LED-Phosphors

Novel White Emitting Phosphor as Converter for UV-LEDs

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Introduction

White emitting pcLEDs based on a blue emitting LED and a yellow emitting phosphor, for example YAG:Ce^{3+}, are commonly used as solid state light sources for general lighting. However, such systems suffer from rather low color rendering and luminous efficacy, due to missing radiation in the green and deep red spectral range. In addition to that, the color point of the chip/converter stack depends strongly on the thickness of the phosphor layer located on the LED-chip. On this scale it is a manufacturing challenge to maintain constant layer thickness and therefore stability of color points. Another approach to obtain white light is the conversion of UV radiation by a white emitting phosphor. In this approach the color point depends only on the phosphor blend. One possibility to generate a white emitting phosphor is the incorporation of Ce^{3+} and Mn^{2+} in a host structure. The broad emissions bands in the blue and red spectral region of Ce^{3+} and Mn^{2+} yield white light due to additive color mixing. Since the emitting transitions in Mn^{2+} are spin- and parity-forbidden, it has to be sensitized by energy transfer from Ce^{3+} to Mn^{2+}.

To synthesize a new white emitting phosphor samples, of monoclinic $Ca_3Y_2(Si_3O_9)_2$ doped with Ce^{3+} and Mn^{2+} were prepared and its luminescent properties were investigated.

Table 1
Crystal structure data of $Ca_3Y_2(Si_3O_9)_2$ (Data from Endo et al., Acta Crystallogr. C 1997, C53, 1533–1536.).

$Ca_3Y_2(Si_3O_9)_2$	
Crystal system	monoclinic
Space group	C_2/c
Cell parameters	a = 13.320 Å b = 7.729 Å c = 14.785 Å β = 90.256°

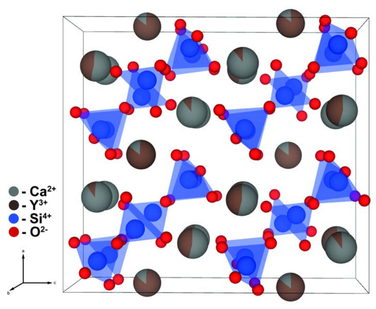

Fig. 1. Unit cell of $Ca_3Y_2(Si_3O_9)_2$ (Drawn with VESTA, K. Momma, F. Izumi, J. Appl. Crystallogr. 2011, 44, 1272-1276.).

Experimental Section

The phosphor samples were synthesized by conventional solid state synthesis. The high purity starting materials $CaCO_3$ (Ph. Eur., Dr. Paul Lohmann), Y_2O_3 (99,99%, Treibacher), SiO_2 (99,0%, Merck), CeO_2 (99,9%, Atomergic Chemetals Co.) and $MnC_2O_4 \cdot 2H_2O$ (chem. Pure, Dr. Paul Lohmann) were grinded in an agate mortar in Acetone and transferred subsequently into an alumina crucible. The samples were calcinated between 1200 and 1400 °C for 8 h in a reductive CO atmosphere.

Phase purity was investigated by application of powder X-ray diffraction. Therefore the diffractometer Miniflex II from Rikgaku with Bragg-Brentano geometry was used. Optical properties of the phosphors were characterized by recording excitation and emission spectra as well as reflectance spectra. Furthermore decay times of the phosphors were measured. Excitation and emission spectra were recorded with a fluorescence spectrometer from Edinburgh Instruments Ltd (FLS920) equipped with 450 W Xe lamp. For reflectance measurements the spectrometer was additionally equipped with an Ulbricht sphere coated with $BaSO_4$. Decay time measurements were performed using a picosecond pulsed laser.

Results

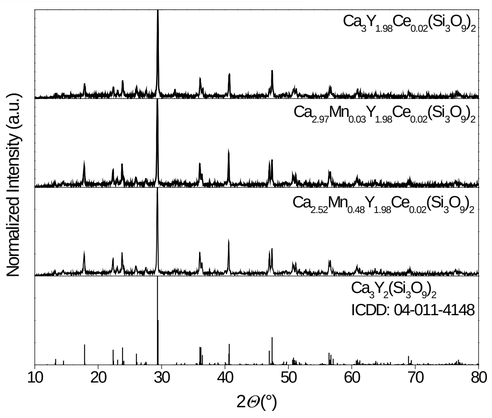

Fig. 2. Randomly selected X-ray diffraction patterns of $Ca_3Y_2(Si_3O_9)_2$:Ce^{3+},Mn^{2+} as well as the ICDD reference card of $Ca_3Y_2(Si_3O_9)_2$.

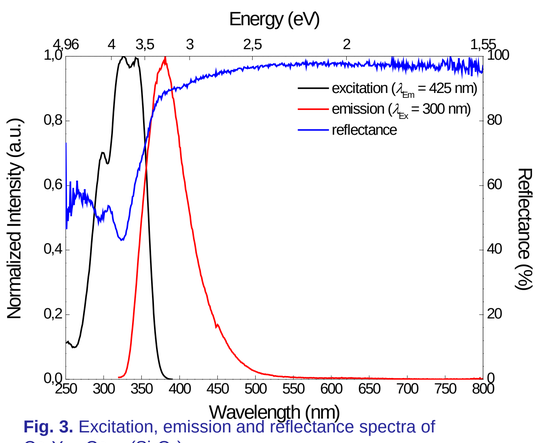

Fig. 3. Excitation, emission and reflectance spectra of $Ca_3Y_{1.98}Ce_{0.02}(Si_3O_9)_2$.

