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A new dual-emission phosphor $Ca_4Si_2O_7F_2$:Ce^{3+}, Mn^{2+} with energy transfer for near-UV LEDs

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ABSTRACT

Ce^{3+} and Mn^{2+} co-doped $Ca_4Si_2O_7F_2$ phosphors have been synthesized by high temperature solid state reaction and their luminescence properties are investigated. The effect of Ce^{3+} concentration on the emission intensity of $Ca_4Si_2O_7F_2$: Ce^{3+} is studied, and the emission intensity reaches a maximum at 4% Ce^{3+}. Energy transfer from Ce^{3+} to Mn^{2+} is observed. The emission spectra of the phosphors show a blue broad band at 460 nm of Ce^{3+} and a yellow band at 580 nm of Mn^{2+}, originate from the allowed 5d→4f transition of the Ce^{3+} ion and the $^4T_{1g}(^4G)\rightarrow{}^6A_{1g}(^6S)$ transition of the Mn^{2+} ion, respectively. Results indicate that the varied emitted color from blue to yellow can be achieved by tuning the relative ratio of the Ce^{3+} to Mn^{2+} ions based on the principle of energy transfer. We have demonstrated that $Ca_4Si_2O_7F_2$: Ce^{3+}, Mn^{2+} phosphors can be a promising candidate for a color-tunable phosphor applied in a near-UV White light emitting diodes.

1. Introduction

Since light-emitting diodes (LEDs) have brought a significant revolution in the field of illumination for application like general lighting sources and components of backlight for liquid-crystal displays (LCDs), they have an impact on research on luminescent materials (phosphors). Many of the phosphors presently used are obtained by doping rare earth ions into host material. In particular, Ce^{3+}-activated phosphors have been subjected to considerable number of researches because Ce^{3+} ion exhibits good performances for its special optical properties of a broad band emission depending on the hosts. For example, the commonly used are down converting yellow emitting $Y_3Al_5O_{12}$:Ce^{3+} phosphor and silicate garnet Sr_3SiO_5: Ce^{3+} and $Ca_3Sc_2Si_3O_{12}$:Ce^{3+} phosphors [1–4]. Moreover, Ce^{3+} ion can also act as an excellent sensitizer, transferring a part of its energy to activator ion such as Mn^{2+} [5–8]. As we have known, Mn^{2+} doped luminescent materials have wide-range emissions from 500 to 700 nm depending on the crystal field of the host materials. However, the Mn^{2+} d–d transitions are difficult to pump, because they are forbidden by spin and parity for electric dipole radiation. Thus, the Mn^{2+} emission can be realized efficiently by energy transfer from Ce^{3+} to Mn^{2+}, which plays an important role in development of efficient phosphor materials.

In this work, we have demonstrated a new dual-tunable $Ca_4Si_2O_7F_2$: Ce^{3+}, Mn^{2+} phosphor by energy transfer mechanism between the luminescence centers Ce^{2+} and Mn^{2+}, and 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 $Ca_4Si_2O_7F_2$: Ce^{3+}, Mn^{2+} phosphor exhibits great potential for use in white UV-LED applications.

2. Experimental

The $Ca_{4-x-y}Si_2O_7F_2$ (CSF): xCe^{3+}, yMn^{2+} phosphors were synthesized by a high-temperature solid-state reaction. The constituent oxides or carbonates $CaCO_3$ (99.9%), SiO_2 (99.9%), CaF_2 (99.9%), CeO_2 (99.99%), and $MnCO_3$ (99.99%) were employed as the raw materials, which were mixed homogeneously by an agate mortar for 30 min, placed in a crucible with a lid, and then sintered in a tubular furnace at 1200 °C for 2 h in CO reducing atmosphere. Powder X-ray diffraction (XRD) data was collected using Cu Kα radiation ($\lambda = 1.54056$ Å) on a Bruker D8 Advance diffractometer equipped with a linear position-sensitive detector (PSD-50 m, M. Braun), operating at 40 kV and 40 mA with a step size of 0.02° (2θ). Crystal structure refinement employed the Rietveld method as implemented in the General Structure Analysis System (GSAS) program [9]. 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.

