$M_9Gd_2W_4O_{24}:Eu^{3+}$ ($M^{2+} = Ca^{2+}$ and Sr^{2+}) Red Phosphors for NUV and Blue InGaN-based WLEDs

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$M_9Gd_2W_4O_{24}:Eu^{3+}$ ($M^{2+} = Ca^{2+}$ and Sr^{2+}) phosphors were prepared by solid-state reaction, and the phosphors show intense red emission under 395 and 465 nm excitations, which matched the emission wavelength of a near-UV (NUV) chip and a blue chip, respectively. Bright white LEDs were fabricated, and the performances of the LEDs demonstrate that the tetratungstate phosphors are suitable for application to NUV and blue InGaN-based WLEDs.

White light-emitting diodes (WLEDs) as a novel generation of illumination technology have great potential for application in the lighting domain. Currently, the dominant commercial method to obtain white light is by combining a blue (ca. 460 nm) chip with a yellow-emitting phosphor YAG:Ce^{3+}. However, the most conspicuous problem for such "blue and yellow" WLEDs is that the color temperature is too high (6000–7000 K) to be applied as an indoor warm-lighting because of the lack of red light.[1–3] Another method is by combing a NUV (ca. 400 nm) chip with red, green, and blue phosphors.[1–3] The commonly used phosphors are blue phosphor $BaMgAl_{10}O_{17}:Eu^{2+}$, green phosphor $ZnS:Cu^+/Al^{3+}$, and red phosphor $Y_2O_2S:Eu^{3+}$.[2] Compared with the blue and green phosphors, $Y_2O_2S:Eu^{3+}$ shows lower efficiency[2] and instability.[3] Therefore, it is urgent to search for new red phosphors with high efficiency and stability.

As important optical materials, tungstates and molybdates[2,4,5] have attracted particular interest. In our previous paper,[6] we report the luminescence of tetratungstate $Sr_9Gd_2W_4O_{24}:Eu^{3+}$. The phosphors show intensely red emission under 395 and 465 nm excitations and are considered to be suitable application of NUV and blue InGaN-based WLEDs. As systematic and further work, in the present letter, other tetratungstate $Ca_9Gd_2W_4O_{24}:Eu^{3+}$ phosphors were found and compared with $Sr_9Gd_2W_4O_{24}:Eu^{3+}$.

Phosphors were prepared by solid-state reaction. The stoichiometric mixtures of $CaCO_3$, $SrCO_3$, WO_3 (A.R. grade), and M_2O_3 (99.99% purity, $M^{3+} = Eu^{3+}$ and Gd^{3+}) were first ground and then sintered at 1400 °C for 4 h. The commercial yellow phosphor YAG:Ce^{3+} was provided by Jiangmen Kanhoo Industry Co., Ltd. The synthesized phosphors were characterized by X-ray diffraction (XRD, Rigaku D/max 2200 vpc, Cu Kα radiation), field emission scanning electron microscopy (FESEM, JEOL JSM-6330F), photoluminescence spectrometry (EDINBURGH FLS920), and LED spectrophotocolorimetry (EVERFINE PMS-50).

Figure 1a shows the XRD patterns of $Sr_{9-x}Ca_xEu_2W_4O_{24}$. With increasing values of x in $Sr_{9-x}Ca_xEu_2W_4O_{24}$, the XRD patterns transfer gradually from $Sr_9Gd_2W_4O_{24}$ (JCPDS 50-0375) to $Ca_9Gd_2W_4O_{24}$ (JCPDS 41-0186). The radius of Eu^{3+} (0.95 nm) is almost equal to that of Gd^{3+} (0.94 nm); therefore, Eu^{3+} and Gd^{3+} can form a solid solution in both $Ca_9Gd_2W_4O_{24}$ and $Sr_9Gd_2W_4O_{24}$ hosts, showing that Eu^{3+} doping did not change the lattice of the hosts, and no concentration quenching of Eu^{3+} was observed in either hosts. $Ca_9Eu_2W_4O_{24}$ and $Sr_9Eu_2W_4O_{24}$ show a uniform morphology and an average particle size of 4–8 μm (Figures 1b and 1c), indicating that both the phosphors can meet the demands of the LED application basically.