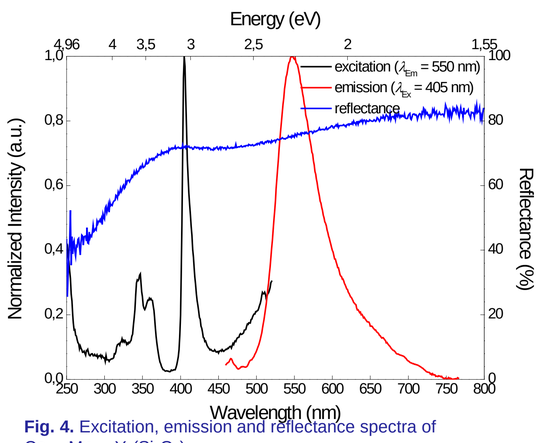

Fig. 4. Excitation, emission and reflectance spectra of $Ca_{2.91}Mn_{0.09}Y_2(Si_3O_9)_2$.

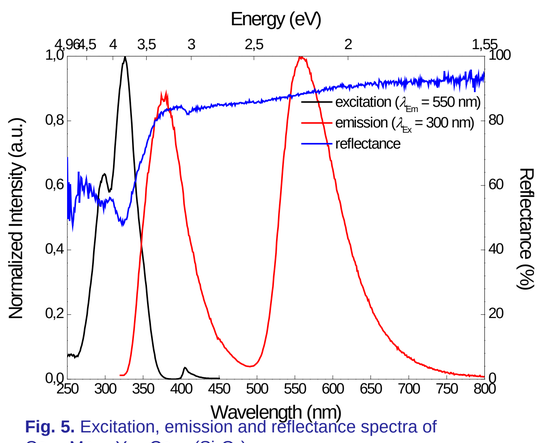

Fig. 5. Excitation, emission and reflectance spectra of $Ca_{2.52}Mn_{0.48}Y_{1.98}Ce_{0.02}(Si_3O_9)_2$.

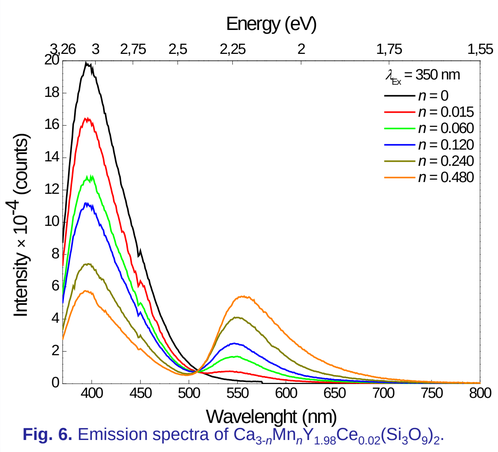

Fig. 6. Emission spectra of $Ca_{3-n}Mn_nY_{1.98}Ce_{0.02}(Si_3O_9)_2$.

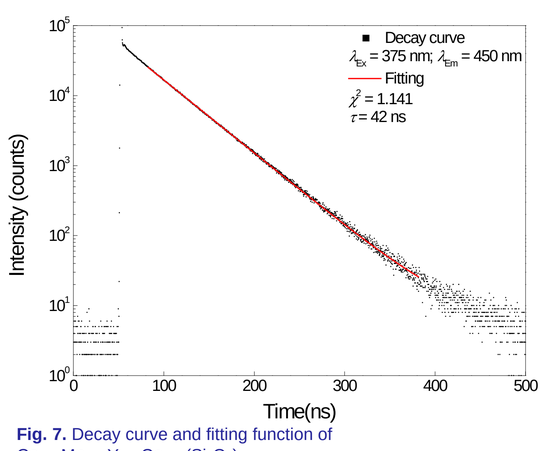

Fig. 7. Decay curve and fitting function of $Ca_{2.97}Mn_{0.03}Y_{1.98}Ce_{0.02}(Si_3O_9)_2$.

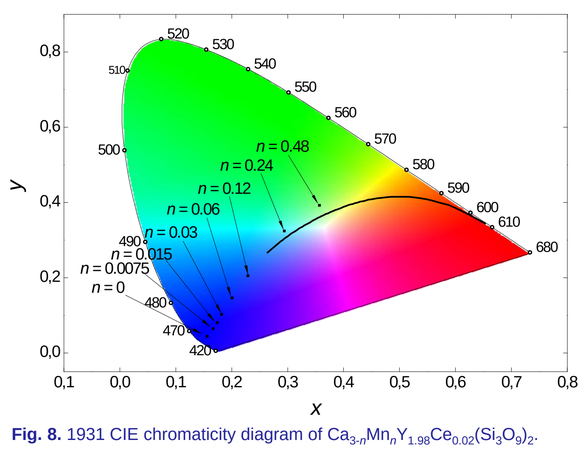

Fig. 8. 1931 CIE chromaticity diagram of $Ca_{3-n}Mn_nY_{1.98}Ce_{0.02}(Si_3O_9)_2$.

