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Review paper

Luminescence and energy transfer of a color tunable phosphor: $Ba_2CaLa_{1-x}M_x(PO_4)_3$ (M = Dy, Tm, Eu) for warm white UV LEDs

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Abstract

A series of Dy^{3+}-, Tm^{3+}-, Eu^{3+} co-activated $Ba_2CaLa(PO_4)_3$ phosphors were synthesized via a standard solid state reaction under normal ambient air, and the emission colors could be tuned from blue to white and then to red. It was discovered that the energy is transferred from Tm^{3+} to Dy^{3+} by directly observing overlap of the excitation spectrum of Dy^{3+} and the emission spectrum of Tm^{3+} and Dy^{3+}. By utilizing the principle of energy transfer, we have demonstrated that with appropriate tuning of activator content, $Ba_2CaLa_{1-x-y-z}(PO_4)_3{:}xDy^{3+}{-}yTm^{3+}{-}zEu^{3+}$ phosphors exhibit great potential for use as single-component phosphors for warm white ultraviolet light-emitting diodes (UV LEDs).

Keywords: White LED; Energy transfer; Photoluminescence; $Ba_2CaLa_{1-x-y-z}(PO_4)_3{:}xDy^{3+}{-}yTm^{3+}{-}zEu^{3+}$

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1. Introduction

White light-emitting diodes (w-LEDs) are the new emitting light source for common illumination due to their application in the lighting industry based on the advantages of small size, long lifetime, small size, energy saving and environmental friendliness, regarded as the fourth generation solid-state light [1–3]. Several techniques have been developed for the preparation of white LEDs. The first way to obtain the white LEDs is to combine yellow YAG:Ce^{3+} phosphor with a gallium nitride (GaN)-based blue chip. However, such white LEDs have high color temperature and poor color rendering index high color temperature due to lack of red components in the color. Another kind of white LEDs can

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be fabricated by employing blue, green and red emitting phosphors excited by ultraviolet (UV) InGaN chip. However, these white LEDs encounter the following drawbacks: the luminescent efficiency is low, poor chemical stabilities against humidity and low color rendering index. The current academic interests in white light are displaced by pursuing single-component white-light phosphors to get lower production cost, great color rendering index and small color aberration [2–7]. Rare earth Dy^{3+} ions have two dominant emission bands in the blue region (470–500 nm) due to $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition and in the yellow region (560–600 nm) due to $^4F_{9/2}\rightarrow{}^6H_{15/2}$ transition. It is possible to achieve the white light emission by adjusting the yellow to blue intensity ratio value [7]. However, the quality of the white light is not ideal since the distance between the energy equal point and the color coordinates of Dy^{3+} single-doped phosphor is a little far. When the blue emission was stronger than yellow emission, the color coordinates of phosphor can be modulated by co-doping Eu^{3+} ions. For example: $Gd_2(MoO_4)_3$:Dy^{3+}–Eu^{3+} [8], Sr_3AlO_4F:Dy^{3+}–Eu^{3+} [9], $LiInW_2O_8$:Dy^{3+}–Eu^{3+} [10], $CaMoO_4$:Dy^{3+}–Eu^{3+} [11]. To the contrary, the color coordinates of phosphor can be modulated by co-doping Tm^{3+} ions, such as: $KSr_4(BO_3)_3$:Tm^{3+}–Dy^{3+} [12], $Ca_9Y(PO_4)_7$:Tm^{3+}–Dy^{3+} [13]. For the phosphates, the eulytite type structure $MI_3MII(PO_4)_3$ (MI=Ca, Sr, Ba and Pb; MII=La, Y, Sc, Bi, Tb and In) (space group I-43d) has attracted extensive attention as host materials for lanthanide activators [14]. For example, the energy transfer from Eu^{2+} to Mn^{2+} in $Sr_3Sc(PO_4)_3$, $Ba_3Lu(PO_4)_3$ and $Ba_3Gd(PO_4)_3$ has been validated, and the emission color of the phosphors can be tuning by properly tuning the relative doping composition of Eu^{2+}/Mn^{2+} [15,16]. The luminescence and energy transfer from Tb^{3+} to Mn^{2+} in $Sr_3Tb(PO_4)_3$:Mn^{2+} has also been researched [17]. Keeping in view the above interesting results, in the present work, we investigate new color-tunable borate phosphor $Ba_2CaLa_{1-x-y-z}(PO_4)_3$:$xDy^{3+}$–$yTm^{3+}$–$zEu^{3+}$, the energy transfer from Tm^{3+} to Dy^{3+}, and the warm white light emission.

