

## ENERGY TRANSFER AND COLORFUL EMISSION of Eu<sup>3+</sup> and Tb<sup>3+</sup> CO-DOPED CaWO<sub>4</sub> PHOSPHORS

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*Eu<sup>3+</sup>/Tb<sup>3+</sup> co-doped CaWO<sub>4</sub> phosphors were synthesized by a simple green co-precipitation process. The structure of the samples was investigated by X-ray diffraction. The photoluminescence spectra and fluorescence decay lifetimes of the samples were measured to investigate the luminescence properties. We analyzed the energy transfer process between Eu<sup>3+</sup> and Tb<sup>3+</sup> co-doped-CaWO<sub>4</sub>. As the Tb<sup>3+</sup> to Eu<sup>3+</sup> energy transfer process was confirmed, Eu<sup>3+</sup> and Tb<sup>3+</sup> co-doped-CaWO<sub>4</sub> phosphors showed a color-tunable emission from green to red under a 365 nm UV lamp.*

**Keywords:** rare earth ions, CaWO<sub>4</sub>, photoluminescence, energy transfer, colorful emission.

## ПЕРЕНОС ЭНЕРГИИ И ИЗЛУЧЕНИЕ ЛЮМИНОФОРОВ CaWO<sub>4</sub>, СОВМЕСТНО ДОПИРОВАННЫХ ИОНАМИ Eu<sup>3+</sup> И Tb<sup>3+</sup>

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*Люминофоры CaWO<sub>4</sub>, легированные ионами Eu<sup>3+</sup>/Tb<sup>3+</sup>, синтезированы простым способом “зеленого” соосаждения. Структура образцов исследована методом рентгеновской дифракции. Измерены спектры фотолюминесценции и времена затухания флуоресценции образцов. Проанализирован процесс переноса энергии между Eu<sup>3+</sup> и Tb<sup>3+</sup> в солегированном CaWO<sub>4</sub>. Поскольку процесс передачи энергии от Tb<sup>3+</sup> к Eu<sup>3+</sup> подтвержден, люминофоры CaWO<sub>4</sub>, легированные совместно Eu<sup>3+</sup> и Tb<sup>3+</sup>, демонстрируют перестраиваемое по цвету излучение от зеленого до красного под воздействием света УФ-лампы с длиной волны 365 нм.*

**Ключевые слова:** редкоземельные ионы, CaWO<sub>4</sub>, фотолюминесценция, перенос энергии, цветное излучение.

**Introduction.** During the past decades, more and more attention has been paid to rare-earth-ion-based luminescent materials owing to their excellent luminescent properties and colorful emission [1–3]. They are widely applied in displays [4]. One general route is to combine blue, green and red phosphors excited with UV light (360–410 nm) to obtain white light [5]. Therefore, the synthesis and development of rare-earth-based colored fluorescent powder are essential for displays. The selection of an appropriate host matrix is important for efficient emission. Among the many optical materials, tungstate has excellent photoelectric properties and chemical stability. WO<sub>4</sub><sup>2-</sup> can absorb energy in the UV region, transferring the energy to rare earth ions. However, tungstate phosphors were usually studied via UV excitation – for example, CaWO<sub>4</sub> nanospindles with Eu<sup>3+</sup> or Dy<sup>3+</sup> cations emitted multicolor (red for Eu<sup>3+</sup>; white for Dy<sup>3+</sup>) luminescence when excited by UV radiation (250 nm) [6], whereas Eu<sup>3+</sup>, Tb<sup>3+</sup> codoped-CaWO<sub>4</sub> emitted color from blue to pink blue, white and green on excitation into the WO<sub>4</sub><sup>2-</sup> at 260 nm [7]. The emission intensity ratio of Tb<sup>3+</sup>/Eu<sup>3+</sup> in the case of the CaWO<sub>4</sub> lattice showed a linear relationship with the excitation wavelength in the range

of 240–330 nm [8]. However, recent research on rare-earth-ion-based  $\text{CaWO}_4$  phosphors pumped by near-UV (NUV) excitation is limited [9–12]. In this study, we synthesized a series of  $\text{Eu}^{3+}/\text{Tb}^{3+}$  co-doped  $\text{CaWO}_4$  phosphors by a simple and green co-precipitation process. Energy transfer from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  in  $\text{CaWO}_4$  phosphor excited by near ultraviolet excitation (378 nm) was investigated. The results of the fluorescence lifetimes of the samples revealed that the classic energy transfer process from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  was confirmed to exist in the  $\text{CaWO}_4$  host, leading to tunable color emission by changing their relative contents under 365-nm excitation.

