



Intense green/yellow emission in $\text{Ca}_8\text{Zn}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}, \text{Mn}^{2+}$ through energy transfer for blue-LED lighting

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ABSTRACT

Eu^{2+} and Mn^{2+} co-doped $\text{Ca}_8\text{Zn}(\text{SiO}_4)_4\text{Cl}_2$ phosphors have been synthesized by a high temperature solid state reaction. Energy transfer from Eu^{2+} to Mn^{2+} is observed. The emission spectra of the phosphors show a green band at 505 nm of Eu^{2+} and a yellow band at 550 nm of Mn^{2+} . The excitation spectra corresponding to $4f^7-4f^65d$ transition of Eu^{2+} cover the spectral range of 370–470 nm, well matching UV and/or blue LEDs. The shortening of fluorescent lifetimes of Eu^{2+} followed by simultaneous increase of fluorescent intensity of Mn^{2+} with increasing Mn^{2+} concentrations is studied based on energy transfer. Upon blue light excitation the present phosphor can emit intense green/yellow in comparison with other chlorosilicate phosphors such as Eu^{2+} and Mn^{2+} co-doped $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$ and $\text{Ca}_3\text{SiO}_4\text{Cl}_2$, demonstrating a potential application in phosphor converted white LEDs.

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1. Introduction

Phosphor converted white light-emitting diodes (LEDs) are regarded as the next generation light sources because of their high luminous efficiency, long lifetimes, environment friendly features, etc. [1]. At present most of the LED phosphors are activated singly doped luminescent materials such as Ce^{3+} doped garnets (typically $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$) [2,3], Eu^{2+} doped silicates [4,5], and nitrides and oxynitrides [6–9]. While doubly doped luminescent material based energy transfer is an alternative for white LED phosphors [10–13]. This type of phosphor in principle can provide full color emission without phosphor blend.

Eu^{2+} activated chlorosilicate luminescent materials exhibit highly efficient luminescence in blue/green spectral region [14–18]. Co-doping Mn^{2+} as a yellow or longer wavelength emitting center in several chlorosilicate phosphors has been studied through energy transfer from Eu^{2+} to Mn^{2+} to generate white light. Ding et al. [19] studied luminescence properties of $\text{Ca}_3\text{SiO}_4\text{Cl}_2:\text{Eu}^{2+}, \text{Mn}^{2+}$ that which a green emission band at 512 nm of Eu^{2+} and a yellow band at 570 nm of Mn^{2+} . White LEDs are fabricated by combining this phosphor with near-ultraviolet chips. Fang et al. [20] studied luminescence properties of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}, \text{Mn}^{2+}$ which shows a green band at 505 nm and a yellow band at 540 nm.

In our previous work, we synthesized a series of intense green emitting (505 nm) phosphors $\text{Ca}_8\text{Zn}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ that is suitable for either UV or blue LED excitations [21]. Especially, $\text{Ca}_8\text{Zn}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ can emit green light stronger than $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ and $\text{Ca}_3\text{SiO}_4\text{Cl}_2:\text{Eu}^{2+}$ under blue light excitation. As a result, it is expected that an intense green/yellow emission could be achieved in Eu^{2+} and Mn^{2+} co-doped $\text{Ca}_8\text{Zn}(\text{SiO}_4)_4\text{Cl}_2$ materials. Although Lin et al. [22] have mentioned the energy transfer from Eu^{2+} to Mn^{2+} in $\text{Ca}_8\text{Zn}(\text{SiO}_4)_4\text{Cl}_2$ host, there has been no research on the luminescence of Eu^{2+} and Mn^{2+} in $\text{Ca}_8\text{Zn}(\text{SiO}_4)_4\text{Cl}_2$ for blue LEDs published, nor a systematic study on energy transfer reported in the literature. In this paper, $\text{Ca}_8\text{Zn}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}, \text{Mn}^{2+}$ is synthesized and its luminescence properties and energy transfer from Eu^{2+} to Mn^{2+} are investigated. It is demonstrated that $\text{Ca}_8\text{Zn}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}, \text{Mn}^{2+}$ can be effectively excited by blue light to emit strong green/yellow light in comparison with $\text{Ca}_3\text{SiO}_4\text{Cl}_2:\text{Eu}^{2+}, \text{Mn}^{2+}$ and $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}, \text{Mn}^{2+}$ phosphors.

