CaSc$_2$O$_4$:Eu$^{3+}$: A tunable full-color emitting phosphor for white light emitting diodes

Zhendong Hao$^a$, Jiahua Zhang$^{a,*}$, Xia Zhang$^a$, Xiaojun Wang$^{a,b}$

$^a$Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 3888 Eastern South Lake Road, Changchun 130033, China

$^b$Department of Physics, Georgia Southern University, Statesboro, GA 30460, USA

**Article info**

Article history:
Received 6 July 2010
Received in revised form 19 September 2010
Accepted 20 September 2010
Available online 30 October 2010

Keywords:
CaSc$_2$O$_4$
Eu$^{3+}$
Full-color

**Abstract**

We report an intense full-color emission originating from $^5D_{0,1,2,3}$ to $^7F_{0,1,2,3,4}$ transitions of Eu$^{3+}$ in CaSc$_2$O$_4$ upon 395 nm excitation. The emission spectra vary with increasing Eu$^{3+}$ concentration, demonstrating tunable color coordinates from white to red region in the CIE chromaticity diagram. Considering the relaxation from $^5D_J$ to $^5D_J/C_0$ through cross energy transfer, the Eu$^{3+}$ concentration dependent emission spectra are well simulated based on the analysis of steady state rate equations and the measured lifetimes of the $^5D_J$ levels. It is suggested that CaSc$_2$O$_4$:Eu$^{3+}$ could be a potential single-phased full-color emitting phosphor for near-ultraviolet InGaN chip pumped white light emitting diodes.

1. Introduction

In recent years, single-phased full-color emitting phosphors for near ultraviolet (UV) chip-based white light emitting diode (LED) have attracted more attention because they can facilitate high color rendering index and prevent the loss of luminous efficiency which often exists in phosphor blend systems due to the reabsorption between different phosphors [1–12]. The single-phased full-color phosphors are usually conducted by activators codoped systems in which energy transfer occurs, for instance, (Ba,Sr)$_3$MgSi$_2$O$_6$:Eu$^{2+}$, Mn$^{2+}$ [1,2], La$_{0.82}A_{11.19}O_{19.02}$:Eu$^{2+}$, Mn$^{2+}$ [3], Sr$_6$Al$_2$O$_{11}$Cl$_2$:Ce$^{3+}$, Eu$^{2+}$ [4], SrZn$_2$(PO$_4$)$_2$:Eu$^{2+}$, Mn$^{2+}$ [5], Sr$_2$Al$_2$Ge$_2$O$_7$:Ce$^{3+}$, Tb$^{3+}$ [6], Sr$_2$B$_2$P$_2$O$_{10}$:Eu$^{2+}$, Mn$^{2+}$, Ba$^{2+}$ [7], and NaYF$_4$:Yb$^{3+}$, Ho$^{3+}$, Tm$^{3+}$ [8], etc. Recently, Eu$^{3+}$ singly doped full-color emissions were observed in CaIn$_2$O$_4$:Eu$^{3+}$ and BaY$_2$ZnO$_5$:Eu$^{3+}$ [9–12], in which the full-color emissions of Eu$^{3+}$ were achieved by mixing the simultaneous red emission from the $^5D_0$ and blue and green emissions from the higher $^5D$ levels ($^5D_1$, $^5D_2$, and $^5D_3$) with comparable intensities. The performance of intense emissions from the higher $^5D$ levels requires low cutoff phonon frequency of the host lattice to meet small multi-phonon relaxation rates. In this case, the cross-relaxations among the higher $^5D$ levels [13] play an important role on tuning the populations of the $^5D$ levels through only controlling Eu$^{3+}$ concentration. However, to the best of our knowledge, few of suitable hosts for this type of full-color emission are reported.