**Experimental.** A series of  $\text{CaWO}_4:\text{Eu}^{3+},\text{Tb}^{3+}$  phosphors were synthesized by a simple co-precipitation process. In this work, all reagents used were of analytical grade. In a typical procedure, a mixture of  $\text{CaCl}_2$ ,  $\text{EuCl}_3$ , and  $\text{TbCl}_3$  at a specific molar ratio was dissolved in 25 mL of deionized water, forming a 0.2 M solution of metal ions. Separately,  $\text{Na}_2\text{WO}_4$  was dissolved in another 25 mL of deionized water. The molar ratio of the total metal ions and tungstate ions was the theoretical stoichiometric ratio of 1:1. Then, the metal ions solution was added dropwise into the solution of sodium tungstate, and stirred for 5 min. Next, the turbid liquid was immediately filtered under reduced pressure, and washed with distilled water 3 times. Finally, the resultant precipitate was dried at 80°C for 12 h to obtain white  $\text{CaWO}_4:\text{Eu}^{3+},\text{Tb}^{3+}$  powders.

The XRD patterns of the samples were conducted on a Brucker D8 ADVANCE X-ray diffractometer in the range of 10–80°. The photoluminescence (PL) spectra were recorded on F-7000 fluorescence spectrophotometer, and fluorescence decay curves were obtained at 546 nm by exciting with 378 nm using Edinburgh FLS980. The duration of the excitation pulse was about 1  $\mu\text{s}$ .

**Results and discussion.** *Crystal structure of the sample.* The XRD patterns of  $\text{CaWO}_4$  and  $\text{CaWO}_4:\text{Ln}^{3+}$  ( $\text{Ln} = \text{Eu, Tb}$ ) were displayed in Fig. 1. All the peaks of samples agreed well with that of the tetragonal phase of  $\text{CaWO}_4$  (JCPDS card#14-1431), indicating the formation of the pure phase. This is because the ionic radii of  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  are very close to that of  $\text{Ca}^{2+}$ ; therefore, the phases do not change when part of the  $\text{Ca}^{2+}$  is exchanged with  $\text{Tb}^{3+}$  or  $\text{Eu}^{3+}$  in the crystal lattice.

