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Journal of The Electrochemical Society

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J. Electrochem. Soc. 2009, Volume 156, Issue 3, Pages H193-H196.
doi: 10.1149/1.3060382

Journal of The Electrochemical Society, **156** (3) H193-H196 (2009)
0013-4651/2009/156(3)/H193/4/$23.00 © The Electrochemical Society

Blue-Green-Emitting Phosphor $CaSc_2O_4$:Tb^{3+}: Tunable Luminescence Manipulated by Cross-Relaxation

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Blue-green $CaSc_2O_4$:Tb^{3+} phosphors have been prepared by solid-state reaction. Under 254 or 276 nm light excitation, both blue and green emissions are observed, which are attributed to the characteristic 4f-4f transitions ($^5D_{3,4}$–^7F_J, $J = 6, 5, 4, 3$) of Tb^{3+}. The cross-relaxation from $^5D_3$ to $^5D_4$ states are investigated by spectroscopic and dynamic measurements. The luminescent color of $CaSc_2O_4$:Tb^{3+} can be tuned from blue to green by manipulating the cross-relaxation. Moreover, efficient white light is generated for fluorescence lamps by blending the blue-green $CaSc_2O_4$:Tb^{3+} with a red $CaSc_2O_4$:Eu^{3+} phosphor.
[DOI: 10.1149/1.3060382]

Manuscript submitted November 9, 2008; revised manuscript received December 8, 2008. Published January 15, 2009.

Nowadays, phosphors with high-efficiency, good thermal, and chemical stability and free environmental pollution have attracted more and more attention, due to their wide applications on modern lighting and display fields.[1-5] Undoubtedly, rare-earth (RE) ions have always been playing an important role in the design and synthesis of phosphors due to their abundant emission colors based on 4f-4f or 5d-4f transitions. Among the RE ions, the trivalent terbium ion (Tb^{3+}) is well known as an efficient green-emitting activator for application in the display field such as Y_2O_2S:Tb^{3+} used in color television and $LaPO_4$:Ce^{3+},Tb^{3+} in fluorescence lamps. The green emissions of Tb^{3+}-activated phosphors are originated from $^5D_4$–^7F_J transitions ($J = 3, 4, 5, 6$).[6] Besides the green emission lines, the blue emissions from higher level $^5D_3$ are also observable, depending on the host lattice (phonon frequency as well as the crystal structure) and the doping concentration of Tb^{3+}.[7,8] To detect the blue emissions, host lattice with low phonon frequency and low doping concentration of Tb^{3+} are required to avoid the multiphonon relaxation and cross-relaxation occurring among Tb^{3+} ions, which will suppress the $^5D_3$–$^5D_4$ nonradiative relaxation.[9] Therefore, Tb^{3+} activated efficient phosphors with various emission colors can be achieved by choosing a suitable host and appropriate concentration of Tb^{3+}.

Calcium scandates ($CaSc_2O_4$) has the calcium ferrite ($CaFe_2O_4$) structure, which is a crystal structure synthesized with a large divalent cation and a small trivalent cation.[10] Recently, Shimomura et al.[11] reports that Ce^{3+}-activated $CaSc_2O_4$ shows intense green luminescence with a peak wavelength of 515 nm under excitation with blue light. Its emission intensity is comparable to the commercial yellow yttrium aluminum garnet (YAG):Ce phosphor, suggesting that Ce^{3+}-activated $CaSc_2O_4$ is a great candidate for color conversion of white-light emitting diodes. It also implies that $CaSc_2O_4$ has the potential to serve as a host material in phosphor applications.

In this paper, a series of Tb^{3+}-doped $CaSc_2O_4$ phosphors have been prepared by solid-state reaction and the results on the cross-relaxation and tunable luminescence properties of $CaSc_2O_4$:Tb^{3+} as a function of Tb^{3+} concentration are reported. White light is generated by blending the blue-green $CaSc_2O_4$:Tb^{3+} with a red $CaSc_2O_4$:Eu^{3+} phosphor upon 254 nm excitation, showing $CaSc_2O_4$:Tb^{3+} phosphor can be a promising phosphor for tricolor fluorescence lamps.