Table 2
Decay times τ, quantum efficiency *QE*, luminous equivalent *LE* and color points of $Ca_3Y_2(Si_3O_9)_2Ce^{3+},Mn^{2+}$.

Sample (n)	τ (ns)	*QE* (%)	*LE* (lm·W^{-1})	Color Point (x|y)
0	42	75	22	(0.156|0.044)
0.003	43	77	24	(0.161|0.048)
0.0075	42	72	32	(0.167||0.064)
0.015	42	61	41	(0.174|0.080)
0.03	42	71	52	(0.182|0.102)
0.06	42	59	79	(0.201|0.146)
0.12	41	59	117	(0.229|0.205)
0.24	39	49	212	(0.294|0.324)
0.48	37	62	279	(0.357|0.392)

Discussion

- As shown in Figure 2 X-ray diffraction patterns of the as-synthesized $Ca_3Y_2(Si_3O_9)_2$:Ce^{3+},Mn^{2+} samples with various doping concentrations fit well to the ICDD reference card and show the monoclinic $Ca_3Y_2(Si_3O_9)_2$ phase.
- Luminescence and reflectance spectra of $Ca_3Y_{1.98}Ce_{0.02}(Si_3O_9)_2$ are depicted in Figure 3. The excitation spectrum of $Ca_3Y_{1.98}Ce_{0.02}(Si_3O_9)_2$ consists of various bands due to the $5d^1$ multiplets of the Ce^{3+} excited states. The emission spectrum shows a broad band peaking at 380 nm with a tail on the long-wavelength side due to the spin-orbit splitting of the Ce^{3+} ground state ($^2F_{7/2}$ and $^2F_{5/2}$). The reflectance spectrum shows high reflectance in the visible range of light and therefore $Ca_3Y_{1.98}Ce_{0.02}(Si_3O_9)_2$ exhibits a white body color.
- Luminescence and reflectance spectra of $Ca_{2.91}Mn_{0.09}Y_2(Si_3O_9)_2$ are depicted in Figure 4. The excitation spectrum shows four bands at 324, 345, 360 and 405 nm which can be assigned to transitions from the $^6A_1(^6S)$ ground state to the $^4T_1(^4P)$, $^4E(^4D)$, $^4T_2(^4D)$ and [$^4E(^4G)$, $^4A_1(^4G)$] excited states. The emission spectrum shows a broad band with a maximum at 548 nm due to the spin- and parity-forbidden $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ transition. The $Ca_{2.91}Mn_{0.09}Y_2(Si_3O_9)_2$ exhibits a slightly brownish body color due to the absorption in the visible range of light.
- Figure 5 shows the luminescence and reflectance spectra of $Ca_{2.52}Mn_{0.48}Y_{1.98}Ce_{0.02}(Si_3O_9)_2$. The excitation spectrum of $Ca_{2.52}Mn_{0.48}Y_{1.98}Ce_{0.02}(Si_3O_9)_2$ shows the $^2F_{7/2}$, $^2F_{5/2} \rightarrow 5d^1$ excitation of Ce^{3+} as well as the $^6A_1(^6S) \rightarrow$ [$^4E(^4G)$, $^4A_1(^4G)$] excitation of Mn^{2+}. Since the excitation spectrum was recorded for the Mn^{2+} emission the observed Ce^{3+} excitation is an indication for the energy transfer from Ce^{3+} to Mn^{2+}.
- Figure 6 shows the emission spectra of $Ca_3Y_2(Si_3O_9)_2$:Ce^{3+},Mn^{2+} with different Mn^{2+} concentrations. The emission intensity of Ce^{3+} was found to decrease with increasing Mn^{2+} content. The Mn^{2+} emission increases with increasing Mn^{2+} content. Concentration quenching was not found in the examined samples.
- The decay curve and its fitting function of $Ca_{2.97}Mn_{0.03}Y_{1.98}Ce_{0.02}(Si_3O_9)_2$ is depicted in Figure 7. Its shape is representative for all codoped $Ca_3Y_2(Si_3O_9)_2$:Ce^{3+},Mn^{2+} samples. The corresponding decay times can be best fitted with a first-order exponential function. The determined decay times are summarized in Table 2.
- To visualize the color hue chromaticity coordinates were calculated and mapped onto a 1931 CIE chromaticity diagram as it can be seen in Figure 8 and onto Table 2. The chromaticity coordinates range from (0.156|0.044) to (0.357|0.392) and indicate that the color hue is tunable from deep blue to green.
- Furthermore quantum efficiencies QE as wells as luminous equivalents LE were calculated. The results are summarized in Table 2. The quantum efficiencies QE decrease with increasing Mn^{2+} content which indicates a decrease in sample quality with increasing Mn^{2+} content. The luminous equivalents increase with increasing Mn^{2+} content due to an increasing fraction of green emission.

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