

PFS, $K_2SiF_6:Mn^{4+}$: the Red-line Emitting LED Phosphor behind GE's TriGain Technology™ Platform.

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Abstract

The red-line emission of PFS, $K_2SiF_6:Mn^{4+}$, phosphor centered at 631 nm results in phosphor converted LED package efficacy improvements of >10% relative to packages using conventional Eu^{2+} doped nitride broad-band red-emitting phosphors. Improvements in absorption, quantum efficiency and stability under high humidity and high light flux will be presented that have resulted in commercialization of this material under GE TriGain™ Technology.

Author Keywords

PFS; phosphor; manganese; $K_2SiF_6:Mn^{4+}$; luminescence

Light emitting diode (LED)-based systems are revolutionizing the display and lighting industries due to higher efficiencies and increased functionality [1,2]. For general illumination and LCD backlights, most white LED systems use blue InGaN LEDs combined with various green and red phosphors to convert part of the blue LED emission with typical red LED phosphors being Eu^{2+} -doped nitrides with emission maxima from 610-655 nm and FWHMs of 50-90 nm [3,4,5]. These phosphors can have quantum efficiencies greater than 90%, but there are significant losses at high color rendering indices (CRIs) or high color gamuts for general lighting or LCD backlights, respectively, due to the large fraction of red phosphor emission in the deep red and near-IR where eye sensitivities are low [2,5]. Therefore, one U. S. Department of Energy goal for LED development has been the development of narrow linewidth (<40 nm full width at half maximum or FWHM) red phosphors or downconverters with λ_{max} ~615-635 nm that are excited by blue (λ_{max} =420-470 nm) LEDs [1]. Red emitting phosphors with these spectral characteristics could enable lighting systems with >10% higher efficacy at >90 CRI and high color gamuts (>90% NTSC) if they can meet all requirements for LED usage.

It is possible to use semiconductor quantum dots (QDs) as downconverters since they can have narrow emission linewidths and large absorption cross-sections for blue light [6,7]. However, reliability concerns limit many CdSe-based QD downconverters to hermetically sealed optical components that are remotely placed away from blue LED light engines instead of direct implementation in LED packages [6,8]. Configurations using remote downconverters may lead to lower LCD system efficiencies [8] and could also increase the cost and complexity for QD-based lighting or display systems. Alternately, Mn^{4+} -doped complex fluoride phosphors, such as $K_2SiF_6:Mn^{4+}$ (PFS) or $K_2TiF_6:Mn^{4+}$ (PFT), have a combination of high efficiency, narrow red emission, and reasonable absorption at blue LED wavelengths (Figure 1) to make these materials interesting for LED lighting and display backlights [9,10,11,12,13]. The narrow line spectrum of these phosphors is spectrally equivalent to a Gaussian with a peak at ~630 nm and ~30 nm FWHM, meeting spectral requirements for both high CRI lighting and

high color gamut LCD backlights. However, while it is possible to achieve high quantum efficiencies (QEs) [9,10,11,12,13], the major issues for typical PFS and other Mn^{4+} -complex fluoride phosphors include low absorption of the phosphor at the onset of concentration quenching, photosaturation, and general reliability issues. In this paper, we will discuss how GE's research and development work on these materials has nearly eliminated many of these issues and the subsequent impact on LED packages for backlighting and general lighting.

Figure 1 shows the normalized excitation and emission spectra of a typical Eu^{2+} doped nitride in comparison to PFS. From Figure 1, two of the main advantages of PFS relative to using a nitride are clear. First, the narrow-band red emission from PFS centered at 631nm results in no emission in the orange and near infrared portions of the electromagnetic spectrum. Second, the excitation spectra shows that while PFS does not absorb beyond 510 nm, Eu^{2+} doped nitrides continue to absorb significantly out to 570nm which in a package would result in both absorbing some green phosphor emission and self-absorption of red phosphor emission. Relative to Eu^{2+} doped nitrides, PFS would simplify LCD color filter choices and improve the system efficiency by more than 10%.

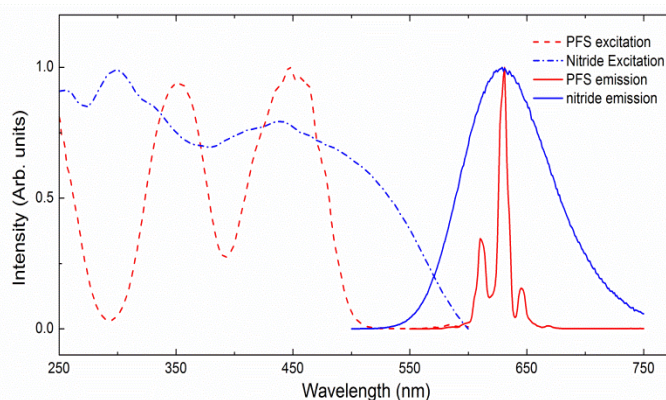


Figure 1. Normalized excitation and emission spectra of $K_2SiF_6:Mn^{4+}$ (PFS) in comparison to a Eu^{2+} doped nitride.

