

A Study on the Luminescence and Energy Transfer of Green-Emitting $\text{Ca}_9\text{Y}(\text{PO}_4)_7:\text{Ce}^{3+}, \text{Tb}^{3+}$ Phosphor for Fluorescent Lamp Application

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Abstract

A series of green-emitting $\text{Ca}_9\text{Y}(\text{PO}_4)_7:\text{Ce}^{3+}, \text{Tb}^{3+}$ (CYP:Ce,Tb) phosphors were synthesized by a solid state reaction. Under excitation at 254 nm, the as-synthesized CYP:Ce,Tb phosphors showed two typical emission bands, peaking at 366 nm for Ce^{3+} and 544 nm for Tb^{3+} , respectively. The energy transfer from Ce^{3+} (sensitizer) to Tb^{3+} (activator) in the $\text{Ca}_9\text{Y}(\text{PO}_4)_7$ host was demonstrated to be a resonant type via a dipole-dipole mechanism with the critical distance of 6.88 Å. The thermal quenching stability of the composition-optimized $\text{Ca}_9(\text{Y}_{0.35}\text{Ce}_{0.15}\text{Tb}_{0.5})(\text{PO}_4)_7$ was found to be higher than that of $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$ commodity. The CIE chromaticity coordinates for the CYP:Ce,Tb phosphor and fluorescent lamp were found to be (0.342, 0.543) and (0.314, 0.532), respectively. Our results demonstrated that CYP:Ce,Tb can serve as a potential green-emitting phosphor for fluorescent lamp application.

Keywords: $\text{Ca}_9\text{Y}(\text{PO}_4)_7:\text{Ce}^{3+}, \text{Tb}^{3+}$; Green-emitting; Photoluminescence; Energy transfer; Fluorescent lamps.

1. Introduction

Rare-earth doped luminescent materials are widely applied in lighting and display devices, such as plasma display panels, fluorescent lamps, lighting emitting diodes (LED) and so on.^[1] The study of seeking new luminescent materials, thus, is of great research interest. Fluorescent lamps are essentially consisted of a glass tube lined on the inside with a phosphor coating and filled inside with a mixture of mercury vapor and argon.

As electric current flows through the lamp, the mercury atoms are bombarded by electrons and excited to emitted wavelengths at 254 nm (~ 65 %) and 185 nm (10 ~ 20 %),^[2] as well as longer wavelengths at 365, 405, 436, 546 and 577 nm.^[3] Thus, the phosphors must have a strong optical absorption in the short ultra-violet region of 254 nm. Tb^{3+} is a good candidate for green-emitting (sharp band at 544 nm) phosphors as an activator; however, the absorption wavelength of solely-doped these phosphors at the short ultra-violet region of 254 nm is weak. Therefore, by doping the sensitizer into a crystalline host is an efficient way to improve the luminescence intensity of phosphors. As a promising Tb^{3+} activator, Ce^{3+} can act as an efficient sensitizer transferring energy to Tb^{3+} and has been investigated in various hosts such as LaPO_4 ,^[4] BaBPO_5 ,^[5] $\text{LaMgAl}_{11}\text{O}_{19}$,^[6] $\text{Y}_3\text{Si}_2\text{O}_8\text{Cl}$,^[7] $\text{Sr}_3\text{Al}_{10}\text{SiO}_{20}$,^[8] $\text{CaAl}_2\text{B}_2\text{O}_7$,^[9] and $\text{Ca}_2\text{Al}_2\text{SiO}_7$.^[10]

To the best of our knowledge, the luminescence properties and the corresponding study on the energy transfer mechanism of $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$ in the $\text{Ca}_9\text{Y}(\text{PO}_4)_7$ host have not been reported. In this study, we firstly reported the luminescence properties, energy transfer efficiency and mechanism, critical distance, as well as thermal quenching stability and the applications for fluorescent lamps. We have demonstrated that a green-emitting phosphor can be achieved by co-doped Ce^{3+} and Tb^{3+} ions in the CYP host. The result demonstrated that the CYP:Ce,Tb green-emitting phosphor exhibits great potential in fluorescent lamp application.

