Novel Tunable Green-Red Luminescence in Mn$^{2+}$ Doped Ca$_9$Tb(PO$_4$)$_7$ Phosphors Based on the Mn$^{2+}$ Regulation and Energy Transfer

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Abstract: β-Ca$_3$(PO$_4$)$_2$ type phosphors Ca$_9$Tb(PO$_4$)$_7$:Mn$^{2+}$ were fabricated by high temperature solid state reaction. Under 377 nm light excitation, the Ca$_9$Tb(PO$_4$)$_7$ host displays the green emission attributable to the characteristic emission of Tb$^{3+}$ ions peaking at 488, 542, 586, and 620 nm, respectively. The red broadband emission is observed when Ca$_9$Tb(PO$_4$)$_7$ is doped with Mn$^{2+}$ ions. The emission is attributed to the energy transfer from Tb$^{3+}$ to Mn$^{2+}$ ions; this facilitates the realization of the tunable green–red emission. The energy transfer mechanism from Tb$^{3+}$ to Mn$^{2+}$ is defined as quadrupole–quadrupole interaction. Furthermore, the thermal stability of Ca$_9$Tb(PO$_4$)$_7$:Mn$^{2+}$ samples has been studied, and it can maintain half the emission intensity exceeding 424 K. This demonstrates their potential applications in white light LEDs (w-LEDs).

Keywords: high thermal stability; β-Ca$_3$(PO$_4$)$_2$; tunable emission

1. Introduction

Phosphate-based phosphors can form various crystal field environments that impose on the emitting center [1]. β-Ca$_3$(PO$_4$)$_2$ and its derivatives are important compounds that have been widely researched for use in white light LEDs (w-LEDs), temperature sensing and plasma display panels. Their advantages include high luminescent efficiency, as well as good physical and chemical stability. Recently, researchers have developed numerous single-component phosphate phosphors with tunable color emission and white light emission that can be used in UV-excited w-LEDs which have been developed by researchers, such as Sr$_9$Mg$_{15}$f(PO$_4$)$_7$:Eu$^{2+}$, (Ca,Sr)$_9$(PO$_4$)$_7$:Eu$^{2+}$/Mn$^{2+}$, Ca$_2$Sr(PO$_4$)$_2$:Eu$^{2+}$/Mn$^{2+}$, Ca$_9$Bi(PO$_4$)$_7$:Ce$^{3+}$/Tb$^{3+}$/Mn$^{2+}$, Ca$_8$MgLu(PO$_4$)$_7$:Ce$^{3+}$/Tb$^{3+}$/Mn$^{2+}$, (Ca,Mg,Sr)$_9$(PO$_4$)$_7$:Eu$^{2+}$/Mn$^{2+}$ and Ca$_{9-x-y}$Mg$_x$Sr$_y$Ba$_z$Ce(PO$_4$)$_7$:Eu$^{2+}$/Mn$^{2+}$ [2–8]. Furthermore, β-Ca$_3$(PO$_4$)$_2$ and its derivatives have garnered interest for application in temperature sensing, owing to the excellent thermal stability of Mn$^{2+}$ emission which originates from the energy compensation of stored electrons [9,10]. To manufacture an efficient solid-state lighting equipment, it is crucial for the phosphors to possess the following characteristics: adjustable emission color to regulate the ratio of each color in the spectra, environmental friendliness, and appreciable thermal stability to maintain increased luminous efficiency at high temperature.