Experimental

Synthesis of the powder samples was conducted by solid-state reaction. The starting materials, analytical grade, Sc_2O_3, $CaCO_3$, and Tb_4O_7 were homogenized by an agate mortar, pestled for 1 h, and placed in a crucible with a lid. The crucible was buried by carbon sticks and sintered at 1500°C for 4 h in CO reducing atmosphere. The concentration of Tb^{3+} was varied from 0.1 to 12 mol %. The red $CaSc_2O_4$:$0.08Eu^{3+}$ phosphor for mixing with $CaSc_2O_4$:$0.03Tb^{3+}$ to realize white-light emission was also synthesized by the same process as described above.

The structure of sintered samples was identified by X-ray powder diffractometer [(XRD), Rigaku D/M AX-2500 V]. The morphology was investigated by using field-emission scanning electron microscopy [(FESEM), Hitachi S-4800]. The measurements of photoluminescence (PL) and photoluminescence excitation (PLE) spectra were performed by using a Hitachi F4500 fluorescent spectrometer. In fluorescence lifetime measurements, the fourth harmonic (266 nm) of a Nd–YAG laser (Spectra-Physics, GCR 130) was used as an excitation source, and the signals were detected with a Tektronix digital oscilloscope (TDS 3052).

Results and Discussion

XRD patterns of the $CaSc_2O_4$:$0.05Tb^{3+}$ sample are shown in Fig. 1. All the peaks are indexed based on orthorhombic structure and match well with JCPDS card no. 20-0234 [space group: *Pnam* (62), $a = 9.46$ Å, $b = 11.12$ Å, and $c = 3.143$ Å]. There are no impurity

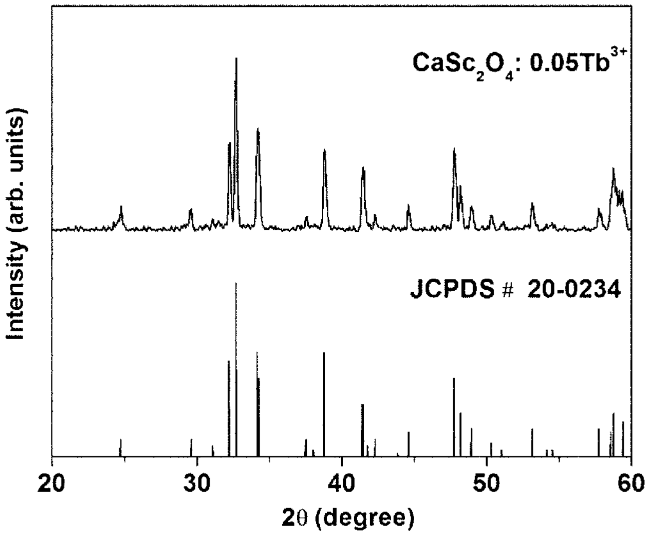

Figure 1. XRD patterns of $CaSc_2O_4$:$0.05Tb^{3+}$ sample sintered at 1500°C for 4 h.

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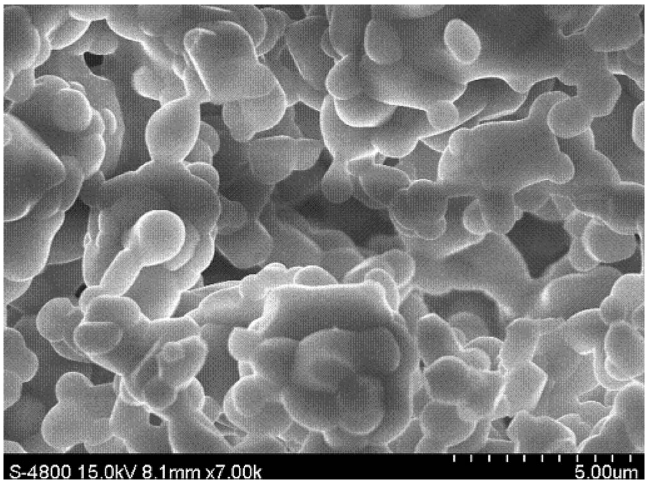

