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

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doi:10.5618/chem.2011.v1.n1.2 || Received: 22-03-2011, Accepted: 12-04-2011, Available online: 29-04-2011

Abstract

A series of green-emitting Ca$_9$Y(PO$_4$)$_7$:Ce$^{3+}$,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 Ca$_9$Y(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 Ca$_9$(Y$_{0.35}$Ce$_{0.15}$Tb$_{0.5}$)(PO$_4$)$_7$ was found to be higher than that of LaPO$_4$:Ce$^{3+}$,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: Ca$_9$Y(PO$_4$)$_7$:Ce$^{3+}$,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. 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%). As well as longer wavelengths at 365, 405, 436, 546 and 577 nm. 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$_4$,[6] BaBPO$_4$,[5] LaMgAl$_2$O$_{19}$,[6] Y$_2$Si$_2$O$_7$Cl,[7] Sr$_2$Al$_{10}$Si$_{20}$O$_{70}$,[8] CaAl$_2$O$_7$,[9] and Ca$_2$Al$_2$SiO$_7$.[10]

To the best of our knowledge, the luminescence properties and the corresponding study on the energy transfer mechanism of Ce$^{3+} \rightarrow$ Tb$^{3+}$ in the Ca$_9$Y(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 Ca$_3$(Y$_{0.85}$Ce$_{0.15}$Tb$_{0.5}$)(PO$_4$)$_7$ (CYP:0.15Ce$^{3+}$,0.5Tb$^{3+}$) phosphors were synthesized by a solid-state route from starting materials of CaCO$_3$(Aldrich, 99.9%), Y$_2$O$_3$(Aldrich, 99.9%), (NH$_4$)$_2$HPO$_4$(Merck, >99%), CeO$_2$(Aldrich, 99.9%), and Tb$_4$O$_7$(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% H$_2$/60% N$_2$ in an alumina crucible and then cooled slowly.

Characterizations: The crystal structure of the as-synthesized Ca$_3$(Y$_{0.85}$Ce$_{0.15}$Tb$_{0.5}$)(PO$_4$)$_7$ was refined using powder X-ray diffraction analysis with an advanced automatic diffractometer (Bruker AXS D8) with Cu K$_\alpha$ radiation (λ = 1.5418 Å) collected with 2θ = 10° - 80° 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’Eclaireur (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:0.15Ce$^{3+}$, xTb$^{3+}$ 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 coated into a helical configuration, and the green-emitting Ca$_3$(Y$_{0.85}$Ce$_{0.15}$Tb$_{0.5}$)(PO$_4$)$_7$ 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 Ca$_3$Y(PO$_4$)$_7$.

The Ca$_3$Y(PO$_4$)$_7$ crystallizes in a rhombohedral structure with the space group R3c (No.161) and the lattice parameters are a = 10.4442 Å, c = 37.324 Å, V = 3525.89 Å$^3$, 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 Å, 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 in JCPDS file no. 46-0402. 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 Ce$^{3+}$/Tb$^{3+}$ ions would not cause any observable change in the crystal structure of the CYP host. These results indicate that the Ce$^{3+}$/Tb$^{3+}$ co-doped CYP retained as single phased. As shown in Fig. 2, the particle size and the SEM image of the CYP:0.15Ce$^{3+}$,
0.5Tb$^{3+}$ phosphor. The particle sizes of CYP:0.15Ce$^{3+}$, 0.5Tb$^{3+}$ 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: 0.15Ce$^{3+}$, 0.5Tb$^{3+}$ phosphor, which consists of particles that are aggregated and irregular.

### 3.2 Luminescence properties of CYP:Ce$^{3+}$, Tb$^{3+}$

Fig. 3 shows the PL and PLE spectra of CYP:Ce$^{3+}$ and CYP:Tb$^{3+}$ phosphors. The PL spectrum of CYP:Ce$^{3+}$ phosphor shown a broad band emission ranging from 340 to 440 nm and centered at 366 nm, which was contributed to the 5d$^1 → 4f^1$ transition of Ce$^{3+}$ ions.$^{[12]}$

The PLE spectra of the CYP:Ce$^{3+}$ sample exhibited five excitation wavelengths at 204, 224, 246, 264, and 287 nm due to the crystal field splitting of Ce$^{3+}$ 5d states.$^{[13]}$

