Quantum Confined Atom based Nanophosphors for Solid State Lighting

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Abstract

When an atomic impurity is incorporated in a nanoparticle of size 2 to 10 nm, the quantum-confinement provided by the dielectric-boundary of the host-nanoparticle modulates the properties of the atom. This Quantum Confined Atom (QCA) shows extraordinary changes in its luminescent properties and is associated with the modulation of the excited states of the caged atom. These “atomically engineered nanomaterials”, pioneered and developed by Nanocrystals Technology, yield several novel properties and are expected to be a major contributor to the future of nanotechnology. Efficient QCA-Nanophosphors that emit different colors depending on the specific choice of the ‘caged atom’ are being developed for applications to solid-state lighting. We have made two key contributions to development of SSL. (1) By embedding nanoparticles in the encapsulant, the refractive index is enhanced to 1.8 that allows us to enhance Light Extraction Efficiency (LEE) of the LED chip. (2) Incorporation of appropriate nanophosphors enables efficient down-conversion with high color-quality. The combination of an optically transparent downconverter and high refractive index in an encapsulant has yielded Phosphor-Converted LEDs (PC-LEDs) that yield higher package optical efficiency at lower package-level cost. The LEE and wall plug efficiency enhancement due to the HRI encapsulant is applicable across the entire visible spectrum of monochromatic HB-LED lamps.

Key words: Quantum Confined Atom, Nanophosphors, High Refractive Index Encapsulants, High-Brightness LEDs.

Background and Introduction

The cost of producing electricity is $60 Billion per year in the US. Lighting accounts for 22% of the electricity consumption in the US. Solid State Lighting (SSL) devices promise to replace conventional light sources such as incandescent lamps and eventually fluorescent lamps in the long term. A significant economic and environmental savings of approximately $100 Billion over the period 2000 to 2020, with a 50% reduction in electricity consumption for lighting in year 2020 sparing the atmosphere 28 million metric tons of carbon emission annually, is anticipated. This is predicated upon SSL attaining target luminous efficacy values for white-light in excess of 150 lm/W at a cost target of <5 $/klm, in order to replace fluorescent lamps[1].

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[1] See for example: “Solid State Lighting : Roadmap projects significant LED penetration of lighting market by 2010” J.Y. Tsao, Laser Focus World, pp. S11-S14, (May 2003)

Third International Conference on Solid State Lighting, edited by Ian T. Ferguson,
Nadarajah Narendran, Steven P. DenBaars, John C. Carrano, Proc. of SPIE Vol. 5187
(SPIE, Bellingham, WA, 2004) · 0277-786X/04/$15 · doi: 10.1117/12.515432

The three approaches to solid state white light being actively pursued are summarized in Table 1 below[2]. The *first approach* using a combination of saturated color LEDs offers the highest luminous efficacy (best case ~ 60 lm/W, assuming the following monochromatic LED WPE values: 25% @ 470nm, ~10% @ 550nm, 30% @ 610nm) with good color quality along with the ability to tune/vary the color quality, but has the disadvantage of a more complex system due to drive circuitry for both lumen-maintenance, color-maintenance, and secondary-optics for color mixing. The *second approach* using yellow and red emitting phosphor combination excited by Blue LED offers the second-best luminous efficacy (best case ~ 45 lm/W, assuming a 470nm monochromatic LED WPE value of 25%). For this case, the color quality as shown in the table I has been enhanced from original value of CT= 8000K and CRI =75 by using a single or multiple phosphors with red emission in addition to external yellowish-green (or greenish- yellow) emission but with lower energy efficiency. The *third approach* using Blue, Green and Red emitting phosphor combination excited by UV/Violet LED, offers very high color quality (CT = 4000K, CRI=90) with ability to tune color quality during lamp fabrication and achieve higher yield, with a less complex system. But this approach, currently has the disadvantage that it offers the lowest luminous efficacy (best case ~30 lm/W, assuming a 400nm monochromatic LED WPE value of 25%). The lower luminous efficacy is often due to lower absorption efficiency (~ 0.5) of the UV/Violet LED emission by the phosphor, An attempt to increase conversion efficiency of the transmitted UV emission to phosphor emission, by increasing thickness of the phosphor layer results in a detrimental effect on the luminous efficacy of the LED lamp. The decrease in optical transparency at visible emission wavelengths in a thicker phosphor layer due to optical scattering by micron size phosphor particles limits light extraction and decreases luminous efficacy. *In second and third approach, the package optical efficiency (POE) containing down-converting phosphors is limited to about 50%, further decreasing the light extraction from the package.*