Phosphors doped with Mn$^{2+}$ have exhibited a broad emission band ranging from 500 to 700 nm, which is determined by the matrix crystal field. Green emission is usually displayed in weak crystal fields (tetrahedrally coordinated sites) and red emission is demonstrated in strong crystal fields (octahedral coordinated sites) [11–13]. In addition, the Mn$^{2+}$ ion usually exhibits red emission in Ca$_9$Ln(PO$_4$)$_7$ structure compounds. However, the absorption and emission bands of
Mn$^{2+}$ d–d transitions are relatively weak due to parity and spin confinement. Therefore, it is necessary to enhance their emission intensity via energy transfer using sensitizers like Ce$^{3+}$, Tb$^{3+}$, Eu$^{2+}$ ions. Moreover, the efficient sensitization of Mn$^{2+}$ emission and tunable color should be realized, for example, Ca$_8$BaCe(PO$_4$)$_2$:Tb$^{3+}$/Mn$^{2+}$, Ca$_9$Y(PO$_4$)$_2$:Ce$^{3+}$/Mn$^{2+}$, Ca$_9$Ce(PO$_4$)$_2$:Eu$^{2+}$/Mn$^{2+}$ and 0.1Ca$_9$Y(PO$_4$)$_2$·0.9Ca$_{10-z}$Na$_{1+z}$PO$_4$:Eu$^{2+}$, Mn$^{2+}$ [3,4,10,14–16]. However, the Ce$^{3+}$ and Eu$^{2+}$ ions are typically formed in a reducing atmosphere, and the Tb$^{3+}$ ions are formed in an air atmosphere with a lower, more stable consumption. In addition, Tb$^{3+}$ ions have previously been used as one of the matrix ions, and as a sensitizer to enhance the red emission [17,18]. A series of the whitlockite structure Ca$_9$Ln(PO$_4$)$_2$ (Ln = lanthanide) materials with matrix luminescence originating from the β-Ca$_3$(PO$_4$)$_2$ derivatives are receiving increasing interest in this field of research [19]. In this Ca$_9$Ln(PO$_4$)$_2$ group, Ln includes all the non-radioactive rare earth (Eu, Ho, Tb, Dy, Pr, Sm, Yb, Nd, Er and Tm) elements. These matrix materials exhibit the characteristic emission of Ln ions. Therefore, the possibility of using Tb$^{3+}$ ions as sensitizers to improve the luminescence properties of Mn$^{2+}$ in the whitlockite structure can be considered. Based on this, it can be concluded that Ca$_9$Tb(PO$_4$)$_2$ (CTP) will be an important candidate for strengthening the Mn$^{2+}$ emission.

In this study, we have reported green–red tunable color Mn$^{2+}$-doped CTP phosphors synthesized via high-temperature solid method. The CTP host displays a characteristic green emission of Tb$^{3+}$ ion upon 377 nm light excitation. In addition, the red emission is observed while Mn$^{2+}$ doped into CTP, owing to the energy transfer from Tb$^{3+}$ to Mn$^{2+}$ ions. Additionally, the fluorescence lifetimes have been studied systematically. The Mn$^{2+}$ emission reaches the maximum at $x = 0.3$, and then monotonically decreases with an increase in the Mn$^{2+}$ concentrations, owing to the concentration quenching. Besides, the thermal stability of the phosphors CTP:Mn$^{2+}$ phosphors we prepared has been researched: they can maintain half the strength even at temperatures above 424 K, indicating that these whitlockite structure phosphors have promising applications in w-LEDs.

2. Experimental

2.1. Materials and Synthesis

Whitlockite structure luminescent materials of CTP:Mn$^{2+}$ were synthesized by high-temperature solid-state method. The raw materials were CaCO$_3$ (99.7%), Tb$_4$O$_7$ (99.99%), (NH$_4$)$_2$HPO$_4$ (99.7%) and MnCO$_3$ (99.7%), and they were weighed according to the stoichiometric ratio of Ca$_9$$_{-x}$Tb(PO$_4$)$_2$•xMn$^{2+}$ ($x = 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7$), ground thoroughly, and mixed in an agate mortar and ground thoroughly to obtain the mixtures. Firstly, the mixtures were pre-sintered in a tube furnace at 500 °C for 2 h. The intermediate products were then reground thoroughly and transferred to a high-temperature tube furnace, sintered at 1200 °C for 4 h in the ambient atmosphere. Finally, the obtained products were ground to a fine powders for the following measurements.

