Highly efficient all-nitride phosphor-converted white light emitting diode

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1 Introduction

Progress in blue and green light emitting diodes (LEDs) based on GaN [1, 2] with respect to light generation efficiency and manufacturability enables many different pathways to new sources of white light for specialty lighting and in the longer run for general illumination. We report here about the development and demonstration of an all-nitride white LED. The concept adopted is termed phosphor converted LED (i.e. pc-LED), in which a short wavelength emitting LED is used to excite luminescent materials (phosphors) which emit light of longer wavelengths and then mix with the remains of the pump light to compose a desired color – e.g. white. Our approach employs an (In,Ga) N–GaN quantum well primary blue emitter and novel Eu^{2+} doped nitride and oxonitride phosphors for color conversion of the primary blue emission into a mixed white of excellent color quality. Only chemically very stable materials with no environmental hazards in service and disposal are used. Excellent efficiency values have been achieved and, vital for many applications, very high stability of the color parameters with temperature and drive current can be claimed.

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The concept of 1-pc-LEDs has been commercially realized using a blue LED and yttrium aluminium garnet doped with Ce^{3+} ($YAG:Ce^{3+}$) to produce a blue-yellow mix, which is best described as 'plain white' [3]. A better light quality is achieved by using a combination of a Ce^{3+} doped garnet phosphor with a red emitter [4–7].

Other combinations, especially the combination of blue pump, green and red emitting phosphors (2-pc-LED), but also UV LED plus 3 phosphors (3-pc-LED) have been proposed [8]. All phosphors in more-than-one-phosphor pc-LEDs have to be excitable by a single pump wavelength and, from manufacturing yield considerations, the excitation spectrum should be broad. The rare earth ions Eu^{2+} and Ce^{3+} are therefore suitable since both show parity-allowed fast 5d–4f emissions, host lattice sensitivity in spectral position and stability up to very high excitation intensities. The Eu^{2+} dopant, being narrower in emission, is the preferred option for all 2- and 3-pc-LED applications while Ce^{3+} is more versatile for 1-pc-LEDs. The spectral positions of Eu^{2+} states in classic oxidic host materials have been extensively investigated and reported by Dorenbos [9] giving little hope for finding reasonable positions for white LEDs except in sulfides like red emitting $CaS:Eu^{2+}$ and green emitting thiogallate $SrGa_2S_4:Eu^{2+}$ [10]. But the chemical and thermal stability of these compounds is quite poor requiring a complicated treatment against hydrolysis.

Crucial key values describing the quality of the obtained white light are the General Color Rendering Index (CRI) *Ra* [11] and the Correlated Color Temperature (CCT) [12]. $Ra > 80$ is regarded as 'good', in the 70ies as 'plain' or acceptable.

All these so far mentioned requirements for 'good' phosphors are met by our herein presented realization of an efficient 2-pc-LED based on the two new phosphors: $Sr_2Si_5N_8:Eu^{2+}$ (red) and $SrSi_2O_2N_2:Eu^{2+}$ (green).

2 The novel nitride phosphors

Both new phosphors are chemically and thermally extremely stable nitridosilicates. The structures of nitridosilicates typically consist of condensed corner sharing SiN_4 tetrahedra with nitrogen atoms connecting up to four neighboring Si atoms, thus significantly extending the structural chemistry of classical oxosilicates [13]. The red emitting phosphor in our 2-pc-LED, $Sr_2Si_5N_8:Eu^{2+}$, contains a three-dimensional rigid network structure of corner sharing SiN_4 tetrahedra with half of the nitrogen atoms being connected to two ($N^{[2]}$) and three ($N^{[3]}$) Si atoms, respectively. The $N^{[3]}$ atoms are arranged in corrugated highly condensed layers built up of Si_3N_3 rings. The Sr^{2+} ions are coordinated by ten N atoms, mainly $N^{[2]}$. $Eu_2Si_5N_8$ and $Ba_2Si_5N_8$ are isotypic with $Sr_2Si_5N_8$ [14, 15].