One issue that determines loading levels of most phosphors in LED packages is the onset of concentration quenching. Given the relatively low absorption coefficient of PFS (~30 cm^{-1} at 0.7 wt% Mn), this is especially important. The loss of phosphor quantum efficiency at high activator concentrations, or concentration quenching, is a typical phosphor property. When research groups analyze concentration quenching in either new or previously reported phosphors, the "critical" activator concentration is typically defined as the point where either the quantum efficiency (QE) or brightness begins to decrease.

However, one item that is rarely noted in most studies is how synthesis parameters can affect critical concentrations and (possibly) microscopic mechanisms for energy transfer. Since improved synthesis and post synthesis processes could eliminate quenching defects, they could also lead to higher critical concentrations. Practically, increasing Mn^{4+} concentration in PFS without QE losses helps to alleviate one of the drawbacks for this material, the relatively low absorption coefficient for blue light. Improving phosphor absorption then reduces PFS phosphor loading in LED packages to make LED packaging significantly easier.

Figure 2 shows the quantum efficiency and photoluminescence decay time of PFS as a function of activator concentration, $[Mn^{4+}]$. Through evaluation of commercial samples and our own internal synthesis efforts, concentration quenching in PFS becomes significant around 0.85 wt% Mn. Through process development, we have reduced defect concentrations that lead to nonradiative pathways such that concentration quenching effects are not observed until significantly above 2.0 wt% Mn. More than doubling the activator concentration while maintaining >90% quantum efficiencies enables LED packages to be made with much lower phosphor loading.

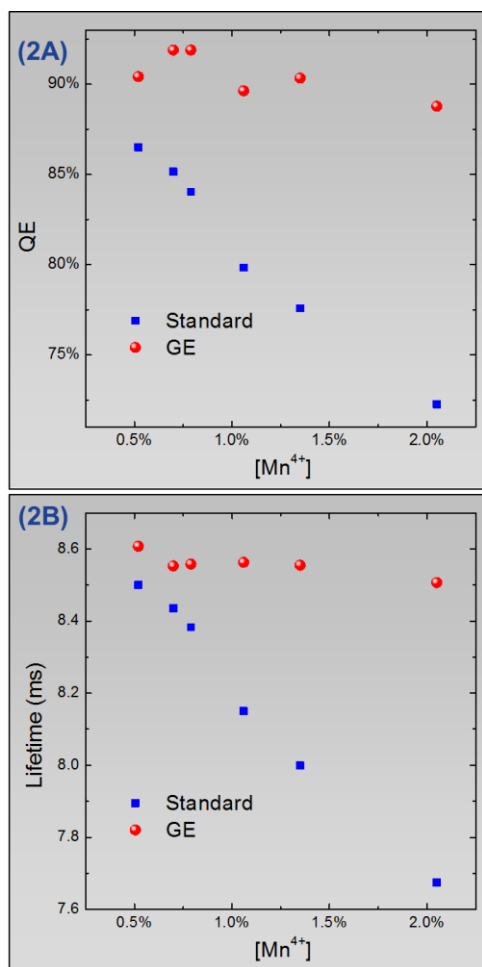
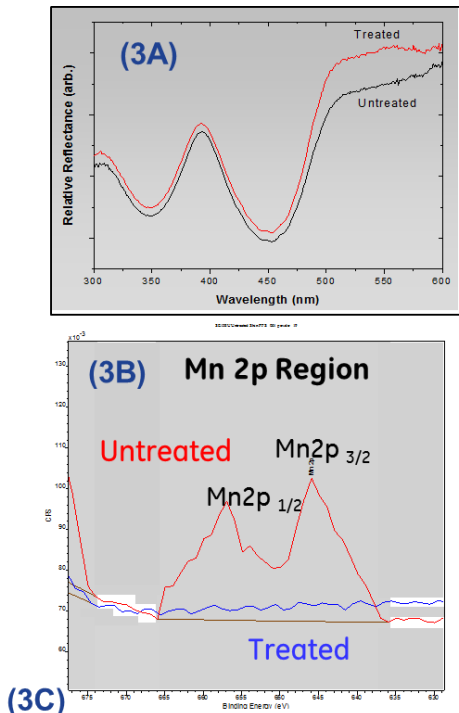


Figure 2. Quantum efficiency (2A) and photoluminescence decay time (2B) of standard PFS vs. GE TriGain™ with improved processing.

Another issue that may limit the use of PFS in phosphor on chip medium/high-powered packages is photosaturation since Mn^{4+} in PFS has a relatively long decay lifetime ($\tau \sim 8.8$ ms). In the least, photosaturation leads to photobleaching where the excited ion cannot absorb additional blue photons but the quantum efficiency of the phosphor is unaffected. However, it is also possible that excited Mn^{4+} ions can absorb blue light or undergo Auger-like energy transfer processes, leading to lower quantum efficiencies at higher excitation fluxes. It is possible to place the downconverter further away from the LED chip in a remote phosphor configuration [14] to decrease the incident flux density. However, with this approach the phosphor usage and costs can become prohibitively high, negating any potential advantage for PFS versus current QD-based systems. Our measurements and experience have shown that the onset for intensity saturation ($\sim 2\%$ quantum efficiency loss versus low flux measurements) is at ~ 25 W/cm². This indicates that TriGain™ PFS can be used in most on-chip medium power package applications without significant losses in phosphor efficiency. The intensity saturation in Mn^{4+} -complex fluorides is much less severe versus Eu^{2+} - Mn^{2+} phosphors that have similar decay times [14], suggesting different mechanisms for saturation. For example, Mn^{4+} excited-state absorption could occur at high excitation fluxes, similar to other d^3 ions like Cr^{3+} [15].

