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Photoluminescence Properties and Fabrication of Red-Emitting LEDs based on Ca₉Eu(VO₄)₇ Phosphor

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We study the photoluminescence properties of the red-emitting phosphor Ca₉Eu(VO₄)₇ and establish a strong red emission centered at 613 nm under excitation at 395 nm (near ultra violet light, near-UV light) due to the intra-configurational ⁵D₀ → ⁷F₂ transition within the ⁴f configuration of the Eu³⁺ ions. The intensity of the emitted light decreases with increasing temperature and at T = 470 K about 50% of the intensity of the emitted light at room temperature is lost. Five different red-LED prototypes were constructed by applying a mixture of Ca₉Eu(VO₄)₇ phosphor and silicone gel on the headers of near-UV LED chips. The prototypes showed a color output from violet for the lowest phosphor concentration (133 g phosphor/l silicone gel), reaching an almost pure red-light output for the highest phosphor concentration (670 g phosphor/l silicone gel). The luminous efficiency of optical radiation (LER) was found to decrease slightly with increasing applied current. For the highest phosphor concentration, the LER decreases from 238 lmW⁻¹ for 1 mA current supply to 235 lmW⁻¹ for 18 mA current supply. The external quantum efficiency decreased from 7.33% for the lowest phosphor containing LED prototype to 4.13% for the highest one.

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The environmental and economic benefits of phosphor-converted white light emitting diodes (pc-WLEDs) have been increasingly appreciated in recent years. An important challenge in this field pertains to developing phosphors emitting in the red wavelength region, under excitation in either the near-UV range (380–410 nm) or the blue range (450–480 nm). Amongst the most promising red phosphors, particularly important are those based on intra-configurational 4f-4f transitions of Eu³⁺. Great attention has been paid on Eu³⁺-doped molybdates (e.g., Ba₂Ga₂(MoO₄)₄:Eu³⁺,² and NaEu(MoO₄)₂:Eu³⁺),¹⁴ buorosilicates (e.g., (K,Li,Na)ₓ(Y,Gd,La,Eu)ᵧTizO₁₂),¹⁴ and vana-
DeltaDiode DD-450L laser connected to a DD-C1 picosecond diode controller from Horiba Scientific. Emission spectra were recorded on an Ocean Optics USB2000+ UV-Vis spectrometer.

Phosphor-converted red LED prototypes.—Red-emitting pc-LED prototypes were developed by integrating Ca₉Eu(VO₄)₇ phosphor powder on near-UV LED chips as purchased from Semilens Corporation. The LED chip dimensions were 400 × 400 μm² and featured a 115 μm bond pad on the surface and an Au-plated back side. The active region consisted of InGaN epi-layers with an emission maximum at 390 nm. The LEDs were capable of delivering 20 mA at 3.8 V forward voltage with a junction temperature of 125°C. Au-plated Schott 8 pin TO5 headers were used as LED holders. Mounting was done using In-204 soldering paste from Indium Corporation and heating the headers on a hot plate to 200°C before mechanical transfer of the LED chip to the header. Another heating to 200°C was performed with the LED chip mounted. Contacts to two of the pins were made from the LED top bond pad as well as the back side of the Au-plated chip using a K&S 4123 wedge bonder and 17 μm Au-wire.

The Ca₉Eu(VO₄)₇ phosphor was dispersed in Elastosil RT 601 silicone gel procured from Wacker Chemicals. Elastosil RT 601A and 601B components were mixed in a 10:1 ratio. After component mixing, 75 μl of the gel was mixed with different ratios of phosphor powder. A series of five samples with a phosphor concentration of 133, 270, 400, 530, and 670 μg/ml silicone gel was prepared. These gels were then mechanically transferred to the headers to coat the LED and left to solidify overnight. A reference LED, of 75 μl pure silicone gel (without phosphor), was prepared in order to measure the absorption of the silicone gel alone. For the reproducibility of results, all the 75 μl of gel + phosphor was applied to the LEDs. The 8-pin headers with the coated LEDs were mounted in an Optronic Laboratories OL 770 Multichannel spectroradiometer integrating sphere for the optical measurements. Current was supplied using a Yokogawa 7651 Programmable DC source and simultaneous voltage was measured using a Keithley 2400 SourceMeter (to monitor the maximum allowed voltage of the LEDs).