We and others reported about the optical properties (fluorescence, thermoluminescence and upconversion) of the Eu^{2+} doped alkaline earth compounds already [16, 17]. Within the orthorhombic solid solution $(Ba_{1-x-y}Sr_xCa_y)_2Si_5N_8:Eu^{2+}$ the spectral position of the emission band can be tuned from the yellow to the deep red by either increasing the concentration of the smaller sized host lattice cations or by increasing the Eu^{2+} concentration (Fig. 1). SiAlONs crystallizing in the orthorhombic $M_2Si_5N_8$ structure type are obtained by substituting part of the $N^{[2]}$ by $O^{[2]}$ atoms and, in order to maintain charge neutrality, by substituting a respective part of Si by Al to form compounds $M_2Si_{5-x}Al_x(N^{[2]})_{4-x}(O^{[2]})_x(N^{[3]})_4$. An increase of x in $M_2Si_{5-x}Al_xN_{8-x}O_x:Eu^{2+}$ leads to a red shift of the Eu^{2+} emission band and an increased Stokes' shift.

Recently, our synthetic approach leading to nitridosilicates has been applied to novel oxonitridosilicates, namely $M^{II}Si_2O_2N_2$ with M^{II} = Ca, Sr [18]. These compounds represent an unprecedented type of single-layer silicates: The molar ratio of $Si:(O/N) = 1:2$ of the $[Si_2O_2N_2]^{2-}$ substructure suggests a three-dimensional framework silicate (cf. SiO_2) rather than a two-dimensional layer structure. The corrugated layers in $SrSi_2O_2N_2$ are made up of $SiON_3$ tetrahedra forming condensed Si_3N_3 rings. Each nitrogen atom connects three Si, while all oxygen atoms are terminally bound to silicon.

Figure 2 gives the excitation spectra of two of the new nitride phosphors used in this work in comparison to the classic $YAG:Ce^{3+}$. Obviously, the excitation band of the latter is much narrower than the others, while its emission is broader. Relative to oxide hosts the Eu^{2+} excitation and emission bands of both nitridic compounds are remarkably red-shifted. This can be explained by a strong nephelauxetic effect [19–21] that leads to a lowered net positive charge of the Eu^{2+} ions because of significant bonding interactions between Eu^{2+} and its nitride ligands [22].

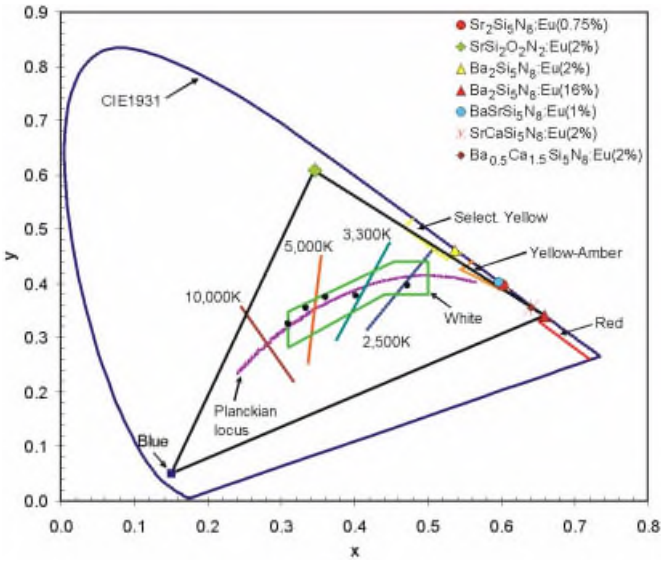

Fig. 1 Positions of selected phosphor emissions of (Ba, Sr, Ca)$_2$Si$_5$N$_8$:Eu^{2+} and SrSi$_2$O$_2$N$_2$:Eu^{2+} in the CIE diagram, together with some white points (•) experimentally realized by mixing SrSi$_2$O$_2$N$_2$:Eu^{2+} (green) with M$_2$Si$_5$N$_8$:Eu^{2+} (red). The system is obviously able to realize amber and red as well as white, especially at the most wanted CCT range around 3300 K.

The coordination polyhedra of both cation sites in M$_2$Si$_5$N$_8$ are very similar and they cannot be resolved by low-temperature Mößbauer spectroscopy [23]. However, electronic structure calculations [24] show that Eu^{2+} has a lower net positive charge on site M(1) with respect to M(2) and thus a smaller separation of the 4f and 5d block levels can be expected for Eu^{2+} on site M(1). Assuming a similar Stokes' shift for both lattice sites, the slightly different chemical environments of M(1) and M(2) result in a broadened emission band actually composed of two separate bands.

The Stokes' shift of orthorhombic M$_2$Si$_5$N$_8$:Eu^{2+} is small (~2700 cm^{-1}) and therefore the materials are well excitable in the blue to green spectral region. Moreover, the small Stokes' shift leads to an excellent temperature stability of the luminescence quantum efficiency (QE) [25]. Even at a temperature of 200 °C remarkably high QEs > 90% were measured for optimized materials.

