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Ceramics International 39 (2013) 6363–6367

CERAMICS INTERNATIONAL

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Preparation of $Ca_4Mg_5(PO_4)_6:Eu^{2+}$, Mn^{2+} phosphor and its photoluminescence properties

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Received 5 October 2012; received in revised form 19 January 2013; accepted 21 January 2013
Available online 29 January 2013

Abstract

Eu^{2+} and Mn^{2+} singly doped and Eu^{2+}/Mn^{2+}-codoped $Ca_4Mg_5(PO_4)_6$ phosphors were synthesized via combustion synthesis. Mn^{2+}-singly doped $Ca_4Mg_5(PO_4)_6$ phosphor exhibits a single red emission in the wavelength range of 500–700 nm due to the $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ transition of Mn^{2+}. Eu^{2+}/Mn^{2+} co-doped phosphor emits two distinctive luminescence bands: a blue one centered at 442 nm originating from Eu^{2+} and a broad red-emitting one peaked at 609 nm from Mn^{2+}. Energy transfers from Eu^{2+} to Mn^{2+} were discovered by directly observing significant overlap of the excitation spectrum of Mn^{2+} and the emission spectrum of Eu^{2+} as well as the systematic relative decline and growth of emission bands of Eu^{2+} and Mn^{2+}, respectively. Based on the principle of energy transfer, the relative intensities of blue and red emission could be tuned by adjusting the contents of Eu^{2+} and Mn^{2+}.

Keywords: C. Optical properties; Phosphate; X-ray diffraction; Energy transfer

1. Introduction

Mn^{2+} ions have been widely investigated in the materials for the luminescence properties [1]. The emission color of Mn^{2+} depends strongly on the crystal field of the occupied sites in the host lattice, varying from green to deep red [2,3]. Generally, tetrahedrally coordinated Mn^{2+} (weak crystal-field) usually gives a green emission, whereas octahedrally coordinated Mn^{2+} (strong crystal-field) exhibits a red emission due to the d–d transition ($^4T_1(^4G) \rightarrow {}^6A_1(^6S)$) of Mn^{2+}. Owing to forbidden d–d transition of Mn^{2+}, the Mn^{2+} single doped phosphor generally does not show considerable emission [4]. The method to enhance the emission intensity of Mn^{2+} is by introducing Eu^{2+} as a sensitizer. Eu^{2+} can transfer its absorbed energy fully or partly to Mn^{2+}; consequently single-phase and multicolor-emitting phosphors can be obtained [5]. Hence, Eu^{2+} and Mn^{2+} co-doped luminescent materials have been studied extensively over the past few years.

As an important family of luminescent materials, phosphate compounds have attracted more and more attention because of their excellent thermal and chemical stability [6–8]. Compound $Ca_4Mg_5(PO_4)_6$ was first confirmed to exist as a single phase in the system of $CaO–MgO–P_2O_5$ by Fuchs in 1967 [9,10]. Currently, $Ca_4Mg_5(PO_4)_6$ has been considered to be an efficient luminescent host [11]. Our group has synthesized the phosphor $Ca_4Mg_5(PO_4)_6:Eu^{2+}$ and investigated the luminescence properties. To the best of our knowledge, no paper has been published on the preparation of Eu^{2+} and Mn^{2+} doubly activated $Ca_4Mg_5(PO_4)_6$ phosphors. Based on these considerations, in this paper, we report the preparation of phosphors $Ca_4Mg_5(PO_4)_6:Eu^{2+}$, Mn^{2+} and discuss the energy transfer process between Eu^{2+} and Mn^{2+}.

