Development of Phosphors for LEDS

By L. S. Rohwer and A. M. Srivastava

Light emitting diodes are based on semiconductors, which emit spontaneous radiation under suitable forward bias conditions. The basic principle is based on low field injection electroluminescence where light is generated when injected minority carriers recombine with the majority carriers radiatively across the band gap of the crystal. Thus, electrons are injected into *p*-type semiconductors and holes are injected into *n*-type semiconductors. The physics of LED devices is not dealt with here and the reader is referred to an article by DenBaars.[1]

The recent burgeoning interest in the field of LEDs is traceable to the breakthrough in the epitaxial growth of InGaN compound semiconductor material which has led to the development of blue light emitting diodes (and blue laser diodes). The semiconductor is an efficient blue light emitter with emission maximum near 450 nm to 470 nm. There is growing commercial use of blue LEDs based on the GaN semiconductor technology in such diverse applications as full-color flat-panel displays, traffic signals (where they replace the short lived and energy-hungry incandescent lamps), and high-resolution printing, to name a few.

According to the U.S. Department of Energy, lighting accounts for 14% of the total U.S. energy use in the building sector and 21% of the total electricity consumed in the U.S. as a whole. Fluorescent lighting accounts for 67% of this total. Solid-state lighting (SSL)-LEDs have the potential for significantly improving lighting efficiency leading to a reduction in lighting energy use and a concurrent reduction in pollution from fossil fuel power plants. A recent study predicts that SSL-LEDs with an electrical-to-optical conversion efficiency of 50%, and 200 lm/W, could benefit the U.S. by a 50% decrease in the 600 TW-hr of electricity per year used for lighting. This translates into cost savings of $25B/year. However, significant technical challenges must be overcome to meet these efficiency goals. These challenges create opportunities for national laboratories, universities, and industries to work together to develop the science and technology base required to make SSL-LEDs a reality for general illumination. Table I shows the targets for LEDs set for the year 2002, 2007, 2012, and 2020.[2] Achieving the targets for 2007 would enable SSL-LEDs to compete with incandescent bulbs, and the 2012 targets would enable SSL-LEDs to compete with fluorescent lamps. By 2020, if the targets are met, SSL-LEDs are expected to penetrate all the lighting markets.

Over the past four decades, LEDs have been increasing in efficiency and dropping cost at startling rates, as shown in Fig. 1.[3] For red LEDs, the luminous efficiency (lm/W) has improved at a rate of 30X per decade, while the cost has dropped at a rate of 10X per decade. Another significant accomplishment is the availability of blue LEDs as a result of advancements in nitride materials. The technology continues to progress with the announcement of a 100 lm/W orange/red LED by Lumileds and Philips. Lumileds also reported 50 lm/W green InGaN LEDs.

The technical challenges in SSL can be grouped into three primary technologies:[2]

- Substrates, Buffers, and Epitaxy
- Physics, Processing, and Devices
- Lamps, Luminaires, and Systems

Luminescent materials (phosphors) significantly impact the third technology area. The function of a phosphor in SSL-LEDs is to absorb the primary wavelength emitted by the LED chip (near-UV or blue light) and convert it to visible luminescence. This paper focuses on the role of phosphors in solid-state lighting.

The requirements of phosphors for use in SSL-LEDs include: high absorption in the near-UV to blue spectral region, high quantum efficiency, color rendering index (CRI) > 80, resistance to elevated temperature (up to 150°C), and mainte-

Table I. Technology performance targets of SSL-LEDS.[2]

Technology	SSL-LED 2002	SSL-LED 2007	SSL-LED 2012	SSL-LED 2020	Incandescence	Fluorescent
Luminous Efficacy (lm/W)	25	75	150	200	16	85
Lifetime (hr)	20,000	>20,000	>100,000	>100,000	1,000	10,000
Flux (1m/lamp)	25	200	1,000	1,500	1,200	3,400
Input Power (W/ lamp)	1	2.7	6.7	7.5	75	40
Lumens Cost ($/klm)	200	20	<5	<2	0.4	1.5
Lamp Cost ($/lamp)	5	<5	<5	<3	0.5	5
Color Rendering Index (CRI)	75	80	80	80	95	75

