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

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

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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.\textsuperscript{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 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$_2$O$_3$: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$_{5/2}$ transitions (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$_2$O$_4$: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$_2$O$_4$:Tb$^{3+}$ with a red CaSc$_2$O$_4$:Eu$^{3+}$ phosphor.

Blue-green CaSc$_2$O$_4$: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 ($^3D_1$–$^7F_j$, J = 6, 5, 4, 3) of Tb$^{3+}$. The blue emissions of higher level 5D$_2$ are also observable, depending on the host lattice (phonon frequency as well as the crystal structure) and the doping concentration of Tb$^{3+}$.\textsuperscript{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$_2$–5D$_1$ nonradiative relaxation.\textsuperscript{9} Therefore, Tb$^{3+}$-activated phosphors with various emission colors can be achieved by choosing a suitable host and appropriate concentration of 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.\textsuperscript{10} Recently, Shimomura et al.\textsuperscript{11} 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 commercially available 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 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$_4$:Tb$^{3+}$ as a function of Tb$^{3+}$ concentration are reported. White light is generated by blending the blue-green CaSc$_2$O$_4$:Tb$^{3+}$ with a red CaSc$_2$O$_4$:Eu$^{3+}$ phosphor upon 254 nm excitation, showing CaSc$_2$O$_4$: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$_2$O$_3$, CaCO$_3$, and Tb$_2$O$_7$ 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$^{3+}$ varied from 0.1 to 12 mol%. The red CaSc$_2$O$_4$:0.08Eu$^{3+}$ phosphor for mixing with CaSc$_2$O$_4$:0.03Tb$^{3+}$ 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 fluorescence spectrometer. In fluorescence lifetime measurements, the fourth harmonic 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$_4$:0.05Tb$^{3+}$ 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 peaks observed in the XRD patterns, indicating that the samples are highly crystalline.

![Figure 1. XRD patterns of CaSc$_2$O$_4$:0.05Tb$^{3+}$ sample sintered at 1500°C for 4 h.](image)

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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, λex = 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−4I5d transitions allowed by the electric dipolar parity.12 These broad excitation bands cannot be assigned to Tb3+ − O2− charge-transfer (CT) states have much higher energy 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 5D3−7FJ (J = 3, 4, 5, 6) and 5D4−7FJ (J = 3, 4, 5, 6) transitions of Tb3+ ions, respectively. Specifically, the emission bands at 388, 436, and 456 nm are attributed to the emission transitions of 5D3 → 7F4, 5D4 → 7F5, and 5D4 → 7F6, respectively, and 488, 542, 584, and 619 nm emissions to the transitions of 5D4 → 7FJ, 5D3 → 7FJ, 5D3 → 7FJ, and 5D3 → 7FJ, respectively.

Among these transitions, the green emission 5D4 → 7F4 at 542 nm is the most intense, which is a magnetic dipole transition and satisfies the selection rule ΔJ = ±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 (λem = 276 nm) are given in Fig. 4. It shows that the relative intensities of 5D3−FJ and 5D4−FJ transitions are strongly dependent on the Tb3+ concentration. As the Tb3+ concentration increases, the emission intensities of 5D3−FJ decrease, whereas the intensities of 5D4−FJ increase. This is mainly due to the cross-relaxation that is Tb3+ concentration dependent, and the process can be described as Tb3+ (5D4) + Tb3+ (5F3) → Tb3+ (5D3) + Tb3+ (5Fj).14,15 It is evidenced that the cross-relaxation enhances the decay from the high energy level 5D3 to the low energy level 5D4. 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 5D3. Both fluorescence lifetimes of 5D3 (τ1) and 5D4 (τ2) are measured and represented in Fig. 6. τ2 remains nearly unchanged, indicating the nonexistence of Tb3+ concentration quenching within the range of Tb3+ contents interested in this work. Although τ1, as expected, reduces with increasing Tb3+ concentration, demonstrating the occurring of cross-relaxation from 5D3 excited state to 5D4. The cross-relaxation rate (WCR) can be obtained using

![Figure 2](image2.png)

Figure 2. FESEM image of CaSc2O4:0.05Tb3+ sample.

![Figure 3](image3.png)

Figure 3. PL and PLE spectra of CaSc2O4:0.05Tb3+: λex = 542 nm (dotted line), λex = 276 nm (dashed line), and λex = 254 nm (solid line).

![Figure 4](image4.png)

Figure 4. PL spectra (λex = 276 nm) of CaSc2O4:xTb3+ (x = 0.001–0.12).

