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White-light emission in a single-phase $Ca_{9.3}Mg_{0.7}K(PO_4)_7$:$Eu^{2+}$,$Tb^{3+}$,$Mn^{2+}$ phosphor for light-emitting diodes

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A B S T R A C T

To explore new white-emitting phosphor material for LEDs, a series of $Ca_{9.23-x-2y}Mg_{0.7}K_{1+y}(PO_4)_7$:0.07$Eu^{2+}$,x$Mn^{2+}$,y$Tb^{3+}$ (CMKP:0.07Eu^{2+},xMn^{2+},yTb^{3+}, $0 \le x \le 0.2$, $0 \le y \le 1.0$) phosphors were prepared using the solid-state reaction method, and their photoluminescence properties were studied. Upon 365-nm excitation, the CMKP:0.07Eu^{2+} phosphor shows an asymmetric bluish-green emission band with a dominant peak at 460 nm. By introducing Tb^{3+} and Mn^{2+} into the CMKP:0.07Eu^{2+} phosphor, white emission can be obtained, whose chromaticity coordinates and correlated color temperature are (0.366, 0.362) and 4306 K, respectively, for the CMKP:0.07Eu^{2+},0.05Mn^{2+},0.3Tb^{3+} sample. The excitation spectra cover a wide wavelength region from 240 to 450 nm, which could well match the emission wavelength of a near-ultraviolet LED chip. In Eu^{2+}-Tb^{3+}-Mn^{2+} tri-doped CMKP, three energy-transfer (ET) types have been found, i.e., $Eu^{2+} \rightarrow Tb^{3+}$, $Eu^{2+} \rightarrow Mn^{2+}$, and $Tb^{3+} \rightarrow Mn^{2+}$. The corresponding ET processes and mechanism are discussed. The results of the above investigation imply that the CMKP:0.07Eu^{2+},xMn^{2+},yTb^{3+} phosphors could apply to white LEDs.

1. Introduction

White-light-emitting diodes (w-LEDs) are considered next-generation solid-state lighting systems due to their excellent properties, such as high luminous efficiency, energy savings, long operation time, reliability, and lack of toxic mercury [1–4]. They are widely seen as a superior replacement for conventional inefficient incandescent and fluorescent lighting [5]. In w-LEDs, the luminescence carrier is a phosphor, which is responsible for converting radiation energy into visible light [6]. The traditional method used to obtain w-LEDs is to combine a GaN blue LED chip with YAG:Ce^{3+}, a yellow phosphor. However, the resulting w-LED suffers from a low color rendering index (Ra < 80) and a high correlated color temperature (CCT > 6500 K) owing to the lack of a red spectral component [7,8]. To avoid the above disadvantages, near-ultraviolet (NUV) or UV chips coated with red-green-blue (RGB) tri-color phosphors are considered to be another attractive way to realize white light with high Ra and color uniformity [3,9]. Unfortunately, white LEDs fabricated using two or three different kinds of phosphors could cause fluorescence re-absorption and non-uniformity of luminescent properties, resulting in the loss of luminous efficiency and color variation against time [10]. Recently, a second fabrication method, namely using a single-phased white-light-emitting phosphor that can be excited effectively by UV light, has attracted much attention due to its merits of color stability and excellent color rendering [6,11]. One of the strategies for generating white light from single-phase phosphors is the doping of multi-luminescent ions into the same host, in which energy transfer (ET) plays an important role. As the eventual performance of w-LED-based devices strongly depends on the luminescence properties of the phosphor used [1,12], designing and searching for novel and efficient white-light-emitting, single-phase phosphors have become hot topics in lighting.

It is known that some of the rare-earth (RE) and transition-metal ions can be employed as the sensibilizers or activators, such as Eu^{2+}, Tb^{3+}, and Mn^{2+}. Eu^{2+} shows broad excitation and emission bands based on the electron $4f^6 5d^1 - 4f^7$ transition, whose emission color is strongly dependent on the host lattice and can be shifted from the UV to the red region [3,13]. Tb^{3+} is also a widely used RE activator that gives a green emission. However, two problems exist for the Tb^{3+} ion: One is the lack of efficient and broad excitation band in the NUV region, and the other is the weak emission intensity due to the spin-forbidden f-f transition [14]. The transition-metal Mn^{2+} can play an important role as orange/red emitting activators in the phosphors, which is strongly affected by the crystal field of the host materials [6]. The optical intensity of Mn^{2+} is quite weak, however, because the d-d transition of Mn^{2+} is spin forbidden and difficult to pump [15]. Based on these aspects, it is necessary to enhance the emission intensities of Tb^{3+} and