Calcium scandates (CaSc$_2$O$_4$) is an oxide host crystal with calcium ferrite (CaFe$_2$O$_4$) structure [14]. Shimomura et al. reports the photoluminescence properties of Ce$^{3+}$ doped CaSc$_2$O$_4$ phosphor [15], in which the emission and excitation peak were located at 515 and 450 nm, respectively, and the luminescence efficiency was greater than that of a commercial yttrium aluminum garnet (YAG), demonstrating that CaSc$_2$O$_4$:Ce$^{3+}$ is a good candidate for color conversion of a white LED consisting of a blue GaN LED. In our previous work, we have successfully prepared Tb$^{3+}$ doped CaSc$_2$O$_4$ phosphors [16]. By manipulating the $^5D_3$ $\rightarrow$ $^5D_4$ cross-relaxation rate through controlling Tb$^{3+}$ concentrations, the luminescence colors of CaSc$_2$O$_4$:Tb$^{3+}$ can be tuned from blue to green. In a word, CaSc$_2$O$_4$ is an attractive host for the design of novel phosphors. However, to our best of knowledge, there are no reports on the luminescence properties of Eu$^{3+}$ doped CaSc$_2$O$_4$. In this paper, the tunable full-color emission of CaSc$_2$O$_4$:Eu$^{3+}$ as a function of Eu$^{3+}$ concentration has been investigated. Considering the relaxation from $^5D_0$ to $^5D_1$, through cross energy transfer, the Eu$^{3+}$ concentration dependent emission spectra are well simulated based on the analysis of steady state rate equations and the measured lifetimes of the $^5D_0$ levels.

2. Experimental

Synthesis of the powder samples was conducted by solid-state reaction. The starting materials, analytical grade, Sc$_2$O$_3$, CaCO$_3$, and Eu$_2$O$_3$ were homogenized by an agate mortar and sintered at 1500 °C for 4 h in air. For comparison, the CaIn$_2$O$_4$:0.01Eu$^{3+}$ phosphor was prepared following 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 using field emission scanning electron microscopy (FE-SEM) (Hitachi S-4800). The measurements of photoluminescence (PL) and photoluminescence excitation (PLE) spectra were performed using a Hitachi F4500 fluorescent spectrometer. In fluorescence lifetime measurements, the fourth harmonic (266 nm) of an 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).

3. Results and discussion

XRD patterns of CaSc$_2$O$_4$:Eu$^{3+}$ samples are shown in Fig. 1. All the peaks are indexed based on orthorhombic structure and match well with JCPDS card 20-0234 (space group: Pnam (62), $a = 9.46$ Å, $b = 11.12$ Å, and $c = 3.143$ Å) [17], indicating the well formed single phase of the samples. It is found that all the diffraction peaks shift to higher angles gradually in varying degrees with increasing of the Eu$^{3+}$ concentration, demonstrating reduction of the lattice parameters of CaSc$_2$O$_4$. This is attributed to the replacement of Ca$^{2+}$ with the different effective ionic radii of Ca$^{2+}$ and Eu$^{3+}$ [Ca$^{2+}$:1.12 Å, Eu$^{3+}$:1.07 Å, Sc$^{3+}$:0.87 Å; all for coordination number (CN) 8], which may modify the crystal structure or distort the metal oxide polyhedrons [18,19]. Although the charge of Eu$^{3+}$ ion is different from that of Ca$^{2+}$, there is no charge compensator induced. The mechanism is not sure, but some cation vacancies as a mechanism of the charge compensation may exist which is similar to that of Ce$^{3+}$ doped CaSc$_2$O$_4$ [15]. FE-SEM observation of the powders in Fig. 2 exhibits that the particles are agglomerate in block shape with the particle size of 0.5–3 μm.

