Narrow-Band Emitting Phosphors for Energy Efficient SSL

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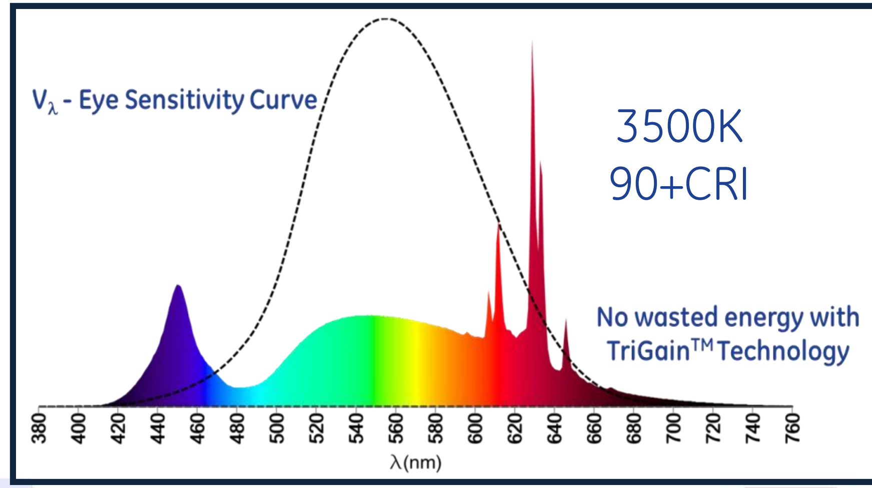

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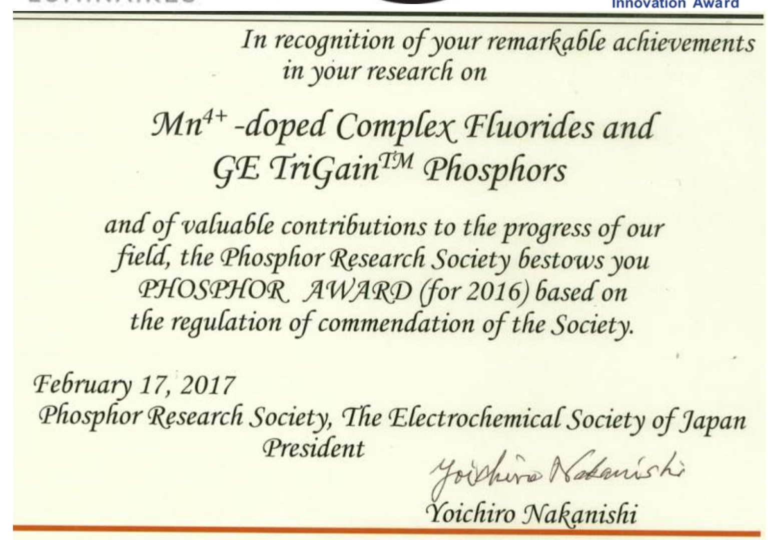
Next Generation LUMINAIRES

2014 IES PROGRESS Report SELECTION

LIGHTFAIR INTERNATIONAL 2015 Innovation Award


In recognition of your remarkable achievements in your research on

Mn^{4+}-doped Complex Fluorides and GE TriGain™ Phosphors

and of valuable contributions to the progress of our field, the Phosphor Research Society bestows you PHOSPHOR AWARD (for 2016) based on the regulation of commendation of the Society.

February 17, 2017
Phosphor Research Society, The Electrochemical Society of Japan
President
Yoichiro Nakanishi