2. Experimental

2.1. Synthesis of $Ca_4Mg_5(PO_4)_6:Eu^{2+}$, Mn^{2+} phosphor

$Ca_4Mg_5(PO_4)_6:Eu^{2+}$, Mn^{2+} was prepared by the combustion synthesis technique [8]. Raw materials are $NH_4H_2PO_4$ (AR), $Ca(NO_3)_2 \cdot 4H_2O$ (AR), $Mg(NO_3)_2 \cdot 6H_2O$ (AR) and

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http://dx.doi.org/10.1016/j.ceramint.2013.01.062

urea (AR). Eu_2O_3 and $MnCO_3$ with purity of 99.99% were dissolved in dilute HNO_3. Stoichiometric amounts of raw materials were added and dissolved in a minimum amount of distilled water, then transferred to a porcelain crucible and introduced into a muffle furnace maintained at 600 °C. Initially, the solution boiled and underwent dehydration, followed by decomposition with evolution of a large amount of gases. Then, spontaneous ignition occurred and underwent smoldering combustion. The reaction duration was approximately 3–5 min, and then the product was cooled to room temperature naturally in its self-generating atmosphere. The obtained powder was placed in a porcelain boat inside a tubular furnace and heated slowly to 900 °C under a reducing atmosphere (5% H_2/95% N_2), flowing at a rate of 50 mL/min. The sample was obtained by reducing at this temperature for 3 h and then cooled to room temperature. Gas flow was maintained until the furnace was cooled to room temperature.

2.2. Characterizations of $Ca_4Mg_5(PO_4)_6$:Eu^{2+}, Mn^{2+} phosphor

Phase characterization was carried out on a Bruker D8 diffractometer (Bruker Co. Ltd., Karlsruhe, Germany) operating at 40 kV, 40 mA with Bragg–Brentano geometry using Cu Kα radiation (λ=1.54056 Å). PL measurements were performed using an RF-5301 fluorescence spectrometer (Shimadzu, Japan) with a xenon lamp as the excitation source. The PL decay curves of Eu^{2+} were measured with an FLS920 Combined Steady State and Lifetime Spectrometer (Edinburgh Instrument) with a nanosecond flash lamp as the light source. For comparison, all measurements were performed at room temperature with identical instrumental parameters.

3. Results and discussion

3.1. Phase analysis

Fig. 1 shows the XRD patterns of $Ca_{3.92}Mg_5(PO_4)_6$:$0.08Eu^{2+}$ and $Ca_{3.92}Mg_{4.85}(PO_4)_6$:$0.08Eu^{2+}$, $0.15Mn^{2+}$. The predominant phase in the samples is the $Ca_4Mg_5(PO_4)_6$ phase (JCPDS Card no. 11-0231) with a small amount of secondary $Ca_{2.86}Mg_{0.14}(PO_4)_2$ phase (JCPDS Card no. 70-0681, ♦). Results indicate that the introduction of activator Eu^{2+} or Mn^{2+} does not cause any significant change in the host structure and the dopants have been incorporated in the lattice.

There are 10 cation sites excluding the 6 tetrahedral P sites in the structure of $Ca_4Mg_5(PO_4)_6$ [12]. Of these 10, four (Cal-4) are fully occupied by Ca, coordinated to either 7 or 8 oxygens. A fifth nominally Ca site (Ca5) is partially occupied by Mg, shows 6-fold coordination. The remaining 5 sites (Mgl-5) are either six or seven coordinated and are occupied only by Mg. Eu^{2+} ions probably occupy the Ca^{2+} sites in $Ca_4Mg_5(PO_4)_6$, because ionic radii of Eu^{2+} and Ca^{2+} are very close in magnitude, (that is Eu^{2+}: r=1.17 Å with CN=6, r=1.20 Å with CN=7 and Ca^{2+}: r=1.00 Å with CN=6, r=1.06 Å with CN=7) [5]. In the lattice of $Ca_4Mg_5(PO_4)_6$, the ionic radius of Mg is about 0.72 Å (CN=6). In the case of $Ca_4Mg_5(PO_4)_6$:Eu^{2+}, Mn^{2+} phosphor, Mn^{2+} (r=0.67 Å with CN=6) easily substitutes the Mg site because of its similarity in ionic size and valence. The external crystal field affects the emission wavelength of Mn^{2+}. Therefore, when Mn^{2+} substitutes the Mg site in $Ca_4Mg_5(PO_4)_6$, we can expect that Mn^{2+} will show red emission.