Results and Discussion

Powder X-ray diffraction.—Fig. 1a shows the room temperature PXRD pattern of Ca₉Eu(VO₄)₇, phosphor sample along with Rietveld refinement of the PXRD pattern. The PXRD pattern shows that the sample is single-phase with no detectable amounts of impurities, having a chi-square value of 2.52. In agreement with previous studies of Ca₉Eu(VO₄)₇, the PXRD pattern can be indexed to a whitlockite-type structure (space group R3c) with a hexagonal unit cell built up of VO₄ tetrahedra with the Ca/Eu ions occupying the space between the VO₄ tetrahedra, and with the Eu³⁺ ions randomly distributed on four individual Ca crystallographic sites (Fig. 1b). The unit cell parameters are \( a = b = 10.8663 \, \text{Å}, \) and \( c = 38.0863 \, \text{Å}, \) and the unit cell volume is \( V = 3894.62 \, \text{Å}^3. \) These values are in agreement with earlier crystallographic studies of Ca₉Eu(VO₄)₇.13,14

Photoluminescence spectroscopy.—Fig. 2a shows the PL emission and excitation spectra for Ca₉Eu(VO₄)₇, as measured at \( T = 293 \, \text{K}. \) The excitation spectrum (in black color), as measured upon a LED chip dimensions were 400 μm² and featured a 115 μm bond pad on the surface and an Au-plated back side. The active region consisted of InGaN epi-layers with an emission maximum at 390 nm. The LEDs were capable of delivering 20 mA at 3.8 V forward voltage with a junction temperature of 125°C. Au-plated Schott 8 pin TO5 headers were used as LED holders. Mounting was done using In-204 soldering paste from Indium Corporation and heating the headers on a hot plate to 200°C before mechanical transfer of the LED chip to the header. Another heating to 200°C was performed with the LED chip mounted. Contacts to two of the pins were made from the LED top bond pad as well as the back side of the Au-plated chip using a K&S 4123 wedge bonder and 17 μm Au-wire.

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Ca₉Eu(VO₄)₇ phosphor, as described below. The spectrum contains two particularly strong emission lines, at 613 nm (\( ^{5}D_{0} \rightarrow ^{7}F_{2} \)) and 700 nm (\( ^{5}D_{0} \rightarrow ^{7}F_{4} \)), in agreement with the literature.23

Fig. 2c shows the PL emission spectra (550–750 nm), as a function of temperature from room temperature up to \( T = 793 \, \text{K}, \) for excitation at 454 nm. The intensity of the emitted light decreases systematically with increasing temperature. Nevertheless, virtually no shift in wavelength length of the emission bands is observed, the latter being an important characteristic for technological applications. The PL emission spectra also showed some background in the 550–575 nm region, which is not observed for excitation at 395 nm, cf. Fig. 2a. The origin of this emission is unclear but may be related to the sensitization of Eu³⁺ emission under 454 nm excitation as this wavelength region also corresponds to the emission from the lowest \( ^{5}T_{2} \rightarrow ^{1}A_{1} \) and \( ^{5}T_{1} \rightarrow ^{1}A_{1} \) transitions of VO₄²⁻ at around 462 and 468 nm with a total separation of 278 cm⁻¹.23