2.2. Characterization

The X-ray diffraction (XRD) patterns were performed on a D8 ADVANCE X-ray diffractometer (Bruker, Billerica, MA, USA) with Cu Kα irradiation ($\lambda = 1.5406$ nm). Photoluminescence excitation (PLE) and photoluminescence (PL) spectra were collected on an Edinburgh FLS 980 Fluorescence Spectrophotometer (Edinburgh Instruments, Edinburgh, Britain). The temperature-dependent PL spectra were also measured on the Edinburgh FLS 980 Fluorescence Spectrophotometer equipped with the variable temperature accessories. SEM images were characterized using a scanning electron microscope (Sipra 55 Sapphire, Zeiss, Oberkochen, German), and the elemental mapping was collected via EDX spectroscopy (Oxford X-max 20, Oxford, London, UK).
3. Results and Discussion

3.1. Phase Characterization and SEM Analysis

The phase purity of the CTP:Mn$^{2+}$ samples was verified using XRD measurements; the representative XRD patterns are shown in Figure 1. Ca$_9$Tb(PO$_4$)$_7$ can not be found in the Joint Committee on Powder Diffraction Standards (JCPDS); however, the obtained samples are indexed to the JCPDS data PDF#46-0402 (Ca$_9$Y(PO$_4$)$_7$), demonstrating that the obtained phosphors are crystallized in a single phase. There is no any clear impure phase that occurs after the Mn$^{2+}$ ion was doped into the CTP host. These results demonstrate that Mn$^{2+}$ ion doping can preserve the crystal structure. The CTP host has three types of Ca$^{2+}$ ions positions with six-fold, eight-fold and nine-fold coordination, respectively.

In addition, Figure 1b indicates that certain diffraction peaks move towards a large angle direction while the content of Mn$^{2+}$ ions increase. This movement can be attributed to the Mn$^{2+}$ ions doping. Based on the charge balance and effective ionic radius, the Ca$^{2+}$ ion (1.00 Å, coordination (CN) = 6; 1.12 Å, CN = 8; 1.18 Å, CN = 9), Mn$^{2+}$ ion (0.83 Å, CN = 6; 0.96 Å, CN = 8), we suggest the simultaneous substitution of Ca$^{2+}$ ions with Mn$^{2+}$ ions at three sites. Therefore, the shift of the diffraction peaks to a larger angle direction can be interpreted by the Bragg’s equation $2d \times \sin\theta = n\lambda$, when the Mn$^{2+}$ ions with a smaller radius replace the Ca$^{2+}$ ions with a larger radius.

![Figure 1](image)

Figure 1. (a) Typically XRD patterns of CTP:xMn$^{2+}$ together with the standard data, (b) The XRD patterns ranging from 30.8 to 31.4°.

The SEM images and EDS element mapping for the morphology investigations of the CTP:Mn$^{2+}$ phosphor are shown in Figure 2. The CTP:Mn$^{2+}$ phosphor displays appreciable crystallinity and the crystal shape is irregular with an approximate size of 10 μm. The element mapping images exhibit the uniform distribution of Ca, Tb, P, O, and Mn on the as-prepared phosphor, demonstrating that the Mn$^{2+}$ ion was successfully doped into the CTP matrix.