2. Experimental

The $\text{Ca}_{8-x}\text{Zn}_{1-y}(\text{SiO}_4)_4\text{Cl}_2(\text{CZSC}):x\text{Eu}^{2+}, y\text{Mn}^{2+}$ phosphors were synthesized by a high-temperature solid-state reaction. The constituent oxides or carbonates CaCO_3 (99.9%), CaCl_2 (99.9%), SiO_2 (99.9%), ZnO (99.9%), Eu_2O_3 (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

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900 °C for 4 h in reductive atmosphere (10% H₂+90% N₂ mixed flowing gas). An excess of CaCl₂ and ZnO was added to the reactants when the phosphors were synthesized. The synthesis procedure of samples Ca₃SiO₄Cl₂(CSC) and Ca₈Mg(SiO₄)₄Cl₂(CMSC) are similar to that described previously [16,18].

Powder X-ray diffraction (XRD) data were collected using Cu K α radiation ($\lambda=1.54056$ Å) on a Bruker D8 Advance diffractometer equipped with a linear position-sensitive detector (PSD-50m, M. Braun), operating at 40 kV and 40 mA with a step size of 0.02° (2 θ) in the range of 15–75°. The measurements of photoluminescence (PL) and photoluminescence excitation (PLE) spectra were performed using a Hitachi F4500 spectrometer equipped with a 150 W xenon lamp under a working voltage of 700 V. The excitation and emission slits were both set at 2.5 nm. 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. Result and discussion

Fig. 1 shows the XRD patterns of CZSC:0.15Eu²⁺ and CZSC:0.15Eu²⁺, 0.05Mn²⁺. The main XRD peaks are in good agreement with the standard data of JCPDS No. 39-1421. Some weak impurity peaks are also observable, which are assigned to the Ca₃SiO₄Cl₂ phase and marked with circle symbols. The intensity of impurity phases is too small that the effect on luminescence and energy transfer of CZSC:Eu²⁺, Mn²⁺ could be neglected.

The PLE and PL spectra of CZSC:0.15Eu²⁺, CZSC:0.05Mn²⁺ and CZSC:0.15Eu²⁺, 0.05Mn²⁺ are shown in Fig. 2. CZSC:0.15Eu²⁺ shows a green emission band at about 505 nm, which corresponds to the 5d¹→4f transition of Eu²⁺. The excitation spectrum monitored at 505 nm shows a broad PLE band within the 300–470 nm range, which is due to the transition from the 4f⁷ ground state to the 4f⁶5d¹ excited state of Eu²⁺ (Fig. 2(a)). CZSC:0.05Mn²⁺ phosphor presents a broad emission band at 550 nm, which corresponds to the ⁴T₁(⁴G)→⁶A₁(⁶S) transition of Mn²⁺ (Fig. 2(b)). The intensity of the Mn²⁺ emission is much weaker than that of Eu²⁺ due to the forbidden d–d transition of Mn²⁺. Obviously, there is a significant spectral overlap between the Eu²⁺ PL and Mn²⁺ PLE spectra, which implies the possibility of energy transfer from Eu²⁺ to Mn²⁺. (Fig. 2(c)) illustrates the PLE and PL spectra of CZSC:0.15Eu²⁺,