2. Materials and Methods

Materials Preparation: The green-emitting $\text{Ca}_9(\text{Y}_{0.85-x}\text{Ce}_{0.15}\text{Tb}_x)(\text{PO}_4)_7$ (CYP:0.15 Ce^{3+} , $x\text{Tb}^{3+}$) phosphors were synthesized by a solid-state route from starting materials of CaCO_3 (Aldrich, 99.9%), Y_2O_3 (Aldrich, 99.9%), $(\text{NH}_4)_2\text{HPO}_4$ (Merck, >99%), CeO_2 (Aldrich, 99.9%), and Tb_4O_7 (Aldrich, 99.9%) with stoichiometric molar ratios of $9 : (0.85-x)/2 : 7 : 0.15 : x/4$. The reactant mixture was then thoroughly ground and mixed in an agate mortar, pressed into pellets and calcined at 1250°C for 8 h. The obtained samples are then reduced at 1000°C for 8 h under a reducing atmosphere of 40 % $\text{H}_2/60$ % N_2 in an alumina crucible and then cooled slowly.

Characterizations: The crystal structure of the as-synthesized $\text{Ca}_9(\text{Y}_{0.85}\text{Ce}_{0.15}\text{Tb}_x)(\text{PO}_4)_7$ was refined using powder X-ray diffraction analysis with an advanced automatic diffractometer (Bruker AXS D8) with $\text{Cu } K_\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) collected with $2\theta = 10^\circ - 80^\circ$ at room-temperature with the operating voltage/current of 40 kV/40 mA. The photoluminescence (PL) and PL excitation (PLE) spectra of the samples were measured using a Spex Fluorolog-3 Spectrofluorometer equipped with a 450-W Xe light source. The Commission International de l'Eclairage (CIE) chromaticity coordinates for all samples were measured by a Laiko DT-101 color analyzer equipped with a CCD detector (Laiko Co., Tokyo, Japan). The temperature-dependent PL spectra were obtained with a spectrophotometer (Jobin-Yvon Spex, Model FluoroMax-3).

Fabrication and testing of fluorescent lamps: To test the potential application of CYP:0.15 Ce^{3+} , $x\text{Tb}^{3+}$ phosphors in lighting, we have fabricated a low-pressure mercury vapor fluorescent lamp (FL) derived, in which the envelope contains argon (~ 3.4 torr) and mercury (~ 1.2 mg) and is coiled into a helical configuration, and the green-emitting $\text{Ca}_9\text{Y}(\text{PO}_4)_7:0.15\text{Ce}^{3+}, 0.5\text{Tb}^{3+}$ phosphors was coated on the interior surface of the envelope, and a pair of tungsten electrodes arranged at the sealed ends of the lamp envelope.

3. Results and Discussion

3.1 Crystal structure and morphology of

$\text{Ca}_9\text{Y}(\text{PO}_4)_7$.

The $\text{Ca}_9\text{Y}(\text{PO}_4)_7$ crystallizes in a rhombohedral structure with the space group $R3c$ (No.161)^[11] and the lattice parameters are $a = 10.4442 \text{ \AA}$, $c = 37.324 \text{ \AA}$, $V = 3525.89 \text{ \AA}^3$, and $Z = 6$. Seven crystallographically independent cation sites were found to consist of two eight-coordinated Ca^{2+} , one nine-coordinated Ca^{2+} , one six-coordinated Y^{3+} and three four-coordinated P^{5+} . The Ce^{3+} and Tb^{3+} are 1.01 and 0.923 \AA , respectively.