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Mn^{2+} in a phosphor, and one important strategy is to co-dope sensitizers with broad absorption and emission bands, such as Eu^{2+}, during which a part of the excitation energy of the sensitizer can be transferred to Tb^{3+} and Mn^{2+}. In addition, by controlling the ET efficiency from the sensitizer to activator, tunable emission as well as white light can be obtained. To obtain efficient phosphors, the host material is also an important factor in addition to the luminescent ions. It has been reported that phosphate-based phosphors have good physical and chemical stability, require modest preparation conditions, and exhibit excellent optical properties [16,17]. The compound $Ca_{10}K(PO_4)_7$ (CKP) is known to be iso-structural with β-$Ca_3(PO_4)_2$, and various Ca^{2+} sites exist in CKP [18]. Thus, abundant spectral features could be expected when the luminescent ions are doped into different Ca^{2+} sites. Liu*et al.* reported that four Eu^{2+} emission centers could be obtained in Eu^{2+}-activated CKP [19]. We synthesized CKP: xEu^{2+},ySr^{2+},zMg^{2+} ($0 \le x \le 0.02$, $0 \le y \le 0.5$, $0 \le z \le 0.1$) phosphors and investigated the tunable-emission properties and found that the CKP:$0.07Eu^{2+}$,$0.07Mg^{2+}$ phosphor has a quantum efficiency of 26.6%, and that the emission spectrum from 500 to 700 nm was enhanced by doping Mg^{2+} into CKP:$0.07Eu^{2+}$ [20]. Thus, to obtain white emission, $Ca_{9.3}Mg_{0.7}K(PO_4)_7$ (CMKP) was chosen in this work. To the best of our knowledge, the luminescence properties of the single-phase Eu^{2+}-Tb^{3+}-Mn^{2+} tri-doped CMKP phosphor for white emission and the detailed ET processes have not been studied.

In this work, to develop new white-emitting phosphor materials, a series of CMKP:Eu^{2+},Tb^{3+},Mn^{2+} phosphors were designed and their spectral characteristics under NUV excitation were investigated.

2. Experimental

The powder samples of $Ca_{9.23\text{-}x\text{-}2y}Mg_{0.7}K_{1+y}(PO_4)_7$:$0.07Eu^{2+}$, xMn^{2+},yTb^{3+} (CMKP:$0.07Eu^{2+}$,xMn^{2+},yTb^{3+}, $0\le x \le 0.2$, $0 \le y \le 1.0$) were prepared using the conventional solid-state reaction method. The starting materials included K_2CO_3 (99%), $CaCO_3$ (99%), $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ (99%), $(NH_4)_2HPO_4$ (99%), $MnCO_3$ (99%), Tb_4O_7 (99.99%), and Eu_2O_3 (99.99%). Part of the K_2CO_3 was used as a charge compensation reagent when the Tb^{3+} was doped. Stoichiometric amounts of the starting materials were thoroughly mixed and ground together in an agate mortar. The reactant mixture was firstly fired at 600 °C for 3 h in air, re-ground, and then calcined at 1230 °C for 5 h in a reduction atmosphere (N_2:H_2 = 95:5). The phase purity was determined by using an ARL X'TRA powder X-ray diffractometer (XRD) with Cu Kα radiation (λ = 1.5418 Å) operating at 40 kV and 35 mA. The photoluminescence (PL) was recorded on an EI-FS5 fluorescence spectrophotometer with a 150-W xenon lamp as the light source. The spectral resolution and wavelength accuracy are 0.1 and ± 0.5 nm, respectively. The excitation and emission spectra were corrected by using the standard light source of the halogen tungsten lamp and deuterium lamp. The decay curves were measured by the EI-FS5 apparatus equipped with a 360-nm pulsed EPLED. The time resolution for recording decay curves was 95 ps. The temperature-dependent measurement was carried out using an EI-FS5 fluorescence spectrophotometer, and the samples were mounted on a heating device, the temperature of which could be changed from room temperature to 473 K in steps of 0.1 K.

3. Results and discussion

Fig. 1 shows the XRD patterns of the CMKP:$0.07Eu^{2+}$,xMn^{2+},yTb^{3+} ($0 \le x \le 0.2$, $0 \le y \le 1.0$) samples. It was found that all the diffraction peaks could be indexed to the $Ca_{10}K(PO_4)_7$ (CKP) structure (JCPDS Card No. 45–0138), and the introduction of the luminescent ions does not cause any obvious impurity. It was also found that the diffraction peaks exhibit a shift toward the large-angle direction compared with those for the JCPDS Card. This is because the ionic radius of Mg^{2+} introduced into the CKP host lattices is smaller than that of Ca^{2+}.

