



Luminescence and energy transfer in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+},\text{Mn}^{2+}$ white LED phosphors

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ABSTRACT

Expanded emission spectra ranging from green to red are reported in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ (CSS): $\text{Ce}^{3+},\text{Mn}^{2+}$ silicate garnets. Mn^{2+} may occupy Ca^{2+} site ($\text{Mn}^{2+}(\text{I})$) to generate a yellow emission band at 574 nm or Sc^{3+} site ($\text{Mn}^{2+}(\text{II})$) with red emission band at 680 nm. Efficient energy transfers from the green emitting Ce^{3+} to both $\text{Mn}^{2+}(\text{I})$ and $\text{Mn}^{2+}(\text{II})$ occur upon blue excitation into Ce^{3+} . Concentration dependence of Mn^{2+} emission is analyzed based on $\text{Ce}^{3+}-\text{Mn}^{2+}$ energy transfer, steady state rate equations, and fluorescence lifetimes. Energy transfer efficiency (η_T) and rate (W) are calculated with values as high as 45% and $14.01 \times 10^6 \text{ s}^{-1}$, respectively.

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1. Introduction

Phosphor converted white light emitting diodes (PC-LEDs) have attracted much attention in recent years for its significant potential in solid-state lighting of the next generation. Presently, the main strategy for producing PC-WLEDs is to combine near UV (NUV) or blue LEDs with phosphors. The most commercially available PC-WLEDs employ yellow emitting $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG: Ce^{3+}) [1,2] phosphor combined with blue LEDs. Although YAG: Ce^{3+} has the high efficiency of converting LED's blue emission to yellow, the deficient red emission leads to the color rendering index (CRI) of white LEDs below 80. To enrich the red emission, a red emitting nitride phosphor is blended [3]. The phosphor mixture causes fluorescence re-absorption and non-uniformity of luminescent properties, resulting in the loss of luminous efficiency and color variation against time. A single phase phosphor with full color emissions is therefore expected.

Recently, the green-emitting $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ (CSS: Ce^{3+}) has attracted much attention due to its high emission intensity and high thermal stability superior to YAG: Ce^{3+} [4]. However, CSS: Ce^{3+} lacks yellow and red emissive components. In view of our previous research on successfully creating intense red luminescence through energy transfer (ET) by designing activators co-doped phosphors, such as $\text{Ca}_2\text{P}_2\text{O}_7:\text{Eu}^{2+},\text{Mn}^{2+}$ [5] and

$\text{BaMg}_2\text{Si}_2\text{O}_7:\text{Eu}^{2+},\text{Mn}^{2+}$ [6], we tentatively introduce Mn^{2+} into CSS: Ce^{3+} to enrich the red or yellow components through the proposed ET of $\text{Ce}^{3+}-\text{Mn}^{2+}$ pairs. Mn^{2+} can give rise to a broad emission, ranging from green to red, depending on the interaction of crystal field with the d–d transition, ${}^4\text{T}_1(\text{G}) \rightarrow {}^6\text{A}_1(\text{G})$ [7,8]. Although the excitation of Mn^{2+} d–d transitions is electric dipole forbidden and is very inefficient, it can be realized efficiently by $\text{Ce}^{3+}-\text{Mn}^{2+}$ ET [9,10], as occurred in $\text{Eu}^{2+}-\text{Mn}^{2+}$ ET [5,6].

In this paper, we report the yellow and red emissions through ET in the green emitting CSS: Ce^{3+} by co-doping Mn^{2+} . The two new bands are originated from Mn^{2+} ions substituting for Ca^{2+} and Sc^{3+} . The dynamical processes of ET from Ce^{3+} to the two Mn^{2+} sites are analyzed based on both emission spectra and fluorescence decay curves. Full color emissions are obtained in a single phosphor, CSS: $\text{Ce}^{3+},\text{Mn}^{2+}$, showing a very promising application for PC-WLEDs.

2. Experimental

Samples were synthesized by mixing high purity CaCO_3 , Sc_2O_3 , SiO_2 , CeO_2 , and MnCO_3 and sintering them in a tubular furnace at 1350 °C for 4 h with 5% $\text{H}_2+95\%$ N_2 reductive atmosphere. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured using F-4500 spectrometer. The short fluorescence decays of Ce^{3+} were measured by FL920 Fluorescence Lifetime Spectrometer with an nF900 hydrogen flash lamp (Edinburg Instruments, UK), while the longer decays of Mn^{2+} were recorded by TDS3052 oscilloscope upon the excitation of a YAG:Nd pumped optical parametric oscillator (Spectra-Physics, Newport, USA).

