

## Photoluminescence properties and energy transfer of Dy<sup>3+</sup> and Tm<sup>3+</sup> co-activated CaZrO<sub>3</sub> phosphor for white LEDs

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Single-phased CaZrO<sub>3</sub>: Dy<sup>3+</sup>, Tm<sup>3+</sup> series have been successfully synthesized by solid-state reaction, and their luminescence properties were investigated. Under 355 nm excitation, CaZrO<sub>3</sub>: Dy<sup>3+</sup> series showed characteristic emission of Dy<sup>3+</sup>, which exhibited yellowish white color. By introducing Tm<sup>3+</sup> into the matrix, the emitted hue of the Dy<sup>3+</sup>-doped sample could be easily tailored to white, and simultaneously, energy transfer from Tm<sup>3+</sup> to Dy<sup>3+</sup> was observed. The color coordinates of the optimum white-emitting sample were (0.321, 0.323), which were very close to the data of the National Television Standard Committee (0.33, 0.33). The co-activated phosphors presented good match to ultraviolet light-emitting diodes (LEDs), which revealed that they could be novel promising phosphors utilized in white LED application.

**Keywords:** photoluminescence, phosphor, white LEDs, energy transfer

### 1. Introduction

White-light-emitting diodes (WLEDs) are considered to be the most promising solid-state light source, owing to higher energy efficiency, longer lifetime, better environmental friendliness and a low temperature performance compared with those of the conventional bulbs of phosphorescent tubes [1–4]. Among the approaches used for fabricating WLEDs, a consuming incentive is dedicated to the phosphor-converted WLEDs based on the blue and ultraviolet (UV) (350–420 nm) light-emitting diodes (LEDs) [5–9]. Compared with the commercial WLEDs fabricated with blue chip and yellow phosphor YAG: Ce<sup>3+</sup>, the ones fabricated with UV chip and corresponding phosphors have higher color rendering index, because all the colors are determined by the phosphors [10,11]. However, in the multiphosphor-converter WLEDs, re-absorption of emission colors could lead to low luminous efficiency, and several mixed phosphors may increase the difficulties during the fabricating process. Hence, it should be advantageous to find a single-host full-color-emitting phosphor that matches the UV chips well for the WLEDs.

As a luminescent center, trivalent dysprosium ion (Dy<sup>3+</sup>) has been extensively studied to generate white light in various hosts, in respect that the ion has two main fluorescence parts: the blue emission at ~470 nm and yellow emission at ~580 nm, respectively. They are attributed to the characteristic transitions from <sup>4</sup>F<sub>9/2</sub> level to the <sup>6</sup>H<sub>15/2</sub>

and <sup>6</sup>H<sub>13/2</sub> levels. However, the combined luminescence color of the Dy<sup>3+</sup> is usually a yellowish white light in many hosts, resulting from the lack of the blue emission part [12–14], since the ratio of yellow/blue (Y/B) parts is not appropriate for obtaining good color purity. With the expectation of acquiring pure white light for the application in display or illumination, trivalent thulium (Tm<sup>3+</sup>) has been introduced into the Dy<sup>3+</sup>-activated systems as Tm<sup>3+</sup> could produce single blue emission and adjust the ratio of Y/B [15–17]. Based on this point, we consider it as an effective and straightforward approach to generate white light which could reach to the standard set by the National Television Standard Committee (NTSC).

Apropos of the host, the preferential selection is ABO<sub>3</sub>-like compounds with perovskite-type structure. This is because they are sufficiently conductive to release electric charges stored on the phosphor particle surfaces, which results in their potential applications in solid oxide fuel cells, hydrogen sensors, field emission display and plasma display panel [18]. Among these materials, alkaline earth zirconates (AZrO<sub>3</sub> (A = Ca, Sr, Ba)) activated by rare-earth ions, including Tm<sup>3+</sup>, Pr<sup>3+</sup>, Eu<sup>3+</sup> and Tb<sup>3+</sup> [19–23], have attracted considerable interest for their good luminescence properties at room temperature. Moreover, to the best of our knowledge, there have been no reports concerned with the photoluminescence of Dy<sup>3+</sup> and Tm<sup>3+</sup> co-doped CaZrO<sub>3</sub>. Hence, in this work, we synthesized the above-mentioned

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samples, characterized their luminescence properties under UV excitation and discussed their potential application for WLEDs.