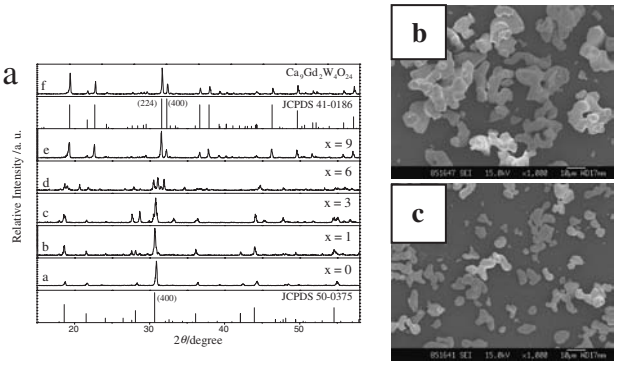

Figure 1. a) XRD patterns of $Sr_{9-x}Ca_xEu_2W_4O_{24}$ ($x = 0$, 1, 3, 6, and 9) (curves a–e) and $Ca_9Gd_2W_4O_{24}$ (curve f), b) FESEM image of $Ca_9Eu_2W_4O_{24}$, and c) FESEM image of $Sr_9Eu_2W_4O_{24}$.

The excitation and emission spectra of $Sr_9Eu_2W_4O_{24}$ and $Ca_9Eu_2W_4O_{24}$ are shown in Figure 2a. The profiles of both excitation spectra (curves 1 and 2) are similar except for the intensity. The broad band from 250 to 350 nm is attributed to the charge transfer of $O^{2-} \rightarrow W^{6+}$ and $O^{2-} \rightarrow Eu^{3+}$, and the sharp lines in the 360–500 nm range are attributed to 4f–4f transitions of Eu^{3+}. Both excitations at 395 and 465 nm are very strong, and the $^7F_0 \rightarrow {}^5D_2$ at 465 nm is the strongest absorption which may be favorable to resolve the problem of the high color temperature of YAG:Ce^{3+}-WLEDs.[7,8] The emission spectra (curves 3–6) under 395 and 465 nm excitations are composed of groups of sharp lines, which belong to the characteristic emission of Eu^{3+}. However, the main emission ($^5D_0 \rightarrow {}^7F_2$) of Eu^{3+} in $Ca_9Eu_2W_4O_{24}$ shows red shift compared with that in $Sr_9Eu_2W_4O_{24}$, which may result from different covalency of Eu–O bond between $Ca_9Eu_2W_4O_{24}$ and $Sr_9Eu_2W_4O_{24}$.[9] Other f–f transitions of Eu^{3+} are very weak, which is advantageous to obtain good Commission International de l'Eclairage (CIE) chromaticity coordinates.

Figure 2b depicts the dependence of the Eu^{3+} emission intensities on Ca^{2+} content (x) in $Sr_{9-x}Ca_xEu_2W_4O_{24}$ under 395 and 465 nm excitations. With the increase of Ca^{2+} content, the emission intensities initially decrease and then increase which is in good agreement with the XRD patterns. As indicated above,

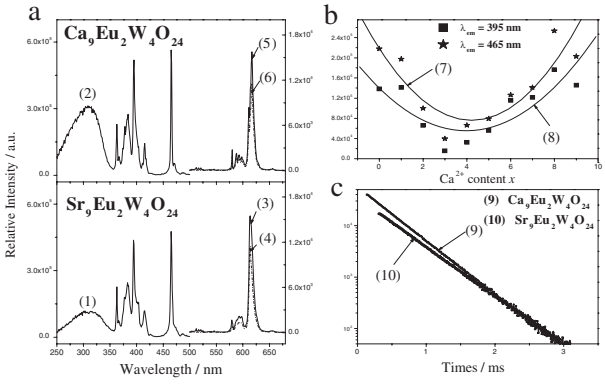

Figure 2. a) The excitation (left, $\lambda_{em} = 617$ nm) and emission spectra (right, dashed: $\lambda_{ex} = 395$ nm, solid: $\lambda_{ex} = 465$ nm) of $Sr_9Eu_2W_4O_{24}$ and $Ca_9Eu_2W_4O_{24}$; b) The integrated intensities in the range from 500 to 680 nm as a function of the doped Ca^{2+} content (x) in $Sr_{9-x}Ca_xEu_2W_4O_{24}$; and c) The decay curves of the Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ emission of $Ca_9Eu_2W_4O_{24}$ and $Sr_9Eu_2W_4O_{24}$ ($\lambda_{ex} = 395$ nm; $\lambda_{em} = 617$ nm).

the increase of Ca^{2+} content (x) in $Sr_{9-x}Ca_xEu_2W_4O_{24}$ will lead to a phase transfer from $Sr_9Gd_2W_4O_{24}$ to $Ca_9Gd_2W_4O_{24}$. When the phosphors are used with $Sr_9Gd_2W_4O_{24}$ or $Ca_9Gd_2W_4O_{24}$ phase, they exhibit superior photoluminescence properties, showing that both $Sr_9Gd_2W_4O_{24}$ and $Ca_9Gd_2W_4O_{24}$ are excellent matrixes for phosphors.