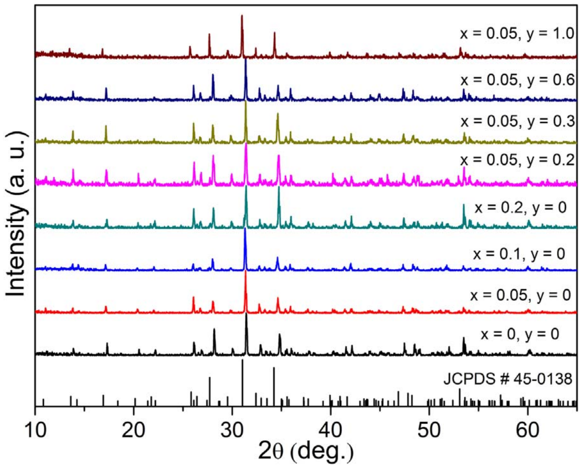

Fig. 1. XRD patterns of CMKP:$0.07Eu^{2+}$,xMn^{2+},yTb^{3+} ($0 \le x \le 0.2$, $0 \le y \le 1$).

Fig. 2(a) presents the emission spectra of the CMKP:$0.07Eu^{2+}$,xMn^{2+} ($0\le x \le 0.2$) samples measured upon 365-nm excitation at a temperature of 298 K. It can be observed that the emission band of the Eu^{2+}-single-doped CMKP covers a broad wavelength region of 400–750 nm that could be attributed to the $4f^7-4f^65d^1$ transition of Eu^{2+} [20]. However, the emission spectrum shape is asymmetrical, indicating there is more than one Eu^{2+} emission center in this phosphor, which is in agreement with the analysis in Ref. [20]. When the Mn^{2+} is co-doped, a new emission band around 647 nm appeared. To identify this new red emisison band, a Mn^{2+}-single-doped CMKP phosphor was prepared. Fig. 2(b) shows its excitation and emisison spectra measured at a temperature of 298 K. By monitoring 647 nm, the Mn^{2+} characteristic excitation peaks were observed, and the excitation peaks at approximately 340, 372, 403, 417, and 446 nm could be attributed to the Mn^{2+} transitions from the $^6A_1(^6S)$ ground state to the $^4E(^4D)$, $^4T_2(^4D)$, $[^4A_1(^4G),^4E(^4G)]$, $^4T_2(^4G)$, and $^4T_1(^4G)$ levels, respectively [21]. Under 403-nm excitation, a red emisison band from 500 to 800 nm was found, which could be ascribed to the $^4T_1(^4G)$-$^6A_1(^6S)$ transition of Mn^{2+} [21]. This band shape of the Mn^{2+} emisison is the same as those at approximately 647 nm in Fig. 2(a), revealing that the new red emisison bands in Fig. 2(a) also belong to the $^4T_1(^4G)$-$^6A_1(^6S)$ transition of Mn^{2+}. In addition, it can be also found from Fig. 2(a) that the Mn^{2+} emission intensity exhibits an increase with increasing Mn^{2+} content until x = 0.1 and starts to decay beyond this Mn^{2+} concentration due to the concentration quenching of Mn^{2+}. The above observation implies that an ET from Eu^{2+} to Mn^{2+} could occur. To investigate this implication, Fig. 2(c) represents the excitation spectra of the typical CMKP:$0.07Eu^{2+}$,$0.1Mn^{2+}$ sample monitored at 460 and 647 nm at a temperature of 298 K. Obviously, both excitation bands are strong and broad, covering a wavelength region of 240–450 nm, which could well match the emission wavelength of the NUV LED chip. These excitation bands can be attributed to the $4f^7-4f^65d^1$ transition of Eu^{2+}, which reveals that the ET between Eu^{2+} and Mn^{2+} has occurred. To further verify this ET, Fig. 3 shows the decay curve of the CMKP:$0.07Eu^{2+}$,xMn^{2+} ($0 \le x \le 0.2$) phosphors with 360-nm excitation and 460-nm emission at a temperature of 298 K. The decay curve can be well fitted by a double-exponential function as

$$I = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2), \tag{1}$$

where τ_1 and τ_2 are the fast and slow components of the luminescent lifetimes, and A_1 and A_2 are the fitting parameters, respectively. τ_i and A_i (i = 1, 2) are summarized in Table 1. The average lifetime can be determined according to the following equation [22]:

$$<\tau> = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2). \tag{2}$$

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