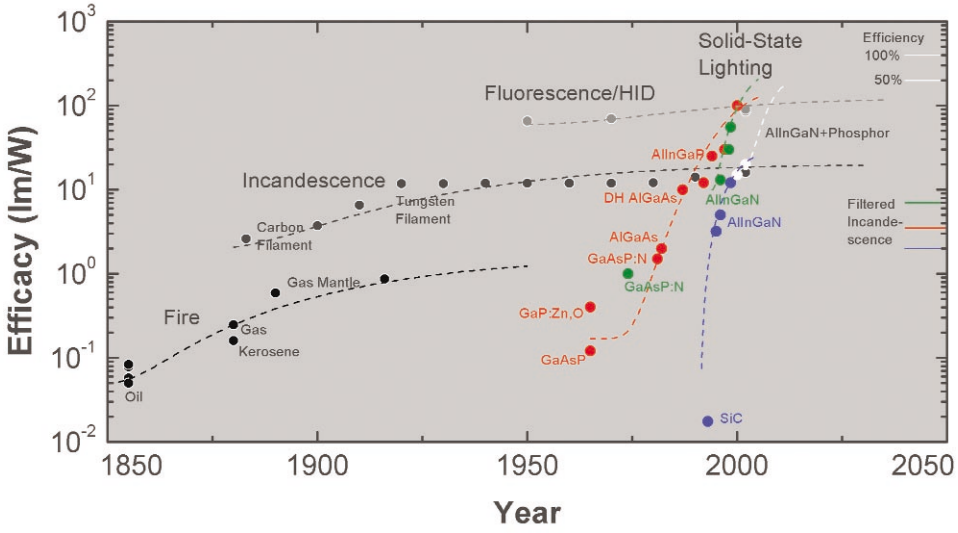

FIG. 1. Performance in lumens/watt of light sources is shown as a function of time in history. Milestones in materials development and performance are indicated. Luminous efficiencies of incandescent and fluorescent lighting technologies are plotted for comparison.

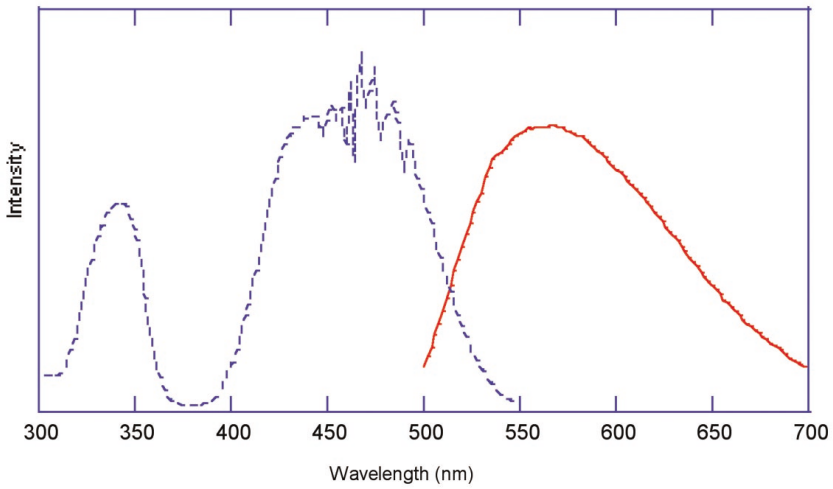

FIG. 2. Room temperature excitation (left, λ_{em}= 570 nm) and emission spectra (right, λ_{ex} = 450 nm) of $Y_3Al_5O_{12}:Ce^{3+}$.

nance of high quantum efficiency in an encapsulating matrix. Quantum efficiency is defined as the ratio of the number of photons emitted to the number of photons absorbed. The quantum efficiencies of fluorescent lighting phosphor compositions are in the range: 80-100%.

Fluorescent lamp phosphors convert the ultraviolet discharge of rare-gas/mercury (primarily at 254 nm) plasma into visible light. The efficiency of conversion of primary UV energy into visible light of wavelength 555 nm (this average wavelength of the visible light is fixed by the human spectral response) in the conventional fluorescent lamp is approximately 45 percent. The rather low energy conversion efficiency arises from the fact that each individual ultraviolet photon incident on the phosphor carries nearly 5 electron volts of energy, while each visible photon in a mercury-based discharge carries (on average) barely over 2 electron volts. This single factor accounts for nearly 55 percent of the energy loss in the conventional fluorescent lamp. Therefore, the efficiency of a lighting device would increase as the ultraviolet wavelength is moved closer to the average visible light wavelength. For example, the energy conversion efficiency of a 370 nm UV and a 450 nm blue radiator into visible light would be about 65 percent and 80 percent, respectively. Consequently, the development of a high-efficiency, low cost source of 370-450 nm radiation would be highly beneficial to general purpose illumination. Two such commercially available devices are UV (emission at 370 nm) and blue (emission near 450 nm to 470 nm) LEDs. It should be noted, however, that the emission intensity of InGaN LEDs decreases very quickly at emission wavelengths less than 400nm.