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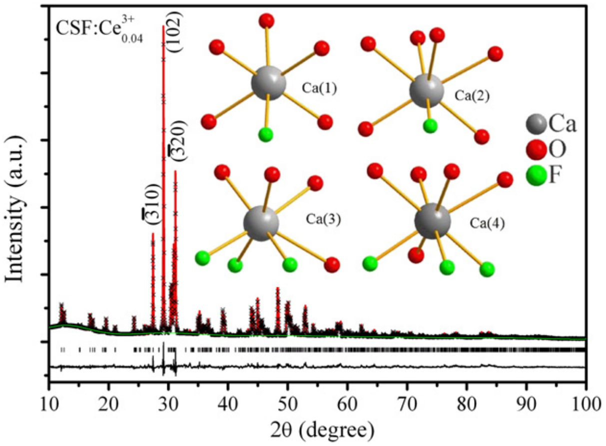


Fig. 1. Rietveld analysis patterns for X-ray powder diffraction data of CSF: Ce^{3+}. The cross marks represent the experimental intensities, and the red solid line is the calculated one. A difference (obsd–calcd) plot is shown beneath. Tick marks above the difference data indicate the reflection positions.

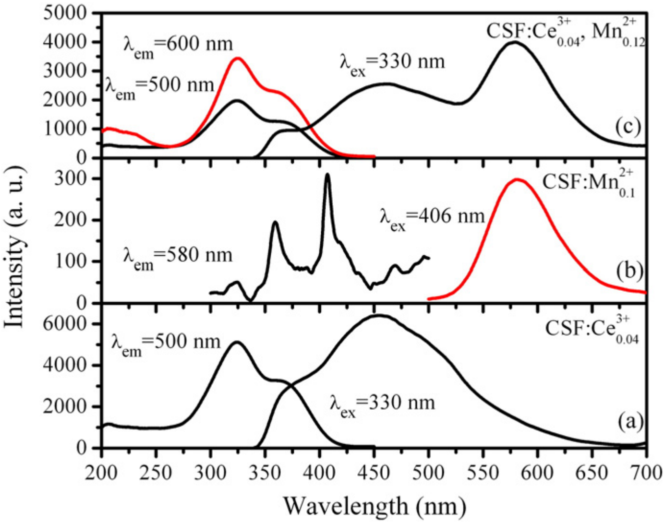


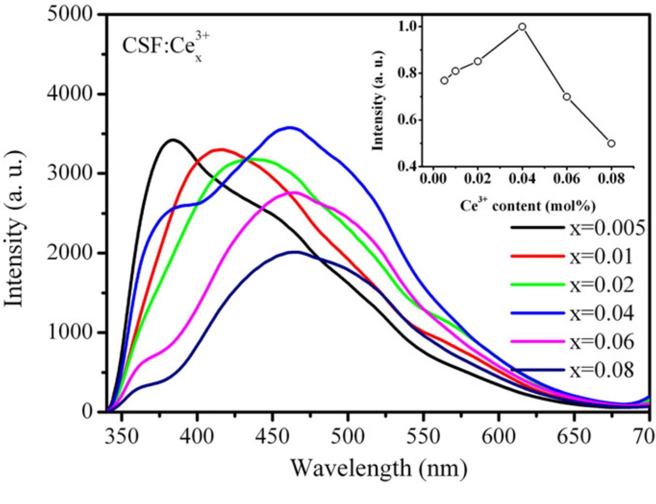
Fig. 3. The excitation and emission spectra of CSF: $0.04Ce^{3+}$(a), CSF: $0.1Mn^{2+}$ (b), CSF: $0.04Ce^{3+}$, $0.1Mn^{2+}$ and (c) phosphors.

3. Results and discussion

Fig. 1 shows the experimental, calculated, and their difference results of the XRD refinement of CSF: $0.04Ce^{3+}$. The initial structural model was constructed with crystallographic data previously reported for $Ca_4Si_2O_7F_2$ (JCPDS 41–1474) [10]. All of the observed XRD peaks are obtained with goodness of fit parameters $R_{wp}=8.34\%$ and $\chi^2=4.98$. CSF crystallizes as a monoclinic structure with a space group of P 1 21/c 1 and lattice constants of a = 7.5422 Å, b = 10.5442 Å, c = 10.9171 Å. Our XRD refinement indicate that Ca^{2+} ions have four different coordination numbers (CNs) as shown in Fig. 1 inset. Ca(1) is six coordinated surrounding by five oxygen and one fluorine atoms; Ca(2) and Ca(3) are both seven coordinated with six oxygen and one fluorine atoms, and four oxygen and three fluorine atoms, respectively; Ca(4) is eight coordinated surrounding by five oxygen and three fluorine atoms. The ionic radii of Ca(1)(CN = 6), Ca(2) and Ca(3) (both CN = 7), Ca(4)(CN = 8) are approximately 1.00, 1.06, and 1.12 Å, respectively. In this study, it is reasonable to propose that Ce^{3+} and Mn^{2+} are expected to randomly occupy the Ca^{2+} sites in the host structure.