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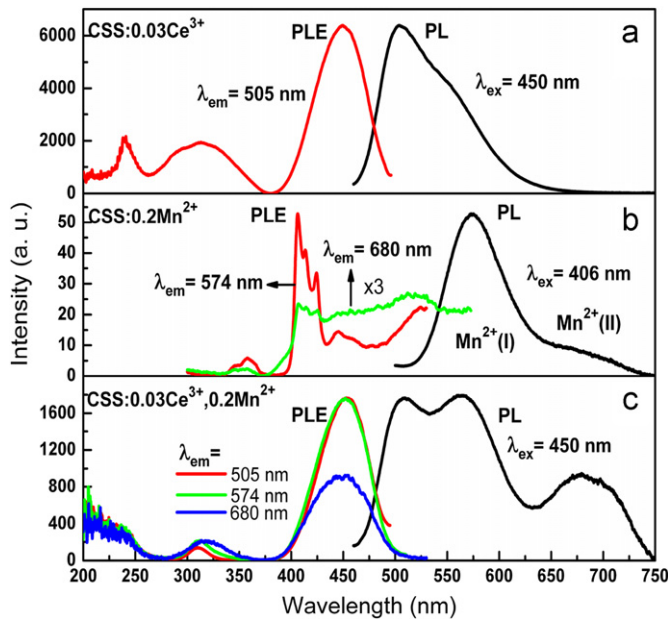


Fig. 1. PLE and PL spectra for CSS:0.03Ce³⁺ (a), CSS:0.2Mn²⁺ (b), and CSS:0.03Ce³⁺, 0.2Mn²⁺ (c).

3. Results and discussion

3.1. Luminescence of Ce³⁺ and Mn²⁺ in CSS

Fig. 1 shows three set PL and PLE spectra in CSS:0.03Ce³⁺ (a), CSS:0.2Mn²⁺ (b), and CSS:0.03Ce³⁺, 0.2Mn²⁺ (c). CSS:0.03Ce³⁺ exhibits a typical green PL band peaked at 505 nm with a shoulder around 540 nm, originating from the transitions of the lowest 5d state to ²F_{5/2} and ²F_{7/2} of Ce³⁺, respectively [4]. Meanwhile, the PLE spectrum for the green emission shows an intense band around 450 nm, well matching the emitting wavelength of blue InGaN LEDs. The PL spectrum of CSS:0.2Mn²⁺ exhibits two emission bands, a yellow band around 574 nm (named Mn²⁺(I)) and a red one around 680 nm (named Mn²⁺(II)), indicating that there are two kinds of Mn²⁺ sites in CSS. The emissions of Mn²⁺ are due to ⁴T₁(⁴G) → ⁶A₁(⁶S) transitions and their corresponding PLE spectra are also recorded.

The silicate garnet CSS belongs to cubic crystal system with space group Ia3d, and there is only one coordinated site for both Ca²⁺ and Sc³⁺ with coordination numbers (CNs) of 8 and 6, respectively [11]. Thus, the observed two emission bands due to Mn²⁺(I) and Mn²⁺(II) suggests that Mn²⁺ ions can occupy both Ca²⁺ and Sc³⁺ sites. Inspection of the crystal structure of CSS shows that the average distance for Ca–O (2.390(4) Å) is significantly longer than that for Sc–O (2.099(6) Å) [11]. Accordingly, the covalency and crystal field effects on the Ca²⁺ site are weaker than that on the Sc³⁺ site. For this reason, the higher-energy Mn²⁺(I) emission can be attributed to the Mn²⁺ occupying the Ca²⁺ site (characterized by a weaker crystal field and lower nephelauxetic effect), and the lower-energy Mn²⁺(II) emission to the Mn²⁺ occupying the Sc³⁺ site. Similar luminescence for Pr³⁺ doped Ca₃R₂Si₃O₁₂ (R = Sc, Y, Lu) was also reported by Ivanovskikh et al. [12], who described that Pr³⁺ exhibits a high-energy and a low-energy emissions for two distinct sites with significantly different bond distances.