In SrSi$_2$O$_2$N$_2$:Eu^{2+} the chemical environment of Eu^{2+} is comparable to that found in (Sr,Ba)$_2$SiO$_4$ with β-K$_2$SO$_4$ structure; the cations are coordinated by terminal O atoms in both compounds. Stokes' shift

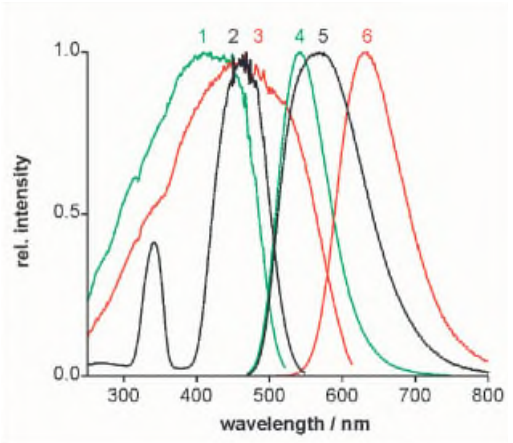

Fig. 2 Typical excitation and emission spectra of the phosphors M$_2$Si$_5$N$_8$:Eu^{2+} (red, 3: excitation spectrum, 6: emission spectrum) and M^{II}Si$_2$O$_2$N$_2$:Eu^{2+} (green, 1: exc, 4: em) compared to YAG:Ce^{3+} (black, 2: exc, 5: em).

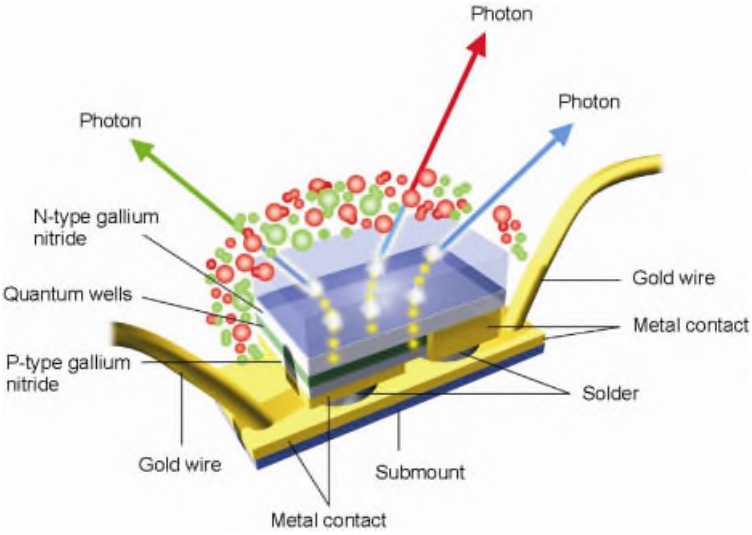

Fig. 3 Artist's view of our 2-pc-LED: On a copper slug and underneath a plastic lens a 'flip-chip' is soldered to metal contacts; 'flip-chip' meaning the substrate on which the stack of GaN and InGaN layers has been deposited is used as light exit, the (bottom) p-contacts being highly reflective. The color converting phosphors are placed on top of the chip, embedded in silicone.

(2700 cm^{-1}), position (λ_{max} = 538 nm) and width (FWHM = 78 nm) of the emission band of $SrSi_2O_2N_2:Eu^{2+}$ is almost identical with that of $Sr_{1.4}Ba_{0.7}SiO_4:Eu^{2+}$. Surprisingly, $SrSi_2O_2N_2:Eu^{2+}$ shows a very efficient luminescence (QE > 90%) even above 200 °C in contrast to $(Sr,Ba)_2SiO_4:Eu^{2+}$ that is most likely due to the measured larger band gap of $SrSi_2O_2N_2:Eu^{2+}$ (E_g = 5.88 eV) compared to $(Sr,Ba)_2SiO_4:Eu^{2+}$ (E_g = 5.66 eV, 70% Ba^{2+}) [26].

3 Technical realization of the all-nitride pc-LED

We built the 2-pc-LED from suspensions of systematically varied amounts of two phosphors in silicone, which were applied to the reflector cup of high-power LEDs of the LUXEON type. These can be driven up to 3 W electrical input by designed-in heat management (Fig. 3). The silicone gel improves the optical coupling. A plastic lens gives mechanical protection and optical lens action. The pump wavelength and the phosphor amounts were selected in a way, to have the final emission color within the white space box around the Planckian locus in the CIE diagram (Fig. 1).