3.2. Luminescence spectra of solely Eu^{2+} or Mn^{2+} doped $Ca_4Mg_5(PO_4)_6$

Fig. 2 shows the emission (PL) and the excitation (PLE) spectra of Eu^{2+} doped $Ca_4Mg_5(PO_4)_6$ phosphor. The PLE spectrum consists of a broad band absorption in the range of 300–420 nm centered at 350 nm, due to the 4f5d multiplets of the Eu^{2+} excited state. Under the excitation of UV light, the PL spectrum presents a broad blue emission band centered at around 420 nm, which is attributed to the well-known $4f^65d^1(t_{2g})\rightarrow 4f^7(^8S_{7/2})$ transition of Eu^{2+} [13]. No other characteristic emission peaks from Eu^{3+} are observed in the PL spectrum, indicating that Eu^{3+} have been reduced to Eu^{2+} completely in our experiments. Moreover, the dependence of the PL intensities of $Ca_{4-x}Mg_5(PO_4)_6$:xEu^{2+} on the concentration of Eu^{2+} (x) is shown in the inset of Fig. 2. The PL intensity increases with increasing Eu^{2+} content until it reaches a maximum at x=0.08; then it decreases as the content of Eu^{2+} further increases because of the concentration quenching which is caused by the energy transfer between the identical Eu^{2+} ions. The luminescence properties agree well with that reported [11].

The PL and PLE spectra of $Ca_4Mg_{4.85}(PO_4)_6$:$0.15Mn^{2+}$ are shown in Fig. 3(a). The PLE spectrum shows a band centered at 402 nm, corresponding to the transition from $^6A_1(^6S)$ to [$^4A_1(^4G)$, $^4E(^4G)$]. Upon excitation with 402 nm light, the broad red emission located at 609 nm due to the spin-forbidden $^4T_1(^4G)\rightarrow$ $^6A_1(^6S)$ transition of Mn^{2+} has clearly been obtained. Comparing the PLE spectrum of the Mn^{2+} ions in Fig. 3(a) with the PL spectrum of the Eu^{2+} ions in Fig. 2, a significant spectral overlap is observed by comparing the excitation band of Mn^{2+} with the emission band of Eu^{2+}. Therefore, it is expected that a possibility of resonance-type energy transfer from Eu^{2+} to Mn^{2+} would happen.

3.3. Luminescence properties of Eu^{2+} and Mn^{2+} co-doped $Ca_4Mg_5(PO_4)_6$

Resonance-type energy transfer generally plays a central role in the Eu^{2+} and Mn^{2+} codoped host, such as $Sr_2Mg_3P_4O_{15}$ [14], $BaMg_2(PO_4)_2$ [15], $Na(Sr,Ba)PO_4$ [16] and so on. Eu^{2+} has been proven to be an efficient sensitizer for Mn^{2+}; thus it is possible to obtain a phosphor with blue and red double colors emission by the introduction of two activators Eu^{2+} and Mn^{2+} simultaneously if the energy