APPROACHES TO LED - BASED SOLID-STATE WHITE LIGHTING	**Current Luminous Efficacy**	**Color Rendering Index**	**Color Temperature**
3 or More LEDs of Different Colors	~ 60 lm/W	80	5000K
Blue LED with Phosphor(s)	~ 45 lm/W	75-80	6000-4000K
UV LED with 3 or More Phosphors	~ 30 lm/W	90	4000K

Table 1. {The numbers above are based on the best estimates from current literature.}

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[2] See for example: "Illumination With Solid State Lighting Technology" D. Steigerwald et.al., IEEE Journal On Selected Topics In Quantum Electronics, Vol. 8, No.2, pp 310-320 (2002)

To date, the Phosphor-Converted LED (PC-LED) offer the best cost effective solution to white LED lamps and only this solution has been addressed in this paper.

To better understand both (i) the limitations encountered by the current phosphors and the encapsulants and (ii) the potential improvements in luminous efficacy that can be realized in LED light sources, we discuss Equation 1 below that defines the different contributions from the LED die, phosphor and package to the efficiency of the PC-LED.

When excited by an LED die emitting at λ_1, the downconverter luminous-efficacy (DCLE) of the phosphor emission at wavelength λ can be expressed as:

$$\mathbf{DCLE^{\lambda} = \{WPE\} . Lm^{\lambda} . \propto^{\lambda 1} . S^{\lambda 1-\lambda} . QE^{\lambda} . POE^{\lambda}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(1)}$$

where die ‘Wall Plug Efficiency’ (WPE) = {IQE x LEE x ($E^{\lambda 1}$/ V_F)},
IQE = ‘Internal Quantum Efficiency’,
LEE = ‘Light Extraction Efficiency’ from the LED die into the package,
$E^{\lambda 1}$/ V_F = diode electrical efficiency,
Lm^{λ} = phosphor luminous output in lumens/watt;
$\propto^{\lambda 1}$ = Absorption efficiency of LED radiation λ_1 into phosphor,
$S^{\lambda 1-\lambda}$ = Stokes shift-multiplier representing transfer efficiency,
QE^{λ} = Quantum efficiency of the phosphor emission at λ,
POE = Package Optical Efficiency (light extraction from package and phosphor into the ambient).

Our objective is to achieve the highest Downconverter Luminous Efficacy (DCLE) by maximizing the Light Extraction Efficiency (LEE), Absorption Efficiency ($\propto$), Quantum Efficiency (QE^{λ}) and Package Optical Efficiency (POE).

Performance Limitations of Phosphor-Converted LED Lamps using Bulk Phosphors and Encapsulant with Refractive Index of ~ 1.5

Conventional phosphor based downconverter in PC-LED, has the following characteristics:

- phosphor particle size is typically larger than ~ 1 micron.
- phosphor particles are dispersed in a matrix such as silicone or epoxy that has a Refractive Index (RI) ~ 1.5, whereas the phosphor particles have a RI greater than or equal to ~ 1.85.

As a consequence of the RI mismatch and the phosphor particle size being larger than the optical scattering limit (30 nm), both the LED die emission and the phosphor emission experience optical scattering at every interface between phosphor particle and matrix material in the downconverter. Scattering imparts an optically-opaque or translucent appearance to the downconverter limiting the external-light output as discussed below.