## 2. Experiments

Calcium nitrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99.0%), zirconium oxide ( $\text{ZrO}_2$ , 99.0%) and dysprosium oxide ( $\text{Dy}_2\text{O}_3$  (99.99%)) (or thulium oxide ( $\text{Tm}_2\text{O}_3$  (99.99%))) were used as raw materials. All of them were weighed according to the stoichiometric amounts. The reagents with the composition of  $\text{Ca}_{1-x}\text{ZrO}_3: x\text{Dy}$  ( $0.01 \leq x \leq 0.05$ ) and  $\text{Ca}_{0.96-y}\text{ZrO}_3: 0.04\text{Dy}^{3+}, y\text{Tm}^{3+}$  ( $0.01 \leq y \leq 0.04$ ) were, respectively, commixed in agate mortar with an appropriate amount of ethanol, and then sintered at  $1400^\circ\text{C}$  for 4 h.

Crystal phase of the obtained materials was determined by powder X-ray diffraction (XRD, Rigaku D/MAX-2400 X-ray diffractometer with Ni-filtered  $\text{Cu K}\alpha$  radiation at a scanning step of  $0.02^\circ$  in the  $2\theta$  range from  $10^\circ$  to  $80^\circ$ ). The emission and excitation spectra were measured by FLS920T fluorescence spectrophotometer. All measurements were carried out at room temperature.

## 3. Results and discussion

The crystallinity and phase purity of the as-prepared samples were examined by XRD patterns. For example, Figure 1 shows the patterns of the single-doped samples with the maximum  $\text{Dy}^{3+}/\text{Tm}^{3+}$  concentration, and that of the  $\text{Dy}^{3+}$  and  $\text{Tm}^{3+}$  co-doped one with the optimum concentration. All diffraction peaks of the samples could be well indexed to the pure orthorhombic structured  $\text{CaZrO}_3$  (Joint Committee for Power Diffractions Standards, JCPDs Card No. 35-0645), and all the other samples in the doped series are also in good agreement with the card. The results demonstrate that the single phase of all the doped samples is formed completely without any impurity phase, and that the introduction of  $\text{Dy}^{3+}$  and  $\text{Tm}^{3+}$  did not cause the breakage of the lattice structure.

Figure 2(a) characterizes the UV excitation spectrum of the typical  $\text{Ca}_{0.96}\text{Dy}_{0.04}\text{ZrO}_3$  acquired by fixing the monitor wavelength at 575 nm. The curve consists of a number of excitation bands of f-f transitions, which are ascribed to the different transitions from the ground-state  ${}^6\text{H}_{15/2}$  to the various excited states of  $4f^9$  electronic configuration of the  $\text{Dy}^{3+}$  ions [13]. The band ranging from 200–250 nm could be assigned to the host absorption, and the maximum excitation peak located at 355 nm corresponds to the hypersensitive transition from the ground-state  ${}^6\text{H}_{15/2}$  level to the excited-state  ${}^6\text{P}_{7/2}$  level of  $\text{Dy}^{3+}$ , which matches well with UV-LED chips. Hence, all the emission spectra in the present work are obtained by 355 nm excitation.

