Narrow-Band Phosphors for Next Generation MiniLED and MicroLED Displays

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Abstract

Both phosphors and quantum dots are currently used in liquid crystal displays (LCDs), with GE's KSF narrow red phosphor demonstrating the best possible red color point, reliability, and efficiency. Next generation miniLED and microLED based displays require excellent color quality (gamut) and high brightness which will require color conversion materials with high EQE and narrow emission peaks. Here we describe recent advancements in narrow-band phosphors which are being implemented in next-generation miniLED displays, and being considered for enabling full-color microLED displays of the future due to their excellent optical performance and robust nature.

Author Keywords

Phosphor; KSF; PFS; Wide color gamut; microLED; miniLED; Quantum Dot; color conversion; ink.

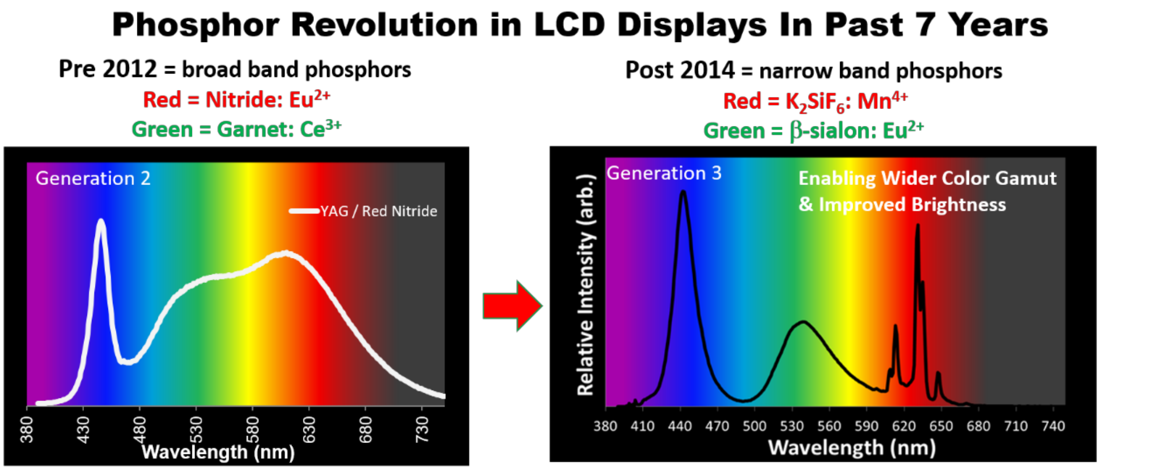
1. Phosphor History

Color quality is one of the most important differentiating features in modern display technology. As a result, there has been a revolution in phosphor technology used in LCDs over the past 7 years. Broad-band emitting phosphors are being replaced by narrow-band emitting phosphors to achieve wide color gamut and increased brightness/efficiency. These improvements may be grouped into three generations of phosphor technology based on the phosphors that are combined in a silicone and deposited on a blue emitting LED chip to achieve the CIE standard illuminant D65 color point.

Early LED LCD models used a single broad-band emitting phosphor deposited onto a blue emitting LED chip to provide color conversion throughout the visible, however green and red color quality was then largely determined by the LCD color filters. Cerium doped garnet phosphors such as $Y_3Al_5O_{12}:Ce^{3+}$ ($YAG:Ce^{3+}$) are very impressive luminescent materials having a quantum efficiency greater than 90%, strong absorption, and excellent reliability to high temperature, high humidity, and high blue flux providing a good on-chip LED package solution (Generation 1). The downside was the lack of red emission in $YAG:Ce^{3+}$ and a full width at half maximum (FWHM) emission that is > 100 nm resulting in good brightness but poor color gamut; typically less than 80% NTSC.

To achieve wider color gamut, a second generation of LED packages emerged in the LED LCD display market which used a two-phosphor solution. "Generation 2" LED packages used both green and red broad-band phosphors to improve color quality, but this approach had to balance inherent tradeoffs between brightness, energy efficiency, and color quality due to the near infrared emission from broad-band emitting red phosphors such as Eu^{2+} doped nitrides. This approach still requires heavy filtering in order to separate the green phosphor emission from the red (Figure 1).

