

Phosphors:

The driving force behind white LEDs

Faiz Rahman and Wojciech Jadwisienczak from Ohio University review the progress of phosphors, the key ingredient in the white LED

THANKS TO THE INCREASING USE of the LED in car headlights and light bulbs, sale of this white-emitting source continue to rocket.

To produce its broad emission profile, this device feature a blue-emitting LED chip with a yellow phosphor coated on top. Some of the blue emission pumps the yellow phosphor, and white light results from the mixing of these two colours (see Figure 1).

The quality of white light produced by this class of LED is almost exclusively dependent on the properties of the phosphor. So to make better illumination-quality LEDs, which hold the key to the penetration of this light source into new markets, it is essential to develop better phosphors.

Although it is possible to make phosphors with organic light converting materials, all commercial white LEDs use inorganic phosphors that are much more robust. They typically consist of a host crystal doped with a small amount of one or more 'activator' ions, which are usually rare-earth atoms. Colour conversion results from electronic transitions within the rare-earth ions.

The rare-earth series of elements, which are also known as the lanthanides, are ideal for making phosphors, because they absorb light at shorter wavelengths (typically, blue and ultra-violet), before efficiently emitting at longer wavelengths. The inherent downside of this process is an energy loss, called the Stokes loss, which stems from the lower energy of longer wavelength photons compared to shorter wavelength ones. In a phosphor-driven light emitter, this down-conversion process accounts for most of the energy loss in the LED.

Most phosphors are two-component systems, consisting of a host crystal matrix containing luminescent ionic centres. An example of such a system is one of the first phosphors used for making white LEDs: cerium-doped yttrium aluminium garnet (Ce:YAG). Here, cerium ions that enable the production of cool-white LEDs are doped into a host crystal formed from a mixed oxide of aluminium and yttrium.

Note that in a two-component system such as this, the host matrix plays a crucial role, affecting the energy levels of the dopant atoms and thus determining the absorption and emission wavelengths of the phosphor.

The spectral characteristics of this phosphor govern the quality of white light emitted by the LED. It requires several parameters to quantify the quality of this emission, including the colour or chromaticity point (x,y) on a chart of saturated and unsaturated colours, called a chromaticity diagram (see figure 2). Another parameter is the colour-rendering index (CRI), which describes how closely the light from a white LED matches that of natural daylight. If the match is perfect, the CRI is 100 – the lower the value, the poorer the approximation to natural white light.

Making phosphors

Phosphors are made by high temperature solid-state reactions. Usually, finely ground inorganic salts of various elements are thoroughly mixed in stoichiometric proportions, before this concoction is heated to temperatures that may exceed 1000 °C.

Heating occurs in phosphor firing furnaces, which can hold anywhere from 100 grams to several kilograms of material. Once the phosphors have been heated under an atmosphere of nitrogen or similar inert gases and the reaction is complete, material is removed, reground and may be washed in either water or organic solvents to remove any unreacted compounds. Following mandatory testing, the phosphor is ready to be deployed in blue-pump LEDs.

To make a white LED, most device manufacturers prepare a slurry of phosphors mixed with a thermoplastic resin. Polycarbonate and silicones are widely used, with the polymer acting as a binder to keep the phosphor in place. The high-viscosity liquid slurry is dispensed on to pump LED chips resting in their packages, using precision dispensing machines (see figure 2). Heat or ultraviolet radiation cures the coating, while the assembly is placed in vacuum to remove any air bubbles that might form. In some instances, a dome lens is added on top of the phosphor-coated LED chip using a polymer-moulding step.

Today, much of the effort associated with the development of phosphors for high CRI, high-efficacy light sources is directed towards the use of phosphors with one or more rare-earth ions. Their electronic excitation and subsequent de-excitation can produce narrow spectral emission, such as that resulting from $4f-4f$ transitions in triply-charged +3 rare-earth ions; and it can also deliver a broad emission, such as that coming from $5d$ transitions in doubly-charged +2 rare-earth ions. Thanks to the