Finally, in Fig. 1(c), the PL and PLE spectra are measured for a codoped sample, CSS:0.03Ce³⁺, 0.2Mn²⁺. The PL spectrum upon Ce³⁺ excitation at 450 nm exhibits not only the Ce³⁺ emission at 505 nm but also the Mn²⁺(I) and Mn²⁺(II) emissions at 574 and 680 nm, respectively. The PLE spectra of the two Mn²⁺ emissions

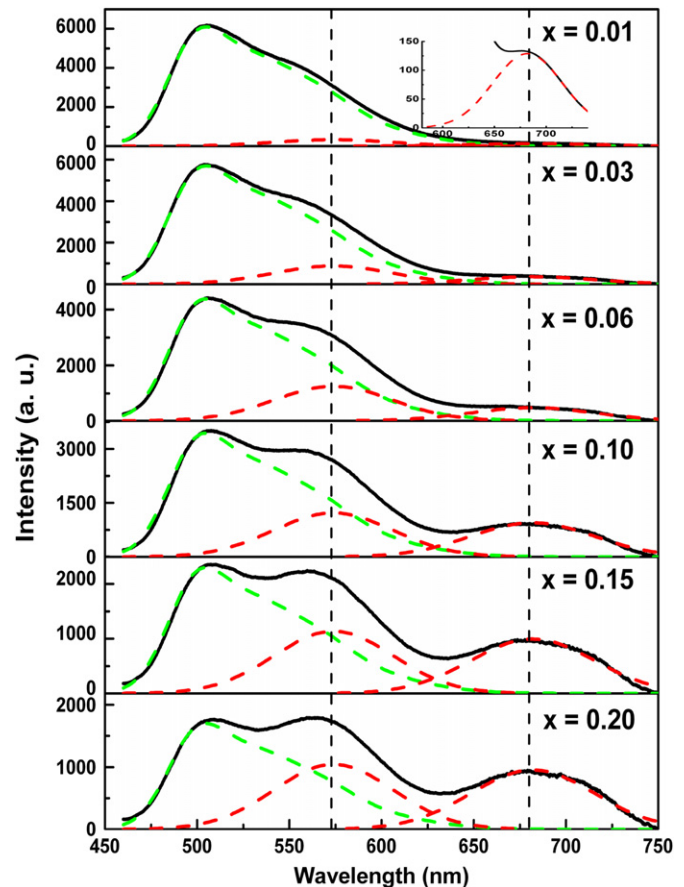


Fig. 2. PL spectra (solid lines) of CSS:0.03Ce³⁺, xMn²⁺ under 450 nm excitation. The resolved individual emissions of Ce³⁺ (505 and 640 nm), Mn²⁺(I) (574 nm), and Mn²⁺(II) (680 nm) are also presented (dashed lines).

are dominated by Ce³⁺ PLE band at 450 nm, giving a strong evidence of the effective Ce³⁺–Mn²⁺ ET. The results are very consistent with the spectral overlap between Ce³⁺ emission in CSS:0.03Ce³⁺ and Mn²⁺ excitation in CSS:0.2Mn²⁺. The increased Mn²⁺(II) emission upon 450 nm excitation also reflects the better overlapping between the spectra of Ce³⁺ emission and Mn²⁺(II) excitation, as shown in Fig. 2(b). Due to the efficient ET of Ce³⁺–Mn²⁺, which greatly enhanced the Mn²⁺ emissions in yellow and red regions, the full color emissions are obtained in CSS:Ce³⁺, Mn²⁺ phosphor with potential application for blue-based PC-WLEDs.

3.2. Energy transfer in CSS:Ce³⁺, Mn²⁺

Fig. 2 depicts the PL spectra of CSS:0.03Ce³⁺, xMn²⁺ under excitation of Ce³⁺ at 450 nm for different Mn²⁺ concentration (x = 0.01–0.2). Three typical emission bands due to Ce³⁺, Mn²⁺(I), and Mn²⁺(II) are overlapped and resolved, as shown by dashed lines, based on three Gaussian distributions in frequency. Mn²⁺(I) and Mn²⁺(II) emission bands can be well fitted with peaks at 574 nm and 680 nm with widths of 74 nm and 83 nm, respectively. Due to Ce³⁺–Mn²⁺ ET, the Ce³⁺ emission intensity reduces followed by the enhancement of Mn²⁺(I) and Mn²⁺(II) emissions as x increases. The decay curves of Ce³⁺ exhibit a similar behavior, as shown in Fig. 3. The decays of Ce³⁺ fluorescence speed up and depart from single exponential function at high Mn²⁺ contents due to the ET. An average fluorescence