Fig. 2d shows the temperature dependence of the emission intensity, as integrated over the wavelength region 605–625 nm, i.e. over the predominant emission line (\( ^{5}D_{0} \rightarrow ^{7}F_{2} \)) band and normalized to the integrated intensity at the lowest temperature measured (\( T = 293 \, \text{K} \)). The integrated emission intensity decreases quite strongly with increasing temperature from \( T = 293 \, \text{K} \) to \( T = 800 \, \text{K}. \) At \( T = 423 \, \text{K}, \) the integrated emission intensity maintains about 65% of that measured at room temperature, which is similar to the previous report by Liu et al.15 (cf. 78% of the room-temperature intensity retained at \( T = 423 \, \text{K}, \) under excitation at 465 nm). The thermal quenching temperature, which is defined here as the temperature at which the PL intensity has dropped to 50% of the low-temperature value, is \( T_{50\%} \approx 470 \, \text{K}. \)
Figure 2. (a) PL spectra of Ca$_9$Eu(VO$_4$)$_7$ phosphor. The excitation (Exc.) spectrum was measured upon a fixed emission wavelength of 613 nm, and the emission (Emi.) spectrum was measured upon excitation at 395 nm. (b) Diffuse reflectance spectrum of Ca$_9$Eu(VO$_4$)$_7$ phosphor between 380 and 500 nm. (c) PL emission spectra of Ca$_9$Eu(VO$_4$)$_7$ phosphor, as a function of temperature, for excitation at 454 nm. (d) Temperature dependence of the normalized emission intensity for Ca$_9$Eu(VO$_4$)$_7$ phosphor under excitation at 454 nm.

| Current (mA) | Intensity near-UV LED (a.u.) | Intensity silicone-gel-coated near-UV LED (a.u.) | Emission loss due to silicone coating (%) |
|-------------|------------------------------|-----------------------------------------------|------------------------------------------|
| 1           | $4.92 \times 10^{-6}$       | $3.15 \times 10^{-6}$                         | 36                                       |
| 2           | $2.09 \times 10^{-5}$       | $1.47 \times 10^{-5}$                         | 30                                       |
| 3           | $4.33 \times 10^{-5}$       | $3.13 \times 10^{-5}$                         | 28                                       |
| 4           | $6.97 \times 10^{-5}$       | $5.08 \times 10^{-5}$                         | 27                                       |
| 5           | $9.79 \times 10^{-5}$       | $7.22 \times 10^{-5}$                         | 26                                       |

| Phosphor concen. (g/l) | Intensity near-UV LED (a.u.) | Intensity red-LED prototype (a.u.) | Emission intensity loss (%) | EQE (%) |
|------------------------|------------------------------|-----------------------------------|-----------------------------|---------|
| 133                    | $8.95 \times 10^{-5}$       | $1.97 \times 10^{-5}$             | 78                          | 7.33    |
| 270                    | $6.39 \times 10^{-5}$       | $3.62 \times 10^{-6}$             | 94                          | 8.13    |
| 400                    | $8.80 \times 10^{-5}$       | $1.43 \times 10^{-6}$             | 98                          | 6.53    |
| 530                    | $7.95 \times 10^{-5}$       | $2.65 \times 10^{-7}$             | 97                          | 5.63    |
| 670                    | $9.13 \times 10^{-5}$       | $2.52 \times 10^{-8}$             | 99.9                        | 4.13    |

Table 1. Upper panel: compilation of measured emission peak intensities for an uncoated near-UV (395 nm) LED (column 2), and for the near-UV LED coated with pure silicone gel (column 3). Column 4 shows the peak (395 nm) emission intensity loss due to the silicone coating. Lower panel: Total intensity of the bare near-UV LED (column 2) and of the red-LED prototypes after phosphor+silicone coating (column 3), total emission intensity loss upon comparison of intensities in column 2 and 3 (column 4); and external quantum efficiency (EQE) for the phosphor-coated red-LED prototypes (column 5). The total emission intensities were measured using an integrating sphere.
The red emission (613 nm) decreases by 78% for the lowest to 99.9% for the highest phosphor to silicone gel concentration. While some decrease (about 30%) can be attributed to absorption in the pure silicone gel, the observed decrease mainly is a consequence of the low EQE for the later ones. This can be considered as a downside of the Eu$^{3+}$ excitation as it is very sensitive to the host-dopant mismatch and to the entire bonding which manifests spectra with very narrow bands in the excitation and emission spectra. Upon comparison of the EQE between Eu$^{3+}$ doped samples, and those with Mn$^{4+}$ and Eu$^{2+}$ doped samples, one can clearly observe the higher EQE for the latter ones. This can be considered as a downside of the Eu$^{3+}$ excitation as it is very sensitive to the host-dopant mismatch and to the entire bonding which manifests spectra with very narrow bands in the excitation and emission spectra.