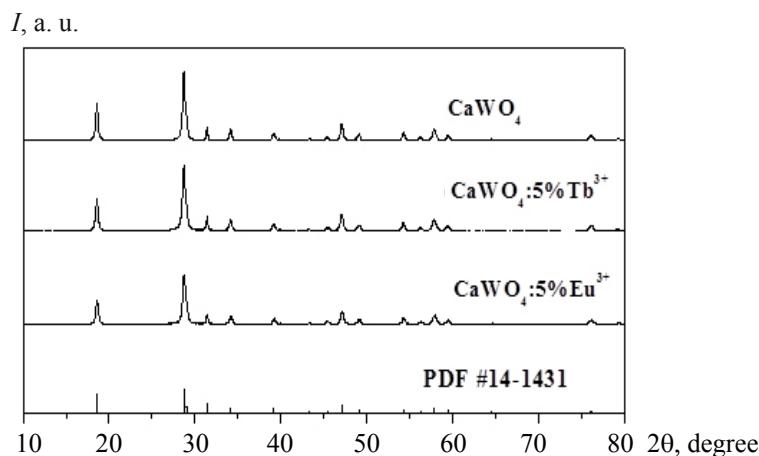
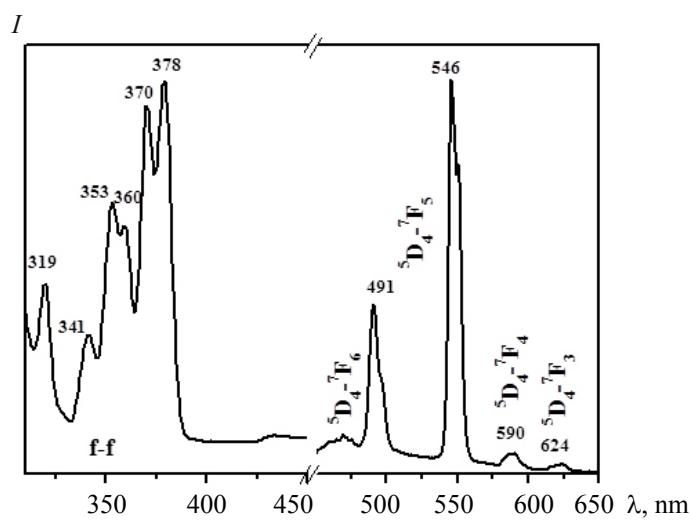
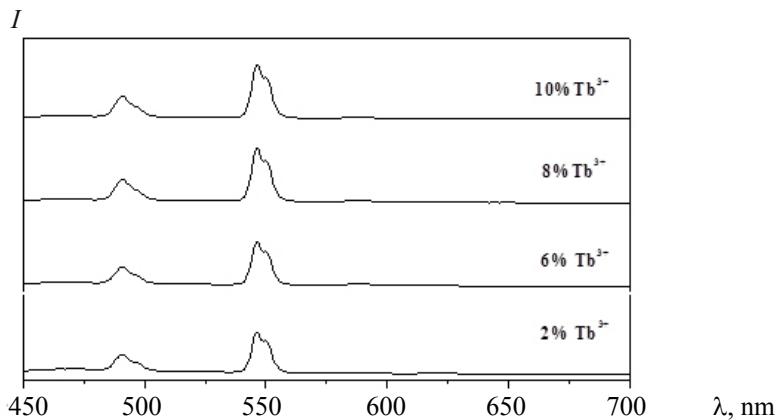
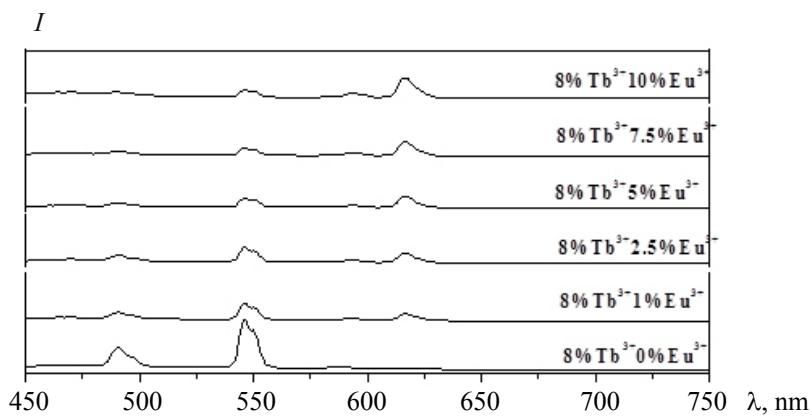


Fig. 1. XRD patterns of  $\text{CaWO}_4$ ,  $\text{CaWO}_4:\text{Eu}^{3+}$ , and  $\text{CaWO}_4:\text{Tb}^{3+}$ .