Therefore, according to the effective ionic radii of cations and electric charge balance, we proposed that Ce^{3+} and Tb^{3+} were expected to occupy the Y^{3+} sites in the host structure. The phase identification for CYP:Ce,Tb samples was characterized by XRD profiles and portrayed in **Fig. 1**. The XRD patterns of CYP:Ce,Tb samples were found to be consistent with that reported

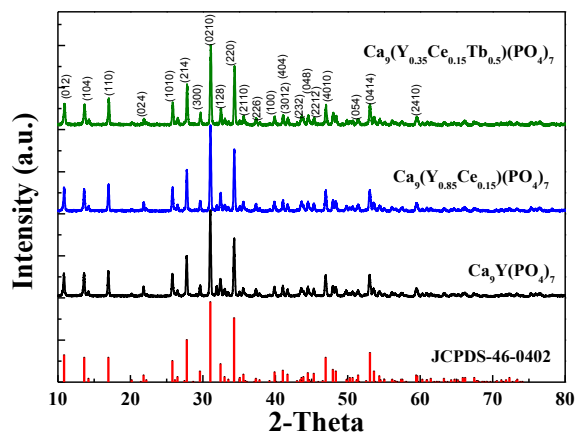


Fig. 1. Powder X-ray diffraction patterns of $\text{Ca}_9\text{Y}(\text{PO}_4)_7$, $\text{Ca}_9(\text{Y}_{0.85}\text{Ce}_{0.15})(\text{PO}_4)_7$, and $\text{Ca}_9(\text{Y}_{0.35}\text{Ce}_{0.15}\text{Tb}_{0.5})(\text{PO}_4)_7$ phosphors. (JCPDS file no. 00-046-0402).

in JCPDS file no. 46-0402.^[11] Our observations clearly revealed that no detectable impurity was presented in the investigated phosphors; even doping of the Ce^{3+} ions or co-doping of $\text{Ce}^{3+}/\text{Tb}^{3+}$ ions would not cause any observable change in the crystal structure of the CYP host. These results indicate that the $\text{Ce}^{3+}/\text{Tb}^{3+}$ co-doped CYP retained as single phased. As shown in **Fig. 2**, the particle size and the SEM image of the CYP:0.15 Ce^{3+} ,

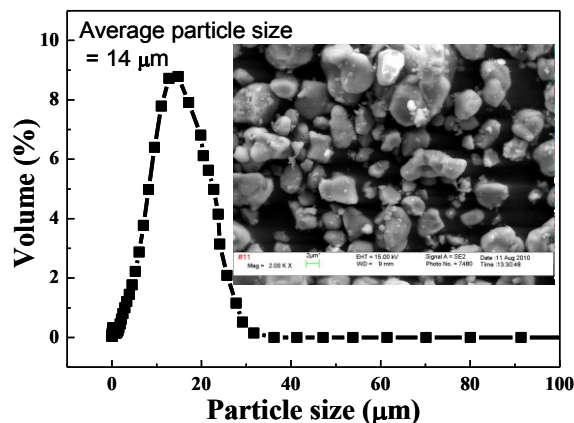


Fig. 2. The distribution of average particle sizes and the SEM image of the CYP:0.15 Ce^{3+} , 0.5 Tb^{3+} phosphors.

0.5Tb³⁺ phosphor. The particle sizes of CYP:0.15Ce³⁺, 0.5Tb³⁺ phosphor were found to vary from 1 to 30 μm, and the average particle size is about 14 μm. The inset of Fig. 2 shows the scanning electron microscopy (SEM) morphology of the CYP: 0.15Ce³⁺, 0.5Tb³⁺ phosphor, which consists of particles that are aggregated and irregular.

3.2 Luminescence properties of CYP:Ce³⁺,Tb³⁺

Fig. 3 shows the PL and PLE spectra of CYP:Ce³⁺ and CYP:Tb³⁺ phosphors. The PL spectrum of CYP:Ce³⁺ phosphor shown a broad band emission ranging from 340 to 440 nm and centered at 366 nm, which was contributed to the 5d¹ → 4f¹ transition of Ce³⁺ ions.^[12] The PLE spectra of the CYP:Ce³⁺ sample exhibited five excitation wavelengths at 204, 224, 246, 264, and 287 nm due to the crystal field splitting of Ce³⁺ 5d states.^[13]