2. Experimental

2.1. Materials and synthesis

The $Ba_2CaLa_{1-x-y-z}(PO_4)_3$:$xDy^{3+}$–$yTm^{3+}$–$zEu^{3+}$ phosphors were synthesized by the conventional solid-state reaction method. $BaCO_3$ (AR), $CaCO_3$ (AR), $NH_4H_2PO_4$ (AR), La_2O_3 (99.99%), Dy_2O_3 (99.99%), Eu_2O_3 (99.99%), Tm_2O_3 (99.99%) were used as starting materials. The materials were weighed according to the ratio of the sum and ground them in the mortar. Then the compound was preheated at 300 °C for 2 h in a muffle furnace, reground, and finally calcined at 1250 °C for 3 h in air atmosphere. After calcining, the samples were slowly cooled to room temperature in the furnace and ground again into powder for subsequent measurement.

2.2. Measurements and characterization

The crystal structures of as-synthesized products were recorded with XD-3 model X-ray powder diffraction (XRD) with Cu-Kα1 (λ=1.5418 Å) radiation generated at 36 kV/20 mA. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the phosphor were measured by a SBP-150 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The resolution of the instruments is 1 nm. All the measurements were investigated at room temperature.

3. Results and discussion

3.1. XRD pattern of $Ba_2CaLa_{1-x-y-z}(PO_4)_3$:$xDy^{3+}$–$yTm^{3+}$–$zEu^{3+}$ phosphor

The phase purity of $Ba_2CaLa_{1-x-y-z}(PO_4)_3$:$xDy^{3+}$–$yTm^{3+}$–$zEu^{3+}$ sample was confirmed by XRD measurements (Fig. 1). It was found to be consistent with that reported in JCPDS Card no. 29-0175. Its lattice parameters are a=10.521 Å, b=10.521 Å, c=10.521 Å, $\alpha=\beta=\gamma=90.0^\circ$, Z=4 [10]. The obtained samples are single phase and the co-doped Tm^{3+} and Dy^{3+} ions do not cause any significant changes in the host structure of $Ba_2CaLa(PO_4)_3$.

3.2. Photoluminescence properties of $Ba_2CaLa_{1-x}(PO_4)_3$:xTm^{3+} and $Ba_2CaLa_{1-y}(PO_4)_3$:yDy^{3+}

Fig. 2 shows the PL and PLE spectra of $Ba_2CaLa_{0.98}(PO_4)_3$:$0.02Tm^{3+}$ phosphor. The main excitation band centered at 359 nm is attributed to the electronic dipole transition of $^6H_6\rightarrow{}^1D_2$ monitored by the emission at 458 nm. It is clearly observed that the strong peak (458 nm) appeared in the emission spectrum of $Ba_2CaLa_{0.98}(PO_4)_3$:$0.02Tm^{3+}$ specimen pumped by 359 nm, corresponding to the transitions of $^1D_2\rightarrow{}^3F_4$ [13].

The PLE and PL spectra of the purely Dy^{3+}-activated $Ba_2CaLa(PO_4)_3$ samples are shown in Fig. 3. Two strong peaks centered at 486 nm and 579 nm as well as a weak band peaked at 666 nm are observed in the emission spectrum of $Ba_2CaLa_{0.92}(PO_4)_3$:$0.08Dy^{3+}$ excited by 350 nm. The blue emission at 486 nm and yellow emission at 579 nm are attributed to the transitions of $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ of Dy^{3+}, and the weak red band at 666 nm is assigned to $^4F_{9/2}\rightarrow{}^6H_{11/2}$ transition of Dy^{3+}. The excitation spectrum by monitoring 579 nm, which are located

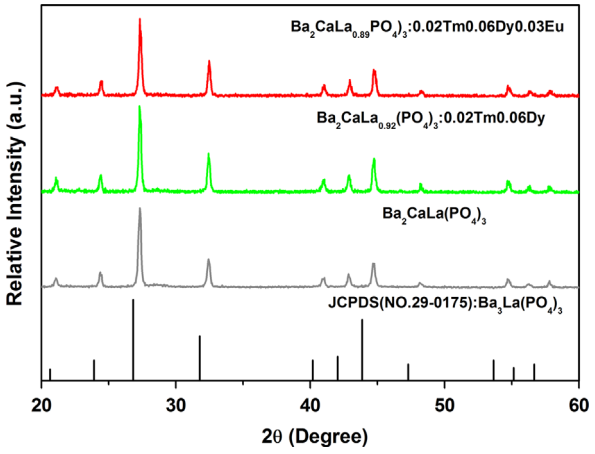

Fig. 1. XRD pattern of $Ba_2CaLa_{1-x-y-z}(PO_4)_3$: xTm^{3+}–yDy^{3+}–zEu^{3+}.