The emission spectra and relative intensity of  $\text{Ca}_{1-x}\text{ZrO}_3: x\text{Dy}^{3+}$  ( $0.01 \leq x \leq 0.05$ ) by 355 nm excitation are depicted in Figure 3. The spectra consist of three parts, centered at 482, 575 and 668 nm, which correspond

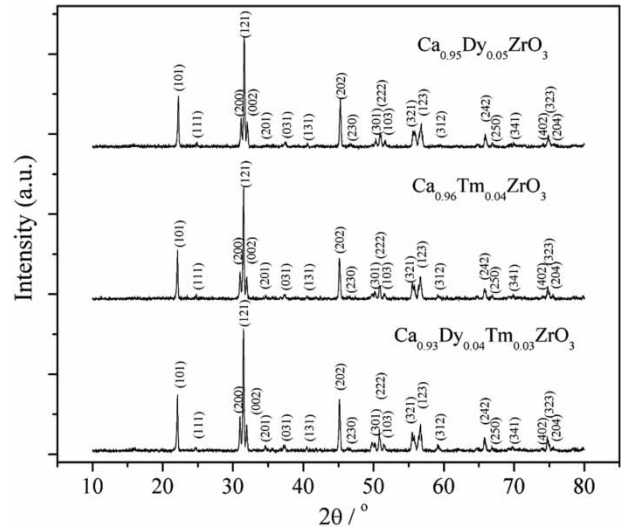


Figure 1. XRD patterns of the typical  $\text{Ca}_{0.95}\text{Dy}_{0.05}\text{ZrO}_3$ ,  $\text{Ca}_{0.96}\text{Tm}_{0.04}\text{ZrO}_3$  and  $\text{Ca}_{0.93}\text{Dy}_{0.04}\text{Tm}_{0.03}\text{ZrO}_3$  samples.

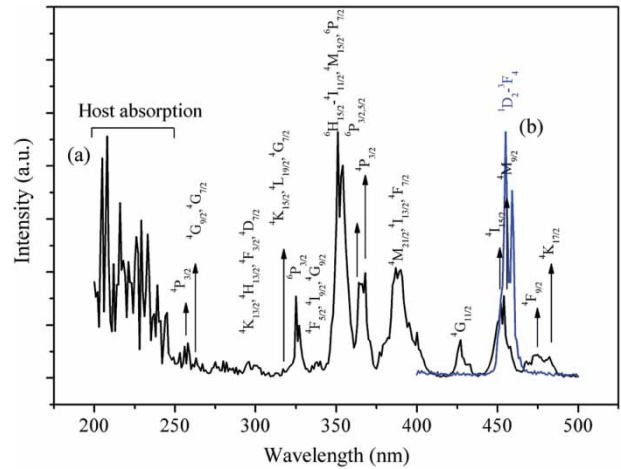


Figure 2. Normalized excitation spectrum of  $\text{Ca}_{0.96}\text{Dy}_{0.04}\text{ZrO}_3$  (a:  $\lambda_{\text{em}} = 575$  nm) and emission spectrum of  $\text{Ca}_{0.97}\text{Tm}_{0.03}\text{ZrO}_3$  (b:  $\lambda_{\text{ex}} = 355$  nm).

to the  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ ,  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$  and  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$  transitions of  $\text{Dy}^{3+}$ , respectively [12]. All the  $\text{Dy}^{3+}$ -doped samples possess the same shape and distribution of emission spectra, except for the difference of emission intensity between them. The inset of Figure 3 shows the variational tendency of the yellow emission intensity (575 nm) for  $\text{Ca}_{1-x}\text{ZrO}_3: x\text{Dy}^{3+}$  ( $0.01 \leq x \leq 0.05$ ) series with  $\text{Dy}^{3+}$  content increasing, revealing that the concentration quenching occurs between  $x = 0.03$  and  $0.05$ . The  $\text{Ca}_{0.96}\text{Dy}_{0.04}\text{ZrO}_3$  sample exhibits the strongest emission intensity, and its color coordinate and color correlative temperature are calculated to be (0.401, 0.436) and 3881 K, respectively, indicating that its combined color is yellowish white when excited by 355 nm. Therefore, in order to improve the color purity, another activated ion,  $\text{Tm}^{3+}$  ion, should be introduced into the  $\text{CaZrO}_3$  host.