Figure 2. FESEM image of $CaSc_2O_4$:$0.05Tb^{3+}$ sample.

peaks in the XRD analysis, indicating the well-formed single phase of the sample. FESEM observation of the powders is depicted in Fig. 2. It exhibits that the particles are agglomeration in shape and have a good crystallinity due to high sintering temperature. The size of the particles is in the range of 500 nm to 3 μm.

Figure 3 presents the PL and PLE spectra of $CaSc_2O_4$:$0.05Tb^{3+}$ sample. The excitation spectrum (dotted line, $\lambda_{em} = 542$ nm) consists of several broadbands with peaks at 276 nm ($36,232\ cm^{-1}$), 258 nm ($38,769\ cm^{-1}$), and 301 nm ($33,222\ cm^{-1}$), respectively, originating from $4f^8$–$4f^7 5d^1$ transitions allowed by the electric dipolar parity.[12] These broad excitation bands cannot be assigned to $Tb^{3+} \leftarrow O^{2-}$ charge-transfer (CT) transition because the CT states have much higher energy ($\sim 60,000\ cm^{-1}$) than 5d states of Tb^{3+}.[13] Under 276 nm (dashed line) or 254 nm (solid line) excitation, the emission spectra yield both blue and green emissions in the regions of 350–480 and 480–650 nm, which are due to the $^5D_3$–^7F_J ($J = 3, 4, 5, 6$) and $^5D_4$–^7F_J ($J = 3, 4, 5, 6$) transitions of Tb^{3+} ions, respectively. Specifically, the emission bands at 380, 414, 436, and 456 nm are attributed to the emission transitions of $^5D_3 \rightarrow {}^7F_6$, $^5D_3 \rightarrow {}^7F_5$, $^5D_3 \rightarrow {}^7F_4$, and $^5D_3 \rightarrow {}^7F_3$, respectively, and 488, 542, 584, and 619 nm emissions to the transitions of $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, and $^5D_4 \rightarrow {}^7F_3$, respectively. Among these transitions, the green emission $^5D_4 \rightarrow {}^7F_5$ at 542 nm is the most intense, which is a magnetic dipole transition and satisfies the selection rule $\Delta J = \pm 1$. In order to investigate the concentration-dependent luminescent properties of Tb^{3+} ion in $CaSc_2O_4$, a series of $CaSc_2O_4$:xTb^{3+} ($x = 0.001$–0.12) have been prepared and their PL emission spectra ($\lambda_{ex} = 276$ nm) are given in Fig. 4. It shows that the relative intensities of $^5D_3$–^7F_J and $^5D_4$–^7F_J transitions are strongly dependent on the Tb^{3+} concentration. As the Tb^{3+} concentration increases, the emission intensities of $^5D_3$–^7F_J decrease, whereas the intensities of $^5D_4$–^7F_J increase. This is mainly due to the cross-relaxation that is Tb^{3+} concentration dependent, and the process can be described as $Tb^{3+}(^5D_3) + Tb^{3+}(^7F_6) \rightarrow Tb^{3+}(^5D_4) + Tb^{3+}(^7F_0)$.[14,15] It is evidenced that the cross-relaxation enhances the decay from the high energy level $^5D_3$ to the low energy level $^5D_4$. An energy level scheme illustrating the characteristic emissions and cross-relaxation of Tb^{3+} in $CaSc_2O_4$ is explained in Fig. 5a.