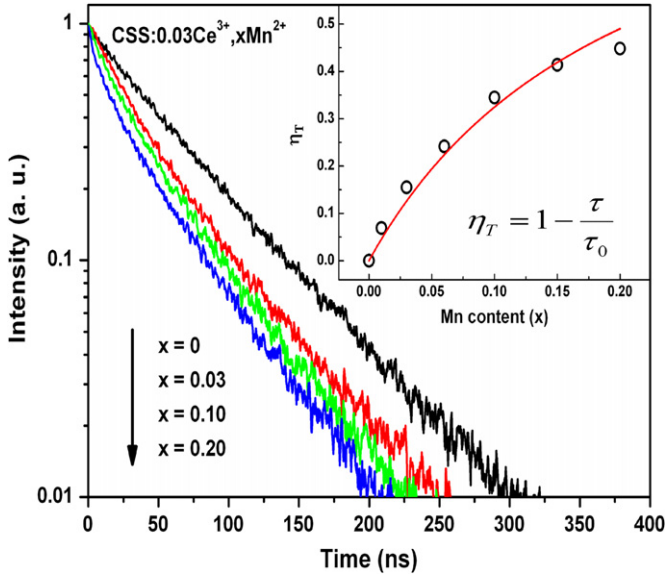


Fig. 3. Fluorescence decays of Ce^{3+} in $\text{CSS:0.03Ce}^{3+}, x\text{Mn}^{2+}$ phosphors ($x=0, 0.03, 0.10,$ and 0.20) and energy transfer efficiency (η_T) as a function of x (inset). τ is the average lifetime calculated using the definition in Eq. (1).

Table 1
Fluorescence lifetimes for Ce^{3+} (τ), $\text{Mn}^{2+}(\text{I})$ (τ_1), and $\text{Mn}^{2+}(\text{II})$ (τ_2) in $\text{CSS:0.03Ce}^{3+}, x\text{Mn}^{2+}$ system.

x	τ (ns)	τ_1 (ms)	τ_2 (ms)
0	58	–	–
0.01	54	4.81	5.27
0.03	49	4.78	5.25
0.06	44	4.83	5.30
0.10	38	4.82	5.24
0.15	34	4.79	5.29
0.20	32	4.81	5.28

lifetime can be defined as

$$\tau = \int_0^{\infty} I(t)dt \quad (1)$$

where $I(t)$ is the fluorescence intensity at time t with normalized unit initial intensity. The fluorescence lifetimes of Ce^{3+} (τ), $\text{Mn}^{2+}(\text{I})$ (τ_1), and $\text{Mn}^{2+}(\text{II})$ (τ_2) are listed in Table 1. The ET efficiency (η_T) can be estimated by $\eta_T = 1 - \tau(x)/\tau_0$, where τ_0 is the fluorescence lifetime of Ce^{3+} for $x=0$. The efficiency increases with the increasing x and reaches 45% for $x=0.20$ (Fig. 3, inset). The fluorescence lifetimes for $\text{Mn}^{2+}(\text{I})$ and $\text{Mn}^{2+}(\text{II})$ are in the order of ms, much longer than that of Ce^{3+} , and the initial rise of the decays is too weak to be detected. The lifetimes also remain nearly unchanged with x for both $\text{Mn}^{2+}(\text{I})$ and $\text{Mn}^{2+}(\text{II})$, indicating that there is no significant concentration-quenching or cross relaxation between Mn^{2+} ions within the range of $x < 0.2$. High emission efficiencies are then expected for both $\text{Mn}^{2+}(\text{I})$ and $\text{Mn}^{2+}(\text{II})$. Under steady state excitation, the rate equations describing the ET from Ce^{3+} to $\text{Mn}^{2+}(\text{I})$ and $\text{Mn}^{2+}(\text{II})$ can be written by

$$W_1 n = n_1 / \tau_1 \quad (2)$$

$$W_2 n = n_2 / \tau_2 \quad (3)$$

where n , n_1 , and n_2 are the populations in the excited states of Ce^{3+} , $\text{Mn}^{2+}(\text{I})$, and $\text{Mn}^{2+}(\text{II})$, respectively; W_1 and W_2 are the ET rates for $\text{Ce}^{3+}-\text{Mn}^{2+}(\text{I})$ and $\text{Ce}^{3+}-\text{Mn}^{2+}(\text{II})$, respectively. The total ET rate W can be written as $W = W_1 + W_2$ and expressed by