3.2. Luminescence Performance and Energy Transfer of CTP:Mn$^{2+}$ Phosphor

The PL and PLE spectra of CTP host are shown in Figure 3. It is evident from a series of peaks that the Tb$^{3+}$ ions are effectively excited, displaying how the different relative intensity obtained the maximum value under 377 nm light excitation. The intense green light peaking at 488, 542, 586, 620 nm are attributed to the transition from the $^5D_4$ level to $^7F_6$, $^7F_5$, $^7F_4$ and $^7F_3$ level, respectively [20–23]. Monitoring at 542 nm, the PLE spectrum shows a series of narrow 4f–4f transition lines of Tb$^{3+}$ in the range of 300–400 nm, which is ascribed to the electron transition from lower energy level $^7F_6$ to the excited level including $^5H_7$ (316 nm), $^5L_6$ (340 nm), $^5G_4$ (351 nm), $^5L_9$ (358 nm), $^5D_2$ (367 nm), $^5D_3$ (377 nm), and $^5D_4$ (482 nm) levels, respectively [17,24,25].
Red emission is observed after the Mn$^{2+}$ ion was doped into the CTP host, which is ascribed to the $^{4}T_{1}(4G) ightarrow ^{6}A_{1}(6S)$ transition of the Mn$^{2+}$ ions, as shown in Figure 4a. The green emission clearly decreases as the Mn$^{2+}$ ion concentration increases, which could be ascribed to the energy transfer from sensitizer (Tb$^{3+}$) to activator (Mn$^{2+}$). In addition, the red emission of Mn$^{2+}$ ions initially increases and reaches its maximum when the Mn$^{2+}$ content is fixed at 0.3, then starts to decrease owing to the concentration quenching as the concentration continues to increase. Green–red tunable color is realized with the Mn$^{2+}$ content increasing in the CTP host—the corresponding Commission Internationale de l’Eclairage (CIE) coordinate diagram and photographs are shown in Figure 4b. Furthermore, the energy transfer diagram from Tb$^{3+}$ to Mn$^{2+}$ ions in the CTP host is illustrated in Figure 5.
which is consistent with the reduction in the PL intensity of Tb\(^{3+}\) ions. The following function is used to estimate the energy transfer efficiency [7,9,17]:

\[ \eta = 1 - \frac{\tau}{\tau_0} \]  

where \(\eta\) is the energy transfer efficiency, \(\tau\) is the average lifetime of Tb\(^{3+}\) ions with Mn\(^{2+}\) ions content, \(\tau_0\) is the average lifetime of Tb\(^{3+}\) ions without Mn\(^{2+}\) ions, respectively.

The calculated energy transfer efficiencies are depicted in Figure 6b. In addition, the efficiency of energy transfer monotonically increases with the increase in Mn\(^{2+}\) ions content, reaching 96.3% at \(x = 0.7\).
Time-resolved spectra are typically employed to explicitly identify the luminescent centers in luminous systems [28,29]. The time-resolved spectroscopy of the sample CTP:0.1Mn2+ is determined for the further verification of energy transfer from the Tb3+ to Mn2+ ion in the CTP host, as shown in Figure 7a. Two emission bands that belong to Tb3+ and Mn2+ ions are clearly observed, and the relative intensity between the Tb3+ and Mn2+ ions decreases with an increase in the decay times increasing as depicted in Figure 7b. In addition, the intensity of Tb3+ ions remains unchanged after 10 ms, and the intensity of Mn2+ ions is persisting to reduce over time, indicating that the energy is gradually transferred from Tb3+ to the Mn2+ ions and the energy transfer process is completed after 10 ms. These results establish the energy transfer from Tb3+ to Mn2+ ions.

Generally, the exchange interaction and electric multipole multipole interaction can lead to a nonradiative energy transfer between the sensitizer and activator [2–8,10,14–16]. If the exchange
is the reason for energy transfer, the emission intensity of Mn$^{2+}$ ions will exhibit the following relationship [30,31]:

$$\ln(I_0/I) \propto C$$  \hspace{1cm} (4)

where $I_0$ and $I$ represent the emission intensity of the Tb$^{3+}$ ions in the absence and presence of Mn$^{2+}$ ions, respectively. $C$ is the total contents of Tb$^{3+}$ and Mn$^{2+}$ ions in the CTP matrix. If electric multipole–multipole interaction is the primary cause of energy transfer from Tb$^{3+}$ to Mn$^{2+}$ ions, the emission intensity of Mn$^{2+}$ ions will be determined using the following function:

$$\ln(I_0/I) \propto \ln C$$  \hspace{1cm} (5)

the slope of the function is $\alpha/3$, where $\alpha$ equals to 6, 8, 10 which stand for dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interactions, respectively. Thus, the relationships of $\ln(I_0/I)$ and $\ln C$ are depicted in Figure 8. It could be observed that the slope of linear fitting curve is 3.2974 in Figure 8, thus, the $\alpha$ is close to 10. This result illustrates that the energy transmission between the Tb$^{3+}$ and Mn$^{2+}$ ion is mainly caused by quadrupole–quadrupole interaction.