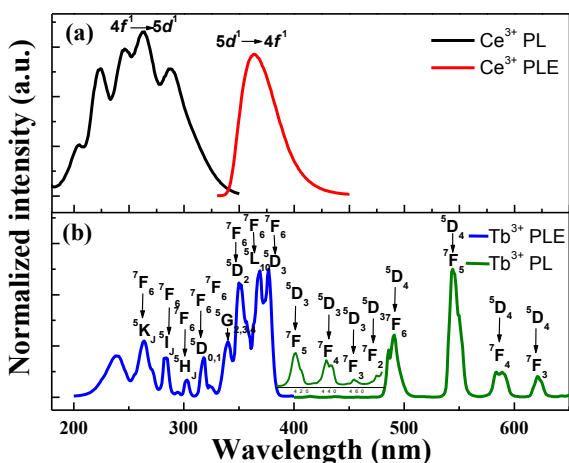


Fig. 3. The PLE and PL spectra of (a) Ca₉Y(PO₄)₇:Ce³⁺ and (b) Ca₉Y(PO₄)₇:Tb³⁺.

As for the CYP:Tb³⁺ samples, the PLE spectrum of these phosphors emitted several bands between 200 and 390 nm centered at 264, 283, 303, 318, 340, 350, 368, and 377 nm, corresponding to the transitions from the ⁷F₆ to ⁵K_J, ⁵I_J, ⁵H_J, ⁵D_{0,1}, ⁵G_{2,3,4}, ⁵D₂, ⁵L₁₀ and ⁵D₃ levels, respectively.^[14] Conversely, their emission spectra showed a series of sharp bands centered at 414, 437, 457, 473, 491, 544, 586, and 622 nm, which were assigned to the ⁵D₃ → ⁷F_J (J = 5-2) and ⁵D₄ → ⁷F_J (J = 6-3) transitions of Tb³⁺.^[15] The effective resonant energy transfer was expected to occur from Ce³⁺ to Tb³⁺ based on the observed significant spectral overlap between PL spectra of CYP:Ce³⁺ and PLE spectra of CYP:Tb³⁺. Thus, the effective resonance-type energy transfer from Ce³⁺ to Tb³⁺ (ET_{Ce→Tb}) was expected.

3.3 Energy transfer mechanism of CYP:Ce³⁺,Tb³⁺

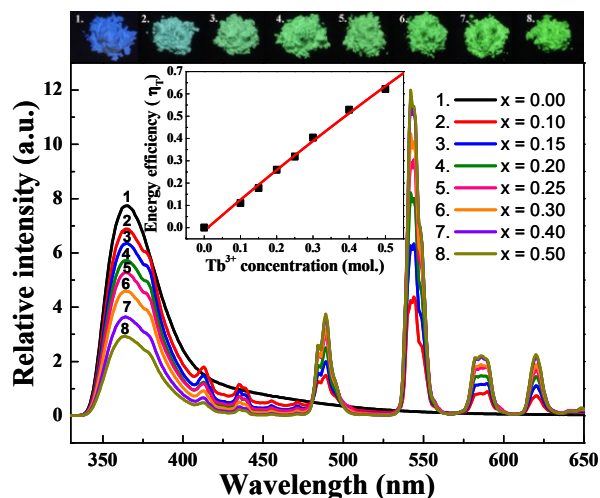


Fig. 4. The emission spectra of Ca₉(Y_{0.85-x}Ce_{0.15}Tb_x)(PO₄)₇ phosphors (x = 0, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4 and 0.5) excited at 254 nm. The inset shows the energy transfer efficiency η_T on Tb³⁺ content x and the Ca₉(Y_{0.85-x}Ce_{0.15}Tb_x)(PO₄)₇ phosphors photos under 254 nm UV box.