Fig. 3 presents the PL and PLE spectra of the CaSc$_2$O$_4$:0.01Eu$^{3+}$ sample. The PLE spectrum (a) consists of two main features, a broad band in the range of 225–325 nm assigned to the charge transfer band (CTB) from O$^-$ to Eu$^{3+}$, and the characteristic f–f transition lines of Eu$^{3+}$ attributed to the transitions from $^7$F$_{0}$ ground state to the different excited states of Eu$^{3+}$, with peaks at 365 nm ($^5$D$_{0}$), 379 nm ($^5$G$_{2}$), 386 nm ($^5$G$_{4}$) and 395 nm ($^5$I$_{6}$), respectively. The PL spectrum (b) yield multi-emission lines from the $^5$D$_{0}$, $^5$D$_{1}$, $^5$D$_{2}$, $^5$D$_{3}$ excited states to the $^7$F$_{0}$ ground states of Eu$^{3+}$, including $^5$D$_{2}$ → $^7$F$_{1}$ (417 nm), $^5$D$_{2}$ → $^7$F$_{2}$ (430 nm), $^5$D$_{2}$ → $^7$F$_{3}$ (446 nm), $^5$D$_{2}$ → $^7$F$_{4}$ (465 nm), $^5$D$_{2}$ → $^7$F$_{5}$ (492 nm), $^5$D$_{2}$ → $^7$F$_{6}$ (510 nm), $^5$D$_{1}$ → $^7$F$_{1}$ (535 nm), $^5$D$_{1}$ → $^7$F$_{2}$ (556 nm), $^5$D$_{0}$ → $^7$F$_{1}$ (590 nm), $^5$D$_{0}$ → $^7$F$_{2}$ (611 nm), $^5$D$_{0}$ → $^7$F$_{3}$ (648 nm), and $^5$D$_{0}$ → $^7$F$_{4}$ transitions (700 nm) [9]. In order to compare with the full-color emission of Eu$^{3+}$ in CaIn$_2$O$_4$ host reported previously [9,10], we also present the emission spectrum (c) for comparison: (c) $\lambda_{em} = 395$ nm. PL spectrum of CaIn$_2$O$_4$:0.01Eu$^{3+}$ can be as high as 218% of that of CaIn$_2$O$_4$:0.01Eu$^{3+}$ under 395 nm excitation, indicating that CaSc$_2$O$_4$:Eu$^{3+}$ is a potential single-phase full-color emitting phosphor for near-ultraviolet (UV) InGaN chip pumped white light emitting diodes. Though the narrow absorption of Eu$^{3+}$ f–f transitions would lead to potentially severe scattering losses in LED packages, it may be improved by codoping with Bi$^{3+}$ or Sm$^{3+}$ into CaSc$_2$O$_4$ host to broaden the absorption band. This part of work is under our consideration and the results will be reported elsewhere.

Fig. 4 shows the emission spectra of CaSc$_2$O$_4$:xEu$^{3+}$ ($x = 0.005–0.06$) under 395 nm excitation. It can be seen that the emissions from the $^5$D$_{j-1}$ enhances relatively to that from its upper level $^5$D$_{j}$ as the Eu$^{3+}$ concentration increase. This result is considered to be the effect of the cross-relaxation from $^5$D$_{j}$ to $^5$D$_{j-1}$, as described by: Eu$^{3+}$($^5$D$_{j}$) + Eu$^{3+}$($^7$F$_{0}$) → Eu$^{3+}$($^5$D$_{0}$) + Eu$^{3+}$($^7$F$_{j}$), Eu$^{3+}$($^5$D$_{j}$) + Eu$^{3+}$($^7$F$_{0}$) → Eu$^{3+}$($^5$D$_{j}$) + Eu$^{3+}$($^7$F$_{j}$), and Eu$^{3+}$($^5$D$_{j}$) + Eu$^{3+}$($^7$F$_{0}$) → Eu$^{3+}$($^5$D$_{j}$) + Eu$^{3+}$($^7$F$_{j}$) [13]. As a result, the luminescence color of CaSc$_2$O$_4$:xEu$^{3+}$ can be tuned by changing the doping concentration of Eu$^{3+}$. Fig. 5 shows the corresponding CIE (Commission Internationale de l’Eclairage 1931 chromaticity) coordinates positions. The CIE coordinates change from $x = 0.28$, $y = 0.20$ (cold white) to $x = 0.38$, $y = 0.28$ (warm white) with
increasing Eu$^{3+}$ concentration from 0.5 to 2 mol%. Though the white color points are not close to the blackbody locus due to the relative weak green emission, it may be improved by mixing CaSc$_2$O$_4$:Eu$^{3+}$ with some other green emission phosphors. As the Eu$^{3+}$ concentration is higher than 2 mol%, the CIE coordinates of the phosphor enters into the orange region and no white light can be produced due to the dominant red emission.