$$W = 1/\tau - 1/\tau_0 \quad (4)$$

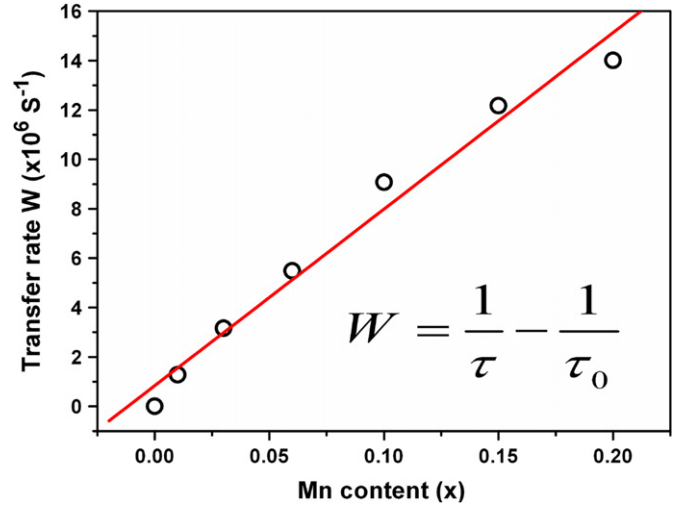


Fig. 4. Energy transfer rate (W) for $\text{CSS:0.03Ce}^{3+}, x\text{Mn}^{2+}$ phosphors as a function of Mn^{2+} concentration ($x=0-0.2$).

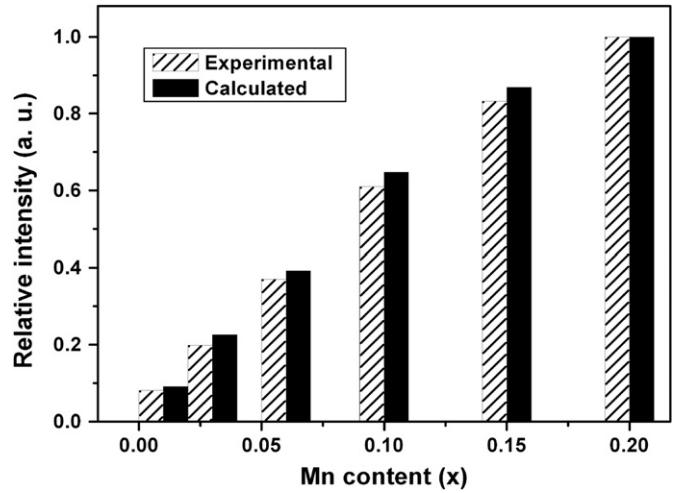


Fig. 5. Comparison of emission intensity ratios obtained by PL spectra in Fig. 2 and calculated by lifetimes listed in Table 1 for $\text{Mn}^{2+}(\text{I})$ and $\text{Mn}^{2+}(\text{II})$ to Ce^{3+} with various x . The maximum ratios are normalized to unity.

As shown in Fig. 4, the ET rate W can reach as high as $14.01 \times 10^6 \text{ s}^{-1}$. Using Eqs. (2) and (3) the emission intensity ratios of $\text{Mn}^{2+}(\text{I})$ to Ce^{3+} , R_1 , and $\text{Mn}^{2+}(\text{II})$ to Ce^{3+} , R_2 , can be calculated as

$$R_1 = W\tau_0 / (R_{2/1} + 1) \quad (5)$$

and

$$R_2 = W\tau_0 / (1 + R_{2/1}^{-1}) \quad (6)$$

where $R_{2/1}$ is the emission intensity ratio of $\text{Mn}^{2+}(\text{II})$ to $\text{Mn}^{2+}(\text{I})$ and $R_{2/1} \cong W_2/W_1$ due to the high emission efficiency and unchanged fluorescence lifetimes of the Mn^{2+} ions. Therefore, the total emission intensity ratio of $\text{Mn}^{2+}(\text{I})$ and $\text{Mn}^{2+}(\text{II})$ to Ce^{3+} (R) can be obtained by

$$R = R_1 + R_2 = W\tau_0 \quad (7)$$

The values of R calculated using Eq. (7) are in good agreement with those directly obtained from PL spectra for various x , as shown in Fig. 5.

4. Conclusions

In summary, Mn^{2+} may either substitute for Ca^{2+} to generate a yellow emission band at 574 nm or for Sc^{3+} to have a red emission band at 680 nm in CSS. High efficient ET from Ce^{3+} to the two Mn^{2+} centers takes place upon blue excitation into Ce^{3+} , resulting in full color luminescence in $\text{CSS}:\text{Ce}^{3+},\text{Mn}^{2+}$. ET dynamical processes are analyzed using steady state rate equation and measured fluorescence lifetimes. ET efficiency (η_{ET}) and rate (W) can reach as high as 45% and $14.01 \times 10^6 \text{ s}^{-1}$, respectively. The full color emissions in $\text{CSS}:\text{Ce}^{3+},\text{Mn}^{2+}$ combining with a blue LED chip potentially provides an idea about PC-WLEDs.

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