Fig. 4 shows the PL spectra and the relative emission intensity (Ce³⁺ monitored at 366 nm, Tb³⁺ monitored at 544 nm) for Ca₉(Y_{0.85-x}Ce_{0.15}Tb_x)(PO₄)₇ phosphors doped with different Tb³⁺ contents of 0, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4 and 0.5 mole upon 254 nm excitation. The PL emission intensity of sensitizer Ce³⁺ at 366 nm decreased with the increasing Tb³⁺ dopant content, and the emission intensity of activator Tb³⁺ at 544 nm increased with the increasing Tb³⁺ content. The results further indicated that the occurrence of energy transfer from the Ce³⁺ to Tb³⁺ ions. The inset of Fig. 4 displays the relationship between energy transfer efficiency (η_T) from Ce³⁺ to Tb³⁺ by the following equation:^[16]

$$\eta_T = 1 - \frac{I_S}{I_{S0}} \quad (1)$$

where I_{S0} is the lifetime of the sensitizer Ce³⁺ in the sample in the absence of Tb³⁺, and I_S is the lifetime of Ce³⁺ in the presence of Tb³⁺. As a consequence, the of CYP:Ce³⁺,Tb³⁺ phosphors was found to increase gradually with increasing Tb³⁺ concentration. The η_T was observed to be above 64 % when dopant concentration of Tb³⁺ ions was 0.5 mole.

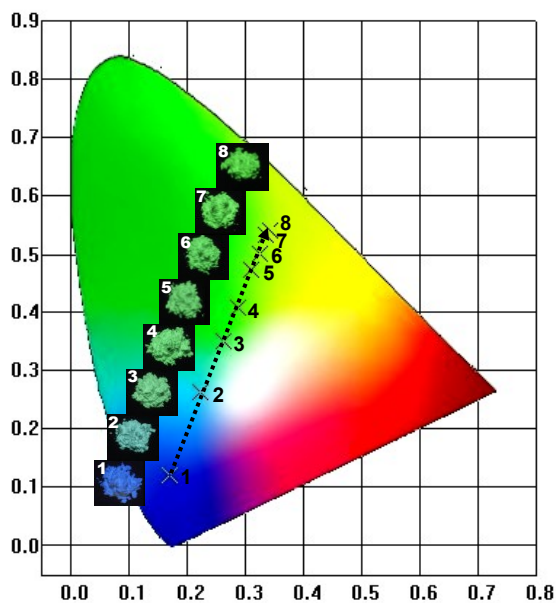


Fig. 5. CIE diagram of $\text{Ca}_0(\text{Y}_{0.85-x}\text{Ce}_{0.15}\text{Tb}_x)(\text{PO}_4)_7$ phosphors ($x = 0, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4$ and 0.5) excited at 254 nm. No.1: $x = 0$. No. 8: $x = 0.5$.

As shown in **Fig. 5**, the CIE diagram for $\text{CYP}:0.15\text{Ce}^{3+}, x\text{Tb}^{3+}$ phosphors exhibited a systematically varied hues from ultraviolet blue (0.170, 0.123) with $x = 0$ to green (0.342, 0.543) with $x = 0.5$ by adjusting the concentration of Tb^{3+} ions in $\text{CYP}:0.15\text{Ce}^{3+}, x\text{Tb}^{3+}$ phosphors. The inset in Fig. 5 shows luminescence image of $\text{CYP}:0.15\text{Ce}^{3+}, x\text{Tb}^{3+}$ phosphors under 254 nm excitation.

Fig. 6 shows the energy level scheme to illustrate the energy transfer from Ce^{3+} ions to Tb^{3+} ions in $\text{CYP}:0.15\text{Ce}^{3+}, x\text{Tb}^{3+}$ phosphors. The following four consecutive processes are proposed to rationalize the energy transfer in $\text{CYP}:0.15\text{Ce}^{3+}, x\text{Tb}^{3+}$ phosphors. First of all, the Ce^{3+} ions were excited from ground state ($4f^1$) to excited state ($5d^1$). Secondly, Ce^{3+} ions relax and emit and energy transfer occurs from Ce^{3+} to Tb^{3+} , part of the energy accounted for Ce^{3+} emission from excited state ($5d^1$) to ground state ($4f^1$, $^2F_{7/2}$ and $^2F_{5/2}$) and the rest of the energy was then transferred from Ce^{3+} to Tb^{3+} . Thirdly, non-radiative relaxation occurred from the high energy levels relaxing to the lowest 5D_3 and 5D_4 levels. Finally, Tb^{3+} ions were found to relax by emitting several sharp bands at 415, 437, 457, 473, 491, 544, 586, and 621 nm, which were attributed to the $^5D_3 \rightarrow ^7F_5$, $^5D_3 \rightarrow ^7F_4$, $^5D_3 \rightarrow ^7F_3$, $^5D_3 \rightarrow ^7F_2$, $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$ transitions of Tb^{3+} .^[17]