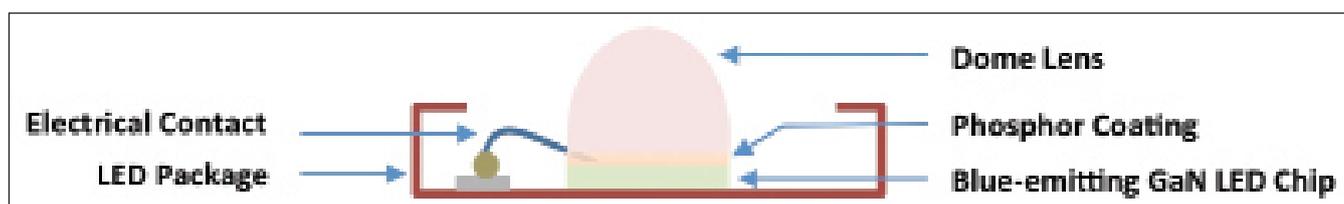


Figure 1. A white LED is formed from a blue-emitting chip pumping a yellow-emitting phosphor.

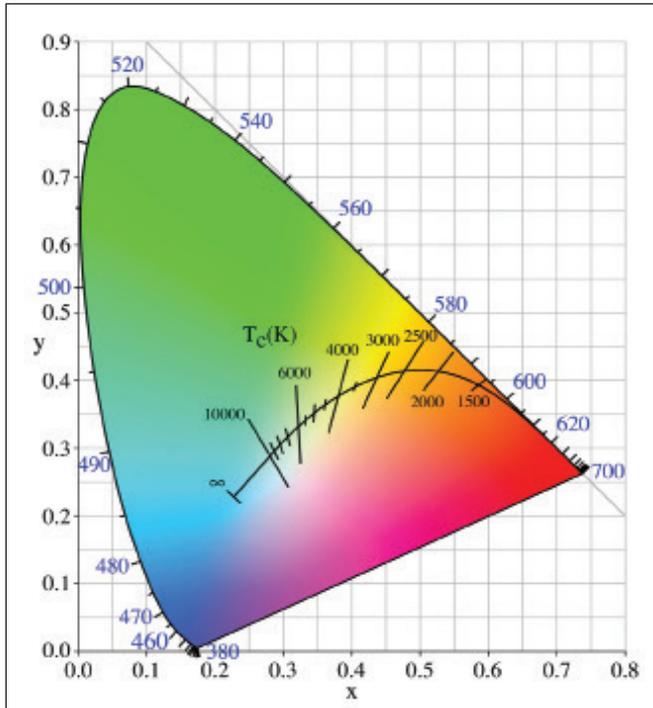


Figure 2. A CIE 1931 chromaticity diagram bounded by monochromatic wavelengths. The curved black line inside the diagram is the blackbody locus, which passes through the colours that would be emitted by a heated black object at different temperatures. The short black lines intersecting the locus show the various correlated colour temperatures (CCTs) – temperatures of non-blackbody emitters emitting light similar to a blackbody.

relatively slow luminescence kinetics of these rare-earth ions – they are in the range 10^{-6} - 10^{-3} s – effective energy transfer can take place between optically-active rare-earth ions and the host matrix. This relaxes pumping requirements, while increasing device efficacy.

Selection of the matrix material plays a large role in determining the emission properties of the phosphor, because it has a profound effect on the active ion coordination chemistry. This allows phosphor makers to engineer the crystal field surrounding the doping sites of the ions. This crystal field determines the covalency of the lattice, and has different effects on the energy levels of $5d$ and $4f$ electrons.

One example of this kind of phosphor engineering is the creation of a new, warm LED phosphor based on a magnesium aluminium silicate, $Mg_2Al_4Si_5O_{18}$ (MASO), crystal matrix doped with Eu^{2+} , Ce^{3+} , Tb^{3+} and Mn^{2+} . Wei Lü and colleagues from the Chinese Academy of Sciences showed that the CRI and CCT of the light source could be successfully controlled by altering the crystal structure and doping ions. The phosphor's luminescence profile was fine-tuned by stimulating different energy migration pathways among active metal ions. However, the quantum efficiency of this phosphor requires further improvement, so work is underway to gain a better understanding of energy exchange in multi-rare-earth phosphors.

The cost and scarcity of rare-earths has encouraged researchers to investigate other types of phosphors. Some

of these resemble the traditional combination of host and luminescent ion, but are based on non-rare-earth elements such as manganese.

Others, meanwhile, are just very small particles of crystalline materials such as cadmium sulphide or cadmium selenide. These so-called quantum dots have sharp, atom-like transitions that give rise to sharp spectral lines with an emission wavelength governed by the size of the dot – the larger it is, the longer the emission wavelength. By combining six or more different sizes of quantum dot together, it is possible to generate customised broadband white light that is tailored to special needs.

