Alan Mills

The use of phosphors by man probably started more than 2000 years ago when they were used in fireworks to modify the colour output, but real phosphor development is a 20th century phenomena starting in the 1940s, and its more recent development has most of the market demand being generated by cathode ray tubes (TVs, PC monitors, test equipment) and fluorescent lighting. However, during the last five years white LEDs have become very important lighting sources and the importance of LED phosphors for white and coloured light generation must be considered an important market driver in the future, and perhaps unfortunately, as a disruptive technology.

Phosphors development for LED lighting

Although the eventual solution for general lighting may yet be a combination of red, green and blue (RGB) LED emitters, plus other LEDs such as orange and yellow if more colour rendition index (CRI) control is required, the vast majority of the current high brightness white LED sources use phosphors [single or in combinations]. These are used to mix or convert blue or near violet LED-sources into white.

Early white LEDs, as introduced by Nichia, used existing phosphors such as cerium doped yttrium aluminium garnet (YAG:Ce), a yellow phosphor, which when combined with the blue LED (~460nm), produces white light (as the eye sees it). It has a low CRI, in the 60 to 70 range, but the benefits are a relatively low cost and its simplicity of use. As may be expected, the inclusion of a small amount of a red phosphor with the YAG:Ce improved the CRI to the acceptable range (a CRI of >80) and increased the light conversion.

However Nichia claims patent rights to the use of this red phosphor and has created potential IP problems for other LED lamp manufacturers. It has also created an industry wide drive to make a new range of phosphors stimulated by blue-violet radiation that are not IP hindered. Preferably, these should be more efficient emitters for these wavelengths and also more efficiently stimulated by 380 to 470nm wavelength radiation.

The need for new phosphors has moved most of the existing suppliers into action including the fluorescent light industry, which, at least in Europe and Japan, will soon have to replace the traditional mercurysources. This may dictate the use of new phosphors for ultra violet activation wavelengths, other than those from mercury.

The need for new phosphor technology and the rapid growth of phosphor based LED market segment has led to the start up of new companies and extensive research into new phosphor materials. Many are hoping to exploit the next generation of phosphors, and develop materials to avoid existing intellectual property situations.

Such is the case for Intematix of Moraga, California, which is using its 'Combinational Discovery Engines' to develop a range of high efficiency phosphors for LED applications. The company is already marketing its phosphors under the Intellectual-Property-free banner, a condition that appears to provide a fully patent protected phosphor family for all to license and that will give pleasant relief from the LED application litigation-wars that are currently on going in this industry.

The planned family of phosphors will provide a range of colours with good colour rendering features, see Figure 1. According to their customers, which includes 'top tier companies' the application results appear to be 'superior to all licensable alternatives and equivalent to the best in class'.

In making these new phosphors, the company used a 'nano discovery engine', which reduced the development time for the first two products to just over a year.

Two of the first phosphors are Y450, which is stimulated by wavelengths of 450nm and shorter and Y460 which is stimulated by the more widely available LEDs emitting at 460nm and below. Both of these phosphors are offered in production quantities.

Evident Technologies, based in Troy New York, is offering a range of phosphors that are mostly based on II-VI materials including cadmium selenides, tellurides and sulphides (CdSe, CdTe & CdS), lead selenide (PbSe), zinc sulphide (ZnS), and also some based on indium phosphide (InP).

The phosphors and phosphor blends of interest to LED lighting have excitation frequencies in the desired range of near-UV and blue excitation (380 to 450nm) and emit in bands across the visible spectrum.

Other Evident phosphors such as PbSe emit in the near IR-spectrum and are presumed to be similar to the PbS nano-crystals tuned by 'the quantum size effect' which were described by Professor Ted Sargent from the University of Toronto in the February issue. Indium phosphide based phosphors have also been developed, but are not as good light emitters at this time.

Evident has received funding from a variety of sources, including New York State Development funds in a joint effort with Rensselayer Polytechnic Institute to demonstrate high efficiency LED lighting sources. This year, Evident also received an NSF Business Innovation grant to develop 'advanced quantum-dot based anti-counterfeiting materials'.