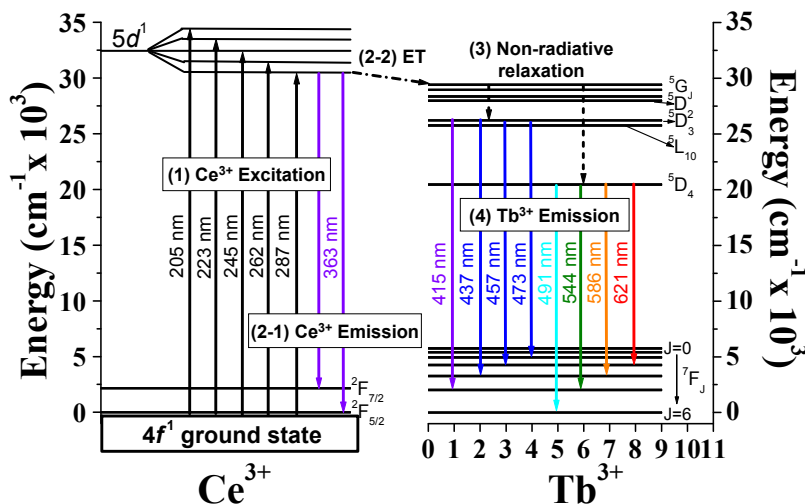


Fig. 6. The energy level scheme illustrating energy transfer from Ce^{3+} to Tb^{3+} in $\text{Ca}_0(\text{Y}_{0.85-x}\text{Ce}_{0.15}\text{Tb}_x)(\text{PO}_4)_7$ phosphors.

According to Dexter's energy transfer formula for exchange and multipolar interaction and Reisfeld's approximation, the following relations can be obtained.^[18,19]

$$\ln\left(\frac{I_{S0}}{I_S}\right) \propto C \quad \text{and} \quad \frac{I_{S0}}{I_S} \propto C^{\alpha/3} \quad (2)$$

where C is the concentration of Tb^{3+} ; as $\ln(I_{S0}/I_S)$ against C corresponds to exchange interaction and (I_{S0}/I_S)

against $C^{\alpha/3}$ with $\alpha = 6$ and 8 , corresponding to dipole-dipole, and dipole-quadrupole interactions, respectively. The plots of $\ln(I_{S0}/I_S)$ against C and (I_{S0}/I_S) against $C^{\alpha/3}$ were represented in Figs 7(a-c), and only

that with $\alpha = 6$ was observed to be a linear behavior, implying that energy transfer from sensitizer Ce^{3+} to the activator Tb^{3+} occurs via the dipole-dipole mechanism.

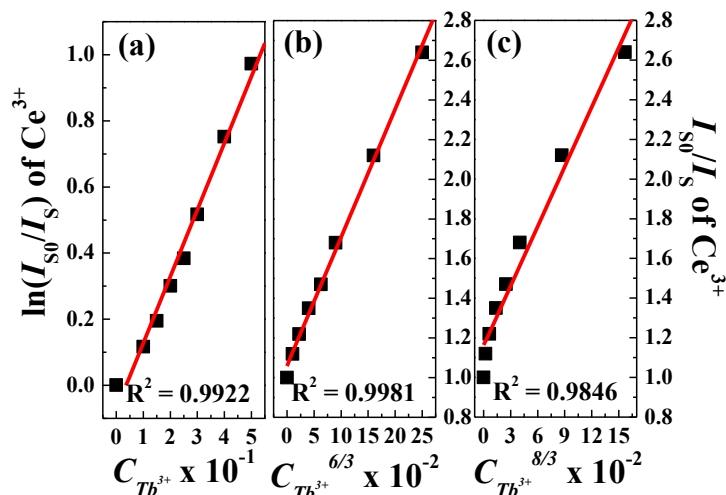


Fig. 7. Dependence of (a) $\ln(I_{S0}/I_S)$ of Ce^{3+} on C ; and I_{S0}/I_S of Ce^{3+} on (b) $C^{6/3}$ and (c) $C^{8/3}$.