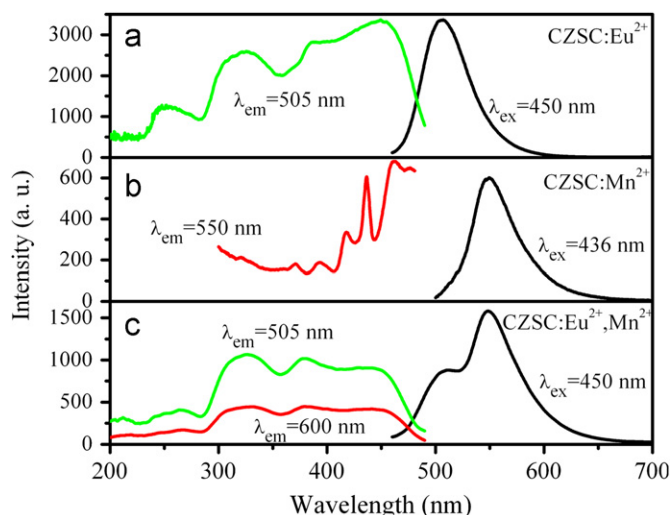


Fig. 2. PL and PLE spectra of CZSC:0.15Eu²⁺ (a), CZSC:0.05Mn²⁺ (b), and CZSC:0.15Eu²⁺, 0.05Mn²⁺ (c).

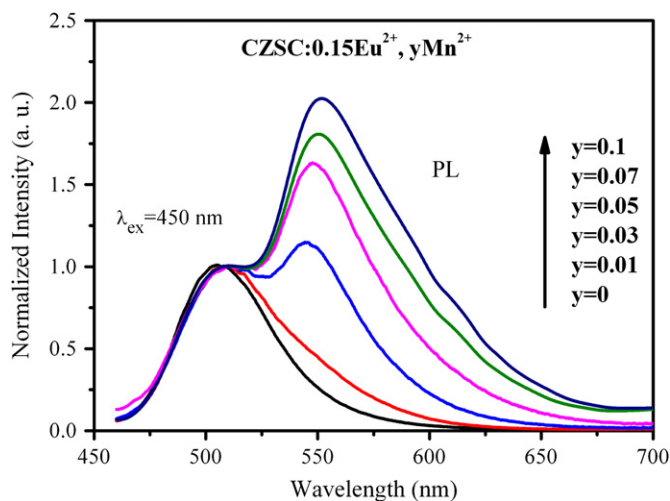


Fig. 3. Normalized emission spectra of CZSC:0.15Eu²⁺, yMn²⁺ for various Mn²⁺ concentrations (y=0.01, 0.03, 0.05, 0.07 and 0.1).

0.05Mn²⁺. It is found that the PLE spectrum of the yellow emission of Mn²⁺ is similar to that of the green emission of Eu²⁺, demonstrating the existence of energy transfer from Eu²⁺ to Mn²⁺ in CZSC. In addition the PL and PLE spectra shape resembling Ca₃SiO₄Cl₂:Eu²⁺, Mn²⁺ is not observed, further confirming that the impurity phases have little effect on the PL spectra and energy transfer. CZSC:0.15Eu²⁺, 0.05Mn²⁺ exhibits a broad and strong PLE band extended to 470 nm, covering almost the full UV–blue region, indicating that CZSC:Eu²⁺, Mn²⁺ can be used as a promising phosphor with green and yellow components applied to near UV and/or blue LED based white LEDs.

Fig. 3 shows the normalized emission spectra of Eu²⁺, Mn²⁺ co-doped CZSC with various Mn²⁺ concentrations (y=0.01, 0.03, 0.05, 0.07 and 0.1). Here, the remarkable enhancements of the yellow band relative to green band are observed with increasing Mn²⁺ concentration. The fluorescence lifetimes of Eu²⁺ (τ_1) and Mn²⁺ (τ_2) with different Mn²⁺ concentrations are presented in Fig. 4. The fluorescence lifetimes of Eu²⁺ (τ_1) reduce and tend to be nonexponential functions with increasing Mn²⁺ concentrations, reflecting the characteristics of energy transfer between donors and acceptors [23]. The energy transfer efficiencies (η_T) are calculated using the equation $\eta_T=1-\tau_1/\tau_0$ and presented in