The LER or the brightness of the light as emitted by the red-LED prototypes, as perceived by the average human was calculated according to the following relationship:

\[
LER = 683 \text{lm/W} \cdot \frac{\int_{\lambda=560}^{\lambda=830} I(\lambda) V(\lambda) d\lambda}{\int_{\lambda=560}^{\lambda=830} I(\lambda) d\lambda}
\]

where the prefactor 683 lm/W is a normalization factor, V(\lambda) is the eye sensitivity, and I(\lambda) the emission spectrum. Under an applied current of 1 mA, the prototype with the highest phosphor concentration exhibits a LER of 238 lm/W, which decreased only very slightly, to 235 lm/W, when increasing the current to 18 mA (Fig. 3c, inset), suggesting a high stability of luminescence toward increasing current of the LED base.

The colors of the emitted light from the five LED prototypes were further evaluated using a CIE 1931 color space diagram (Fig. 4). The color evolves from being dominated by the violet emission from the LED base at the lowest phosphor concentration to bright red color for the highest phosphor concentration, i.e. very close to the red edge of the color space diagram. Furthermore, we observe that the emission spectrum is dominated by the strong emission band at 613 nm ($^7F_2 \rightarrow ^5D_0$), whereas the other emission band at approximately 700 nm ($^7F_0 \rightarrow ^5D_2$) is much weaker, resulting in a high color purity. The high color purity, temperature stability, and LER makes Ca$_9$Eu(VO$_4$)$_7$ a highly promising phosphor for technological applications.

**Conclusions**

To conclude, our results establish that the emission spectrum of the red-emitting phosphor Ca$_9$Eu(VO$_4$)$_7$ is dominated by a sharp emission peak at 613 nm, with a decrease in intensity as the concentration of phosphor increases. The red emission is highly stable under increasing current, with a high color purity and temperature stability, making it a promising candidate for technological applications.
Figure 4. CIE 1931 color coordinate diagram for the five different pc-LED prototypes based on Ca$_9$Eu(VO$_4$)$_7$ phosphor and a near-UV LED [CIE 1931, $(x,y) = (0.434, 0.197)$ for 133 g/l, $(0.544, 0.264)$ for 270 g/l, $(0.589, 0.291)$ for 400 g/l, $(0.624, 0.312)$ for 530 g/l, and $(0.652, 0.328)$ for 670 g/l] under 5 mA current supply at $T = 300$ K.

band at 613 nm under excitation with near-UV light (395 nm). The data presented in the work demonstrates that the Eu$^{3+}$-based phosphor has significant issues with respect to practical implementation. The color of the emitted light is stable upon increasing temperature from $T = 293$ to $T = 793$ K, but shows a strong decrease in the emitted intensity. At $T = 420$ K, the integrated intensity of the 613 nm emission band has decreased to about 65% of that at room temperature, and at $T = 470$ K it has decreased to about 50%. Furthermore, the performance of Ca$_9$Eu(VO$_4$)$_7$ phosphor was evaluated by coating the phosphor on near-UV LED chips with silicone gel as an encapsulating agent. By this relatively simple phosphor capping technique, we obtain red-LEDs featuring a high red color purity and thermal stability.

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