Apart from efficiency and absorption concerns, the reliability of PFS has been another issue. Although minimal temperature quenching of $K_2SiF_6:Mn^{4+}$ phosphors is observed below 150 °C, PFS can darken when exposed to high temperature high humidity (HTHH) conditions for prolonged periods of time. One cause for $K_2SiF_6:Mn^{4+}$ degradation under HTHH conditions is the hydrolysis of near-surface/surface MnF_6^{2-} groups. Surface hydrolysis of MnF_6^{2-} leads to brown, mixed valence Mn species with a resulting drop in QE and an increase in parasitic absorption. A washing process was developed to remove surface manganese from PFS using K_2SiF_6 -saturated solutions in concentrated HF [16] and/or H_2SiF_6 solutions [17]. The resulting “core-shell” phosphor particles [18] have greatly reduced Mn^{4+} near-surface concentrations to significantly reduce HTHH and hydrolysis-based degradation. Figure 3 shows differences between treated and untreated PFS samples after a 150 hr. exposure to 85°C and 85% relative humidity. Figure 3A shows the diffuse reflectance of both treated and untreated samples and the browning of the untreated sample results in a parasitic absorption which becomes significant between 500-600nm. Figure 3B shows x-ray photoelectron spectroscopy (XPS) results that indicate that the particle surface has a significantly reduced Mn concentration after the phosphor powder is treated in $K_2SiF_6/40\%$ HF solutions: the Mn surface concentration for treated phosphors is below the XPS detection limit ($\sim 0.1\%$). Therefore, these treated $K_2SiF_6:Mn^{4+}$ phosphor powders can be described as “core-shell” particles with an inner $K_2SiF_6:Mn^{4+}$ core and a shell of undoped K_2SiF_6 . Figure 3C shows that the treatment step results in decreasing the brightness degradation by a factor of seven during this HTHH exposure.



Sample	Initial QE/Abs	$\Delta(QE*ABS)$
PFS	95/72	-14%
Treated PFS	100/70	-2%

Figure 3. Comparison of Treated and untreated PFS under HTHH conditions. (A) Diffuse Reflectance, (B) X-ray photoelectron spectroscopy, (C) Change in brightness.

Apart from HTHH degradation, there is the potential for color center formation at high excitation fluxes and a loss in phosphor efficiency over time [19]. Accelerated testing of phosphor stability under blue irradiation is measured by irradiating phosphor/silicone tapes with an InGaN diode laser that is coupled to an optical fiber whose output is coupled to a collimator. Again, through improved process methods, we are able to significantly reduce the photodamage (~9x) in GE TriGain™ relative to typical commercial PFS samples (Figure 4).

GE's process improvements for PFS lead to the combination of reduced concentration quenching and higher stability under high excitation flux and HTHH condition. These improved PFS phosphors enable PFS to be used in a wider range of lighting/display applications. When medium-power LED packages are made with improved PFS phosphors deposited directly onto LED chips, we achieve *steady-state system* efficacies of 137 lm/W at CRI>90, CCT=4000K with lumen losses and color shift over >5,000 hours that match commercial LEDs using typical Eu²⁺-doped nitride phosphors. Similar improvements are also possible in LCD backlight units. Consequently, these improvements in the quantum efficiency at high activator concentration, and reliability under high excitation flux and HTHH conditions have resulted in the commercialization of PFS for on chip applications under GE TriGain™ technology.

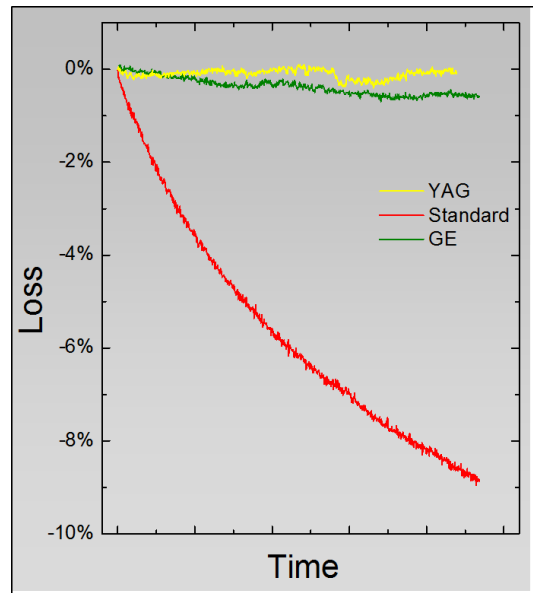


Figure 4. High Excitation flux damage comparison of commercial PFS vs. GE TriGain™

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