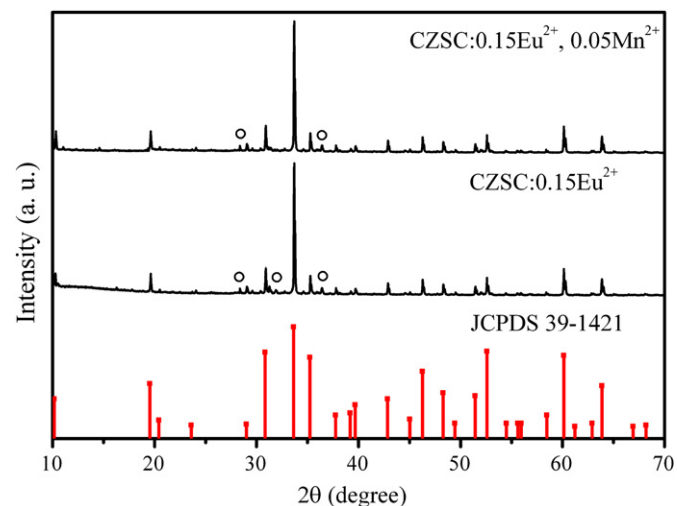


Fig. 1. XRD patterns of CZSC:0.15Eu²⁺ and CZSC:0.15Eu²⁺, 0.05Mn²⁺ samples. The impurity phase is labeled by circle symbols.

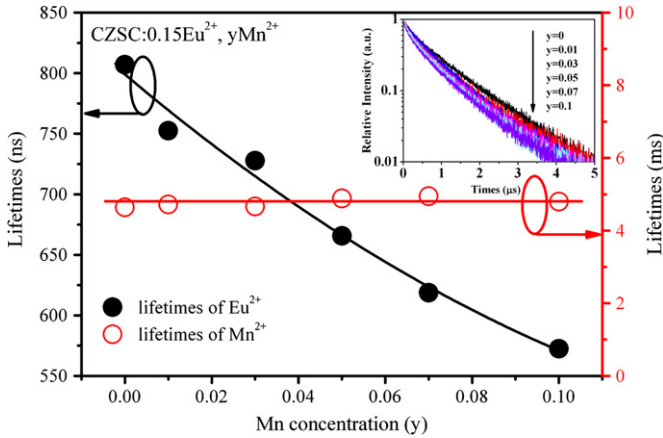


Fig. 4. Fluorescence lifetimes of Eu^{2+} (τ_1) and Mn^{2+} (τ_2) in CZSC:0.15Eu^{2+} , $y\text{Mn}^{2+}$. Inset: fluorescence decay curves of Eu^{2+} (τ_1) with different Mn^{2+} concentrations under 355 nm excitation.

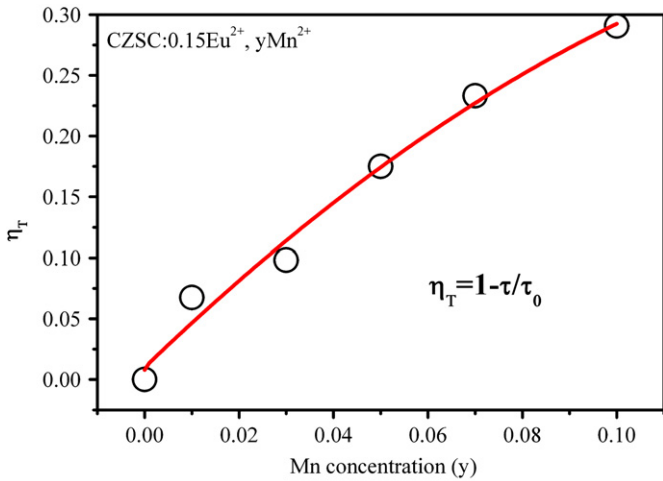


Fig. 5. Dependence of the energy transfer efficiency η_T in CZSC:0.15Eu^{2+} , $y\text{Mn}^{2+}$ on Mn^{2+} content y .