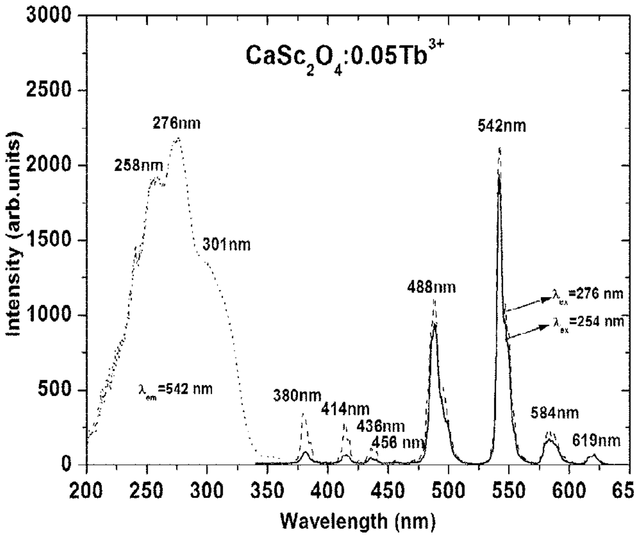

Figure 3. PL and PLE spectra of $CaSc_2O_4$:$0.05Tb^{3+}$: $\lambda_{em} = 542$ nm (dotted line), $\lambda_{ex} = 276$ nm (dashed line), and $\lambda_{ex} = 254$ nm (solid line).

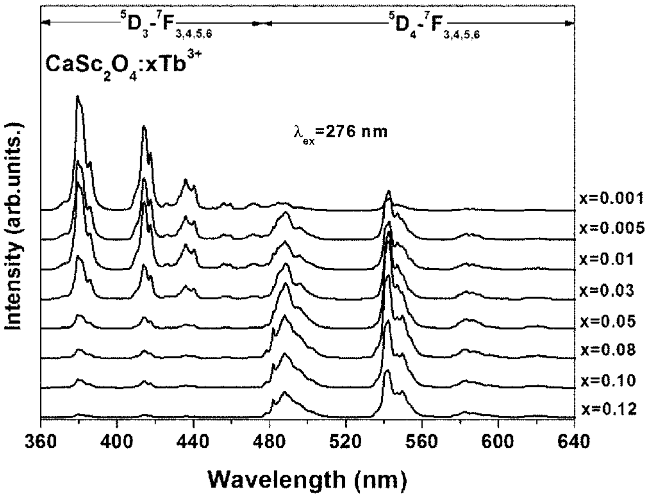

Figure 4. PL spectra ($\lambda_{ex} = 276$ nm) of $CaSc_2O_4$:xTb^{3+} ($x = 0.001$–0.12).

In principle, the cross-relaxation can shorten the lifetime of $^5D_3$. Both fluorescence lifetimes of $^5D_3$ (τ_1) and $^5D_4$ (τ_2) are measured and represented in Fig. 6. τ_2 remains nearly unchanged, indicating the nonexistence of Tb^{3+} concentration quenching within the range of Tb^{3+} contents interested in this work. Although τ_1, as expected, reduces with increasing Tb^{3+} concentration, demonstrating the occurring of cross-relaxation from $^5D_3$ excited state to $^5D_4$. The cross-relaxation rate (W_{CR}) can be obtained using

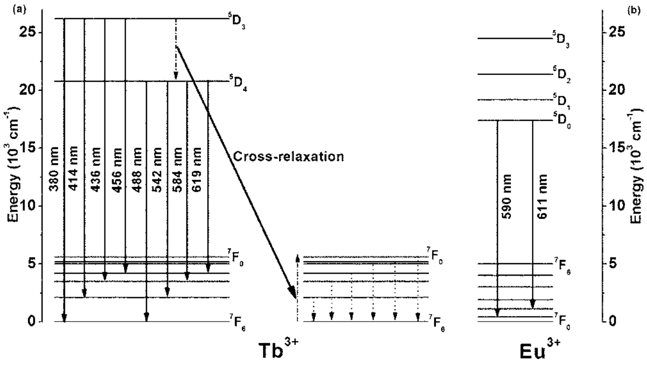

Figure 5. Schematic diagrams of Tb^{3+} and Eu^{3+} energy levels in $CaSc_2O_4$. Cross-relaxation and their characteristic emissions are also illustrated.