It plans to make use of the semiconductor and optical emission properties to produce unique spectral bar codes with security features that are 'difficult to counterfeit or reverse engineer'. Their goal under this grant is to produce advanced quantum dot systems compatible with a range of ink, UV-curable epoxies and polymers that can be used on paper currency and other important documents.

There are several different product types, Core- and Core-Shell-EviDots, EviDot Composite Nano-

Colour samples of Intematix phosphors

Eight years of UK experience

In Europe, Phosphor Technology Ltd, esconsed at Stevenage in Hertfordshire, England,, has been a key developer and manufacturer of phosphors for blue to white LED conversion for over eight years.

It is also working on phosphors for CRTs, FEDs, plasma display panels, X-Ray applications, IR and UV detection, scintillator applications and laser detection

Among the services offered are particle size analysis using a Beckman Coulter Multisizer 3 and scanning electron micro scopy; spectral analysis in the UV, visible and IR regions; consultancy on theory and practical application and R&D on creating new products and improving existing ones

"Following on the mercury issue," says CEO, Gerry Sorce. "it would be interesting to find if anyone has considered what impact QDs based on II-VI materials would have on the environment if used in large scale applications."

"The big issue currently" he says "is the fairly low long term cost of solid state lighting due to the 'fit and forget' factor, relatively low weight and footprint of the individual chip and the low power consumption. The big shaker at the moment is the automotive sector and of course the mobile telephone/PDA/LCD screen backlighting industry."

Sorce also questions any contribution of nanoparticulate work in real-life LED product developments, as he has yet to see any evidence to prove this.

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Phosphor Technology's new building.at Stevenage, Herts.

materials and 'Quantum Dots' with Core being CdSe visible particles and the Shell-dots having coatings such as CdS or ZnS.

Most fall in the category of providing 'novel semiconductor nano-crystals that enhance and expand applications' in several scientific fields, with many of them being available in 'production quantities'. According to its literature, the company can achieve from their 'quantum dots' 'unique specialty wavelengths that are not readily attainable through standard phosphors.'

There are a couple of interesting features of the Evident materials. One is that the differing phosphor colours are obtained by changing particle size, whereas most traditional lighting phosphors emit at different wavelengths by changing the chemical composition of the molecule. The second is that many of the colour shades have enchanting environmental names -- Catskill Green, Maple red-orange, Lake Placid Blue, Hops yellow, which we hope will also brighten up many currencies!

At the Global Phosphor meeting of over 300 attendees, it became obvious that the increasing market demand for LED phosphors and changes in the governance of the fluorescent industry [eg removal of mercury] have provided excitement and a reawakening in the phosphor business for new phosphor research, even to the extent of a re-examination of phosphor libraries, where old or previously non-applicable phosphors [described in expired patents] could alleviate the present IP situations.

The current world market place for phosphors is about $450m annually with an expectation to grow in the 8-10% range. And, they have to compete with and against several display technologies and applications such as liquid crystal, plasma, LEDs, OLEDs, automotive and field emission, which in turn require a growing range of phosphor types to satisfy new and existing uses. These include cathodic, electroluminescent, plasma, LED, colour conversion, micro display, xenon activated, and image panel application. In an atmosphere of heightened awareness, new compounds, materials properties, formats and processes are being examined covering doping activation, particle sizes, particle coatings and even nano-dots, all to provide more efficient and more stable phosphors with improved aging and half-life characteristics. These will all affect the supply, demand, pricing and new business opportunities as the market volumes and values continue to grow.

However, as these developments occur, the centre of activity is moving away from the US and Europe toward Asia, where Japan, for example, has had at least five phosphor technology meetings per year since the 1940s. To support most of the present white LED market demand, the LEDs need phosphors. In turn, this creates a demand and a growing market for a new breed of high efficiency phosphors tuned to LED emissions. It is an important synergy for the future of LED lighting.