(1) *The optical scattering in the downconverter* results in lower light extraction efficiency for both the phosphor emission and for the portion of the LED die emission that is not absorbed by the phosphor. Higher optical loss from scattering is due to increased optical path length through absorbing material and increased number of events at interfaces (such as reflection or transmission) involving lossy surfaces in the LED die and the package. Thus it leads to ~ 50% *optical efficiency for the package (POE).*

(2) *Back-scattering of the exciting LED die emission by the phosphor particle, decreases the effective absorption efficiency (∝)*. This decrease in the effective absorption efficiency can be reduced if the absorption length for the excitation is smaller than the particle size. This effect has been extensively studied in 254nm and 185nm excitable phosphors in fluorescent lamps. Blue wavelength excitable YAG:Ce has a RI mismatch with respect to the conventional encapsulant and phosphor particle size in the 1 to 20 micron range, thus absorption efficiency of the phosphor in the optically-scattering downconverter is compromised.

Results and Discussion

1. YAG:Ce and TAG:Ce Nanophosphors excitable in the Blue wavelength regime

We have prepared broad-band emitting YAG:Ce and TAG:Ce Nanophosphor excitable in the 420nm to 480nm wavelength regime. QCA nanophosphors of the above garnet systems are synthesized using a micellar microemulsion process[3] to form a nanocrystalline matrix of the host-compound and containing the activator. This process was earlier developed for $Y_2O_3:Tb^{3+}$, $Y_2O_3:Eu^{3+}$ and $Gd_2O_3:Tb^{3+}$ nanocrystals which yield very efficient nanophosphors[4] excitable at 254nm. The size distribution of the

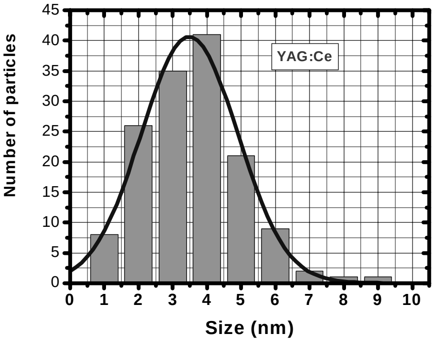

Fig.1

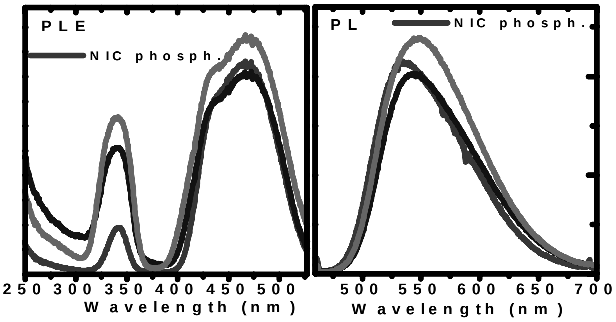

Fig.2

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[3] . V.Chhabra et.al., US Patent # 6,036,886

[4] R.N.Bhargava, V.Chhabra, B.Kulkarni, J.V.D.Veliadis, Phys. Stat. Sol., (b) **210** (1998) 621 and references cited therein.

nanocrystals, as measured by AFM technique[5] is shown in Fig.1. Mean size of the nanocrystals is about 4 nm.

Fig.2 shows Photoluminescent (PL) and Photoluminescent Excitation (PLE) spectra of two commercial bulk-YAG:Ce phosphors (dashed-line) and NCT's nano-phosphor (solid-line).

From these measurements we conclude that NCT's YAG:Ce nanophosphor shows similar luminescent characteristics to that of the best commercial bulk-YAG:Ce phosphors. This similarity is also observed in the temperature dependence of luminescent intensity of the nanophosphors and the commercial bulk-YAG:Ce phosphors. The difference in the PLE (excitation) characteristic at ~350nm between the nanophosphors and the bulk-phosphors measured in samples in the powder form, is under investigation.