By 2015, a huge step forward in LCD color quality occurred as broad band phosphors became replaced by narrow-band phosphors. These "Generation 3" phosphors enabled wider color gamut and improved brightness due to better separation between the blue, green, and red LED package emission which allowed



Gen	Phosphor(s)	Brightness	Gamut
1	Garnet: Ce^{3+}	High	Low
2	green + nitride:Eu^{2+}	Lower	Higher
3	BSiAlON:Eu^{2+} + KSF	Highest	Highest

Narrow-band emitting phosphors enable more efficient, brighter, wider color gamut displays

Figure 1. Phosphor revolution in LCD in the past 7 years has gone from broad phosphors with high brightness, to narrow-band phosphors with the highest brightness and highest color gamut.

for less filtering and produced minimal NIR emission by the narrow-band red phosphor. Specifically, the green phosphor employed in these third generation phosphor converted white LEDs (pc-wLEDs) is $(Si,Al)_6(O,N)_8:Eu^{2+}$, or β-SiAlON:Eu^{2+}, which has peak emission between 535-540 nm and a FWHM of less than 55 nm. The red phosphor $K_2SiF_6:Mn^{4+}$ (also known as PFS or KSF) developed by GE, has peak emission centered at 631 nm and contains 5 emission peaks, each of which are less than 2 nm FWHM [1,2].

This combination has become the dominant wide color gamut color conversion solution having penetrated all major display sectors such as TVs, cell phones, laptops, computer monitors, and tablets. GE licenses its KSF phosphor technology into the display industry with more than 40 billion KSF containing LEDs sold, with many more KSF-containing LEDs being used in the LED lighting industry. Displays utilizing this narrow-band emitting phosphor approach have achieved close to 100% DCI-P3, easily meeting the UHD Alliance definition of wide color gamut displays of 90% DCI-P3. Nonetheless, color quality continues to drive market differentiation and there is a market segment that seeks to further improve color quality. Relative to red-emitting InP quantum dots (QDs), KSF phosphor has more narrow red emission enabling wider color gamut (Figure 2), more saturated red color, higher quantum efficiency in commercialized parts, and on-chip reliability that does not require encapsulation. The insert in figure 2 shows the red color point of an InP QD with peak emission around 630nm vs. KSF phosphor plotted versus NTSC, DCI-P3, and BT. 2020 color spaces. Both phosphor types have color points that extend beyond NTSC and DCI-P3 red color spaces which means that when used in combination with a suitable narrow band green phosphor and proper color filters both phosphor types can fully render colors in these spaces. However, due to the more narrow red emission, KSF phosphor comes closer to the red primary color point for BT.2020 which means that KSF has the potential to render more colors in BT.2020 color space and better serve the ultra-high-definition television color rendering needs of the future.

Green QDs have more narrow emission than green-emitting β-SiAlON:Eu^{2+} so there are development efforts underway by multiple companies to develop a narrow-band emitting green phosphor that improves upon the properties of β-SiAlON:Eu^{2+}. At SID 2020, GE announced that it is developing narrow-band green phosphor compositions that have peak emission between 520-535 nm with a FWHM emission below 35 nm which will enable a color gamut of 88% BT. 2020 when used in combination with KSF red emitting phosphor. Customer sampling of GE narrow-band green phosphor is underway.

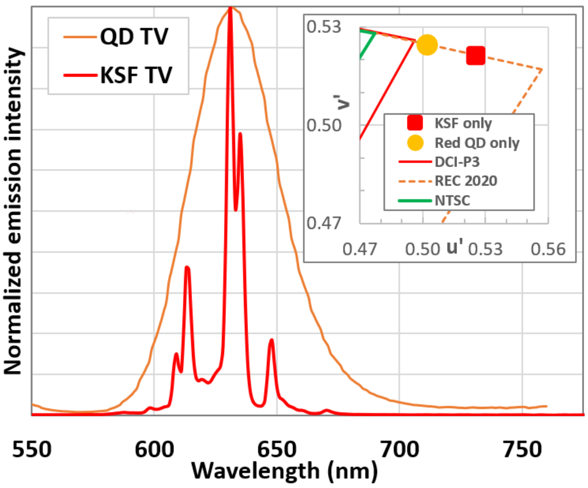


Figure 2. Red region emission spectrum of KSF compared to a QD part from a 2020 commercial QLED display.