![Fig. 3. The PLE and PL spectra of (a) Ca$_9$Y(PO$_4$)$_2$:Ce$^{3+}$ and (b) Ca$_2$Y(PO$_4$)$_3$:Tb$^{3+}$.](image)

As for the CYP:Tb$^{3+}$ 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 $^5$F$_{6}$ to $^7$K$_{1}$, $^7$I$_{1}$, $^7$H$_{8}$, $^5$D$_{0}$, $^5$G$_{23,4}$, $^5$D$_{2}$, $^5$L$_{10}$ and $^3$D$_{3}$ 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 $^5$D$_{3}$ → $^7$F$_{J}$ ($J = 5$-2) and $^5$D$_{4}$ → $^7$F$_{J}$ ($J = 6$-3) transitions of Tb$^{3+}$.$^{[15]}$

The effective resonant energy transfer was expected to occur from Ce$^{3+}$ to Tb$^{3+}$ based on the observed significant spectral overlap between PL spectra of CYP:Ce$^{3+}$ and PLE spectra of CYP:Tb$^{3+}$. Thus, the effective resonance-type energy transfer from Ce$^{3+}$ to Tb$^{3+}$ (ET$_{Ce→Tb}$) was expected.

### 3.3 Energy transfer mechanism of CYP: Ce$^{3+}$, Tb$^{3+}$

![Fig. 4. The emission spectra of Ca$_9$(Y$_{0.85}$Ce$_{0.15}$Tb$_{0.1}$)(PO$_4$)$_2$ 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 $\eta_T$ on Tb$^{3+}$ content $x$ and the Ca$_9$(Y$_{0.85}$Ce$_{0.15}$Tb$_{0.1}$)(PO$_4$)$_2$ phosphors photos under 254 nm UV box.](image)

Fig. 4 shows the PL spectra and the relative emission intensity (Ce$^{3+}$ monitored at 366 nm, Tb$^{3+}$ monitored at 544 nm ) for Ca$_9$(Y$_{0.85}$Ce$_{0.15}$Tb$_{0.1}$)(PO$_4$)$_2$ phosphors doped with different Tb$^{3+}$ 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 Ce$^{3+}$ at 366 nm decreased with the increasing Tb$^{3+}$ dopant content, and the emission intensity of activator Tb$^{3+}$ at 544 nm increased with the increasing Tb$^{3+}$ content. The results further indicated that the occurrence of energy transfer from the Ce$^{3+}$ to Tb$^{3+}$ ions. The inset of Fig. 4 displays the relationship between energy transfer efficiency ($\eta_T$) from Ce$^{3+}$ to Tb$^{3+}$ by the following equation.$^{[16]}

$$\eta_T = 1 - \frac{I_T}{I_{S0}}$$

where $I_{S0}$ is the lifetime of the sensitizer Ce$^{3+}$ in the sample in the absence of Tb$^{3+}$, and $I_T$ is the lifetime of Ce$^{3+}$ in the presence of Tb$^{3+}$. As a consequence, the of CYP:Ce$^{3+}$,Tb$^{3+}$ phosphors was found to increase gradually with increasing Tb$^{3+}$ concentration. The $\eta_T$ was observed to be above 64% when dopant concentration of Tb$^{3+}$ ions was 0.5 mole.
As shown in Fig. 5, the CIE diagram for CYP:0.15Ce³⁺, xTb³⁺ 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 Tb³⁺ ions in CYP:0.15Ce³⁺,xCb³⁺ phosphors. The inset in Fig. 5 shows luminescence image of CYP:0.15Ce³⁺,xCb³⁺ phosphors under 254 nm excitation.

Fig. 6 shows the energy level scheme to illustrate the energy transfer from Ce³⁺ ions to Tb³⁺ ions in CYP:0.15Ce³⁺,xCb³⁺ phosphors. The following four consecutive processes are proposed to rationalize the energy transfer in CYP:0.15Ce³⁺,xCb³⁺ phosphors. First of all, the Ce³⁺ ions were excited from ground state (4f°) to excited state (5d°). Secondly, Ce³⁺ ions relax and emit and energy transfer occurs from Ce³⁺ to Tb³⁺, part of the energy accounted for Ce³⁺ emission from excited state (5d°") to ground state (4f°', 2F7/2 and 2F5/2) and the rest of the energy was then transferred from Ce³⁺ to Tb³⁺. Thirdly, non-radiative relaxation occurred from the high energy levels relaxing to the lowest 2D3 and 2D4 levels.