![Figure 8](image-url)

**Figure 8.** The dependence of $\ln(I_0/I)$ on $\ln C$ in the CTP:xMn$^{2+}$ phosphors.

### 3.3. Temperature-Dependent PL Performance of CTP:Mn$^{2+}$ Phosphor

Thermal stability is one significant factor for phosphors adopted in w-LEDs [32,33]. Normally, the emission intensity of phosphors should be maintained at a temperature above 423 K (150 °C) because the light-emitting diodes generate heat for long durations of time. Typically, the emission intensity monotonically decreases with an increase in temperature, and displays lower luminous efficiency. A series of phosphors with good thermal stability have been reported in recent years [10,34–36]. To investigate the thermal stability of a CTP:Mn$^{2+}$ phosphor, the temperature-dependent (303 to 573 K) PL spectra of the CTP:0.3Mn$^{2+}$ phosphor was collected, as shown in Figure 9a. It can be easily observed that the emission intensity can maintain a half level even with a temperature up to 424 K.

To further study the thermal stability of the CTP:Mn$^{2+}$ phosphor, the corresponding PL intensity of Tb$^{3+}$ and Mn$^{2+}$ ions for each temperature points are depicted in Figure 9b. Significantly, the CTP:0.3Mn$^{2+}$ phosphor we obtained has maintained the half emission intensity at 424 K, a result which demonstrates the good thermal stability for the CTP:Mn$^{2+}$ phosphor. The relationship of $\ln(I_0/I-1)$ on $1/kT$ of the CTP:0.3Mn$^{2+}$ phosphor is shown in Figure 10, and the value of activation energy ($E_a$) is defined as 0.1846 eV. In conclusion, the as-prepared tunable green–red CTP:Mn$^{2+}$ phosphors have promising application in w-LEDs.
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Figure 9. (a) Temperature-dependent PL spectra of the CTP:0.3Mn$^{2+}$ phosphors ranging from 303 to 573 K; and (b) the variation tendency of Tb$^{3+}$ and Mn$^{2+}$ ions from 303 to 573 K.

Figure 10. The relationship of the ln(I/I_0−1) versus 1/kT for the CTP:0.3Mn$^{2+}$ phosphor.

4. Conclusions

In sum, the color-tunable green-red Mn$^{2+}$ doped Ca$_9$Tb(PO$_4$)$_7$ phosphors have synthesized via traditional solid phase method. Under 377 nm light excitation, the Ca$_9$Tb(PO$_4$)$_7$ matrix shows green emission with several peaks belonging to the transition from 5D$_4$ level to 7F$_6$, 7F$_5$, 7F$_4$ and 7F$_3$ level, respectively. Red emission is clearly observed as the Mn$^{2+}$ ions doping into Ca$_9$Tb(PO$_4$)$_7$. Color-tuning from green to red is realized by varying the Mn$^{2+}$ contents. The sensitization of Tb$^{3+}$ to Mn$^{2+}$ ions effectively. The energy transmission efficiency reaches a maximum of 96.3% at $x = 0.7$. In addition, the theoretical mechanism for energy transmission from Tb$^{3+}$ to Mn$^{2+}$ ions has been investigated, and it is found to be dominated by the quadrupole-quadrupole interaction. Meanwhile, the Ca$_9$Tb(PO$_4$)$_7$:Mn$^{2+}$ phosphor indicates good thermal stability, maintained the approximately half emission level at 424 K (150 °C), which demonstrates that the Ca$_9$Tb(PO$_4$)$_7$:Mn$^{2+}$ phosphor can be potentially applied to w-LEDs.

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