*Emission and excitation spectra of  $\text{CaWO}_4:5\%\text{Tb}^{3+}$  phosphors.* The excitation spectrum of  $\text{CaWO}_4:\text{Tb}^{3+}$  comprised  $f-f$  adsorptions in the range of 310–400 nm by monitoring the emission wavelength of 543 nm (Fig. 2). The characteristic absorption peaks were located at 319, 341, 353, 360, 370, 378 nm, corresponding to the transitions of  $^7F_6-^5D_0$ ,  $^7F_6-^5G_2$ ,  $^7F_6-^5D_2$ ,  $^7F_6-^5G_5$ ,  $^7F_6-^5D_6$ , and  $^7F_6-^5D_3$ , respectively. The optimal excitation peak of  $\text{Tb}^{3+}$  was located at 378 nm ( $^7F_6-^5D_3$ ) in the NUV range. Under the excitation wavelength of 378 nm, the emission peaks were located at 491, 546, 590, and 624 nm, which originated from  $^5D_4-^7F_J$  ( $J = 6, 5, 4, 3$ ), respectively. The intense green emission of 546 nm was derived from  $^5D_4-^7F_5$ ; therefore,  $\text{CaWO}_4:\text{Tb}^{3+}$  acted as a classic green phosphor. The PL spectra of  $\text{CaWO}_4:m\text{Tb}^{3+}$  ( $m = 2-10\%$ ) are shown in Fig. 3. With the increase of  $\text{Tb}^{3+}$  concentration in the range of 2–8%, the emission intensity of  $\text{Tb}^{3+}$  increases; however, roughly equal emission intensity of 8 and 10%-doped  $\text{Tb}^{3+}$ -doped  $\text{CaWO}_4$  was observed. The optimal doping concentration of  $\text{Tb}^{3+}$  in  $\text{CaWO}_4$  was 8%; therefore, the 8% $\text{Tb}^{3+}$ -doped  $\text{CaWO}_4$  was selected as the optimum sample in the following study.

Fig. 2. PL spectra of  $\text{CaWO}_4:5\%\text{Tb}^{3+}$  phosphors.Fig. 3. PL spectra of  $\text{CaWO}_4:m\%\text{Tb}^{3+}$  phosphors ( $m = 2-10\%$ ).

*Energy transfer process.* Figure 4 shows the PL spectra of  $\text{CaWO}_4:8\%\text{Tb}^{3+}, n\text{Eu}^{3+}$  ( $n = 0-10\%$ ) upon exciting with 378 nm. In addition to  $^5D_4-^7F_5$  emission (546 nm) of  $\text{Tb}^{3+}$ , the characteristic  $^5D_0-^7F_2$  emission (618 nm) of  $\text{Eu}^{3+}$  was also observed in the spectra [13-15]. As the concentration of  $\text{Eu}^{3+}$  increased, the  $^5D_4-^7F_5$  emission intensity of  $\text{Tb}^{3+}$  fell rapidly, while that of  $^5D_0-^7F_2$  emission intensity of  $\text{Eu}^{3+}$  increased gradually. Therefore, there might have been an energy transfer process from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  in  $\text{CaWO}_4:\text{Tb}^{3+}, \text{Eu}^{3+}$  phosphors.

Fig. 4. PL spectra of  $\text{CaWO}_4:8\%\text{Tb}^{3+}, n\text{Eu}^{3+}$  phosphors ( $n = 0-10\%\text{Eu}^{3+}$ ).

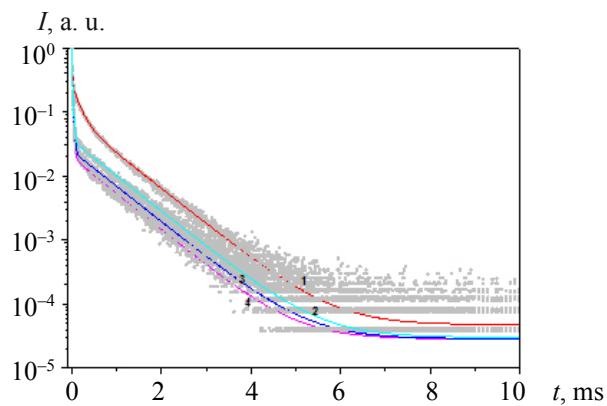


Fig. 5. Luminescence decay curves of  $\text{CaWO}_4:8\%\text{Tb}^{3+}, n\text{Eu}^{3+}$  (1–4: 0, 2.5, 5, 10%) at 546 nm by exciting with 378 nm (the duration of the excitation pulse is about 1  $\mu\text{s}$ ).

