Inorganic phosphors for LED applications

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Abstract

In the nineties the invention of the InGaN blue LED has innovated illumination technology. Currently LCD backlighting and more and more general lighting applications are based on white LEDs comprising of inorganic phosphors and blue emitting InGaN chip. Well established phosphor materials are ortho silicates and garnets like yellow emitting YAG:Ce. In our paper we demonstrate that garnet materials also allow for green light emission for both, general lighting and backlighting LED applications.

1. Introduction

A break through in lighting technology happened in the end of the nineties of last century when Nakamura invented the efficient blue LED [1]. This innovation has made white light generation by LEDs possible: Either by mixing blue, green and red light emitted by different LED chips, or by the so-called phosphor conversion (pc) technology [2]. pcLEDs comprise -in rudimentary approach- of a blue light emitting InGaN LED chip and a yellow inorganic phosphor material distributed in a transparent binder on top of the chip. The phosphor absorbs a part of the blue light (the remaining blue light is transmitted through the binder-phosphor layer) which is converted by the phosphor into yellow fluorescence. Both, the yellow fluorescence and the transmitted blue light mix and finally white light is emitted by the pcLED. The advantages of pcLEDs over multichip-LED approach are among others the less complex layout of the device resulting in cost savings. Well established phosphor materials for pcLED applications are YAG:Ce ($Y_3Al_5O_{12}:Ce^{3+}$) and ortho silicates $(Ba,Sr,Ca)_2SiO_4:Eu^{2+}$ [2, 3]. One big advantage of ortho silicates is their flexibility in terms of fluorescence colors: their emission can be aligned between 515 nm in the green up to deep orange emission of about 610 nm. This allows for the tuning of pcLED emission for different applications like backlighting, general lighting and color-on-demand by applying of specific ortho silicate chromaticity (figure 1). YAG:Ce itself allows only for yellow fluorescent emission.

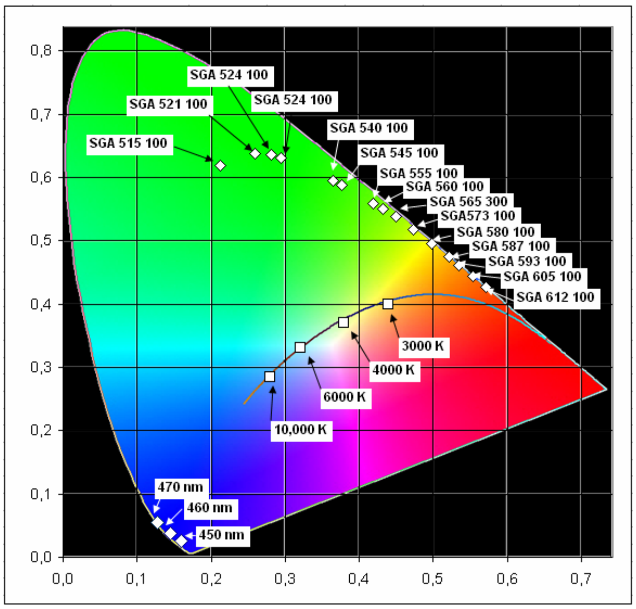

Figure 1: CIE 1931 (x,y) chromaticity of ortho-silicates (ISIPHOR™ SGA 515 100 – SGA 612 100) covering a broad range from green to deep orange fluorescence.

2. Experimental and Results

We varied the YAG:Ce garnet crystal matrix in order to allow for green fluorescence: If Yttrium is replaced with Lutetium the resulting phosphor composition $Lu_3Al_5O_{12}:Ce^{3+}$ is obtained. This material called LuAG:Ce was first published in 1967 [4]. LuAG:Ce powder samples can be excited by means of blue light (figure 2), i.e. with blue LED chip as radiation source.

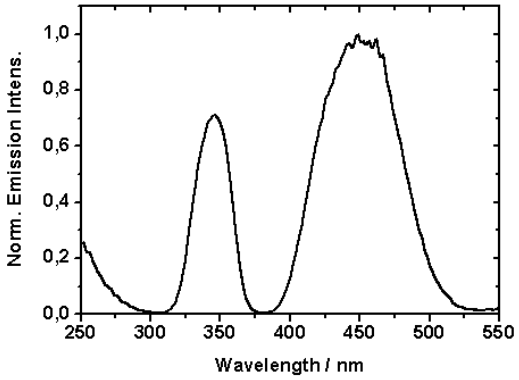

Figure 2: Photoluminescence excitation spectrum of LuAG:Ce with maximum excitability in the region of blue LED light emission of about 450 nm.