Fig. 5 where τ_0 is fluorescence lifetime of Eu^{2+} in the absence of Mn^{2+} . With increasing Mn^{2+} dopant content, η_T was found to increase gradually and reach 30% for Mn^{2+} concentration of 10%.

Based on energy transfer, the dependences of the emission intensity ratios of Mn^{2+} to Eu^{2+} on Mn^{2+} concentration are calculated by the measured fluorescence lifetimes of Eu^{2+} (τ_1) and Mn^{2+} (τ_2). Under steady excitation, the rate equations describing the energy transfers from Eu^{2+} to Mn^{2+} can be written as follows:

$$W_{\text{Eu-Mn}}n_1 = n_2/\tau_2 \quad (1)$$

where n_1 and n_2 are the populations of Eu^{2+} and Mn^{2+} ions, respectively; The energy transfer rates ($W_{\text{Eu-Mn}}$) can be obtained using the equation:

$$W_{\text{Eu-Mn}} = 1/\tau_1 - 1/\tau_0 \quad (2)$$

Since the fluorescence intensity of a specific level is equal to the product of the population and the radiative rate of the level, using Eq. (1), the dependences of the intensity ratio of the yellow to green emissions on Mn^{2+} concentrations can be written as

$$\frac{I_Y}{I_G} = \frac{W_{\text{Eu-Mn}}\gamma_2\tau_2}{\gamma_1} \quad (3)$$

where γ_1 and γ_2 are radiative rates of Eu^{2+} and Mn^{2+} , respectively, which are independent of Mn^{2+} concentrations. $W_{\text{Eu-Mn}}$ has been

calculated according to Eq. (2). τ_2 has been measured and presented in Fig. 4. Therefore, the intensity ratios I_Y/I_G at various Mn^{2+} concentrations can be calculated using Eq. (3) and scaled to the maximum, as shown in Fig. 6. For comparison, the intensity ratios obtained directly from the emission spectra are also given in Fig. 6. It can be seen that the calculated data based on lifetimes are in good agreement with the experimental ones based on PL spectra, clearly demonstrating that the energy of the yellow emission of Mn^{2+} is derived from energy transfer from Eu^{2+} .

Fig. 7 shows comparable PL and PLE spectra of (a) Eu^{2+} singly doped and (b) Eu^{2+} , Mn^{2+} co-doped CSC, CMSC and CZSC phosphors. It can be seen that CZSC:Eu^{2+} shows efficient emission at 505 nm under 450 nm light excitation in (Fig. 7(a)), which is consistent with our previous results. According to the previous result reported by Ding et al.[19], they choose CSC:0.09Eu^{2+} , 0.12Mn^{2+} to fabricate LED with the UV chip. So, in this work, CSC:0.09Eu^{2+} , 0.12Mn^{2+} phosphor was also synthesized. Compared with the CSC:0.09Eu^{2+} , 0.12Mn^{2+} , the CZSC:0.15Eu^{2+} , 0.05Mn^{2+} shows stronger luminescence intensity than CSC in the application for blue LED. As for CMSC:0.15Eu^{2+} , 0.05Mn^{2+} we notice that the PL peak position at 545 nm in CMSC:Eu^{2+} ,