The emission spectra upon 395 nm excitation for various Eu$^{3+}$ concentrations, as shown in Fig. 4, are simulated based on the analysis of steady state rate equations and the lifetimes of the $^5D_J$ states. A simple model illustrating the cross-relaxation and characteristic emission of Eu$^{3+}$ in CaSc$_2$O$_4$ is shown in Fig. 6. Under the 395 nm excitation, the energy relaxes from the $^5I_{6}$ level to the $^5D_J$ levels nonradiatively and then sequentially to the lower $^5D$ levels, and gives the characteristic f–f transition of Eu$^{3+}$. Considering the relaxation from $^5D_{J}$ to $^5D_{J-1}$ through both cross relaxation and multi-phonon relaxation, the steady state rate equation is written as:

$$ (W_{CRI} + W_{MPR})n_i = n_{i-1}/\tau_{i-1} $$

where $W_{CRI}$ and $W_{MPR}$ is the cross-relaxation rate and the multi-phonon relaxation rate of $^5D_i$, respectively. $n_i$ and $\tau_i$ is the population and lifetime of the $^5D_i$ level, respectively. $\tau_{i0}$ (listed in Table 1) is obtained by integrating the decay curve of the fluorescence of the $^5D_i$, of which the initial intensities are normalized. The $W_{CRI}$ can be calculated by the following relationship considering the unchanged multi-phonon relaxation rate with the Eu$^{3+}$ concentrations:

$$ W_{CRI} = \frac{1}{\tau_i - \frac{1}{\tau_{i0}}} $$

where $\tau_{i0}$ is the fluorescence lifetime of $^5D_i$ at the lowest Eu$^{3+}$ concentration of 0.5 mol% in this work, at which the cross-relaxation is negligible. The calculated $W_{CRI}$ is included in Table 1. Using Eqs. (1) and (2), the lifetimes and the cross-relaxation rates of $^5D_i$ can be calculated.

### Table 1

<table>
<thead>
<tr>
<th>Eu$^{3+}$ conc. (mol%)</th>
<th>$\tau_i$ ($\mu$s)</th>
<th>$W_{CRI}$ ($10^3$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_0$ (611 nm)</td>
<td>$\tau_1$ (535 nm)</td>
</tr>
<tr>
<td>0.5</td>
<td>1068</td>
<td>171</td>
</tr>
<tr>
<td>1</td>
<td>1072</td>
<td>166</td>
</tr>
<tr>
<td>2</td>
<td>1082</td>
<td>150</td>
</tr>
<tr>
<td>4</td>
<td>1016</td>
<td>116</td>
</tr>
<tr>
<td>6</td>
<td>1004</td>
<td>95</td>
</tr>
</tbody>
</table>
and (2), the emission intensity ratio of $5D_{i} / C_0$ to $5D_{i} / C_0$, $R_{i}$ is written as

$$R_{i}/C_0 = \frac{c_i}{C_0} \left( W_{CRi} + W_{MPRi} \right)$$

where $c_i$ is the radiative transition rate of the $5D_i$. $R_{i}/C_0$ can be obtained directly from the emission spectra in Fig. 4. The dependence of $R_{i}/C_0$ on $W_{CRi}$ is achieved and depicted in Fig. 7, demonstrating nearly linear relationships with a slope of $c_i/C_0$ and a constant intercept of $(c_i/C_0) - W_{MPRi}$, as described by Eq. (3). Therefore, from the relationship represented in Fig. 7, the relative intensities of $5D_{0,1,2,3}$ can be calculated by Eq. (3) for various $W_{CRi}$ of the Eu$^{3+}$ concentration $x$. The vertical bars in Fig. 4 are the calculated intensities based on the experimental data in Fig. 7, showing a good agreement with the measured spectra. An obvious discrepancy appears only at the lowest Eu$^{3+}$ concentration of 0.5 mol% because we approximately neglect the cross-relaxation process at this concentration.

4. Conclusions

A full-color emission is generated by combining the $5D_{0,1,2,3} - 7F_{0,1,2,3,4}$ radiative transitions of Eu$^{3+}$ in CaSc$_2$O$_4$ upon 395 nm excitation. The white light is tuned from cold to warm white by changing the Eu$^{3+}$ concentration in the range of 0.5–2 mol%. Considering the relaxation from $5D_j$ to $5D_{j-1}$ through energy transfer, the Eu$^{3+}$ concentration dependent white light spectra are well simulated based on the steady state rate equations and the measured lifetimes of the $5D_j$ levels. CaSc$_2$O$_4$:Eu$^{3+}$ may be a candidate as a single-phased full-color emitting phosphor for near-ultraviolet GaN chip pumped white LED.

Acknowledgements

This work is financially supported by the National Nature Science Foundation of China (10834006, 10774141, 10904141, 10904140), the MOST of China (2006CB601104), the Scientific project of Jilin province (20090134, 20090524) and CAS Innovation Program.

References