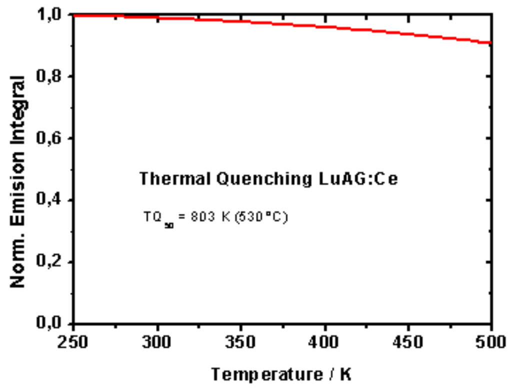

Figure 4: Thermal quenching behavior of LuAG:Ce; the integral of emission band remains nearly constant within the relevant temperature range of LED operation (up to 150°C = 423 K).

The fluorescence of LuAG:Ce is green shifted in comparison to the yellowish emission of YAG:Ce as shown in figure 3. Noteworthy is the thermal stability of LuAG:Ce emission (fig. 4): the phosphor shows only very low thermal quenching resulting in > 90% of initial brightness at temperatures above 150°C compared to room temperature brightness (excitation at 450 nm). Thus, LuAG:Ce is ideally suited for high power LED applications of high temperature operation. Besides the chromaticity of LuAG:Ce fluorescence can be tuned by slightly modifying the chemical composition (figure 5).

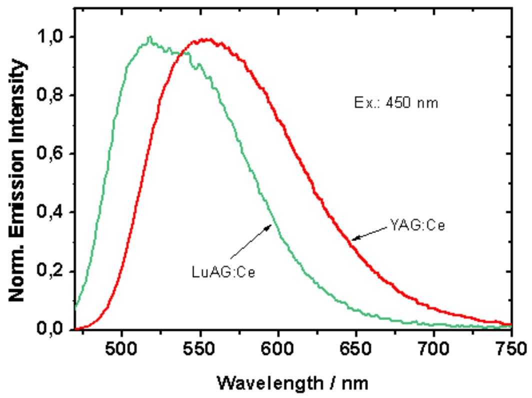

Figure 3: Comparison of LuAG:Ce and YAG:Ce fluorescence spectra.

In order to evaluate some basic properties of LuAG:Ce for LED applications we built prototype pcLEDs with LuAG:Ce as single phosphor but of different concentrations in silicone binder as well as pcLEDs containing phosphor mixtures with LuAG:Ce being the green component of the mixture. The fabrication of prototype pcLEDs was performed in our application laboratory. From our point of view it is very important for phosphor developers and suppliers to be able to build small series of pcLEDs in order to evaluate the phosphor performance in final LED application. A commercial available SMD top view LED package with empty cavity and equipped with a 450 nm emitting bonded blue chip (OSA Opto Light, Berlin) was used as basis for prototype pcLED fabrication.

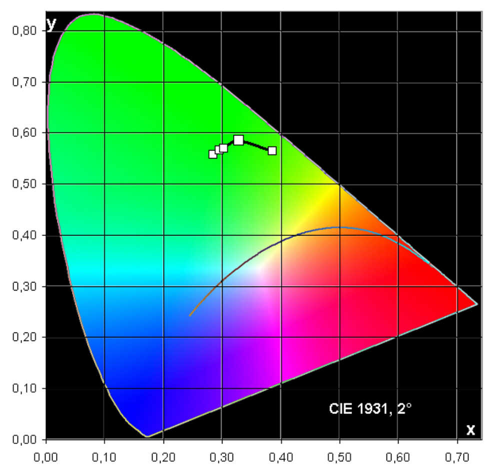

Figure 5: Chromaticity range of the system LuAG:Ce by variation of the composition of the phosphor. Each white square represents one specific LuAG:Ce material.

The phosphor slurry was obtained by dispersing of the single phosphor powder or phosphor mixtures in the two component silicone material OE 6550 (Dow Corning) by means of a speedmixer. After degassing the homogeneous dispersion was used for filling of the LED cavities with a CDS 6200 dispensing machine of Essemtec equipped with a jet valve. The filled LEDs were transferred into a heat cabinet for silicone curing at 150°C. LED spectra were collected with a setup consisting of an Instrument Systems spectrometer CAS 140 CT and integrating sphere 250. LEDs were operated at 20 mA (Keithley 2601 source meter) without cooling.