It is desirable to produce a white light solid-state lighting source that has the potential of replacing "common" lamps such as the linear and compact fluorescent lamp that are in wide use for general and specialized illumination applications. To produce white light, the blue emission from the LED can be combined with complementary yellow emission that may be generated by a phosphor. The high absorption of the blue LED light and the efficient conversion into photons of the desired wavelength are the principal determinants of the phosphor's ability to generate white light in the blue LED + phosphor combination. The yellow luminescence emission with the added transmitted blue light, when carefully matched, can produce white light with color temperatures ranging from 3000 K to greater than 6000 K.

The green-yellow emission of Ce^{3+} in members in the garnet family, $(Y,Gd)_3(Al,Ga)_5O_{12}$, meet most requirements specified for this application. The optical transitions on the activator Ce^{3+} ion are of the allowed $4f^n \leftrightarrow 4f^{n-1}5d$ type. Since the 5d electron interacts strongly with its crystalline environment, broad emission and absorption spectra are obtained. Also, the spectral distribution of emission of the phosphor is a strong function of the composition and structure of the phosphor host lattice. Consequently, the emission color can be conveniently adjusted by changing the composition of the phosphor lattice. The lowest energy Ce^{3+} 4f→5d excitation transition in $Y_3Al_5O_{12}$ (YAG:Ce) is capable of strongly absorbing the emitted blue light from the LED (Fig. 2). The emission of YAG:Ce is efficient and consists of a broad band centered at about 580 nm (Fig. 2). The complementary blue (from the LED) and yellow (from the phos-

phor) emission bands offer a resultant white emission. By careful control of the chemical composition of the garnet phosphor type, the Ce^{3+} emission can be tuned from 510 nm to 590 nm. Consequently, white light with color temperatures ranging from 3000 K to greater than 6000 K can be produced.

The hybrid approach (blue LED +YAG:Ce phosphor) is used in most of the white LED flashlights sold commercially. Users of these flashlights will notice a blue halo surrounding the white light beam. This is a result of the combination of two types of light emitters, directional (LED) and isotropic (powder phosphor). Because of this, the hybrid approach has limitations.

It is also possible to tune the semiconductor emission to 370 nm by changing the indium content in $Ga_{1-x}In_xN$. In such devices, white light can be produced by long-wave UV excitation of a blend of three phosphors, each of which emits one of the three primary colors: red (at 610 nm), green (at 555 nm) and blue (at 450 nm). Phosphors based on the narrow line emission of trivalent rare earth ions like Eu^{3+} (red) and Tb^{3+} (green) and broad band emitters such as Mn^{2+} (green) can supply red and green components and in combination with a suitable blue emitting phosphor can produce the white light with high efficacy. In the "triphosphor," the amount of each color phosphor can be easily adjusted to produce white field corresponding to a wide range of color temperatures with high brightness and excellent color rendering index. It is, of course, necessary that the phosphors strongly absorb the 370 nm long-wave UV. Since a majority of conventional phosphors do not absorb well at these longer wavelengths, it is necessary to custom-make new phosphors to meet the requirements of this application.

The conversion of short and long-wave ultraviolet (emission wavelength: 370-410 nm) LED radiation by a blend of two phosphors to produce a white field corresponding to low color temperature, high CRI and high brightness, is a subject of a U.S. patent.[4] The phosphor blend is composed of two phosphors, a yellow emitting $Sr_2P_2O_7:Eu^{2+}$, Mn^{2+} phosphor and a blue-green emitting phosphor such as commercially available $Sr_4Al_{14}O_{25}:Eu^{2+}$ (SAE).

The efficient blue emission at 420 nm of divalent europium (Eu^{2+}) in $Sr_2P_2O_7$ is well known. The additional incorporation of Mn^{2+} produces a very efficient yellow emission band that is centered at about 580 nm. The enhancement of the Mn^{2+} emission and the quenching of the Eu^{2+} emission are due to the efficient $Eu^{2+} \rightarrow Mn^{2+}$ energy transfer. The phosphor exhibits strong absorption throughout the UV and almost into the visible. Hence, the phosphor luminesces a bright yellow under short and long-wave UV.