Replacing traditional tungsten filament bulbs requires the production of LEDs with yellowish light. In contrast, illumination in museums and art galleries demands a fuller spectrum of white lighting, while medical and rehabilitation applications have their own, often very stringent, specifications.

These differing requirements can also be met by mixing phosphors together to obtain compounded or blended phosphors with desired spectral characteristics. Red-emitting, europium-based phosphors are often combined with yellow-emitting phosphors to reduce the colour temperature of emitted light. This is a cheaper, easier route to producing warm-white-light LEDs than using more expensive, colour-tuned phosphors. But to make a full-spectrum white LED requires phosphor mixtures containing three and even four components.

Blending of phosphors can be performed by a phosphor manufacturer – but most often an LED manufacturer, seeking to meet a specific spectral profile requirement, does it. One example of a blended phosphor LED is a tungsten-halogen lamp simulation LED, which mimics the spectrum of the filament source with a sloping spectral profile (see figure 4). Note that it would not be possible to reproduce this characteristic with a single phosphor.

It is the compounding of the phosphors that is behind much of the recent improvement in the quality of LED-based white lighting. With the continuing development of solid-state lighting, blended phosphor compositions will no doubt lead to speciality LEDs that have no counterpart in conventional incandescent lighting.

Long lifetimes

One of the great strengths of LED-based luminaires over those based on a tungsten filament, and even a fluorescent tube, is their longevity. Even though LED bulbs cost far more than incandescents, their long lifetimes easily compensate for their significantly higher price tags. Of the various components and materials inside a typical LED bulb, phosphors exhibit the longest lifetime. Rather than any malfunctioning of the LED itself, most bulbs fail prematurely because of the failure of one or more electronic components, such as electrolytic capacitors, in their power supply.

The GaN pump chip and the phosphor are extremely reliable, so if a switch-mode power supply itself holds up, the bulb can last for tens of thousands of hours. Unlike filament lamps, which experience catastrophic failure when their filament breaks, phosphor-coated LEDs have no sudden destruction mode. Instead, light output gradually declines over a long period of use.