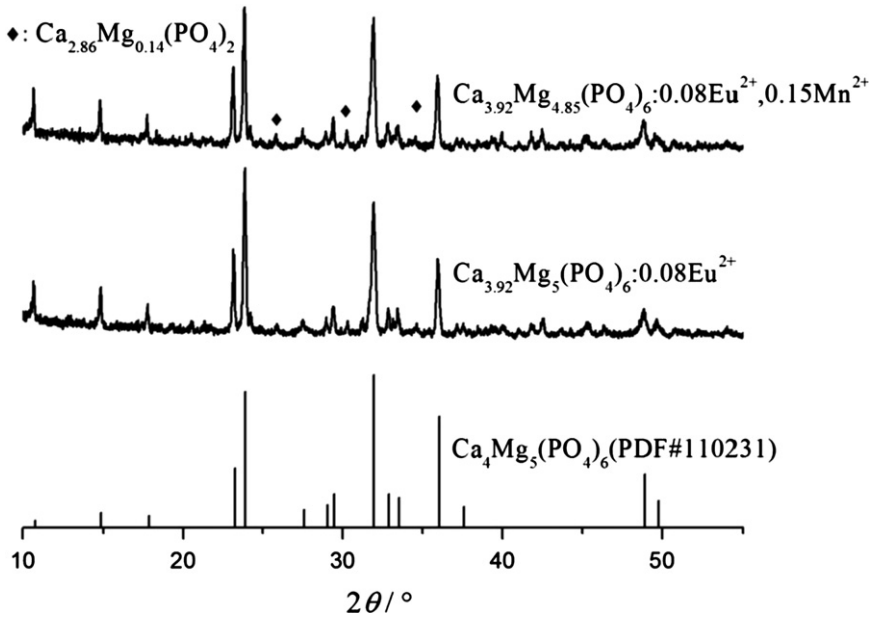

Fig. 1. XRD patterns of the prepared $Ca_{3.92}Mg_5(PO_4)_6$:0.08Eu^{2+} powder and $Ca_{3.92}Mg_{4.85}(PO_4)_6$:0.08$Eu^{2+}$,0.15$Mn^{2+}$ powder.

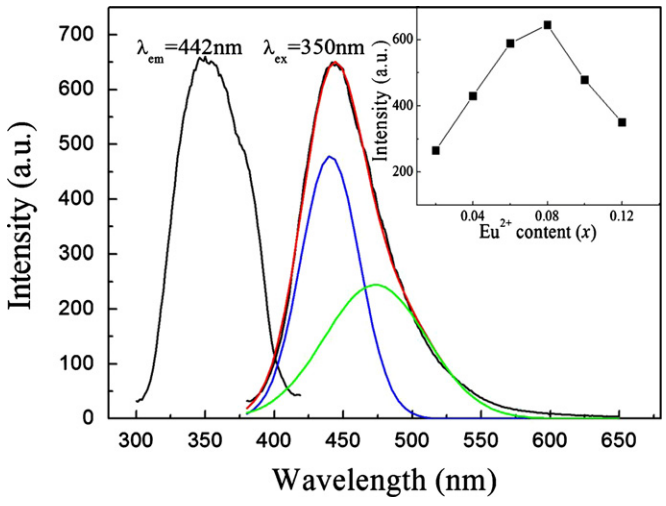

Fig. 2. Excitation and emission spectra of $Ca_{3.92}Mg_5(PO_4)_6$:0.08Eu^{2+}; inset shows the dependence of $Ca_{4-x}Mg_5(PO_4)_6$:xEu^{2+} emission intensity (λ_{ex}=350 nm) on the Eu^{2+} contents (x).

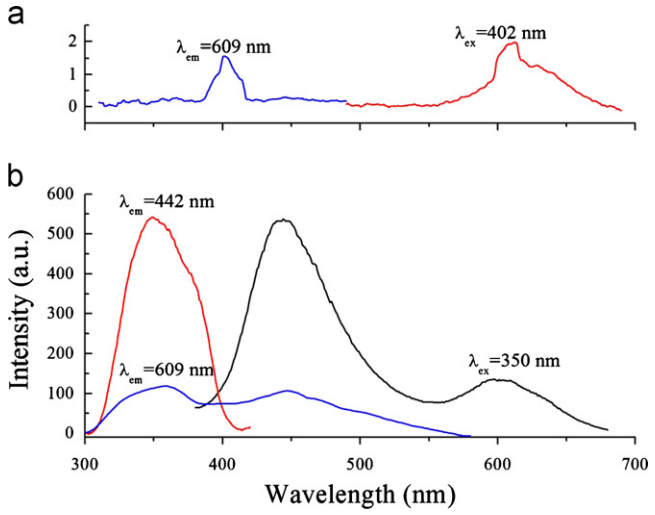

Fig. 3. Emission and excitation spectra of $Ca_4Mg_{4.85}(PO_4)_6$:0.15Mn^{2+} (a) and $Ca_{3.92}Mg_{4.85}(PO_4)_6$:0.08$Eu^{2+}$, 0.15$Mn^{2+}$ (b).

transfer between two activators exists in the $Ca_4Mg_5(PO_4)_6$ host.