In order to analyze the energy transfer process, the fluorescence lifetimes of  $\text{CaWO}_4:8\%\text{Tb}^{3+}, n\text{Eu}^{3+}$  ( $n = 0\text{--}10\%$ ) were investigated. The luminescence decay curves were better fitted by a triple-exponential function (Fig. 5). The average fluorescence lifetime of  $\text{Tb}^{3+}$  could be calculated according to Eq. (1) [16, 17]:

$$\tau_{av} = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2) / (A_1\tau_1 + A_2\tau_2 + A_3\tau_3). \quad (1)$$

The measured fluorescence lifetimes of  $\text{Tb}^{3+}$  in  $\text{CaWO}_4:8\%\text{Tb}^{3+}, n\text{Eu}^{3+}$  ( $n = 0\text{--}10\%$ ) are 0.5279, 0.4817, 0.4110, 0.3492 ms at  $n = 0, 2.5, 5.0, 10.0\%$ , respectively. As seen, the fluorescence lifetimes of  $\text{Tb}^{3+}$  in  $\text{CaWO}_4:8\%\text{Tb}^{3+}, n\text{Eu}^{3+}$  ( $n = 0\text{--}10\%$ ) decreased. This result provides evidence that  $\text{Tb}^{3+}$  transfers the energy to  $\text{Eu}^{3+}$  as expected. The energy transfer efficiency (ET) from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  in  $\text{CaWO}_4$  host could be expressed as follows:

$$ET = 1 - \tau / \tau_0, \quad (2)$$

where  $\tau_0$  and  $\tau$  are the fluorescence time of  $\text{Tb}^{3+}$  ( $^5D_4 - ^7F_3$ ) in  $\text{CaWO}_4:8\%\text{Tb}^{3+}$  and  $\text{CaWO}_4:n\text{Eu}^{3+}, 8\%\text{Tb}^{3+}$ . Figure 6 shows the ET efficiency from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  in the  $\text{CaWO}_4$  host. Results showed that the ET efficiency significantly increased with the concentration of  $\text{Eu}^{3+}$  increased. The ET efficiency was up to 33.8% in  $\text{CaWO}_4:10\%\text{Eu}^{3+}, 8\%\text{Tb}^{3+}$  [15].

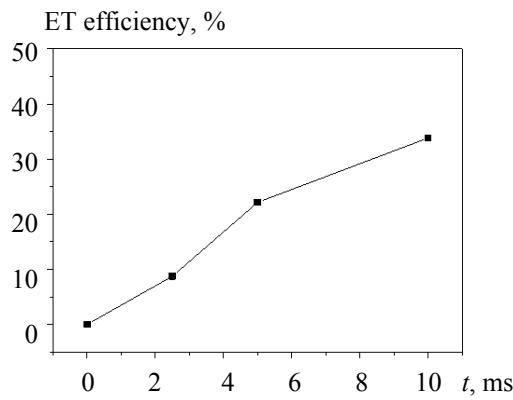


Fig. 6. ET efficiency from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  under 378 nm excitation in  $\text{CaWO}_4:8\%\text{Tb}^{3+}, n\text{Eu}^{3+}$  phosphors ( $n = 0\text{--}10\%\text{Eu}^{3+}$ ) with increasing  $\text{Eu}^{3+}$  concentration.

The energy transfer from a sensitizer to an activator may take place via exchange interaction and multipole-multipole interaction. On the basis of Dexter's energy transfer theory and Reisfeld's approximation, the following relation can be given as:

$$\eta_0/\eta \propto C^{n/3}, \quad (3)$$

where  $\eta_0$  and  $\eta$  are the emission quantum efficiency of the  $\text{Tb}^{3+}$  ions in the absence and presence of the  $\text{Eu}^{3+}$  ions, respectively. The value  $\eta_0/\eta$  can be approximately replaced by the ratio of  $\tau_0/\tau$  [18].  $C$  is the doping concentration of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions, and  $n = 3, 6, 8, 10$  corresponds to the exchange interaction, dipole-

dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively. The  $\eta_0/\eta - C^{n/3}$  plot ( $n = 3$ ) showed a relatively good linear relation in the exchange interaction (Fig. 7), revealing that the exchange interaction might be mainly responsible for the energy transfer from the  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  ions.