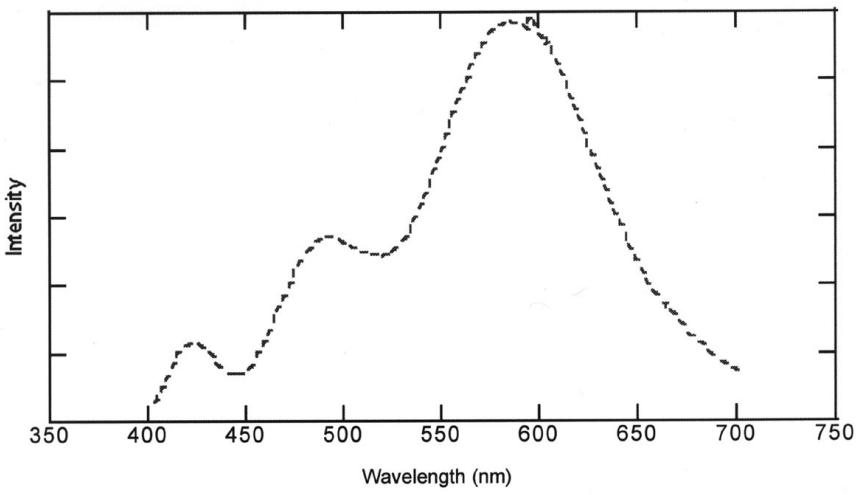

FIG. 3. Room temperature emission spectrum of a bi-phosphor ($Sr_4Al_{14}O_{25}:Eu^{2+}$ and $Sr_2P_2O_7:Eu^{2+}$, Mn^{2+}) white light emitting blend (λ_{ex} = 400 nm).

It is noted that supplementing the yellow emission of $(Sr_{1-x-y}Eu_xMn_y)_2P_2O_7$ phosphor with a blue-green emitting phosphor should produce a white field. The efficient emission of the commercial SAE phosphor in the blue-green at about 490 nm (quantum efficiency of 90 percent) is particularly attractive since the phosphor is well excited by short and long-wave UV and has little or no selective absorption of the visible light. The phosphor blend generates white light with color points in close proximity of the black body locus when energized by line wavelength UV radiation.

The generation of white light by the UV LED/phosphor technology has one very desirable property (just like in fluorescent lamp technology and unlike blue LED/phosphor). It affords very precise control over the color of the resultant white light so that it is possible to develop LEDs with different spectral output for general and specialized applications.

It is also possible to achieve the "triphosphor" scheme of white light generation in the hybrid blue LED and phosphor combination. The strong excitation/absorption spectra of some divalent and trivalent rare earth activated sulfides extend well into the visible and exhibit resonance with the blue LED radiation. It has been proposed to produce white light by combining the blue LED emission with a blue excited complementary green-emitting and red emitting phosphor.[5] Suitable phosphors for such a device are: (1) green emitting, $SrGa_2S_4:Eu^{2+}$ and (2) red emitting $SrS:Eu^{2+}$. The optical transitions on the activator Eu^{2+} ion are of the allowed $4f^n \leftrightarrow 4f^{n-1}5d$ type. By carefully controlling the amount of each phosphor in the blend, white light devices with various color temperatures can be achieved.

Research aimed at developing new phosphors that are superior to existing phosphors for use in LEDs has received much attention. Among the new phosphors that have been investigated are members of the $M_2Si_5N_8$ (M = Ca, Sr, Ba) family of materials activated with divalent europium.[6] Divalent europium-activated $M_2Si_5N_8$ materials display strong absorption in the blue (and into the visible) and exhibit efficient emission in the red.

It is clear that the motivation of many members of the L&DM Division is to develop a triphosphor blend similar in concept to the triphosphor blend of fluorescent lamps, which, when energized by the LED long UV radiation, will produce white light suitable for general-purpose illumination. One of the research activities involves investigating how to improve the quantum efficiency of phosphors for SSL-LEDs. These research activities focus on understanding the materials properties that influence quantum efficiency and develop methods to enhance QE through novel sensitizers, precise control of particle size, and surface chemistry. An additional concern of phosphor researchers is the maintenance of high quantum efficien-

cy at elevated temperatures in an encapsulating matrix. The high input power densities and temperatures generated by the LED chip affect the phosphors, which are in close proximity to the chip. Heat is transferred to the phosphor through an encapsulating matrix such as a silicone gel. Phosphors could experience temperatures up to 150°C in real devices.

The development of highly efficient and inexpensive LED-based white light lamps would certainly represent the most significant revolution in lighting technology since the invention of the fluorescent lamp. Benefits clearly exist for the lighting industry and beyond. Achievement of the project goals will save money for the end-users, while the whole country will benefit from reduced energy consumption, reduced pollution from fossil fuel power plants, and elimination of costly disposal that will result in a safer environment. The targeted market segments are commercial, industrial and retail, all of which are very interested in the higher efficiency products. ■

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