Figure 2c shows the decay curves for $^5D_0 \rightarrow {}^7F_2$ of the Eu^{3+} of the phosphors. These decay curves can be well fitted by a single-exponential function as $I = A\exp(-t/\tau)$, and the lifetimes are 0.424 ms for $Ca_9Eu_2W_4O_{24}$ and 0.449 ms for $Sr_9Eu_2W_4O_{24}$.

Figure 3 (1 and 3–6) shows the emission spectra and corresponding photos of LEDs fabricated with NUV InGaN chips under 20 mA forward bias. Compared with the original NUV LED1, the red LEDs 3 and 5 show an obvious absorption at ca. 395 nm and an emission at ca. 618 nm due to the coated phosphor $Sr_9Eu_2W_4O_{24}$ or $Ca_9Eu_2W_4O_{24}$. Consequently, the WLEDs 4 and 6 were fabricated with the red phosphor $Sr_9Eu_2W_4O_{24}$ or $Ca_9Eu_2W_4O_{24}$, a blue phosphor and a green phosphor which were all prepared by our team. The CIE chromaticity coordinates are (0.3537, 0.3601) for WLED4, (0.3517, 0.3553) for WLED6 which are all located inside the white light domain. The color temperatures are 4718 and 4769 K for WLEDs 4 and 6, respectively, and the luminous efficiencies reach 2.27 and 2.44 lm W^{-1} which is high compared with the value (0.33 lm W^{-1}) of the original NUV chip. Unexpectedly, the color rendering indexes are low (62.5 and 60.0, respectively), which may be due to the poor mixture of the used phosphors under the manual fabrication process. Thus both the phosphors are considered to be candidates as a red component for a three-band WLED.

Curves 2 and 7–9 in Figure 3 show emission spectra of the LEDs fabricated with blue InGaN chips. All WLEDs exhibit bright white emitting (photos 7–9), and the CIE chromaticity coordinates are (0.3075, 0.3376) for WLED7, (0.3181, 0.3407) for WLED8, and (0.3378, 0.3779) for WLED9, respectively. The band between 462 and 490 nm in curves 8 and 9 is lower than that in curve 7 which originates from the absorption of $Ca_9Eu_2W_4O_{24}$ or $Sr_9Eu_2W_4O_{24}$. And the broad band from 515

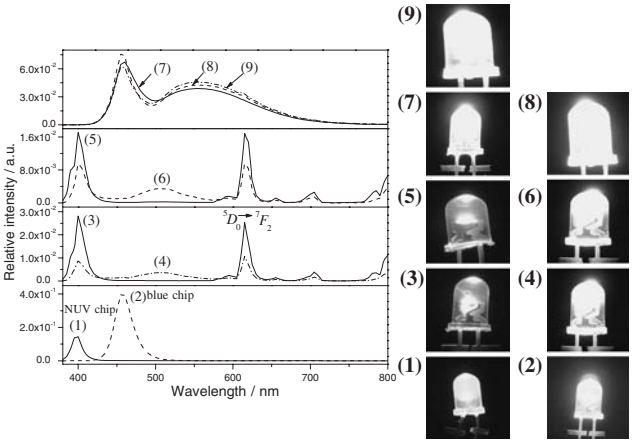

Figure 3. The emission spectra and the corresponding photos of the LEDs made from (1) the original NUV chip, (2) the original blue chip, (3) a NUV chip + $Sr_9Eu_2W_4O_{24}$, (4) a NUV chip + $Sr_9Eu_2W_4O_{24}$ + green phosphor + blue phosphor, (5) a NUV chip + $Ca_9Eu_2W_4O_{24}$, (6) a NUV chip + $Ca_9Eu_2W_4O_{24}$ + green phosphor + blue phosphor, (7) a blue chip + YAG:Ce^{3+}, (8) a blue chip + YAG:Ce^{3+} + $Ca_9Eu_2W_4O_{24}$, and (9) a blue chip + YAG:Ce^{3+} + $Sr_9Eu_2W_4O_{24}$ under 20 mA forward bias excitation.

to 680 nm in curves 8 and 9 is stronger than that in curve 7 which also originates from the emission of $Ca_9Eu_2W_4O_{24}$ or $Sr_9Eu_2W_4O_{24}$. Therefore, compared with WLED7, the CIE chromaticity coordinates of WLEDs 8 and 9 show red shift. The color temperatures, luminous efficiencies, and color rendering indexes are 6710 K, 42.99 lm W^{-1}, and 81.0 for WLED7, 6164 K, 44.71 lm W^{-1}, and 80.0 for WLED8, 5322 K, 43.26 lm W^{-1}, and 76.7 for WLED9, respectively. Compared with WLED7, WLEDs 8 and 9 were improved both on color temperature and luminous efficiency except for color rendering index. The results indicate that both the phosphors can be a promising red component for the commercial YAG:Ce^{3+}-WLEDs.

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