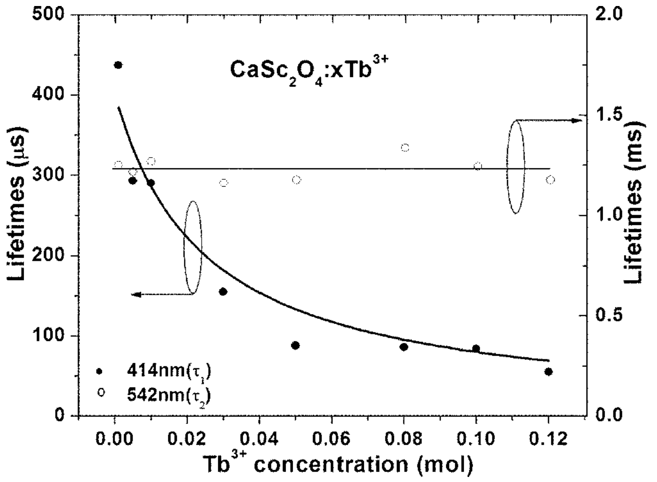

Figure 6. Fluorescence lifetimes of series of $CaSc_2O_4:xTb^{3+}$ ($x = 0.001–0.12$) as a function of Tb^{3+} concentration.

$$W_{CR} = \frac{1}{\tau_1} - \frac{1}{\tau_{10}} \quad [1]$$

where τ_{10} is the fluorescence lifetime of $^5D_3$ at the lowest doping concentration of Tb^{3+} (0.1 mol %) where the cross-relaxation is negligible. τ_{10} is then written as

$$\tau_{10} = \frac{1}{W_0 + \gamma_1} \quad [2]$$

where W_0 is the multiphonon relaxation rate and γ_1 is the radiative transition rate of $^5D_3$, both of which are Tb^{3+} concentration independent. Figure 7 demonstrates the dependence of W_{CR} on Tb^{3+} concentration with a nearly linear relationship. Thus, the energy transfer rates can be written as

$$W_{CR} = Ax \quad [3]$$

where A is a proportional constant and x is the concentration of Tb^{3+} ions. It is known that the multiphonon relaxation rate is independent of concentration for the luminescent centers. Therefore, using Eq. 1-3, τ_1 can be fitted by the function as $\tau_1 = 1/(Ax + B)$ as represented in Fig. 6 (solid line), where B is the sum of W_0 and γ_1.

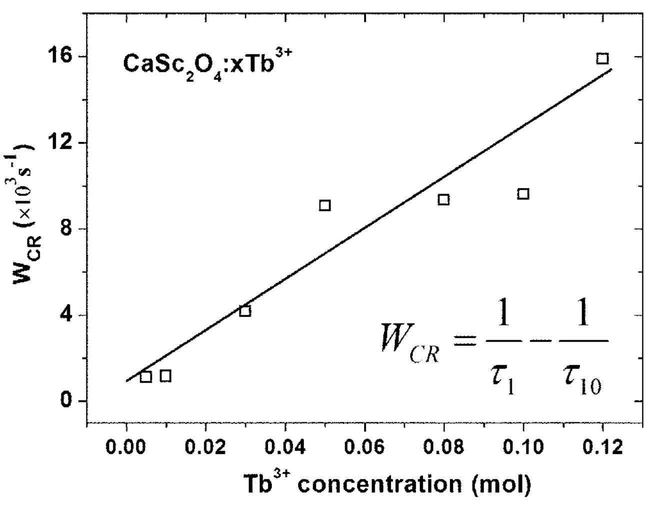

Figure 7. Dependence of the energy transfer rate (W_{CR}) in $CaSc_2O_4:xTb^{3+}$ ($x = 0.001–0.12$) on Tb^{3+} concentration.