Fig. 3(b) presents the PL and PLE spectra of Eu^{2+} and Mn^{2+} doubly doped $Ca_4Mg_5(PO_4)_6$ phosphor. The PLE spectrum monitored at 609 nm consists of both the PLE bands of Eu^{2+} and Mn^{2+}, suggesting the existence of effective resonant energy transfer from Eu^{2+} to Mn^{2+}. The PL spectrum of the codoped sample exhibits not only a broad blue emission band of Eu^{2+} centered at 442 nm but also a red emission band of Mn^{2+} centered at 609 nm upon the optimal excitation of Eu^{2+} at 350 nm, which confirms the expectation of energy transfer process. The corresponding energy levels scheme [18,19] of $Ca_4Mg_5(PO_4)_6$: Eu^{2+}, Mn^{2+} with optical transitions and energy transfer processes is displayed in Fig. 4. Eu^{2+} first absorbs UV light (300–420 nm), electron is pumped to the higher $4f^65d$ level, and then non-radiatively relaxes to the lowest component of $4f^65d$ level. Because the value of energy level of excited $4f^65d$ state of Eu^{2+} is close to the ^4E and other levels of Mn^{2+} ions, it is highly possible that energy transfers from Eu^{2+} to Mn^{2+} ions, promoting it from $^6A_1$ ground state to ^4E and other levels. Then the excited Mn^{2+} relaxes to the $^4T_1$ levels non-radiatively and gives the strong emission of Mn^{2+}.

The PL spectra for $Ca_{3.92}Mg_{5-y}(PO_4)_6$:0.08$Eu^{2+}$, y$Mn^{2+}$ (y=0–0.5) phosphors with varied Mn^{2+} concentrations under excitation of 350 nm are presented in Fig. 5. The PL intensity of the Eu^{2+} emission at 442 nm decreases, and that of the Mn^{2+} emission at 609 nm increases, with increasing Mn^{2+} content. This phenomenon is attributable to the

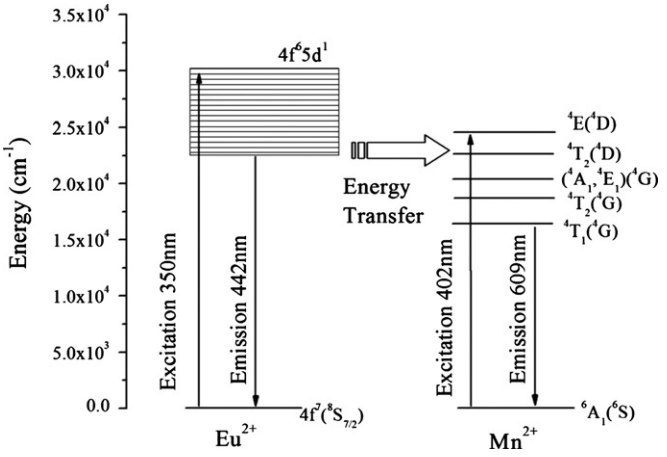

Fig. 4. Schematic energy-level diagram of Eu^{2+} and Mn^{2+}.

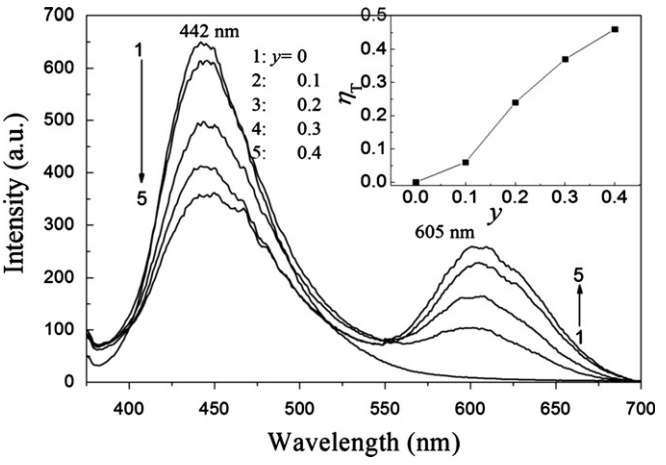

Fig. 5. Emission spectra of samples $Ca_{3.92}Mg_{5-y}(PO_4)_6$:$0.08Eu^{2+}$, yMn^{2+} (λ_{ex}=350 nm) for different Mn^{2+} concentrations: y=0, 0.1, 0.2, 0.3 and 0.4. Inset: dependence of energy transfer efficiency η_T on the Mn^{2+} contents (y).