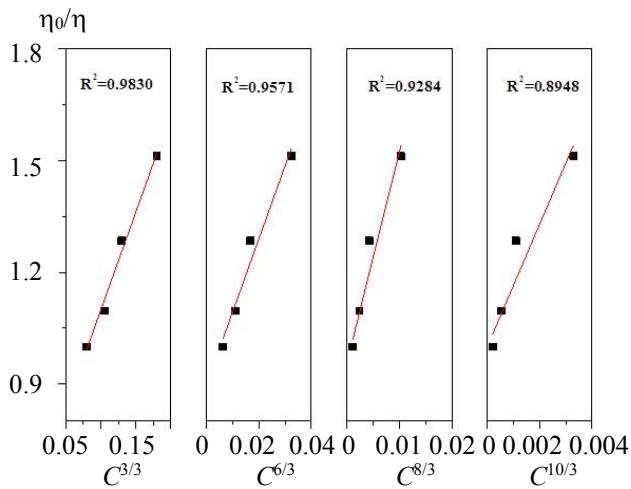


Fig. 7. Dependence of  $\eta_0/\eta$  of  $\text{Tb}^{3+}$  ions on the total doping concentration of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions of  $C^{3/3}$ ,  $C^{6/3}$ ,  $C^{8/3}$ ,  $C^{10/3}$  in the  $\text{CaWO}_4:8\%\text{Tb}^{3+}, n\text{Eu}^{3+}$  phosphors.

The schematics of the ET process from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  were displayed in Fig. 8. When the  $\text{Tb}^{3+}$  ions in  $\text{CaWO}_4:n\text{Eu}^{3+}, 8\%\text{Tb}^{3+}$  ( $n = 2.5\text{--}10\%$ ) were excited by 378 nm, the electrons of  $\text{Tb}^{3+}$  jumped from the  $^7F_6$  level (ground state) to the  $^5D_3$  level (excited state). Then, the electrons at the  $^5D_3$  level jumped to  $^5D_4$  via a nonradiative transition. The energy from the  $^5D_4$  level of  $\text{Tb}^{3+}$  was partly transferred to the  $^5D_1$  level of  $\text{Eu}^{3+}$ , followed by a nonradiative transition to the  $^5D_0$  level. As a result, the characteristic  $^5D_0 - ^7F_J$  ( $J = 1, 2, 3, 4$ ) emissions of  $\text{Eu}^{3+}$  were observed. The rest of the electrons at the  $^5D_4$  level returned to  $^7F_J$  ( $J = 3, 4, 5, 6$ ) of  $\text{Tb}^{3+}$  by radiative transition.

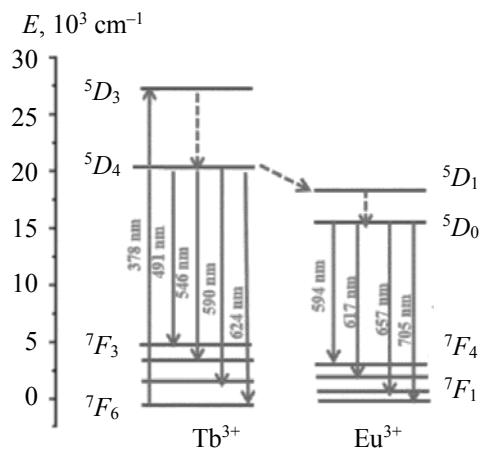


Fig. 8. ET process from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  in co-doped  $\text{CaWO}_4$  phosphors.

*Colorful phosphors under 365 nm UV lamp.* Due to the efficient energy transfer process from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$ , color-tunable emission can be realized. Figure 9 shows the PL spectra of  $\text{CaWO}_4:m\text{Eu}^{3+}, n\text{Tb}^{3+}$  ( $m+n = 5\%$ ) under excitation of 378 nm of  $\text{Tb}^{3+}$ . The fluorescence emission of  $\text{Eu}^{3+}$  gradually enhanced with the increase of the  $\text{Eu}^{3+}$  content, accompanied by the emission of  $\text{Tb}^{3+}$  being gradually reduced. Therefore, it was possible to realize the colorful emission. Figure 10 displays the digital photographs of those phosphors after excitation with 365 nm UV lamp. These fluorescent powders showed green, yellow to red color under the single wavelength, indicating that it could be a candidate for NUV excited-colorful phosphors.