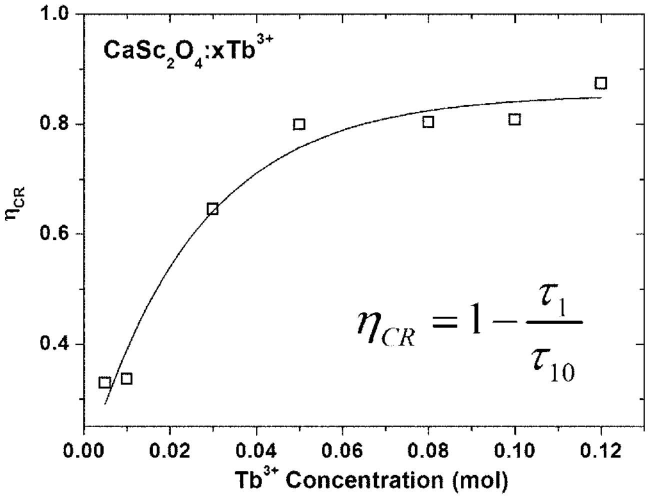

Figure 8. Dependence of the energy transfer efficiency η_{CR} in $CaSc_2O_4:xTb^{3+}$ ($x = 0.001–0.12$) on Tb^{3+} content x.

Furthermore, the cross-relaxation efficiency (η_{CR}) for $^5D_3$ to $^5D_4$ in $CaSc_2O_4:xTb^{3+}$ is also calculated by using

$$\eta_{CR} = 1 - \frac{\tau_1}{\tau_{10}} \quad [4]$$

and is illustrated in Fig. 8. With increasing Tb^{3+} doping content, the relaxation efficiency increases gradually up to 84%.

Owing to cross-relaxation, the intensity ratios ($R_{G/B}$) of green to blue emissions depends on Tb^{3+} concentration, it can be written as

$$R_{G/B} = \frac{R_0(W_{CR} + W_0)\tau_2}{W_0\tau_{20}} \quad [5]$$

where R_0 is the initial value of the ratio and τ_{20} is the lifetime of $^5D_4$ at the lowest concentration of Tb^{3+} ions. τ_2 and τ_{20} can be eliminated because τ_2 remains nearly unchanged with different Tb^{3+} concentrations (Fig. 6). Therefore Eq. 5 is rewritten as

$$\frac{R_{G/B}}{R_0} = 1 + \frac{W_{CR}}{W_0} \quad [6]$$

where $R_{G/B}$ as well as R_0 at different Tb^{3+} concentrations can be obtained directly from the emission spectra (Fig. 4). W_{CR} can be calculated according to Eq. 1. Hence, the relationship of $R_{G/B}/R_0$ and W_{CR} is obtained as plotted in Fig. 9. One can see that the dependence of $R_{G/B}/R_0$ on W_{CR} is close to a linear relationship, indicating a strong dependence of $R_{G/B}$ on Tb^{3+} concentration.

The excitation spectra (Fig. 3) shows that $CaSc_2O_4:Tb^{3+}$ phosphors can also be effectively excited by 254 nm light for the use of fluorescence lamps. Figure 10 illustrates the emission spectra of $CaSc_2O_4:xTb^{3+}$ under 254 nm excitation with the same profile to that under 276 nm excitation. Inset (a) of Fig. 10 shows the emission spectra of $CaSc_2O_4:0.08Tb^{3+}$ compared to the commercial lamp phosphor $LaPO_4$:Ce,Tb. The integral PL intensity of $CaSc_2O_4:0.08Tb^{3+}$ is 34% of $LaPO_4$:Ce,Tb phosphor, indicating that $CaSc_2O_4:Tb^{3+}$ is a potential candidate for fluorescence lamps. The CIE 1931 chromaticity coordinates for the $CaSc_2O_4:xTb^{3+}$ phosphors ($\lambda_{ex} = 254$ nm) are shown in inset (b) (solid squares). It is observed that the CIE coordinates change from $x = 0.19$, $y = 0.19$ to $x = 0.22$, and $y = 0.43$ by changing the doping concentration of Tb^{3+} to $x = 0.26$, $y = 0.56$. The corresponding luminescent color can be tuned from blue to blue-green to green. In order to obtain white-light emission, red emission phosphor, $CaSc_2O_4:0.08Eu^{3+}$ is used to mix with blue-green $CaSc_2O_4:0.03Tb^{3+}$ phosphor. Red $CaSc_2O_4:Eu^{3+}$ phosphor is also an interesting luminescent material and will be reported on later