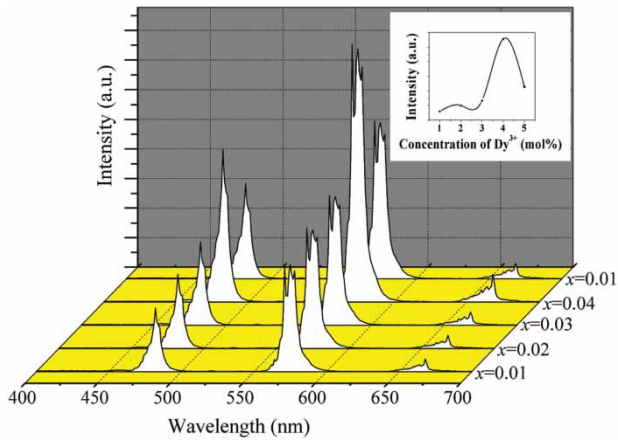


Figure 3. Emission spectra of  $\text{Ca}_{1-x}\text{ZrO}_3: x\text{Dy}^{3+}$  ( $0.01 \leq x \leq 0.05$ ) series ( $\lambda_{\text{ex}} = 355 \text{ nm}$ ). The inset on the left top represents the representative yellow emission intensity (575 nm) of the  $\text{Ca}_{1-x}\text{ZrO}_3: x\text{Dy}^{3+}$  ( $0.01 \leq x \leq 0.05$ ) series with  $\text{Dy}^{3+}$  content increasing.

By 355 nm excitation, the  $\text{Tm}^{3+}$ -doped  $\text{CaZrO}_3$  sample exhibits a single peak at 455 nm, which is attributed to  $^1\text{D}_2 \rightarrow ^3\text{F}_4$  characteristic transition of  $\text{Tm}^{3+}$ , as shown in Figure 2(b). Generally speaking, energy transfer (ET) occurs only when the emission band of the sensitizer overlaps spectrally with the absorption band of the activator [24]. Hence, Figure 2 demonstrates a significant spectral overlapping between the emission curve of  $\text{Tm}^{3+}$  and the excitation peaks of  $\text{Dy}^{3+}$ , indicating that ET from  $\text{Tm}^{3+}$  to  $\text{Dy}^{3+}$  could possibly occur under 355 nm excitation, resulting in the enhancement of the emission intensity for  $\text{CaZrO}_3: \text{Dy}^{3+}$ .

Figure 4 presents the emission spectra of  $\text{Ca}_{0.96-y}\text{ZrO}_3: 0.04\text{Dy}^{3+}, y\text{Tm}^{3+}$  ( $0.01 \leq y \leq 0.04$ ) series by 355 nm excitation. In the co-doped case, all the characteristic

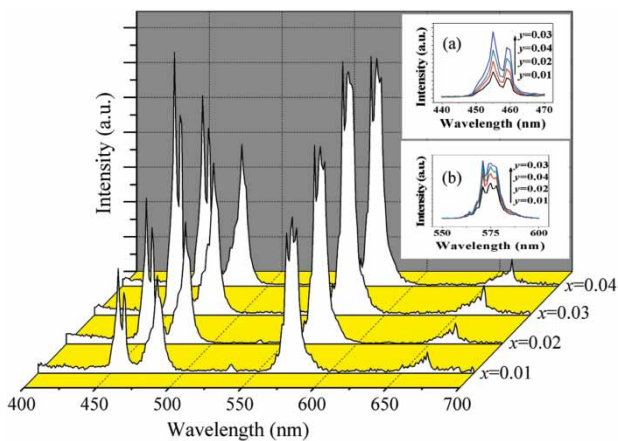


Figure 4. Emission spectra of  $\text{Ca}_{0.96-y}\text{ZrO}_3: 0.04\text{Dy}^{3+}, y\text{Tm}^{3+}$  ( $0.01 \leq y \leq 0.04$ ) series by 355 nm excitation; inset (a) represents the enlarged emission curves of  $\text{Tm}^{3+}$  (455 nm), and inset (b) represents the enlarged yellow emission of  $\text{Dy}^{3+}$  (575 nm).