Chromaticity: *We now discuss the Color-Coordinates Of broad-band emitting YAG:Ce, TAG:Ce Nanophosphors and another complementary-color emitting Wide-Bandgap Semiconductor based Nanophosphor.*
In combination with a 460nm Blue LED die/chip, an appropriate blend of these nanophosphors in a downconverter would enable the attainment of color-temperatures corresponding to Illuminant A (Incandescent Source : 2850K), Illuminant B (Direct Sunlight : 4870K) and Illuminant D (Daylight : 6500K) as shown in figure 3.

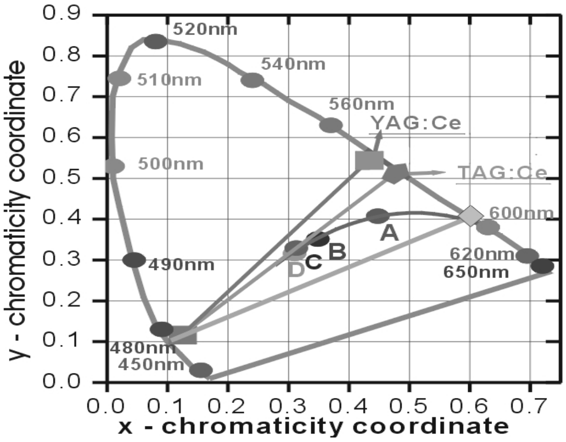

Figure 3. Chromaticity Color-Coordinates of YAG:Ce, TAG:Ce Nanophosphors and a third Wide-Bandgap Semiconductor-based nanophosphor, enable the attainment of color-temperatures corresponding to Illuminant A (incandescent source: 2850K), Illuminant B (direct sunlight : 4870K) and Illuminant D (daylight : *6500K)*

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[5] The size distribution of these nanophosphors was measured using AFM at Oak Ridge National Laboratories by Dr. Adosh Mehta and Dr. Thomas Thundat.

Chromaticity of the downconverted emission and the lamp emission, can be tuned by using an appropriate QCA-nanophosphor blend in the downconverter to achieve a designable CT value between 2500K to 6500K. The downconverter can incorporate a blend of two broad-band emitting QCA-nanophosphors with complementary-color emission at ~ 535nm and ~ 600nm, respectively. The chromaticity coordinates corresponding to these two nanophosphors, in combination with the LED die/chip emission at ~ 460nm can enable the attainment of designable CT values between 2500K to 6500K on the planckian locus in the CIE standard. Figure 4 shows the chromaticity coordinates of the two nanophosphors and the LED die/chip emission, along with the chromaticity coordinates corresponding to the spectra synthesized (shown in inset) using the experimentally measured spectral characteristics of the emission from the LED die/chip and the two nanophosphors (~535nm and ~600nm emission). The 600nm emitting nanophosphor does not exhibit parasitic reabsorption of the emission from the 535nm emitting nanophosphor.

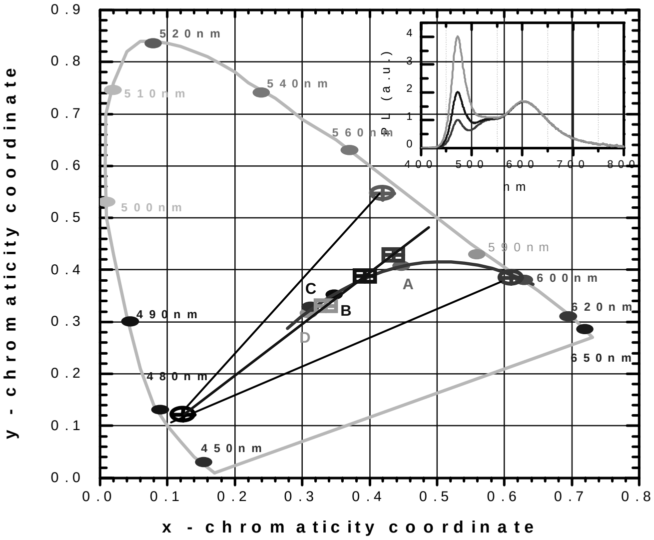

Figure 4. Chromaticity Color-Coordinates of YAG:Ce Nanophosphor and a Wide-Bandgap Semiconductor-based Nanophosphor shown along with the synthesized spectra (inset), enable the attainment of color-temperatures corresponding to Illuminant A (incandescent source: 2850K), Illuminant B (direct sunlight : 4870K) and Illuminant D (daylight : *6500K)*