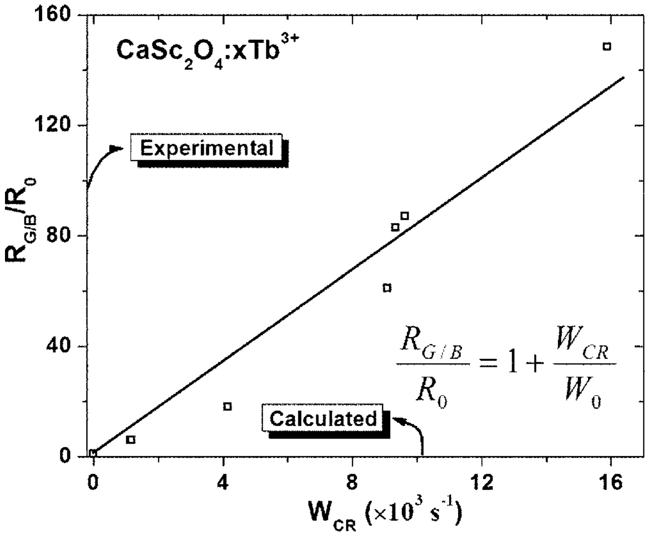

Figure 9. Dependence of $R_{G/B}/R_0$ on W_{CR}.

(Fig. 5b which shows the main energy levels of Eu^{3+} in $CaSc_2O_4$). The PL spectra of the mixed phosphor with different ratios are presented in Fig. 11. For comparison, the emission spectra of $CaSc_2O_4$:0.08Eu^{3+} and $CaSc_2O_4$:0.03Tb^{3+} are also included. Obviously, the red regions of the emission spectra of $CaSc_2O_4$:0.03Tb^{3+} (curve a) have been enhanced gradually by increasing the amount of $CaSc_2O_4$:0.08Eu^{3+} phosphors whose emission bands (curve e) are just located at 590 nm ($^5D_0 \rightarrow {}^7F_1$) and 611 nm ($^5D_0 \rightarrow {}^7F_2$), respectively. The CIE coordinates of two phosphor blends with the ratios of 1:1, 1:2, and 1:3 are presented in inset (b) of Fig. 10 (hollow triangles). For the ratio of 1:1 and 1:2, the higher energy levels $^5D_3$ and $^5D_4$ of Tb^{3+} have comparable intensity with the energy level $^5D_0$ of Eu^{3+} (curves b and c), resulting in a white-light emission with the CIE coordinates of $x = 0.35$, $y = 0.41$, and $x = 0.44$, $y = 0.39$. However, the CIE coordinate of the ratio of 1:3 ($x = 0.51$, $y = 0.38$) enters into the red region due to the dominant red emission (curve d). It is concluded that the white-light emission for fluorescence lamps can be realized by blending $CaSc_2O_4$:Tb^{3+} and $CaSc_2O_4$:Eu^{3+} phosphors with an appropriate ratio.