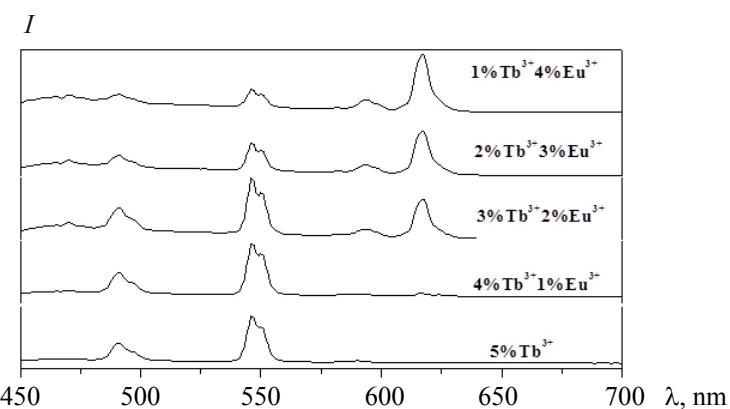


Fig. 9. PL emission spectra of  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ -co-doped  $\text{CaWO}_4$  phosphors.

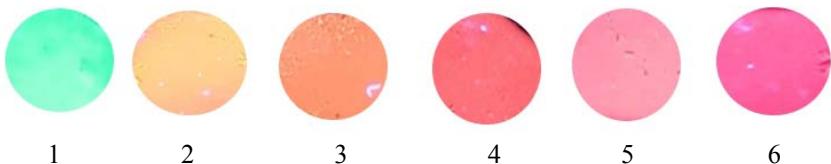


Fig. 10. Photographs under an UV lamp at 365 nm (observed through 400 nm filters): (1)  $\text{CaWO}_4$ :5% $\text{Tb}^{3+}$ ; (2)  $\text{CaWO}_4$ :4% $\text{Tb}^{3+}$ 1% $\text{Eu}^{3+}$ ; (3)  $\text{CaWO}_4$ :3% $\text{Tb}^{3+}$ 2% $\text{Eu}^{3+}$ ; (4)  $\text{CaWO}_4$ :2% $\text{Tb}^{3+}$ 3% $\text{Eu}^{3+}$ ; (5)  $\text{CaWO}_4$ :1% $\text{Tb}^{3+}$ 4% $\text{Eu}^{3+}$ ; (6)  $\text{CaWO}_4$ :5% $\text{Eu}^{3+}$ .

**Conclusions.** A series of  $\text{Eu}^{3+}$ / $\text{Tb}^{3+}$  co-doped  $\text{CaWO}_4$  phosphors were successfully prepared by a simple co-precipitation process.  $\text{CaWO}_4$ : $\text{Eu}^{3+}$  and  $\text{CaWO}_4$ : $\text{Tb}^{3+}$  phosphors exhibited the typical emissions of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ , respectively. As the content of  $\text{Eu}^{3+}$  increased, the fluorescence lifetimes of  $\text{Tb}^{3+}$  ions in  $\text{CaWO}_4$ :8% $\text{Tb}^{3+}$  $n\text{Eu}^{3+}$  ( $n = 0$ –10%) decreased, indicating the energy transfer process from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  in  $\text{CaWO}_4$  host. Under the excitation of 378 nm, the energy transfer efficiency from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  in  $\text{CaWO}_4$ :8% $\text{Tb}^{3+}$ 10% $\text{Eu}^{3+}$  was 33.8%. By adjusting the doping concentrations of  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$ , a series of  $\text{Eu}^{3+}$ / $\text{Tb}^{3+}$  co-doped  $\text{CaWO}_4$  phosphors emitted green, yellow and red colors under 365-nm UV lamp. Therefore,  $\text{Eu}^{3+}$ / $\text{Tb}^{3+}$  co-doped  $\text{CaWO}_4$  phosphor could be used as a candidate for colorful phosphors.

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