transitions of  $\text{Tm}^{3+}$  and  $\text{Dy}^{3+}$  appear in the spectra. This is because there are intense absorption peaks in the excitation spectra of both  $\text{Dy}^{3+}$  and  $\text{Tm}^{3+}$ . Since white light can be combined by an appropriate ratio of blue and yellow components, the extra blue light produced by  $\text{Tm}^{3+}$  could practically compensate the lack of the blue emission of  $\text{Dy}^{3+}$ . As the concentration of  $\text{Tm}^{3+}$  increases, the emission intensity of  $\text{Tm}^{3+}$  (455 nm) first rises and then declines, which is in accordance with the concentration quenching effect (as shown in inset (a) of Figure 4). At the same time, the variations of the three characteristic transitions of  $\text{Dy}^{3+}$  are consistent with that of  $\text{Tm}^{3+}$  (as shown in inset (b) of Figure 4), although the content of  $\text{Dy}^{3+}$  is fixed. Among the samples, the co-doped sample  $\text{Ca}_{0.93}\text{Dy}_{0.04}\text{Tm}_{0.03}\text{ZrO}_3$  exhibits the optimum emission intensity, which exhibits  $\sim 1.56$  times that of the single-doped sample  $\text{Ca}_{0.96}\text{Dy}_{0.04}\text{ZrO}_3$ . These results confirm to some extent that the ET from  $\text{Tm}^{3+}$  to  $\text{Dy}^{3+}$  occurs in the co-doped series.

According to emission and excitation spectra, the potential ET process from  $\text{Tm}^{3+}$  to  $\text{Dy}^{3+}$  is described in the energy level diagram as shown in Figure 5. When the phosphor is irradiated by 355 nm, the electrons of  $\text{Tm}^{3+}$  and  $\text{Dy}^{3+}$  are excited from the ground state to the excited state, and the characteristic emission of the two ions are observed. Since the emission band of  $\text{Tm}^{3+}$  at 455 nm overlaps with the broad absorption band of  $\text{Dy}^{3+}$ , the 455 nm emission light could be possibly absorbed by the transition  $^6\text{H}_{15/2} \rightarrow ^4\text{I}_{15/2}$  of  $\text{Dy}^{3+}$ ; then, the latter relaxes to the  $^4\text{F}_{9/2}$  level and emits the corresponding photon to  $^6\text{H}_{11/2}$ ,  $^6\text{H}_{13/2}$  and  $^6\text{H}_{15/2}$ , and enhances every emission part of  $\text{Dy}^{3+}$  at 482, 575 and 668 nm.

The color coordinates of the co-doped series are presented in Table 1 and illustrated in the CIE chromaticity diagram (Figure 6). It can be noticed that all the color coordinates of the co-doped samples are very close to

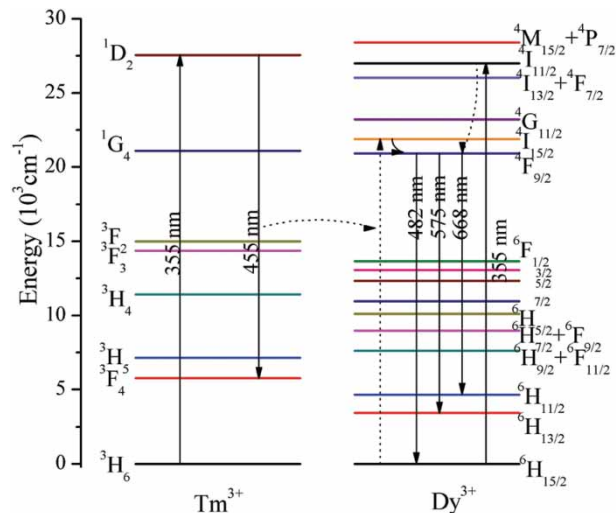


Figure 5. ET process of  $\text{Dy}^{3+}$  and  $\text{Tm}^{3+}$  co-doped  $\text{CaZrO}_3$  phosphor.