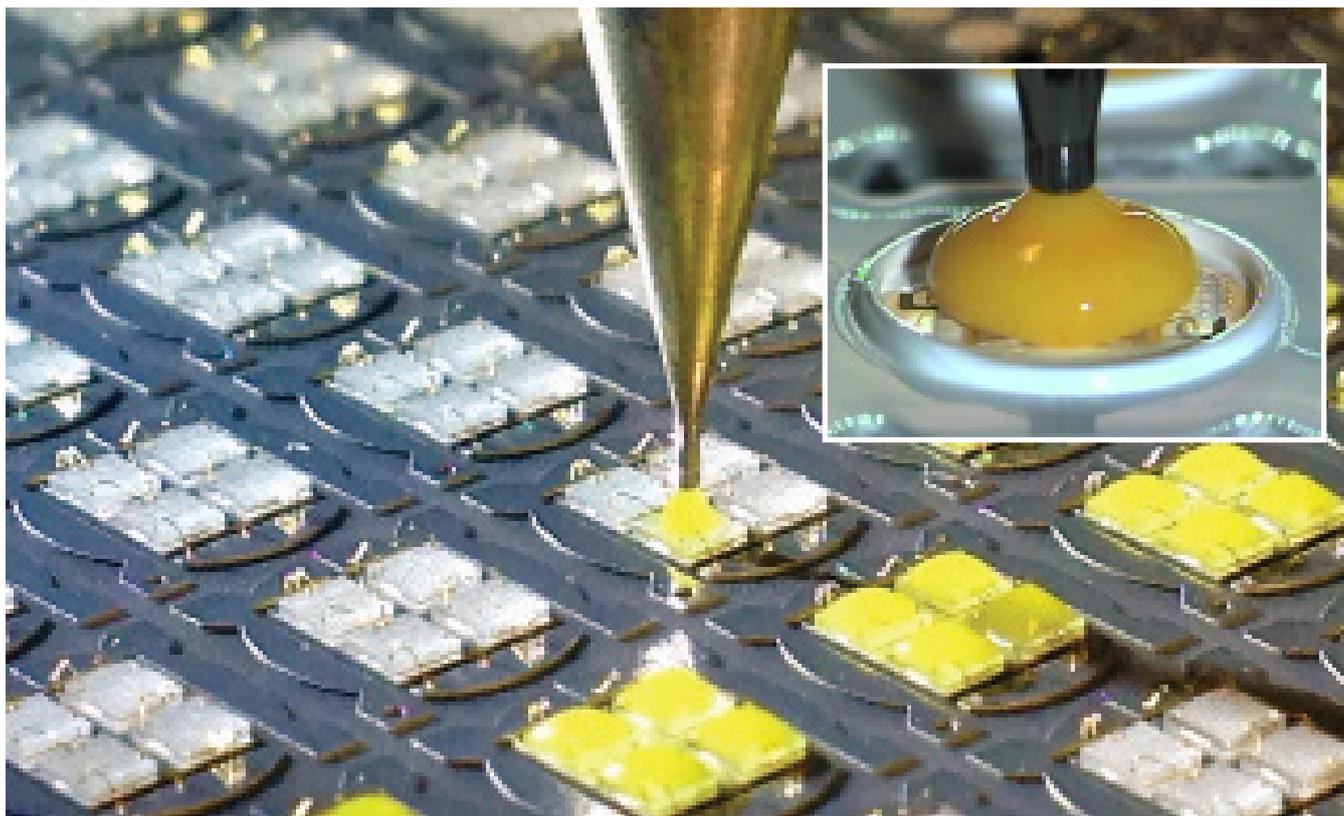


Figure 3. The phosphor that provides wavelength conversion in the LED is embedded in a polymer slurry. Courtesy: GPD-Global Corporation

Due to this behaviour, it makes sense to define the lifetime of the LED as the number of hours before the intensity of emission falls to a certain level. It is common to consider the time taken for intensity to half, and this leads to quoted lifetimes for modern LEDs of 10,000 hours to 50,000 hours.

A steady fall in light output comes from the degradation of the LED's phosphor. Although this class of materials may be considered to be hardy inorganic, thermodynamic processes inside the crystals cause defect formation. Deterioration is accelerated at a higher temperature, due to an increase in the density of defect centres, which seep energy away from the

light-generating, wavelength-down-conversion process. Making matters worse, these crystal defects convert pump light from the LED chip to heat, magnifying defect formation and diminishing light output.

Another problem associated with a high phosphor temperature is that it drives subtle changes in the chemistry of the active ionic species, such as changing the oxidation state. This is bad news, because it leads to changes in colour temperature and colour coordinates. The often talked-about changes in the chromaticity of LEDs are a result of solid-state reactions going on inside the phosphor matrix.

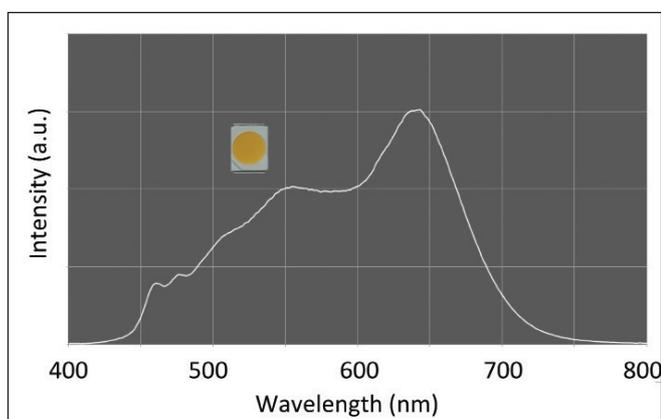


Figure 4. Through careful selection of several phosphors, it is possible to build an LED that can mimic the spectral output of a tungsten-halogen bulb (inset shows a tungsten LED device). Courtesy: ElectrosPELL Corporation

To reduce colour shifts with age and prolong LED life, some manufacturers of solid-state bulbs separate the phosphor from the main source of heat – the pump LED – so it is held at a lower temperature. Thanks to this modification to the design, useful lifetimes are as high as 50,000 hours.

In addition to the inorganic phosphors discussed here, which are deployed in contemporary luminance conversion, some researchers have been investigating luminescent organic compounds that can function as LED phosphors. Their main drawback is their lack of heat and oxidation resistance, which leads to a short operational lifetime. But these phosphors have very promising conversion efficiencies. That makes them an interesting addition to the worldwide effort to improve phosphors and develop new ones, and ultimately aid the growth and diversification of the market for white LEDs.

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