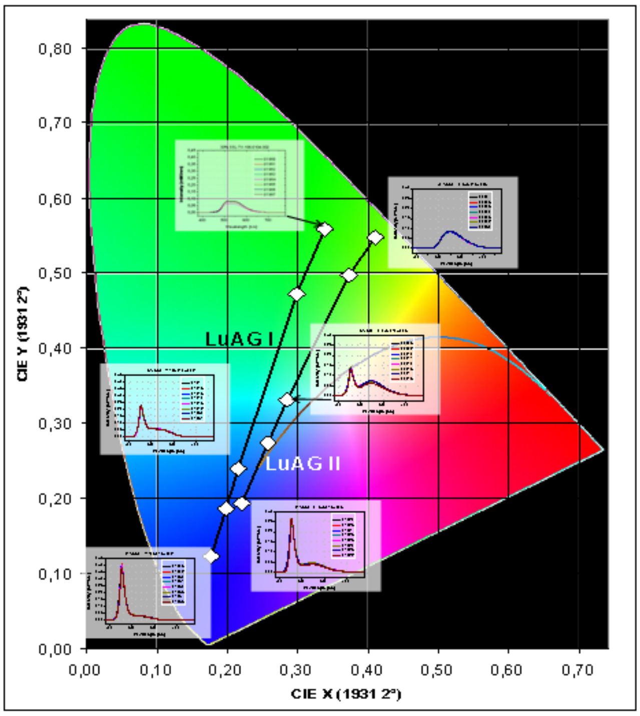

Figure 6: Two series of full converted green LEDs were obtained by increasing the concentration of phosphor. LuAG I and LuAG II are of slightly different composition and of different chromaticity. Each white square within every curve represents a specific concentration of the phosphor in slurry. From bottom to top the concentrations are as follows (in wt-%): 2, 4, 6, 18 and 30. LED spectra belonging to specific LuAG:Ce concentrations are shown.

If LuAG:Ce is used as single phosphor in the slurry full converted green LEDs are obtained by increasing the concentration of the phosphor in the pcLED package. We built series of pcLEDs comprising of two different LuAG:Ce phosphors of different chromaticity (LuAG I and LuAG II). The concentrations of phosphors, the resulting pcLED chromaticity and some LED emission spectra are given in figure 6. Because of the broad emission band of LuAG:Ce with FWHM of about 120 nm the full converted green LEDs are characterized by a broad green emission band.

For lighting applications, high color rendering index (CRI) is required. Dichromatic white pcLEDs (yellow phosphor -emission peak = 560 nm and FWHM = 125 nm- and blue emitting InGaN semiconductor) emit light of poor color rendering in particular at low correlated color temperature (CCT), shown in table 1. CRI increases if a mixture of a green phosphor, the yellow phosphor and a deep red phosphor (broad peak at 650 nm) are applied as converter material for pcLED. With LuAG:Ce as green component high CRI > 90 is possible at both, low and high CCT (table 2).

	neutral white bichromatic LED (blue / yellow)	warm white bichromatic LED (blue / yellow)
Color Temperature [K]	**5000**	**3900**
CIE X / Y(1931 2°)	**0.345 / 0.352**	**0.420 / 0.492**
CRI	**74**	**61**

Table 1: Dichromatic pcLEDs equipped with single yellow emitting phosphor generate poor CRI emission at low CCT of 3900 K (warm white light).

	neutral white tetrachromatic LuAG-LED (blue / green / yellow / red)	warm white tetrachromatic LuAG-LED (blue / green / yellow / red)
Color Temperature [K]	**5600**	**3200**
CIE X / Y(1931 2°)	**0.331 / 0.340**	**0.409 / 0.370**
CRI	**93**	**93**

Table 2: Tetrachromatic pcLEDs with LuAG:Ce as green component allow for higher CRI, in particular at low color temperature of 3200 K (warm white light).

At present, LCD backlighting is the most prominent pcLED application. For high quality displays like TV a large color gamut is necessary. A common standard is the so-called sRGB color gamut comprising of a triangle within CIE diagram [5, 6]. The emission spectrum of pcLED has to be well aligned to the display's color filter transmission curves in order to allow for a high color gamut.

