Blue-Green-Emitting Phosphor CaSc$_2$O$_4$:Tb$^{3+}$: Tunable Luminescence Manipulated by Cross-Relaxation

Zhendong Hao,a,* Jiahua Zhang, a,² Xia Zhang, a Shaozhe Lu, a and Xiaojun Wang,a,b,*

a Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China
b Department of Physics, Georgia Southern University, Statesboro, Georgia 30460, USA

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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 ($\text{Tb}^{3+}$) is well known as an efficient green-emitting activator for applications in the display field such as Y$_2$O$_3$: $\text{Tb}^{3+}$ used in color television and LaPO$_4$:Ce$^{3+}$,$\text{Tb}^{3+}$ in fluorescence lamps. The green emissions of $\text{Tb}^{3+}$-activated phosphors are originated from 5D$_4$–7F emissions of $\text{Tb}^{3+}$. 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 $\text{Tb}^{3+}$. 7,8 To detect the blue emissions, host lattice with low phonon frequency and low doping concentration of $\text{Tb}^{3+}$ are required to avoid the multiphonon relaxation and cross-relaxation occurring among $\text{Tb}^{3+}$ ions, which will suppress the 5D$_3$–5D$_4$ nonradiative relaxation. 9 Therefore, $\text{Tb}^{3+}$-activated efficient phosphors with various emission colors can be achieved by choosing a suitable host and appropriate concentration of $\text{Tb}^{3+}$.

Calcium scandates (CaSc$_2$O$_4$) has the calcium ferrite (CaFe$_2$O$_4$) structure, which is a crystal structure synthesized with a large divalent cation and a small trivalent cation. 10 Recently, Shimomura et al. 10 reports that Ce$^{3+}$-activated CaSc$_2$O$_4$ 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$_2$O$_4$ is a great candidate for color conversion of white-light emitting diodes. It also implies that CaSc$_2$O$_4$ has the potential to serve as a host material in phosphor applications.

In this paper, a series of $\text{Tb}^{3+}$-doped CaSc$_2$O$_4$ phosphors have been prepared by solid-state reaction and the results on the cross-relaxation and tunable luminescence properties of CaSc$_2$O$_4$: $\text{Tb}^{3+}$ as a function of $\text{Tb}^{3+}$ concentration are reported. White light is generated by blending the blue-green CaSc$_2$O$_4$: $\text{Tb}^{3+}$ with a red CaSc$_2$O$_4$: Eu$^{3+}$ phosphor upon 254 nm excitation, showing CaSc$_2$O$_4$: $\text{Tb}^{3+}$ 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$_2$O$_3$, CaCO$_3$, and Tb$_2$O$_3$ 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 $\text{Tb}^{3+}$ was varied from 0.1 to 12 mol %. The red CaSc$_2$O$_4$:0.08Eu$^{3+}$ phosphor for mixing with CaSc$_2$O$_4$:0.03$\text{Tb}^{3+}$ 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$_2$O$_4$:0.05$\text{Tb}^{3+}$ 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: $\text{Pnam}$ (62), $a = 9.46$ Å, $b = 11.12$ Å, and $c = 3.143$ Å]. There are no impurity

Figure 1. XRD patterns of CaSc$_2$O$_4$:0.05$\text{Tb}^{3+}$ sample sintered at 1500°C for 4 h.
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 the CaSc₂O₄:0.05Tb³⁺ 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 \( 4f^9-4f^{10}5d^1 \) transitions allowed by the electric dipolar parity. These broad excitation bands cannot be assigned to Tb³⁺ → O²⁻ charge-transfer (CT) states having much higher energy (≈60,000 cm⁻¹) than 5d states of Tb³⁺. 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 \( ^5D_{4} \rightarrow ^7F_2 (J = 3, 4, 5, 6) \) and \( ^5D_{4} \rightarrow ^7F_7 (J = 3, 4, 5, 6) \) transitions of Tb³⁺ ions, respectively. Specifically, the emission bands at 380, 414, 436, and 456 nm are attributed to the emission transitions of \( ^5D_{4} \rightarrow ^7F_2, ^5D_{3} \rightarrow ^7F_4, ^5D_{3} \rightarrow ^7F_5, \) and \( ^5D_{4} \rightarrow ^7F_6, \) respectively. Among these transitions, the green emission \( ^5D_{4} \rightarrow ^7F_2 \) 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 Tb³⁺ ion in CaSc₂O₄, a series of CaSc₂O₄:xTb³⁺ (x = 0.001–0.12) have been prepared and their PL emission spectra (\( \lambda_{em} = 276 \) nm) are given in Fig. 4. It shows that the relative intensities of \( ^5D_{4} \rightarrow ^7F_1 \) and \( ^5D_{3} \rightarrow ^7F_7 \) transitions are strongly dependent on the Tb³⁺ concentration. As the Tb³⁺ concentration increases, the emission intensities of \( ^5D_{3} \rightarrow ^7F_7 \) decrease, whereas the intensities of \( ^5D_{4} \rightarrow ^7F_1 \) increase. This is mainly due to the cross-relaxation that is Tb³⁺ concentration dependent, and the process can be described as \( ^5D_{4} \rightarrow ^7F_1 + ^5D_{3} \rightarrow ^7F_7 + ^5D_{4} \rightarrow ^7F_1 \). It is evidenced that the cross-relaxation enhances the decay from the high energy level \( ^5D_{4} \) to the low energy level \( ^5D_{3} \). An energy level scheme illustrating the characteristic emissions and cross-relaxation of Tb³⁺ in CaSc₂O₄ is explained in Fig. 5a.