2. Nanoparticle based High Refractive Index (HRI) encapsulant.

Nanocrystals that do not exhibit optical absorption at the LED die/chip emission wavelengths are coated by a ligand and uniformly dispersed without agglomeration in an epoxy based matrix. The nanoparticles are comprised of a host material with a refractive index (RI) value of ~ 2.5 and are in the size range of 7 to 12 nm The effective refractive index of the optically transparent nanocomposite was monitored as a function of volume concentration of the nanocrystals dispersed in the matrix and RI values in excess of 1.8 were achieved. The refractive index value is determined by measuring the deflection of a visible wavelength laser beam passing through a prism with a predetermined angle fabricated from the nanocomposite. Similarly, absorption coefficient measurements at any particular visible wavelength are performed by varying the laser beam path length through the prism, which is achieved by translating the prism perpendicular to the laser beam. The absorption coefficient for an optically transparent nanocomposite with RI = 1.8 was determined to be less than 0.2 cm^{-1}. The dimensions of the prism are typically on the order of 10 mm. Thus, it should be noted that both the RI and absorption coefficient values are obtained in a bulk sample with dimensions similar to those of the encapsulation in a LED lamp, and not in a thin film sample. The nanocomposite serves as a high refractive index (HRI) encapsulant in a LED lamp.

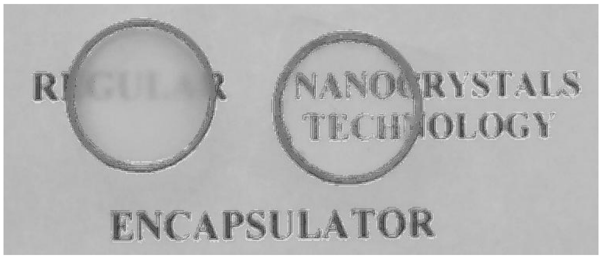

Fig. 5

This refractive index value of ~ 1.8 of the optically transparent nanocomposite HRI encapsulant is close to the refractive index of the YAG:Ce bulk-phosphor (RI = 1.85) which is used as the downconverter in PC-LEDs. This close matching of the RI between the HRI encapsulant and the YAG:Ce bulk-phosphor achieves excellent optical transparency in the downconverter incorporating the HRI encapsulant. Fig.5 compares transparencies of the YAG:Ce bulk-phosphor dispersed in conventional epoxy (n=1.5) and nanocomposite HRI encapsulant (n~1.8), respectively. Concentration of the phosphor is the same for both samples and corresponds to ~ 15 mg/cm^2.

3. Enhanced lumen output from a bulk-YAG:Ce phosphor based downconverter, using HRI encapsulant to achieve higher optical transparency.

We observe an enhancement of approximately 10-20% in lumen output when we compared the light output of YAG:Ce bulk phosphor based downconverter with conventional encapsulant (RI~1.5) and HRI encapsulant (RI~1.8), coupled to a SMD Blue LED lamp in a configuration as described below. In both cases the resulting downconverted emission has similar chromaticity color-coordinates, and the enhancement is shown in the angular candella plot in Fig. 6 (shown on a relative scale). The enhanced optical transparency in the HRI encapsulant based downconverter is due to reduced optical scattering because of matching of the refractive indices of YAG:Ce bulk phosphor and the HRI encapsulant as shown in Fig. 5.