![Figure 5](image5.png)

Figure 5. Schematic diagrams of Tb3+ and Eu3+ energy levels in CaSc2O4. Cross-relaxation and their characteristic emissions are also illustrated.
Dependence of the energy transfer rate can be written as

\[ W_{\text{CR}} = A x \]  \hspace{1cm}  \text{Eq. 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, \( \tau_1 \) can be fitted by the function as \( \tau_1 = 1/(A x + B) \) as represented in Fig. 6 (solid line), where \( B \) is the sum of \( W_0 \) and \( \gamma_1 \).

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

\[ \eta_{\text{CR}} = 1 - \frac{\tau_1}{\tau_{10}} \]  \hspace{1cm}  \text{Eq. 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 \( R_{\text{GB}} \) of green to blue emissions depends on Tb\(^{3+}\) concentration, it can be written as

\[ R_{\text{GB}} = \frac{R_0(W_{\text{CR}} + W_2)\tau_2}{W_0\tau_0} \]  \hspace{1cm}  \text{Eq. 5} \]

where \( R_0 \) is the initial value of the ratio and \( \tau_1 \) and \( \tau_2 \) can be eliminated because \( \tau_2 \) remains nearly unchanged with different Tb\(^{3+}\) concentrations (Fig. 6). Therefore Eq. 5 is rewritten as

\[ \frac{R_{\text{GB}}}{R_0} = 1 + \frac{W_{\text{CR}}}{W_0} \]  \hspace{1cm}  \text{Eq. 6} \]

where \( R_{\text{GB}} \) as well as \( R_0 \) at different Tb\(^{3+}\) concentrations can be obtained directly from the emission spectra (Fig. 4). \( W_{\text{CR}} \) can be calculated according to Eq. 1. Hence, the relationship of \( R_{\text{GB}}/R_0 \) and \( W_{\text{CR}} \) is obtained as plotted in Fig. 9. One can see that the dependence of \( R_{\text{GB}}/R_0 \) on \( W_{\text{CR}} \) is close to a linear relationship, indicating a strong dependence of \( R_{\text{GB}} \) 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 (\( \lambda_{\text{exc}} = 254 \text{ nm} \)) are shown in inset (b) (solid squares). It is observed that the CIE coordinates change from \( x = 0.19, y = 0.19 \) to \( x = 0.22, y = 0.43 \) 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.
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$_2$O$_4$). The PL spectra of the mixed phosphor with different ratios are presented in Fig. 11. For comparison, the emission spectra of CaSc$_2$O$_4$:0.08Eu$^{3+}$ and CaSc$_2$O$_4$:0.03Tb$^{3+}$ are also included. Obviously, the red regions of the emission spectra of CaSc$_2$O$_4$:0.03Tb$^{3+}$ (curve a) have been enhanced gradually by increasing the amount of CaSc$_2$O$_4$: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 $^3D_0$ and $^3D_1$ 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 fluorescent lamps can be realized by blending CaSc$_2$O$_4$:Tb$^{3+}$ and CaSc$_2$O$_4$:Eu$^{3+}$ phosphors with an appropriate ratio.

Figure 10. PL spectra ($\lambda_{ex} = 254$ nm) of CaSc$_2$O$_4$:xTb$^{3+}$ ($x = 0.001–0.12$). Insets: (a) The emission spectra of CaSc$_2$O$_4$:0.08Tb$^{3+}$ compared to the commercial lamp phosphor LaPO$_4$:Ce:Tb; (b) CIE chromaticity coordinates of CaSc$_2$O$_4$:0.03Tb$^{3+}$ (solid squares), and the mixture of two phosphors of CaSc$_2$O$_4$:0.03Tb$^{3+}$ and CaSc$_2$O$_4$:0.08Eu$^{3+}$ (hollow triangles).

Figure 11. PL spectra of (a) CaSc$_2$O$_4$:0.03Tb$^{3+}$, (e) CaSc$_2$O$_4$:0.08Eu$^{3+}$, and (b, c, d) the mixture of two phosphors with different ratios.

Conclusions

The blue-green phosphors CaSc$_2$O$_4$:xTb$^{3+}$ ($x = 0.001–0.12$) have been synthesized by solid-state reaction at 1500°C. Intense blue emissions in the regions of 350–480 nm [$^3D_1 \rightarrow ^7F_j$ ($J = 3, 4, 5, 6$) transitions] and green emissions of 480–650 nm [$^3D_0 \rightarrow ^7F_j$ ($J = 3, 4, 5, 6$) 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 $^5D_3$ to $^7D_2$ can be achieved as 84%. The integral PL intensity of CaSc$_2$O$_4$:0.08Tb$^{3+}$ is 34% of the commercial lamp phosphor LaPO$_4$:Ce:Tb. By mixing the blue-green CaSc$_2$O$_4$:Tb$^{3+}$ with a red CaSc$_2$O$_4$:Eu$^{3+}$, a white-light phosphor can be obtained for the application in fluorescent lamps.

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