2. Phosphors must accommodate miniaturization of LEDs

Along with the quest for improved narrow-band green emitting phosphors, both red and green narrow-band phosphors will continue to evolve to meet the needs of next generation displays. In particular, the trend towards smaller size LEDs such as miniLEDs and microLEDs (μLEDs) will require a decrease in the particle size of conventional phosphors. In order to compete with OLED's deep black levels, LCD manufactures have developed architectures that place a large number of very small LEDs on the back of the display instead of fewer LEDs on the edge of the display. With the implementation of local dimming these displays can achieve high dynamic range similar to OLED, with brightness that far exceeds OLED specifications along with lower cost. The 2020 SID display of the year uses this architecture with a remote phosphor part that contains KSF phosphor technology mixed with a green phosphor which exhibits a narrower emission peak than β-SiAlON:Eu^{2+} to achieve full DCI-P3 color gamut. Traditionally, commercialized displays have used phosphor on-chip as a cost effective and reliable solution to achieve wide color gamut, while QDs used the higher price point remote part configuration because they do not have on-chip reliability.

For applications that can tolerate the higher cost of a remote part, the lower blue flux, and minimal exposure to high temperature and humidity allows KSF to be used in combination with a wider selection of narrow-band green phosphors that may not have on-chip reliability. The result is improved color quality and excellent brightness coupled with the benefits of miniLED backlights leveraging full-array local dimming. This includes hybrid architectures where a green emitting quantum dot may be combined with the narrow-band red emission of KSF phosphor to achieve best in class wide color gamut. KSF is also being used on-chip in a magenta LED + remote part green QD configuration. Specifically, multiple companies are pursuing architectures that combine a green emitting remote perovskite QD sheet used in combination with KSF phosphor to achieve up to 95% rec. 2020 [3].

GE has also reported decreasing the particle size of KSF phosphor down to below 3 microns while maintaining 90% quantum efficiency to meet the needs of these next generation display products using miniLEDs and/or remote downconverter configurations. While a QD remote part loses more than 20% of its emission intensity with band broadening and red shifts at 100 °C, KSF phosphor does not show any thermal quenching or color shifts at elevated temperatures (Figure 3A). Additionally, when exposed to blue fluxes >10 W/cm^2 as an accelerated life test, the QD remote part had a >50% decrease in brightness (Figure 3B) over a 55 hour exposure while a similar part with KSF phosphor had no drop in brightness (Figure 3C) over 168 hours. The KSF color point also did not shift in this accelerated life test in comparison to the QD part (Figure 3D). It is this robustness to temperature and blue flux that allows KSF to be used unencapsulated and directly on-chip.

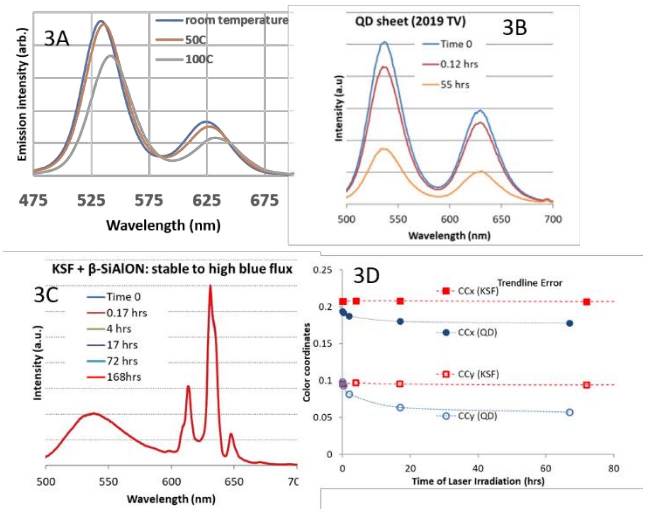


Figure 3. Evaluation of phosphor-containing parts and commercial QD-containing parts