Table 1. Color coordinates of the  $\text{Dy}^{3+}$  and  $\text{Tm}^{3+}$  co-doped samples compared with the NTSC.

Samples $\text{Ca}_{0.96-y}\text{ZrO}_3$ : $0.04\text{Dy}^{3+}$ , $y\text{Tm}^{3+}$ ( $0.01 \leq y \leq 0.04$ )	Color coordinates ( $x, y$ )	Color correlative temperature (CCT) (K)
$y = 0.01$	(0.326, 0.320)	5813
$y = 0.02$	(0.323, 0.312)	5998
$y = 0.03$	(0.321, 0.323)	6078
$y = 0.04$	(0.318, 0.305)	6339
NTSC (white light)	(0.33, 0.33)	5603

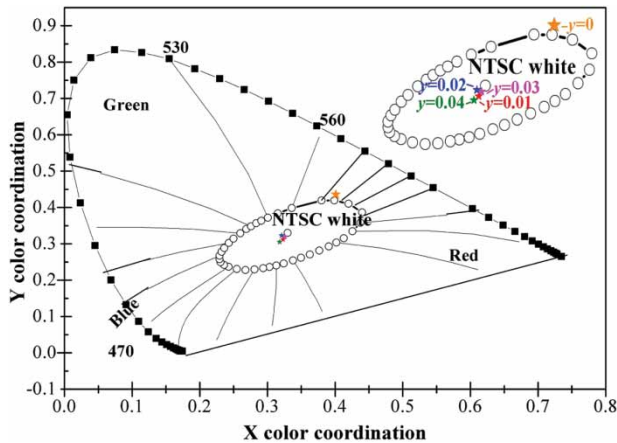


Figure 6. The CIE chromaticity diagram of  $\text{Ca}_{0.96-y}\text{ZrO}_3$ :  $0.04\text{Dy}^{3+}$ ,  $y\text{Tm}^{3+}$  ( $0.01 \leq y \leq 0.04$ ) series represented as solid dots ( $\lambda_{\text{ex}} = 355 \text{ nm}$ ).

the NTSC white light (0.33, 0.33) compared with the single-doped sample, and that the  $\text{Ca}_{0.93}\text{Dy}_{0.04}\text{Tm}_{0.03}\text{ZrO}_3$  sample with the optimum color purity is exactly the one with the best emission intensity. Thus, we could conclude that the introduction of  $\text{Tm}^{3+}$  is actually effective for adjusting the emission color and increase the emission intensity, which makes  $\text{Dy}^{3+}$  and  $\text{Tm}^{3+}$  co-doped  $\text{CaZrO}_3$  potentially applicable in UV WLEDs.

#### 4. Conclusions

$\text{Dy}^{3+}$ - and  $\text{Tm}^{3+}$ -doped  $\text{CaZrO}_3$  phosphors were successfully synthesized by the solid-state reaction. From the investigation of their photoluminescence by 355 nm excitation, it is revealed that the  $\text{CaZrO}_3$ :  $\text{Dy}^{3+}$  exhibits a yellowish white light, which could be improved to reach the NTSC white color by the addition of  $\text{Tm}^{3+}$  due to its single blue emission around 455 nm. Moreover, the ET from  $\text{Tm}^{3+}$  to  $\text{Dy}^{3+}$  is also observed, which could further enhance the intensity of the white emission. Under the irradiation of 355 nm, with the appropriate CIE chromaticity coordinates of (0.321, 0.323) and emission intensity, the phosphor  $\text{Ca}_{0.93}\text{ZrO}_3$ :  $0.04\text{Dy}^{3+}$ ,  $0.03\text{Tm}^{3+}$  could be potentially applied in UV WLEDs.

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