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Synthesis and luminescence properties of $KCaPO_4:Eu^{2+},Tb^{3+},Mn^{2+}$ for white-light-emitting diodes (WLED)

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Abstract: In order to obtain a single-host white-light phosphor, a series of $KCaPO_4$ powder samples tri-doped with Eu^{2+}, Tb^{3+} and Mn^{2+} were synthesized via high-temperature solid-state reaction method. Their structural and luminescence properties were investigated. Under proper ultraviolet excitation (255–405 nm), white light was obtained, consisting of blue, green and red emissions stemming from Eu^{2+}, Tb^{3+}, Mn^{2+} ions respectively. The temperature stability of our sample was analyzed by studying the variation tendency of CIE chromaticity coordinates at different temperatures. The results indicated that this phosphor could yield good color stability when utilized in WLED.

Keywords: single-phase white-light phosphor; photoluminescence; energy transfer; color stability; CIE chromaticity coordinates; rare earths

In recent years, white light emitting diode (WLED) has drawn much attention due to its good performance characteristics, such as high efficiency, long lifespan, energy saving and environmentally-friendly aspects[1,2]. Among different kinds of WLED lamps, it is most promising for phosphors converted WLEDs to be applied in a wide variety of fields such as industrial illumination and solid light-emission devices[3]. There are two main important approaches based on the combination of a single LED chip with phosphors. One is to partially convert the emission of the blue LED chip into appropriate visible light. The most typical example for this is the combination of YAG:Ce^{3+} yellow phosphor with a blue emitting InGaN LED, which has been widely utilized in lighting sources, automobile lamps and backlighting, etc.[4–6] However, YAG:Ce^{3+} phosphor suffers from some drawbacks such as poor color rendering index and low stability of color temperature[4,7,8]. The other approach is usually based on the mixing of red (R), green (G) and blue (B) lights converted from the excitation of UV (or near-UV) LED by different color phosphors. A common path to help us achieve this goal involves mixing different color phosphors, for example, $Y_2MoO_6:Eu^{3+}$ (red), $12CaO\text{-}7Al_2O_3:Ce^{3+},Tb^{3+}$ (green) and $BaMgAl_{10}O_{17}:Eu^{2+}$ (blue)[9–13]. However, the mixture of multiple phosphors may be subjected to color shift due to the host aging, resulting from different hosts involved usually sustaining different aging conditions. In order to enhance the color stability, a single-phase white phosphors is proposed to be a potential solution, since different activators in only one kind of host would experience similar aging condition because of similar atomic surroundings the activators would face.

In recent years, phosphate was widely used in WLED, and it has been reported that $KCaPO_4$ can be used as a potential candidate of UV-LED phosphor host for its high temperature stability[14–16]. To our best knowledge, there has been some reports about the luminescence properties of singly-doped and co-doped $KCaPO_4$ phosphors[15–19], but no report on the tunable color emission of the tri-doped $KCaPO_4:Eu^{2+},Tb^{3+},Mn^{2+}$ phosphor. In this paper, powder samples were successfully synthesized and their luminescence properties were investigated under UV excitation. By studying the variation tendency of CIE chromaticity coordinates with different temperatures, we concluded that $KCaPO_4:Eu^{2+},Tb^{3+},Mn^{2+}$ phosphor could be a candidate for WLED phosphors due to its good temperature stability.

1 Experimental

The samples of $KCaPO_4:Eu^{2+},Tb^{3+},Mn^{2+}$ with different doping concentrations including $KCaPO_4$:0.9%Eu^{2+}, x%Tb^{3+},1.5%Mn^{2+} (x=5, 6, 7, 8), $KCaPO_4$:y%Eu^{2+}, 7%Tb^{3+},1.5%Mn^{2+} (y=0.9, 3.5–7) and $KCaPO_4$:7%Eu^{2+}, 7%Tb^{3+},2%Mn^{2+} were synthesized by high-temperature

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solid-state reaction method. The constituent oxides and carbonates consisted of K_2CO_3 (A.R.), $CaCO_3$ (A.R.), $(NH_4)H_2PO_4$ (A.R.), $MnCO_3$ (A.R.), Eu_2O_3 (99.99%) and Tb_4O_7 (99.99%). Stoichiometric molar ratio of the raw materials were thoroughly mixed, with fully ground and pre-fired at 650 ºC for 6 h under a weak reducing atmosphere (5% H_2 and 95% N_2). Subsequently after being ground again, the obtained sample were re-calcined at 1000 ºC for 10 h. The crystal structures were analyzed by an X-ray diffractometer (Rigaku-TTR-III) with Cu Kα radiation (λ=0.15418 nm) in the 2θ range from 10° to 70°. Excitation and emission spectra were recorded with a spectrometer (HITACHI 850), which utilizes a 150 W Xe lamp as its excitation source.