3. Phosphors for MicroLED

Beyond miniLED/2D backlit displays, the most difficult challenge in color conversion today is color conversion in µLEDs where near-full pump absorption must be achieved in a very thin film. This is in stark contrast to phosphor on-chip magenta LEDs (blue LED + KSF) that do not require absorbing all of the emitted blue light from the LED, and remote parts where the luminescent layer is typically at least 50 micron in thickness. There are some µLED architectures where the thickness of the color converting layer should be similar to the size of the µLED and encapsulation is not a desirable product specification. Although KSF phosphor has better efficiency and reliability relative to QDs, QDs are smaller in size with a higher absorption coefficient than host:activator phosphors. It is unclear if either color conversion technology paired with a blue µLED will have both the reliability and absorption properties required to compete with R, G, B µLED configurations. However, phosphor converted µLEDs will have advantages in avoiding complexities and cost of transferring from three different LED wafer types and accommodating different driving conditions for each color.

Significant research efforts have resulted in the development of inks and photoresists containing either phosphors or QDs for deposition onto blue µLEDs or in color filters. In addition to absorption, the main challenge that phosphors must overcome to be a viable technology for µLED color conversion is size reduction. Sub-micron phosphors must be developed that do not agglomerate and can be successfully incorporated into stable ink suspensions for use with deposition techniques such as inkjet printing, spin coating and slot-die coating. GE has recently developed sub-micron sized KSF phosphor along with KSF inks (Figure 4B) suitable for µLED and color filter applications that may be deposited by ink jet printing (Figure 4A), slot die coating or spin coating (Figure 4C) [4].

µLED technology is still in an early creative phase with many new concepts and designs being developed on a regular basis [5]. With so many architectures being pursued it is worth comparing and contrasting sub-micron KSF to commercially relevant red emitting InP QDs, as both are currently being considered as color-converter technology for µLEDs.

EQE: It has been reported that red-emitting InP QD ink films can reach a maximum of just below 40% when combined with 5-20 wt% TiO_2 scattering agents [6]. It is also known that InP QDs suffer from self-absorption which occurs due to the overlap of the absorption and emission spectrum of the QD [7]. A red photon emitted from a QD can be re-absorbed by another red QD. This manifests itself as a decrease in EQE in highly loaded or optically thick films of QDs, like those desired for µLED color conversion. This QD absorption throughout the visible portion of the electromagnetic spectrum is also responsible for the observed room light excitation that can occur in QD color filter and µLED architectures. As shown in Figure 4D, KSF phosphor shows no self-absorption, allowing highly loaded KSF-containing films to achieve EQEs >70% in densely packed 30-50 µm thick films without the use of any extraneous scattering agents. Scattering agents remain an option for use with small size KSF to further increase blue absorbance in thin films, but KSF has a refractive index of about 1.4 and so at typical sizes used for inks will inherently provide some degree of scattering.

Curing: It has been reported that unencapsulated QD films may degrade more than 20% in luminance even under mild curing conditions of less than 20 minutes at 80 °C [8]. By contrast, small size KSF phosphors that can be suspended in an ink for >48 hours shows less than a 2% loss in luminance when cured at 150 °C in air for 30 minutes.

Photoluminescence decay time: QDs typically have a PL decay time below a few hundred nanoseconds whereas host:activator phosphors tend to have microsecond to millisecond decay times. In LCDs, KSF phosphor TVs show the same decay time as QD TVs because the slowest response time in the display is the liquid crystal. KSF phosphor is also much more prevalent in LCD gaming laptops where color and fast response times are important. In the majority of µLED applications where LCD like response times are sufficient, phosphors like KSF will meet product specifications, although