Fig. 2 shows the PL spectra of CSF: xCe^{3+} with varying Ce^{3+} contents (x = 0.005, 0.01, 0.02, 0.04, 0.06, and 0.08) under an excitation wavelength of 330 nm. The inset shows that the Ce^{3+} concentration dependence of the PL intensity of CSF: Ce^{3+} demonstrated an optimal doping content of Ce^{3+} of 4 mol% in CSF. Beyond the content, the PL intensity was found to decrease dramatically due to concentration quenching. With increasing Ce^{3+} content, the shapes of emission spectra change. Clearly, the emission spectra consist of several broad bands which are ascribed to the different coordination sites in the CSF lattice. For lower doping concentration (<4 mol% Ce^{3+}), the dominated emission from CSF: Ce^{3+} is located at around 400 nm. Thus, In this study, we started at CSF:4% Ce^{3+} and introduced Mn^{2+} into CSF: Ce^{3+} to investigate the effect of Mn^{2+} doping on the luminescence and its energy-transfer mechanism.

The excitation and emission spectra of the Ce^{3+} or Mn^{2+} singly doped phosphors are shown in Fig. 3(a) and (b). The PL spectrum of CSF: $0.04Ce^{3+}$ displays a broad band extending from 340 to 600 nm, which attributed to the transition from 5d level to the ground state of Ce^{3+}. The excitation spectrum monitored at 500 nm shows a broad absorption band within the 300–400 nm UV range, which is due to 4f–5d transition of the Ce^{3+}. CSF: $0.1Mn^{2+}$ phosphor presents a band at 580 nm at 406 nm excitation, which corresponds to the $^4T_1(^4G) \rightarrow {}^6A^1(^6S)$ transition of Mn^{2+}. The excitation spectrum of CSF: Mn^{2+} phosphor consists of several bands centered at 359 and 406 nm, which are assigned to the transitions from $^6A_1(6S)$ to $^4T_2(4D)$ and $^4T_2(^4G)$ levels of Mn^{2+}, respectively



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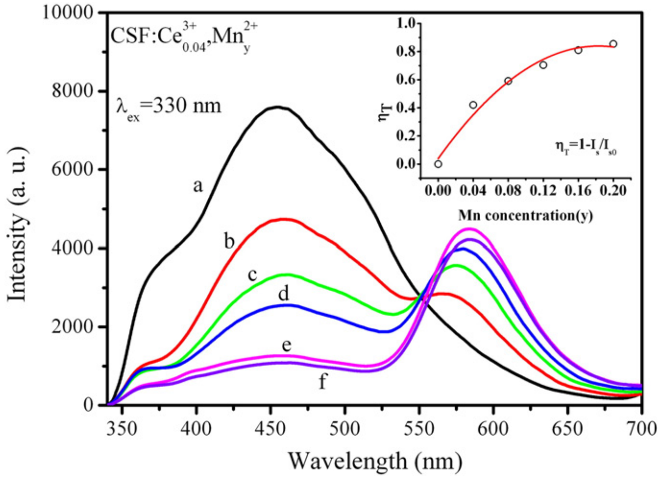

Fig. 4. The emission spectra of Ce^{3+}, Mn^{2+} co-doped CSF at various Mn^{2+} concentrations. (a) y = 0; (b) y = 0.04; (c) y = 0.08; (d) y = 0.12; (e) y = 0.16; (f) y = 0.20.