From the consideration of spectral overlap, the critical distance R_c of $ET_{Ce \rightarrow Tb}$ for dipole-dipole mechanism can be calculated using the following equation:^[20]

$$P_{Ce-Tb}^{DD} = 0.63 \times 10^{28} \frac{Q_A}{\tau_{S0} R_{Ce-Tb}^6 E_S^4} \int F_S(E) F_A(E) dE \quad (3)$$

where $Q_A = 3.5 \times 10^{-21} \text{ cm}^2 \text{ eV}$ is the acceptor absorption cross section of Tb^{3+} ; $E_S = 3.5 \text{ eV}$ is the energy involved in the transfer, and $\int F_S(E) F_A(E) dE$ expresses the spectral overlap between the Ce^{3+} emission and Tb^{3+} absorption, and it was estimated be 0.725 eV^{-1} . The critical distance of energy transfer from sensitizer Ce^{3+} to activator Tb^{3+} absorption is defined as the distance for which the probability of transfer equals the probability of radiative emission of Ce^{3+} ; that is, the distance for which $P_{Ce-Tb}^{DD} \tau_{S0} = 1$. Therefore, R_c can be calculated by the following equation:^[20]

$$R_{Ce-Tb}^6 = 0.63 \times 10^{28} \frac{Q_A}{E_S^4} \int F_S(E) F_A(E) dE \quad (4)$$

The critical distance R_c for energy transfer between Ce^{3+}

and Tb^{3+} ions in the CYP host was calculated to be 6.88 \AA , which was in good agreement with those reported for $Ca_3Y(Si_3O_9)_2:Ce^{3+}, Tb^{3+}$ (6.78 \AA)^[21] and for $K_3La(PO_4)_3:Ce^{3+}, Tb^{3+}$ (6.5 \AA).^[15]

3.4 Thermal quenching stability of CYP:Ce³⁺, Tb³⁺.

Thermal quenching stability is highly critical for phosphor applications in fluorescent lamps. The relative temperature-dependent emission intensities of CYP:0.15Ce³⁺, 0.5Tb³⁺ and LaPO₄:Ce³⁺, Tb³⁺ commodity under excitation at 254 nm are compared in Fig 8. The relative emission intensity of both phosphors decreased with increasing temperature. The PL intensity of CYP:0.15Ce³⁺, 0.5Tb³⁺ and LaPO₄:Ce³⁺, Tb³⁺ was found to decay by 2.62% and 2.84% at 150°C and by 6.54% and 7.76% at 300°C, respectively. These results indicate that CYP:0.15Ce³⁺, 0.5Tb³⁺ phosphors exhibited higher thermal quenching stability than that of the LaPO₄:Ce³⁺, Tb³⁺ commodity.

