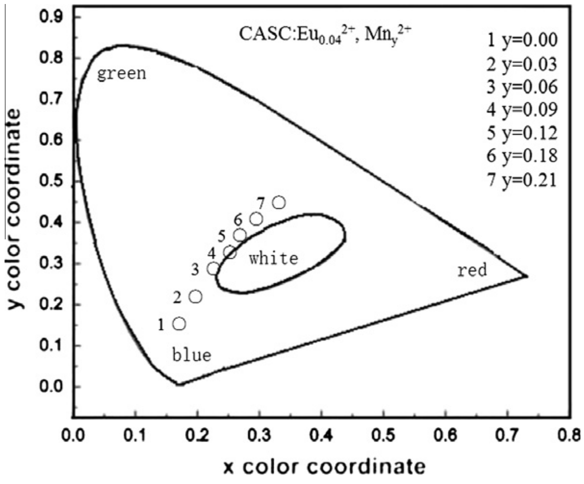

Fig. 7. The CIE 1931 chromaticity diagram of the phosphors CASC:$Eu^{2+}_{0.04}$, Mn^{2+}_{y}.

The excitation and emission spectra of the Eu^{2+} or Mn^{2+} singly doped phosphors are shown in Fig. 4a and b, and the activator mole concentration is 4%. CASC:Eu^{2+} shows a blue emission band at about 460 nm, which corresponds to the $4f^65d^1$ transition of the Eu^{2+}. The excitation spectrum monitored at 460 nm shows a broad absorption band within the 200–450 nm UV range, which is due to the transition from the $4f^7$ ground state of Eu^{2+} to the $4f^65d^1$ excited state. CASC:Mn^{2+} phosphor presents a broad band at 550 nm at 365 nm excitation, which corresponds to the ${}^4T_1({}^4G) \rightarrow {}^6A^1({}^6S)$ transition of Mn^{2+}. The excitation spectrum of CASC:Mn^{2+} phosphor consists of several bands centered at 359, 428, and 440 nm, which are assigned to the transitions from ${}^6A_1(6S)$ to ${}^4E({}^4D)$, ${}^4T_2(4D)$, and ${}^4T_2({}^4G)$ levels of Mn^{2+}, respectively [13]. The intensity of the Mn^{2+} emission is weaker than that of the Eu^{2+} emission in the CASC host, which is due to the forbidden d–d transition of Mn^{2+}. We have observed a significant spectral overlap between the Eu^{2+} PL and Mn^{2+} PLE spectra, indicating the possibility of energy transfer from Eu^{2+} to Mn^{2+} in CASC. Fig. 4c illustrates the PLE and PL spectra of CASC:$Eu^{2+}_{0.04}$, $Mn^{2+}_{0.09}$. It is found that the PLE spectrum monitoring the yellow emission of the Mn^{2+} is similar to that monitoring the blue emission of Eu^{2+}, demonstrating the existence of energy transfer from Eu^{2+} to Mn^{2+} in CASC systems. While a little difference of PLE spectra between the yellow band and blue band may be attributed to small changes in the crystal field around Eu^{2+} with and without Mn^{2+} doping.

Fig. 5 shows the normalized emission spectra of Eu^{2+}, Mn^{2+} co-doped CASC various Mn^{2+} concentrations. The PL intensity of Mn^{2+} at 550 nm increases with increasing Mn^{2+} content further supports the occurrence of the $ET_{Eu\rightarrow Mn}$ mechanism. Moreover, The PL intensity of Mn^{2+} emission band was found to redshift with increasing doped Mn^{2+} concentration. Similar observations reported by Zhang is attributed to stronger crystal field that changes with an increase in Mn^{2+} doping due to shorter Mn–O distances [14].Here, the remarkable enhancements of the yellow band relative to blue band in these phases are observed with increasing Mn^{2+} concentration. The fluorescence lifetimes of Eu^{2+} (τ_1) and Mn^{2+} (τ_2) are both represented in Fig. 6. The reduction of the lifetimes for Eu^{2+} with increasing Mn^{2+} concentrations is observed. These results support the efficient energy transfer from Eu^{2+} to Mn^{2+} ions. The lifetime of the yellow fluorescence of Mn^{2+} remains nearly unchanged, indicating the nonexistence of Mn^{2+} concentration quenching within the range of Mn^{2+}concentrations of interest in this work. The energy transfer rates (η_{Eu-Mn}) can be obtained using the equation $\eta_{Eu-Mn} = 1-\tau_1/\tau_0$. Where τ_1 and τ_0 are fluorescence lifetimes of Eu^{2+} with and without codoping of Mn^{2+}, respectively. Fig. 6 inset shows the dependence of the energy transfer rates (η_{Eu-Mn}) on Mn^{2+} concentration. With increasing Mn^{2+} dopant content, the η_{Eu-Mn} was found out to increase and reach the saturation when x is above 0.21.

The excitation and emission spectra suggest that the phosphors CASC:$Eu^{2+}_{0.04}$, Mn^{2+}_{y} are a series of efficient dual-chromatic emitting phosphors with broad absorption bands, matching well with the widely used NUV LED chips (300–410 nm). Fig. 7 shows the CIE 1931 chromaticity diagram of the phosphors CASC:$Eu^{2+}_{0.04}$, Mn^{2+}_{y}. The coordinate (x, y) of the CASC:$Eu^{2+}_{0.04}$, Mn^{2+}_{y} phosphors varied from (0.16, 0.17) at $y = 0$ to (0.34, 0.43) at $y = 0.21$, corresponding to the color tone from blue to near-white and finally to yellow.

4. Conclusion

In conclusion, a series of single-composition emission-tunable $Ca_3Al_2(SiO_4)_{3-\delta}Cl_{4\delta}$:$Eu^{2+}$,$Mn^{2+}$ phosphors were synthesized and investigated. The energy transfer from sensitizer Eu^{2+} to activator Mn^{2+} in $Ca_3Al_2(SiO_4)_{3-\delta}Cl_{4\delta}$ host has been studied and demonstrated based on the photoluminescence excitation and emission spectra, and decay lifetime data. The $Ca_3Al_2(SiO_4)_{3-\delta}Cl_{4\delta}$:$Eu^{2+}$,$Mn^{2+}$ phosphor can be tuned from blue to near-white and finally to yellow by adjusting the concentration of Mn^{2+}. These results indicated that $Ca_3Al_2(SiO_4)_{3-\delta}Cl_{4\delta}$:$Eu^{2+}$, Mn^{2+} can be a candidate to act as a phosphor for NUV-LEDs.

Acknowledgments

This work is financially supported by the National Nature Science Foundation of China (10834006, 10774141, 10904141, 10904140), the Scientific Project of Jilin province (20090134, 20090346, 20090524) and CAS Innovation Program.

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