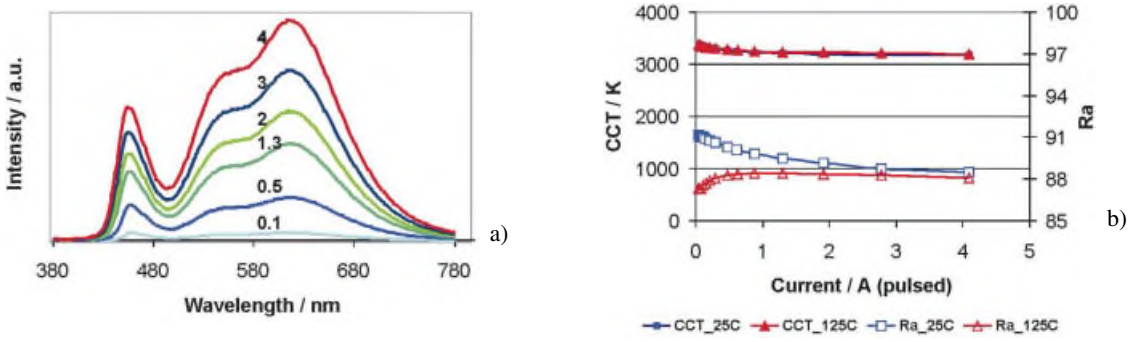

Fig. 4 a) Dependency on drive current of our 2-pc-LED emission up to 4 A (2 W/mm^2 optical pump power) and b) development of CCT and *Ra* with drive current and temperature (shown for 25 and 125 °C).

Table 1 Full set of the 14 CRI and the general color rendering index *Ra* of our 2-pc-LED compared to those of a deluxe fluorescent lamp.

	Ra	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14
fluorescent lamp	83	96	94	57	89	85	80	90	73	11	50	71	54	97	71
2-pc-LED	90	91	96	94	86	89	91	90	80	56	85	81	68	93	96

Figure 4 shows how different currents influence the emission spectra of our 2-pc-LED. The spectra are not discernible if normalized, i.e. the luminescence intensity simply grows with increase in drive. In order to separate temperature and drive dependencies a pulsed voltage was applied while the device temperature was held constant.

All optical measurements were taken using an integrating sphere, calibrated together with a high-end array spectrometer. It provided the functionality to measure not only absolute spectral data but calculated from these spectra colorimetric data as chromaticity, its distance from the Planckian locus, CCT and all 14 CRI according to the CIE procedure 13.3 [27]. The CCT and the General CRI, *Ra*, were determined from the spectra taken at 25 °C and 125 °C and currents up to 4 A, far beyond present product specifications (max. 0.7 A) and thus demonstrate the enormous capability of our system. Both key values are almost independent of temperature and current (CCT remains at 3200 K, *Ra* stays around 89). To our knowledge this is the highest proven color stability of any pc-LED so far.

The excellent illumination properties are even more highlighted by the full set of the 14 CRI given and compared to the ones of a deluxe fluorescent lamp (Table 1). This extraordinary stability with drive and temperature can be traced back to extremely high thermal quenching temperatures of the luminescence well above 200 °C and decay times of some 900 nsec or less for both phosphor components.

Besides the color quality of the emitted light, the ultimate parameter for light sources is the amount of generated luminous flux per used electrical Watt, given in lumen/W. Our all-nitride demonstrator reaches up to 25 lumen/W (1 W input, dc with proper heat sinking). This is already almost twice the efficiency of any incandescent lamp (approx. 15 lumen/W). We believe that this value can be at least doubled by optimizing the phosphor morphology and deposition method, and finally using more efficient blue pump LEDs may give another factor of two in the near future.

4 Conclusions

An important new class of phosphor materials has been discovered and we have used them to demonstrate their superior suitability for white 2-pc-LEDs. The alkaline earth cations of nitridosilicates and oxonitridosilicates can be replaced by Eu^{2+}, which emits for all members of these classes in the visible part of the spectrum; the Stokes' shift is small enough to enable excitation by blue InGaN/GaN LEDs. The new phosphors lend themselves to use in 2-pc-LEDs with excellent properties – a wide range of possible white light with adjustable CCT and simultaneously retained brilliant color rendering properties. CCT and CRI are very stable against temperature changes and drive currents. Moreover, only chemically very stable materials with no environmental hazards in service, production and disposal are used. Further studies to minimize photo-thermal degradation and to select the most stable stoichiometries for long-life operation are underway. White LEDs may well become the next generation of general lighting sources.

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