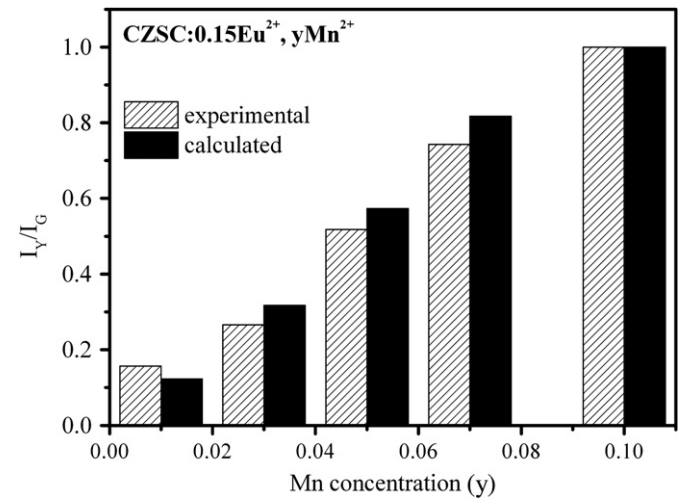


Fig. 6. Calculated and experimental ratios I_Y/I_G of the yellow band to the green band at different Mn^{2+} concentrations. The ratios are scaled to the maximum.

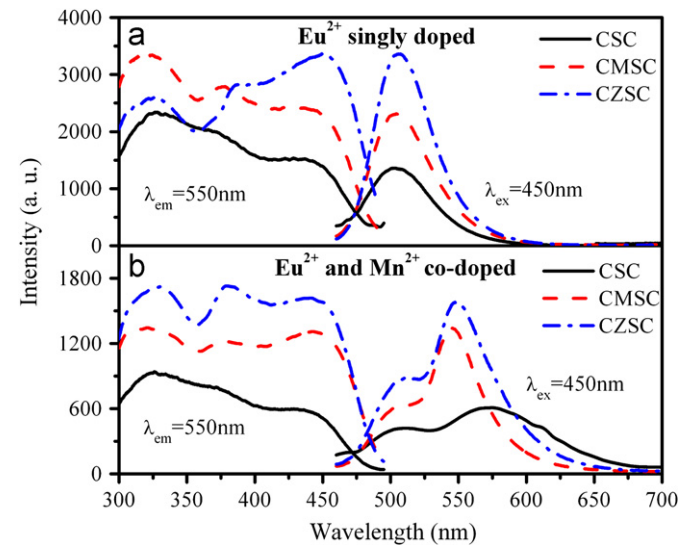


Fig. 7. PLE and PL spectra of (a) Eu^{2+} singly doped and (b) Eu^{2+} , Mn^{2+} co-doped CSC, CMSC, and CZSC phosphors under 450 nm excitation.

Mn^{2+} shifts toward the red side by 5 nm in CZSC:Eu²⁺, Mn²⁺, exhibiting a larger crystal field splitting in CZSC:Eu²⁺, Mn²⁺. The larger crystal field splitting might be caused by a smaller cell volume in CZSC than CMSC because the effective ionic radius for Zn (CN=4) is 0.60 nm and that for Mg (CN=4) is 0.71 nm. The crystal lattices thereby exert larger crystal field on Mn²⁺ ions in CZSC than CMSC. As a result, we can demonstrate that CZSC:Eu²⁺, Mn²⁺ is a potential greenish-yellow phosphor for blue LED based white light devices.

4. Conclusion

In summary, we have prepared Eu²⁺ and Mn²⁺ activated Ca₈Zn(SiO₄)₄Cl₂ phosphors by the high-temperature solid state reaction method. Two emission bands are observed: the one observed at 505 nm is attributed to Eu²⁺ occupying the Ca²⁺ sites and the other band at 550 nm originates from Mn²⁺ occupying Zn²⁺ sites. Luminescence and energy transfer in Eu²⁺ and Mn²⁺ co-doped Ca₈Zn(SiO₄)₄Cl₂ are investigated. The ratio of intensities of the yellow emission (550 nm) to the green (505 nm) obtained from emission spectra is consistent with the theoretical calculation based on energy transfer and lifetime measurements. The luminescence intensity of Ca₈Zn(SiO₄)₄Cl₂:Eu²⁺, Mn²⁺ is compared with related phosphors, indicating that Ca₈Zn(SiO₄)₄Cl₂:Eu²⁺, Mn²⁺ could be a promising green-yellow phosphor for blue LED based white LEDs.

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