Finally, Tb³⁺ 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 2D3 → 7F5, 2D3 → 7F6, 5D4 → 7F0, 5D4 → 7F1, 5D4 → 7F2, 5D4 → 7F3 transitions of Tb³⁺.[17]

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

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

where C is the concentration of Tb³⁺; 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.

\[ F_{CE-Tb}^{DO} = 0.63 \times 10^{28} \frac{Q_A}{\tau_S E_S^{6/3}} \int F_S(E)F_A(E) dE \]  \( \text{3} \)

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 \( |F_A(E)F_A(E)|dE \) expresses the spectral overlap between the \( Ce^{3+} \) emission and \( Tb^{3+} \) absorption, and it was estimated be 0.725 \text{ 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 \( P_{CE-Tb}^{DO} \tau_S = 1 \). Therefore, \( R_c \) can be calculated by the following equation: \( \text{20} \)

\[ R_c^{6/3} = 0.63 \times 10^{28} \frac{Q_A}{E_S^{6/3}} \int F_S(E)F_A(E) dE \]  \( \text{4} \)

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 Å, which was in good agreement with those reported for \( Ca_3Y(Si_3O_8)_2:Ce^{3+},Tb^{3+} \) (6.78 Å) \( \text{21} \) and for \( K_3La(PO_4)_3:Ce^{3+},Tb^{3+} \) (6.5 Å). \( \text{15} \)

3.4 Thermal quenching stability of CYP:Ce\(^{3+},Tb^{3+}\).

Thermal quenching stability is highly critical for phosphor applications in fluorescent lamps. The relative temperature-dependent emission intensities of CYP:0.15Ce\(^{3+},0.5Tb^{3+}\) and LaPO\(_4\):Ce\(^{3+},Tb^{3+}\) 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:0.15Ce\(^{3+},0.5Tb^{3+}\) and LaPO\(_4\):Ce\(^{3+},Tb^{3+}\) 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:0.15Ce\(^{3+},0.5Tb^{3+}\) phosphors exhibited higher thermal quenching stability than that of the LaPO\(_4\):Ce\(^{3+},Tb^{3+}\) commodity.
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 Ca$_9$(Y$_{0.35}$Ce$_{0.15}$Tb$_{0.5}$)(PO$_4$)$_3$ and commercial LaPO$_4$:Ce$^{3+}$,Tb$^{3+}$ phosphors ($\lambda_{ex} = 254$ nm).

![Fig. 9. PL spectrum of FL fabricated using Ca$_9$(Y$_{0.35}$Ce$_{0.15}$Tb$_{0.5}$)(PO$_4$)$_3$ phosphor and the inset shows the operation of FLs at an applied power of 8 W.](image)

In conclusion, a series of Ce$^{3+}$- and Tb$^{3+}$-codoped Ca$_9$(Y$_{0.35}$Ce$_{0.15}$Tb$_{0.5}$)(PO$_4$)$_3$ 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 Ce$^{3+}$ to activator Tb$^{3+}$ in Ca$_9$(Y$_{0.35}$Ce$_{0.15}$Tb$_{0.5}$)(PO$_4$)$_3$ 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 LaPO$_4$:Ce$^{3+}$,Tb$^{3+}$ commodity phosphor, which indicates that CYP:0.15Ce$^{3+}$,0.5Tb$^{3+}$ 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 approximately 544 nm, which was attributed to CYP:0.15Ce$^{3+}$,0.5Tb$^{3+}$ 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:0.15Ce$^{3+}$,0.5Tb$^{3+}$ phosphors are a highly favorable potential candidate for green emission fluorescent lamps.

Acknowledgement

The authors would like to thank the National Science Council of Taiwan for the financial supports from under Contract no. NSC98-2113-M-009-005-MY3 (T. M. C.) and Industrial Technology Research Institute under Contract no. A301AR4150.

Reference