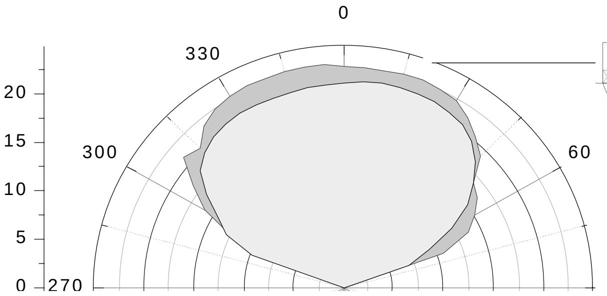

Fig.6 ▨ HRI Encapsulant
□ Conventional Encapsulant

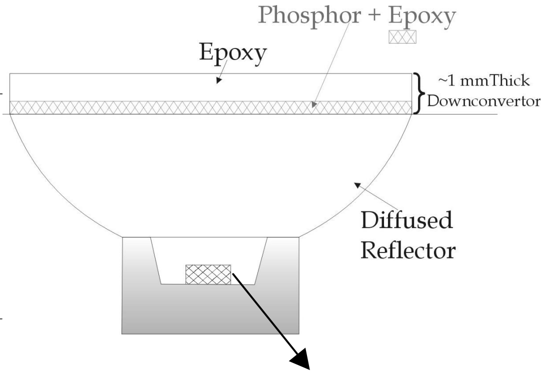

Fig. 7 SMD Blue LED Package

We have coupled a 460nm emitting SMD Blue-LED lamp with a downconverter using a secondary reflector external to the SMD LED lamp (Fig.7). Because the downconverter has very little scattering (due to index matched nanocomposite) we expect more lateral wave guiding of the emission in the downconverter. Since the down converter is not integrated inside the reflector, but is placed above the reflector, the laterally waveguided light is not efficiently directed towards the forward direction for extraction, in the present geometry. Ray-tracing simulations performed for the above geometry and material properties, indicated an enhancement in the lumen output (for the same color-coordinates), in agreement with the experimentally measured value, for an encapsulant RI value of 1.8 compared to that obtained using an encapsulant RI value of 1.5. The absence of an integrated secondary reflector has prevents further enhancement in light extraction from the downconverter. This additional benefit will be realized when the downconverter is integrated within the SMD LED lamp package, besides the additional enhancement in LED die/chip LEE due to the HRI encapsulant.

4. Optical Power and WPE enhancement in AlInGaP Red and Yellow Top-emitting SMD LED lamps using HRI encapsulant

We observe an enhancement of ~ 20% in the ratio of the light output power (and WPE) from an encapsulated lamp to the light output power from the same lamp before encapsulation, when using HRI encapsulant compared to a RI=1.5 conventional epoxy encapsulant. These results are in agreement with the results from Ray-Tracing simulations performed for the specific package, die/chip geometry and the material properties.

The epoxy encapsulant lens from Red (633nm) and Yellow (587nm) Top-emitting SMD LED lamps with an Absorbing-Substrate(AS) AlInGaP LED die/chip was removed using a decapsulating solution. These unencapsulated lamps were re-encapsulated using either a conventional epoxy encapsulant (Hysol HL-1600) or an epoxy-based nanocomposite HRI encapsulant. The lamping ratio (Light Output Power With Encap. / Light Output Power Without Encap.) was monitored for each LED lamp. The mean and standard deviation values for the light output power from the lamps re-encapsulated with the RI=1.5 conventional epoxy, was similar to the corresponding values observed for a random sampling of the as-received lamps from the manufacturer. The standard deviation value for the lamping ratio obtained for both the conventional encapsulant and the nanocomposite HRI encapsulant was ~ 5% of the corresponding mean value in each case.

Conclusion

We have demonstrated blue wavelength excitable, efficient QCA-Nanophosphors capable of enabling downconversion to high color-quality white-light. We have also demonstrated nanocomposite-based HRI encapsulant with RI ~ 1.8, which enhances the LEE of monochromatic LEDs in a cost-effective manner at the package-level. An optically non-scattering downconverter incorporating the HRI encapsulant, enhances the luminous efficacy of PC-LEDs.

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