energy transfer from Eu^{2+} to Mn^{2+} in the $Ca_4Mg_5(PO_4)_6$ matrix [17]. The energy transfer from Eu^{2+} to Mn^{2+}, which results in the improvement of Mn^{2+} emission intensity, is strongly evidenced by the decay behavior of the Eu^{2+} emission in co-doped samples. The PL decay curves of the Eu^{2+} ions in $Ca_{3.92}Mg_{5-y}(PO_4)_6$:$0.08Eu^{2+}$, yMn^{2+} phosphors were measured with excitation at 350 nm and monitored at 442 nm, and are depicted in Fig. 6. The lifetime decay curves have been analyzed by curve-fitting and all the decay curves can be fitted successfully based on the following double-exponential equation:

$$I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1)$$

where I and I_0 are the luminescence intensities at times t and 0, A_1 and A_2 are fitting constants, and τ_1 and τ_2 are the short and long lifetimes for exponential components, respectively.

For $Ca_{3.92}Mg_5(PO_4)_6$:$0.08Eu^{2+}$, the lifetime values were determined to be 0.008 μs and 0.612 μs. The results reveal that there are two lattice sites occupied by Eu^{2+} ions in $Ca_4Mg_5(PO_4)_6$ host [12], which is also supported by the emission spectrum of $Ca_{3.92}Mg_5(PO_4)_6$:$0.08Eu^{2+}$.

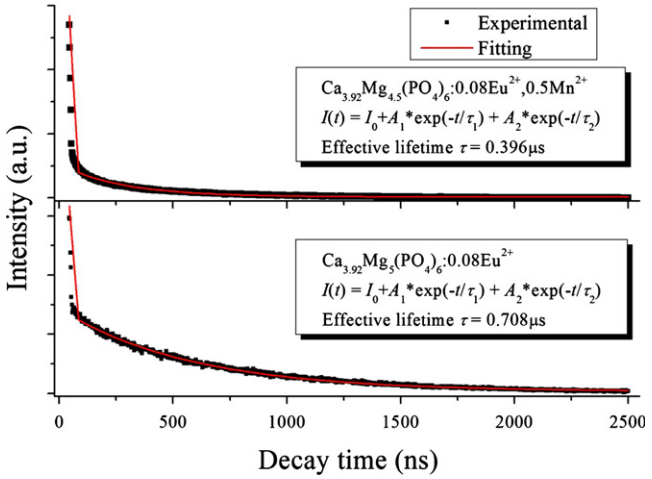

Fig. 6. Selected decay curves of Eu^{2+} emission (442 nm) in the system $Ca_{3.92}Mg_{5-y}(PO_4)_6$:$0.08Eu^{2+}$, yMn^{2+} (y=0 and 0.5) excited by 350 nm UV light.

As shown in Fig. 2, the PL spectrum of $Ca_{3.92}Mg_5(PO_4)_6$:$0.08Eu^{2+}$ exhibits an asymmetrical emission band at 441 nm, tailing toward 475 nm, indicating that two overlapping emission bands exist.

The effective lifetime value can be defined as

$$\tau = \int_0^\infty tI(t)\mathrm{d}t \Big/ \int_0^\infty I(t)\mathrm{d}t \quad (2)$$

From Eq. (2), the effective lifetimes were determined to be 0.708, 0.661, 0.542, 0.472, and 0.396 μs for $Ca_{3.92}Mg_{5-y}(PO_4)_6$:$0.08Eu^{2+}$, yMn^{2+} with y=0, 0.1, 0.2, 0.3, and 0.4, respectively. It can be seen that the decay lifetime for the Eu^{2+} ions decreases monotonically with an increase in the Mn^{2+} doping content, which is a strong evidence for the energy transfer from the Eu^{2+} to Mn^{2+} ions, and the energy transfer process may happen via resonant-type mechanism [20].