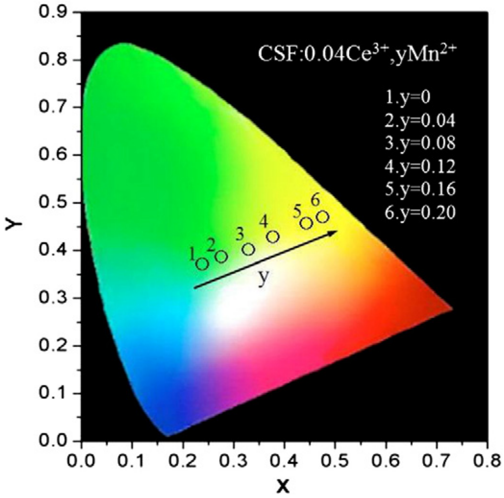

Fig. 5. CIE chromaticity diagram of CSF: 0.04Ce^{3+}, yMn^{2+} phosphors under 365 nm excitation.

[11]. The intensity of the Mn^{2+} emission is weaker than that of the Ce^{3+} emission in the CSF host, which is due to the forbidden d–d transition of Mn^{2+}. We have observed a significant spectral overlap between the Ce^{3+} PL and Mn^{2+} PLE spectra, indicating the possibility of energy transfer from Ce^{3+} to Mn^{2+} in CSF. Fig. 3(c) illustrates the PLE and PL spectra of CSF: 0.04Ce^{3+}, 0.12Mn^{2+}. It is found that the PLE spectrum monitoring the yellow emission of the Mn^{2+} is similar to that monitoring the green emission of Ce^{3+}, demonstrating the existence of energy transfer from Ce^{3+} to Mn^{2+} in CSF systems.

Fig. 4 shows the emission spectra of Ce^{3+}, Mn^{2+} co-doped CSF various Mn^{2+} concentrations(y = 0, 0.04, 0.08, 0.12, 0.16, 0.2). The PL intensity of Mn^{2+} at 580 nm which increases with increasing Mn^{2+} content further supports the occurrence of the $ET_{Ce \rightarrow Mn}$ mechanism. The energy transfer efficiencies (η_T) can be expressed by $\eta_T = 1 - I_s/I_{s0}$ where I_{so} and I_s are the peak intensities of the sensitizer Ce^{3+} without and with the activator Mn^{2+} present. As a consequence, the η_T from Ce^{3+} to Mn^{2+} in CSF was calculated as a function of y and is represented in Fig. 4 inset. With increasing Mn^{2+} content, the η_T was found to increase and reach the saturation when y is above 0.2.

The above results indicate that energy transfer between Ce^{3+} and Mn^{2+} exists in the phosphor CSF: 0.04Ce^{3+}, yMn^{2+}, and the ratio between the blue emission and the yellow emission could be tuned by adjusting the concentration of Ce^{3+} and Mn^{2+}, respectively. The intensity ratio of blue and yellow affects the CIE chromaticity of phosphors, thus the effect of Mn^{2+} dopant contents on the CIE chromaticity coordinates is investigated in CSF: 0.04Ce^{3+}, yMn^{2+} phosphors excited at 365 nm and the corresponding CIE are represented in Fig. 5. It is observed that the (x,y) coordinates of CSF: 0.04Ce^{3+}, yMn^{2+} phosphors vary systematically from (0.24, 0.38), (0.29, 0.39), (0.35, 0.42), (0.40, 0.44) to (0.48, 0.45), with the increase of Mn^{2+} contents from 0 to 20 mol%, corresponding to the change of emission color from blue to yellow. As the contents of Mn^{2+} further increase to 16 and 20 mol%, the value CIE chromaticity of phosphor does not change remarkably, and this may be due to the effect of concentration quenching from Mn^{2+}.

4. Conclusion

In summary, a new dual-tunable $Ca_4Si_2O_7F_2$:Ce^{3+}, Mn^{2+} phosphor is synthesized and investigated. The effect of Ce^{3+} concentration on the emission intensity and energy transfer from sensitizer Ce^{3+} to activator Mn^{2+} in $Ca_4Si_2O_7F_2$ host has been studied. The emission color of the obtained phosphors can be easily modulated from blue to near-white and eventually to yellow by simply adjusting the amount of Mn^{2+} ions due to the different emission compositions of the Ce^{3+} and Mn^{2+} ions. These results indicated that $Ca_4Si_2O_7F_2$: Ce^{3+}, Mn^{2+} may serve as a potential color-tunable NUV phosphor for white-light LED devices.

Acknowledgments

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