2 Results and discussion

2.1 Structural properties

The XRD patterns of some samples with the standard data of $KCaPO_4$ are shown in Fig. 1. At first, to ascertain how Ca^{2+} ions are substituted by the doping ions, we compared two possible charge balanced the molar ratio: (1) a pair of Tb^{3+} ion and K^+ ion substitute for two Ca^{2+} ions, one Mn^{2+} ion replaces one K^+ ion and leaves one K^+ vacancy, and one Eu^{2+} ion occupies one Ca^{2+} site; (2) one Tb^{3+} ion simultaneously replaces one Ca^{2+}-K^+ pair, while the replacement of Eu^{2+} and Mn^{2+} ions are not changed. The doping concentration of the samples we choose to ascertain proper substitution is $KCaPO_4$:7% Eu^{2+},7%Tb^{3+}, 2%Mn^{2+}. The nominal chemical formula for our two possible situation is $K_{1.03}Ca_{0.79}Eu_{0.07}Tb_{0.07}$-$Mn_{0.02}PO_4$ and $K_{0.89}Ca_{0.84}Eu_{0.07}Tb_{0.07}Mn_{0.02}PO_4$ respectively, and the XRD patterns of two samples are exhibited in Fig. 1(1) and (2). It can be seen that Fig. 1(2) shows no obvious impurity phases, while noticeable deviations occur in Fig. 1(1). This result suggests that the second assumption of doping is more reasonable. Then the XRD patterns of three other samples are checked, including $KCaPO_4$:0.9%Eu^{2+},5%Tb^{3+},1.5%Mn^{2+},$KCaPO_4$:0.9%Eu^{2+}, 7%Tb^{3+},1.5%Mn^{2+} and $KCaPO_4$:7%Eu^{2+},7%Tb^{3+}, 1.5%Mn^{2+}. All results show that different doping centers would not lead to unintended phases. Their XRD patterns are shown in Fig. 1(3), (4) and (5) respectively.

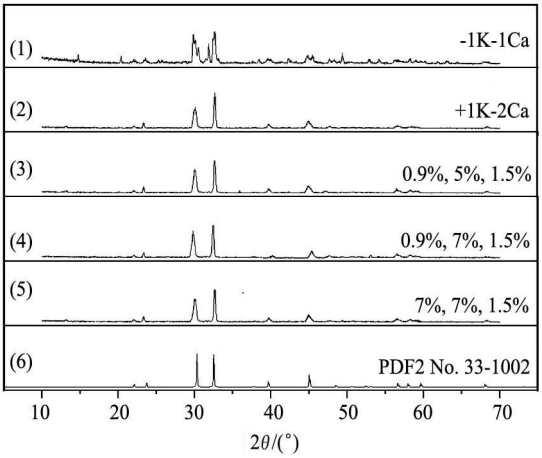

Fig. 1 (1) and (2) XRD patterns of the sample $KCaPO_4$:7%Eu^{2+}, 7%Tb^{3+},2%Mn^{2+} with different nominal chemical formulus ($K_{0.89}Ca_{0.84}Eu_{0.07}Tb_{0.07}Mn_{0.02}PO_4$ and $K_{1.03}Ca_{0.79}Eu_{0.07}Tb_{0.07}Mn_{0.02}PO_4$); (3), (4), (5) XRD patterns of samples $KCaPO_4$:0.9%Eu^{2+},5%Tb^{3+}, 1.5%Mn^{2+},$KCaPO_4$:0.9%Eu^{2+},7%Tb^{3+},1.5%Mn^{2+} and $KCaPO_4$:7%Eu^{2+},7%Tb^{3+},1.5%Mn^{2+} respectively; (6) The standard $KCaPO_4$ data No. 33-1002

2.2 Luminescence properties

The PLE and PL spectra of the sample $KCaPO_4$:0.9% Eu^{2+},7%Tb^{3+},1.5%Mn^{2+} are shown in Fig. 2. The PL spectrum consists of blue, green and orange-reddish emissions. Under UV excitation at 355 nm, a blue broad-band emission with the maximum at 463 nm is generated, which can be attributed to the 5d-4f transition of Eu^{2+}. Besides, some narrow emissions stemming from the transitions between 4f energy levels of Tb^{3+} can be observed, consisting of a green emission centered at around 544 nm which is related to the $^5D_4 \rightarrow {}^7F_5$ transition; a blue emission whose peak locates at near 487 nm which can

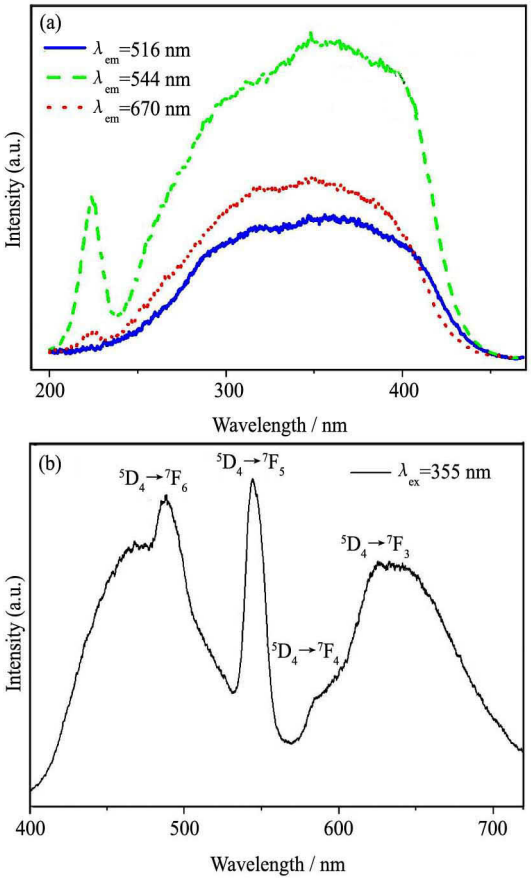

Fig. 2 PLE and PL spectra of the sample $KCaPO_4$:7%Eu^{2+},7% Tb^{3+},2%Mn^{2+} respectively

(a) PLE spectra monitoring the emission wavelength 516 nm (solid line), 544 nm (dashed line) and 670 nm (dotted line) respectively; (b) PL spectrum of tri-doped sample under 355 nm excitation