The energy transfer efficiency of η_T from the Eu^{2+} to Mn^{2+} ions can be obtained experimentally by the decay lifetime; meanwhile, the energy transfer efficiency can be expressed by the equation [21]

$$\eta_T = 1 - \tau/\tau_0 \cong 1 - I_S/I_{S0} \quad (3)$$

where τ_0 and τ are the lifetimes of Eu^{2+} ions in the absence and presence of Mn^{2+} ions, respectively. I_{S0} and I_S are the luminescence intensities of the sensitizer Eu^{2+} in the absence and presence of the activator Mn^{2+}, respectively. η_T is calculated as a function of Mn^{2+} content and illustrated in Fig. 5. Along with the increase of Mn^{2+} content, η_T was found to increase gradually from y=0 to 0.5. The energy transfer efficiency proves that the energy transfer process from Eu^{2+} to Mn^{2+} ions is efficient.

With increase in the content of Mn^{2+}, the ratio of emission intensity of Eu^{2+} to Mn^{2+} changes because of energy transfer from Eu^{2+} to Mn^{2+}. Fig. 7 presents the CIE chromaticity coordinated for $Ca_{3.92}Mg_{5-y}(PO_4)_6$:$0.08Eu^{2+}$, yMn^{2+} phosphors calculated according to the PL spectra. The color tone changes from blue to reddish purple as the

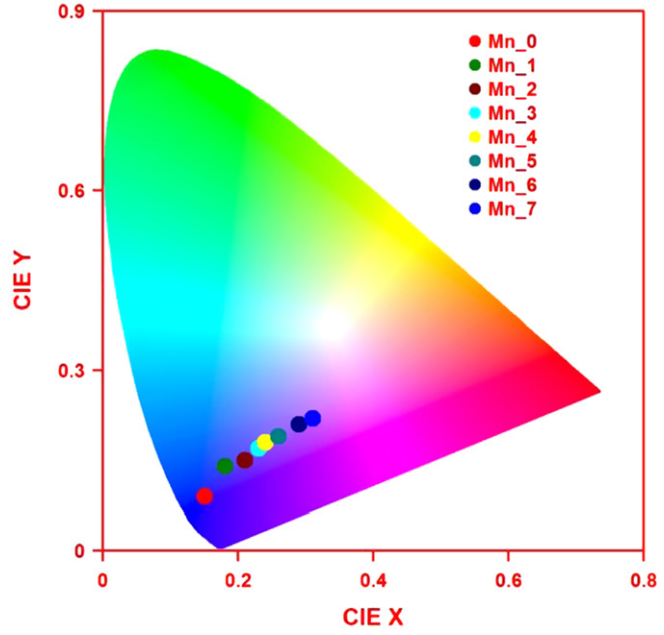

Fig. 7. Color coordinates $Ca_{3.92}Mg_{5-y}(PO_4)_6$:$0.08Eu^{2+}$,$yMn^{2+}$ with different Mn^{2+} concentrations (y=0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4; labeled as Mn_0, Mn_1, Mn_2, Mn_3, Mn_4, Mn_5, Mn_6 and Mn_7, respectively) in CIE 1931 chromaticity diagram.

concentration of doped Mn^{2+} ions is increased. Thus the color coordinates of $Ca_{3.92}Mg_{5-y}(PO_4)_6$:$0.08Eu^{2+}$, yMn^{2+} phosphors can be adjusted, and they can be combined with other phosphors to obtain white light easily.

4. Conclusion

In summary, Eu^{2+} and Mn^{2+} singly or doubly doped $Ca_4Mg_5(PO_4)_6$ were synthesized and their optical properties were also investigated. Broad blue and red emission bands were detected in the emission spectra of $Ca_4Mg_5(PO_4)_6$:Eu^{2+} and $Ca_4Mg_5(PO_4)_6$:Mn^{2+}, respectively. Eu^{2+} and Mn^{2+} codoped $Ca_4Mg_5(PO_4)_6$ phosphor presents blue and red double color emissions, and the effective resonance-type energy transfer plays an important role in this phosphor. The relative intensity ratio of blue emission to the red emission could be tuned by adjusting the contents of Eu^{2+} and Mn^{2+} in the co-doped phosphor.

Acknowledgments

The authors acknowledge the financial support from the Natural Science Foundation of Hubei Province (No. 2011CDB421).

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