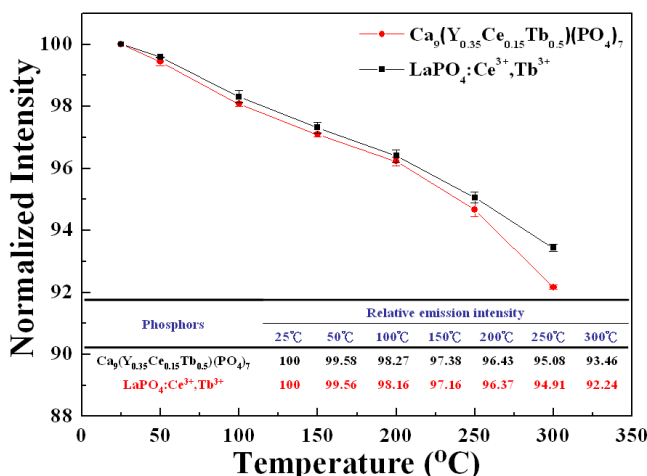


Fig. 8. Temperature dependence of relative emission intensity for Ca₉(Y_{0.35}Ce_{0.15}Tb_{0.5})(PO₄)₇ and commercial LaPO₄:Ce³⁺, Tb³⁺ phosphors (λ_{ex} = 254 nm).

3.5 Fluorescent lamp fabrication and performance.

A low-pressure mercury vapor fluorescent lamp (FL) derived in which the envelope that contains argon (~3.4 torr) and mercury (~ 1.2 mg) is coiled into a helical configuration, the green-emitting Ca₉Y(PO₄)₇:0.15Ce³⁺, 0.5Tb³⁺ phosphors coating provided on the interior surface of the envelope, and a pair of tungsten electrodes arranged at the sealed ends of the lamp envelope. When a power of 8 Watt was applied to the cathodes for inducing discharge, thereby emitting ultraviolet light centered at 404 and 435 nm for mercury,^[22] the excited

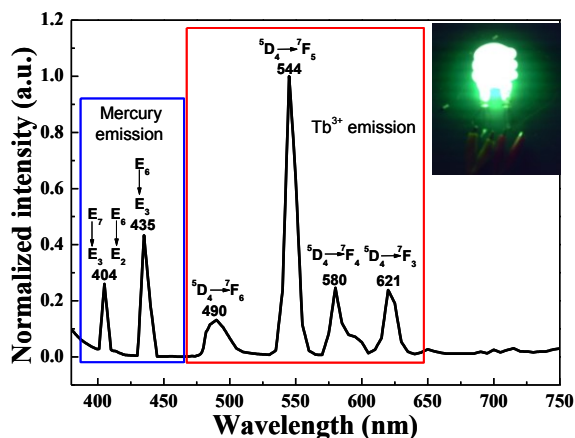


Fig. 9. PL spectrum of FL fabricated using Ca₉(Y_{0.35}Ce_{0.15}Tb_{0.5})(PO₄)₇ phosphor and the inset shows the operation of FLs at an applied power of 8W.

fluorescent layer efficiently emitted green light with a main peak wavelength at approximately 544 nm, which was attributed to CYP:0.15 Ce³⁺, 0.5Tb³⁺ phosphors emission as shown in **Fig.9**. The green-emitting fluorescent lamp shows CIE chromaticity coordinates of x = 0.314, y = 0.532. The inset shows a photograph of a green emission fluorescent lamp under a forward bias of 8 Watt. The results demonstrate that CYP:0.15 Ce³⁺, 0.5Tb³⁺ phosphors are a highly favorable potential candidate for green emission fluorescent lamps.

4. Summary

In conclusion, a series of Ce³⁺- and Tb³⁺-codoped Ca₉Y(PO₄)₇ phosphors were synthesized by a solid state reaction. Their luminescence properties and energy transfer mechanism were investigated. We have demonstrated that the energy transfer from sensitizer Ce³⁺ to activator Tb³⁺ in Ca₉Y(PO₄)₇ is a resonant type via a dipole-dipole mechanism and the critical distance was determined to be ~ 6.88 Å by the spectra overlap method. The phosphor exhibits superior thermal quenching stability to that of the LaPO₄:Ce³⁺, Tb³⁺ commodity phosphor, which indicates that CYP:0.15Ce³⁺, 0.5Tb³⁺ phosphor could be potentially useful for application in green fluorescent lamps. When a power of 8 Watt was applied to the cathodes for inducing discharge, thereby emitting ultraviolet light from mercury, the excited fluorescent layer efficiently emitted green light with a main peak wavelength at around 544 nm. The measured CIE chromaticity coordinates (x, y) for FLs has been found to be (0.314, 0.532), respectively.

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