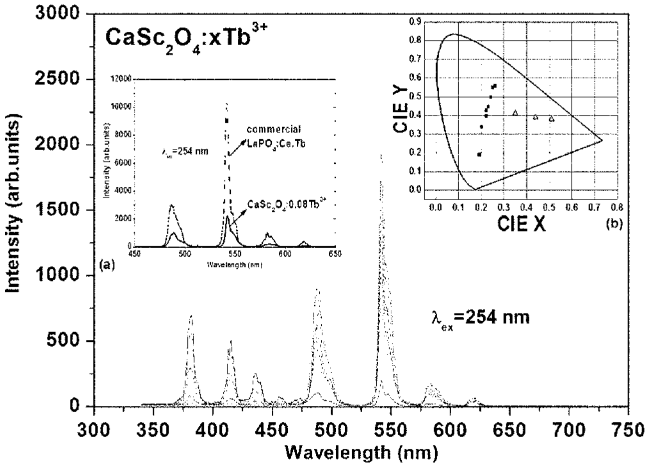

Figure 10. PL spectra (λ_{ex} = 254 nm) of $CaSc_2O_4$:$x$$Tb^{3+}$ (x = 0.001–0.12). Insets: (a) The emission spectra of $CaSc_2O_4$:0.08Tb^{3+} compared to the commercial lamp phosphor $LaPO_4$:Ce,Tb; (b) CIE chromaticity coordinates of $CaSc_2O_4$:$x$$Tb^{3+}$ (solid squares), and the mixture of two phosphors of $CaSc_2O_4$:0.03Tb^{3+} and $CaSc_2O_4$:0.08Eu^{3+} (hollow triangles).

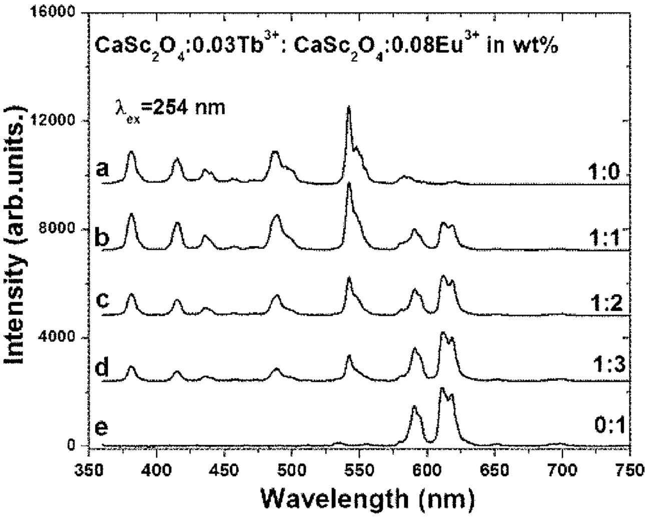

Figure 11. PL spectra of (a) $CaSc_2O_4$:0.03Tb^{3+}, (e) $CaSc_2O_4$:0.08Eu^{3+}, and (b, c, d) the mixture of two phosphors with different ratios.

Conclusions

The blue-green phosphors $CaSc_2O_4$:$x$$Tb^{3+}$ (x = 0.001–0.12) have synthesized by solid-state reaction at 1500°C. Intense blue emissions in the regions of 350–480 nm [$^5D_3$–^7F_J (J = 3, 4, 5, 6) transitions] and green emissions of 480–650 nm [$^5D_4$–^7F_J (J = 3, 4, 5, 6) transitions] of Tb^{3+} ions are observed. In particular, the luminescence color of $CaSc_2O_4$:Tb^{3+} can be tuned from blue to green through cross-relaxation by controlling Tb^{3+} concentrations. The cross-relaxation efficiency from $^5D_3$ to $^5D_4$ can be achieved as 84%. The integral PL intensity of $CaSc_2O_4$:0.08Tb^{3+} is 34% of the commercial lamp phosphor $LaPO_4$:Ce,Tb. By mixing the blue-green $CaSc_2O_4$:Tb^{3+} with a red $CaSc_2O_4$:Eu^{3+}, a white-light phosphor can be obtained for the application in fluorescent lamps.

Acknowledgments

This work is financially supported by the National Natural Science Foundation of China (10834006, 10774141) and the MOST of China (grants no. 2006CB601104, and no. 2006AA03A138)

Chinese Academy of Sciences assisted in meeting the publication costs of this article.

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