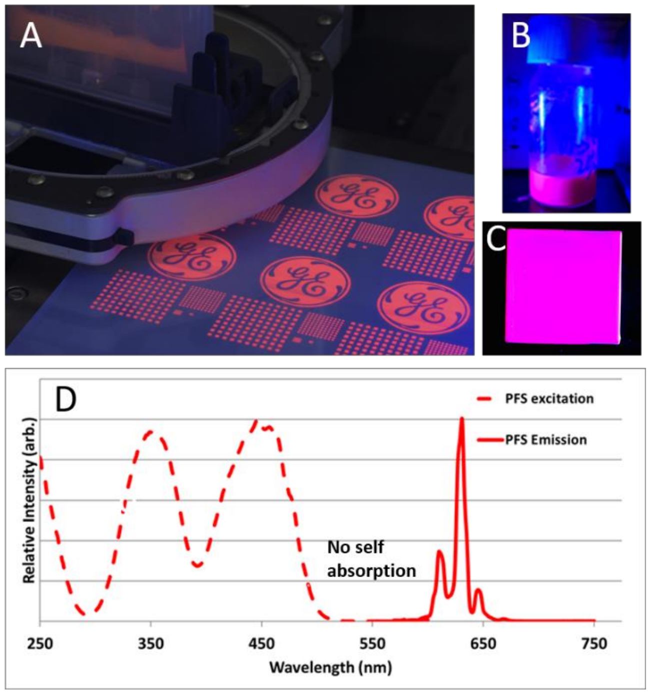


Figure 4. A. ink-jet printing of sub-micron KSF; B. sub-micron size KSF ink; C. spin coated KSF part; D. KSF absorption & emission spectrum showing no self-absorption.

for some niche applications the faster decay time of QDs may be advantageous.

Blue Absorbance: QDs have a clear advantage over typical phosphors when it comes to absorption coefficient of blue light. Most viable phosphor compositions that can be synthesized in submicron size cannot absorb 85% blue flux in a 10 µm thick film with reasonable QE. Higher activator concentrations,

Table 1. Comparing KSF phosphor to InP QDs on important metrics for next generation displays

Property	PFS phosphor	Red InP QD
Color gamut	5 peaks <2nm each	FWHM >40nm
Quantum efficiency (IQE & EQE)	EQE >70%	EQE <40%[6]
Reliability to air	No encapsulation necessary in commercial products	Encapsulation required
Reliability to moisture	No encapsulation necessary in commercial products	Encapsulation required
high temperature quenching	no loss at 100 °C	>20% loss at 100 °C
High temp. curing degradation	<2% at 150 °C for 30 min.	>20% at 80 °C for 20 min. [8]
Reliability to high blue flux	Commercialized on chip	Not commercial on chip
Passivation film required (O_2/H_2O)	no	Yes
Self-absorption	no	Yes, all QD colors
Scatterance	RI = 1.4 so provides some scattering at typical sizes	Must add scattering agent
Photoluminescence decay time	LCD like response time	Faster in microLED with no LCD
Absorption	Requires >2x QD thickness	Higher abs. coefficient

smaller sub-micron particle size, and scattering agents is one viable strategy that can be used to increase blue absorption in very thin (<10 microns) films which are required for some µLED architectures. For applications where an encapsulant is not allowed, one strategy for QDs is to use a thicker Zn-containing shell for improved reliability which results in a penalty of increasing the volume fraction of QDs required to achieve similar absorption when compared to QDs with a thinner shell [9]. Although it is difficult to quantify because of the multiple types of phosphors and core/shell QDs, in general it appears that films containing phosphors should have higher EQEs but need to be at least twice as thick to achieve the blue light leakage levels reported for QD films [6].

µLED architectures that allow for some degree of blue transmission (or use color filter pigments to prevent loss of color quality), or that can tolerate "thicker" luminescent layers will benefit most from the simpler manufacturing and driving scheme used with blue µLEDs in combination with submicron phosphors such as KSF. This combination can provide improvements in color quality, reliability, and brightness when compared to QDs or red emitting µLEDs. A summary of important metrics to be considered when selecting a color-converting material for µLED are summarized in Table 1. Side by side comparison of red InP QDs and KSF phosphor makes it clear why small size phosphors are being considered as a possible technology that will enable full-color µLED across multiple products and cost points.

As the µLED industry matures and the balance between cost and performance determines which architectures prevail for next generation displays, the two most game changing technological advancements in color conversion include commercialization of sub-micron, unagglomerated phosphors that maintain the higher %EQE and reliability; and QDs with improved reliability to enable use on chip without encapsulation. The display industry continues to innovate at a breath-taking speed and color conversion materials that enhance color quality and brightness are at the center of this exciting revolution of next generation, immersive displays.

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