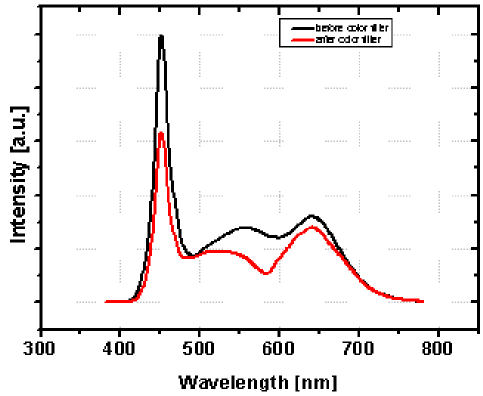

Figure 7: Emission spectrum of pcLED with LuAG:Ce as green phosphor component (black curve) and transmitted pcLED emission after color filter (red curve).

We designed a phosphor mixture comprising of LuAG:Ce and a deep red emitting phosphor and filled LED packages with it. The emission spectrum of resulting pcLED is given in figure 7 (black curve, "before color filter"). Then we positioned a common LCD color filter into optical path between pcLED and detector of spectrometer. The filter itself comprise of a blue transmission band (FWHM = 95 nm) peaking at 452 nm, a green transmission band peak at 525 nm with FWHM = 100 nm and a broad red band of a constant transmission starting from 625 nm up to 780 nm. In the following this set up is referred as "BLU". Resulting BLU set up emission spectrum is shown in figure 7 (red curve, "after color filter"). Finally we computed the color gamut of BLU set up and compared it with the sRGB standard (figure 8): The black triangle representing BLU set up color gamut is fully covering the grey triangle (sRGB color gamut). Furthermore the area of BLU triangle is 107% of sRGB standard. Thus it appears that BLU set up is able to produce higher color fidelity than sRGB. This result shows that broad band emitting green LuAG:Ce phosphor in a mixture with deep red phosphor allows for high color gamut in pcLED backlight applications.

3. Summary

LuAG:Ce is a green emitting material suitable for several LED applications. The fluorescence of the phosphor has high thermal stability resulting in very low thermal quenching. This makes LuAG:Ce ideally suited for high temperature operation, e.g. power pcLEDs. It can be used for green full converted LEDs, for lighting applications if mixed with additional phosphors to obtain high CRI and, last but not least, LuAG:Ce is suitable for LED backlighting of sRGB color gamut.

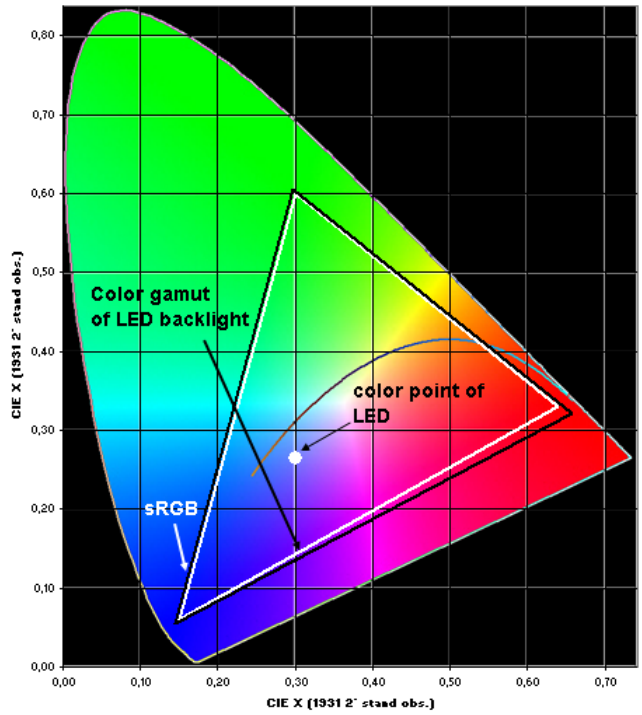

Figure 8: pcLED backlight (BLU set up) comprising of LuAG:Ce as green component allows for full coverage of sRGB (107% sRGB gamut).

4. References

1. S. Nakamura, G. Fasol, The Blue Laser Diode, Springer, Berlin, 1997.
2. F. Schubert, Light Emitting Diodes, Cambridge University Press, Cambridge, 2003.
3. W. Tews, G. Roth, S. Tews, *Silicate Phosphors for White LEDs*, Phosphor Global Summit, San Diego, 2007.
4. W. W. Holloway, M. Kestigian, *Phys. Lett.*, **25A[8]**, 614 (1967).
5. K. Kakinuma, *Japan. J. Appl. Phys.*, **5b[45],** 4330 (2006).
6. M. Stokes, M. Anderson, S. Chandrasekar, R. Motta, A Standard Default Color Space for the Internet – sRGB, Version 1.10 (November 1996), http://www.w3.org/Graphics/Color/sRGB