In principle, the cross-relaxation can shorten the lifetime of \( ^5D_{4} \). Both fluorescence lifetimes of \( ^5D_{1} (\tau_1) \) and \( ^5D_{3} (\tau_2) \) are measured and represented in Fig. 6. \( \tau_2 \) remains nearly unchanged, indicating the nonexistence of Tb³⁺ concentration quenching within the range of Tb³⁺ contents interested in this work. Although \( \tau_1 \), as expected, reduces with increasing Tb³⁺ concentration, demonstrating the occurrence of cross-relaxation from \( ^5D_{3} \) excited state to \( ^5D_{4} \). The cross-relaxation rate (W_CR) can be obtained using
Figure 6. Fluorescence lifetimes of series of CaSc$_2$O$_4$:Tb$^{3+}$ ($x = 0.001$–$0.12$) as a function of Tb$^{3+}$ concentration.

\begin{equation}
W_{CR} = 1 - \frac{1}{\tau_{10}} - \frac{1}{\tau_{10}}\tag{1}
\end{equation}

where $\tau_{10}$ is the fluorescence lifetime of $^{5}$D$_1$ at the lowest doping concentration of Tb$^{3+}$ (0.1 mol%) where the cross-relaxation is negligible. $\tau_{10}$ is then written as

\begin{equation}
\tau_{10} = \frac{1}{W_0 + \gamma_1}\tag{2}
\end{equation}

where $W_0$ is the multiphonon relaxation rate and $\gamma_1$ is the radiative transition rate of $^{5}$D$_1$, 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

\begin{equation}
W_{CR} = Ax\tag{3}
\end{equation}

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, $\tau_1$ 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 $\gamma_1$.

Furthermore, the cross-relaxation efficiency ($\eta_{CR}$) for $^{5}$D$_3$ to $^{5}$D$_4$ in CaSc$_2$O$_4$:Tb$^{3+}$ is also calculated by using

\begin{equation}
\eta_{CR} = 1 - \frac{\tau_1}{\tau_{10}}\tag{4}
\end{equation}

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 ($R_{GB}$) of green to blue emissions depends on Tb$^{3+}$ concentration, it can be written as

\begin{equation}
R_{GB} = \frac{R_0(W_{CR} + W_0)\tau_2}{W_0\tau_2}\tag{5}
\end{equation}

where $R_0$ is the initial value of the ratio and $\tau_20$ is the lifetime of $^{5}$D$_3$ at the lowest concentration of Tb$^{3+}$ ions. $\tau_2$ and $\tau_20$ can be eliminated because $\tau_2$ remains nearly unchanged with different Tb$^{3+}$ concentrations (Fig. 6). Therefore Eq. 5 is rewritten as

\begin{equation}
R_{GB} = \frac{R_0 + W_{CR}}{W_0}\tag{6}
\end{equation}

where $R_{GB}$ 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 $R_{GB}/R_0$ and $W_{CR}$ is obtained as plotted in Fig. 9. One can see that the dependence of $R_{GB}/R_0$ on $W_{CR}$ is close to a linear relationship, indicating a strong dependence of $R_{GB}$ on Tb$^{3+}$ concentration.

The excitation spectra (Fig. 3) shows that CaSc$_2$O$_4$: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$_2$O$_4$:Tb$^{3+}$ 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$_2$O$_4$:0.08Tb$^{3+}$ compared to the commercial lamp phosphor LaPO$_4$:Ce,Tb. The integral PL intensity of CaSc$_2$O$_4$:0.08Tb$^{3+}$ is 34% of LaPO$_4$:Ce,Tb phosphor, indicating that CaSc$_2$O$_4$:Tb$^{3+}$ is a potential candidate for fluorescence lamps. The CIE 1931 chromaticity coordinates for the CaSc$_2$O$_4$:xTb$^{3+}$ phosphors ($x \approx 254$ 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$_2$O$_4$:0.08Eu$^{3+}$ is used to mix with blue-green CaSc$_2$O$_4$:0.03Tb$^{3+}$ phosphor. Red CaSc$_2$O$_4$:Eu$^{3+}$ phosphor is also an interesting luminescent material and will be reported on later.
The blue-green phosphors CaSc$_2$O$_4$·$x$Tb$^{3+}$ ($x = 0.001−0.12$) have been synthesized by solid-state reaction at 1500°C. Intense blue emissions in the regions of 350–480 nm [5D$_{0}→$7F$_{J}$ ($J = 3, 4, 5, 6$) transitions] and green emissions of 480–650 nm [5D$_{0}→$7F$_{J}$ ($J = 3, 4, 5, 6$) transitions] of Tb$^{3+}$ ions are observed. In particular, the luminescence color of CaSc$_2$O$_4$·Tb$^{3+}$ can be tuned from blue to green through cross-relaxation by controlling Tb$^{3+}$ concentrations. The cross-relaxation efficiency from Tb$^{3+}$ to Eu$^{3+}$ has been enhanced gradually by increasing the amount of Tb$^{3+}$.

The higher energy levels 5D$_{0}$, 5D$_{1}$, and 5D$_{2}$ 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 = 0.44, 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$_2$O$_4$·Tb$^{3+}$ and CaSc$_2$O$_4$·Eu$^{3+}$ with different ratios.

Conclusions

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