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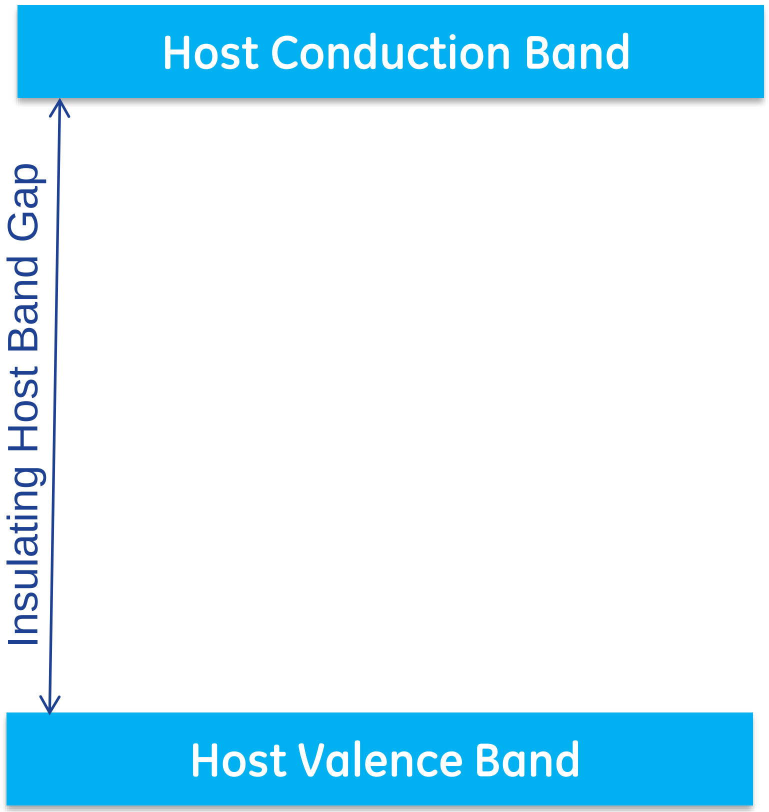
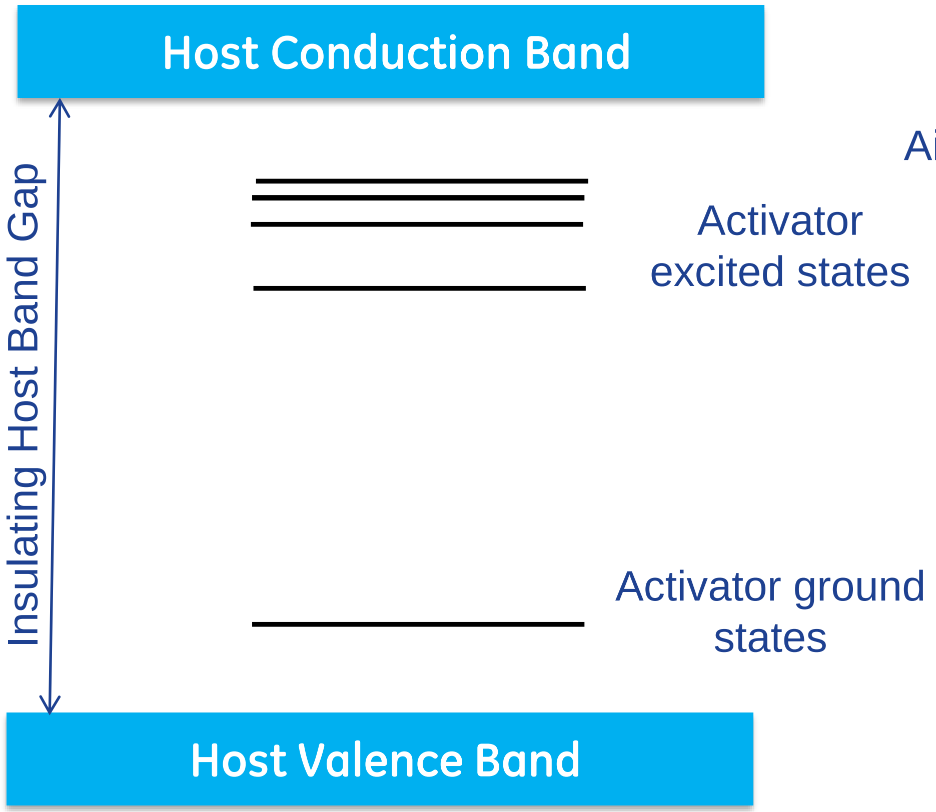
LED Phosphors- Host: Activator Concept

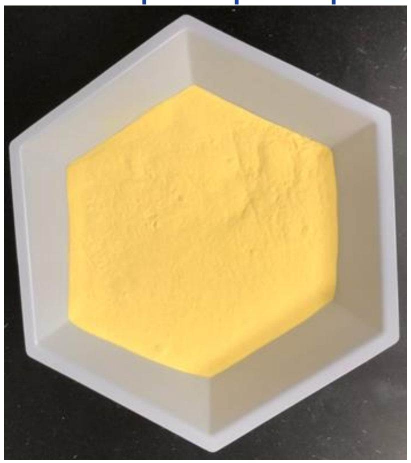


- **Host**: Insulator with band gap in UV = transparent
  ex. K_2SiF_6 (PFS/KSF)

LED Phosphors- Host: Activator Concept



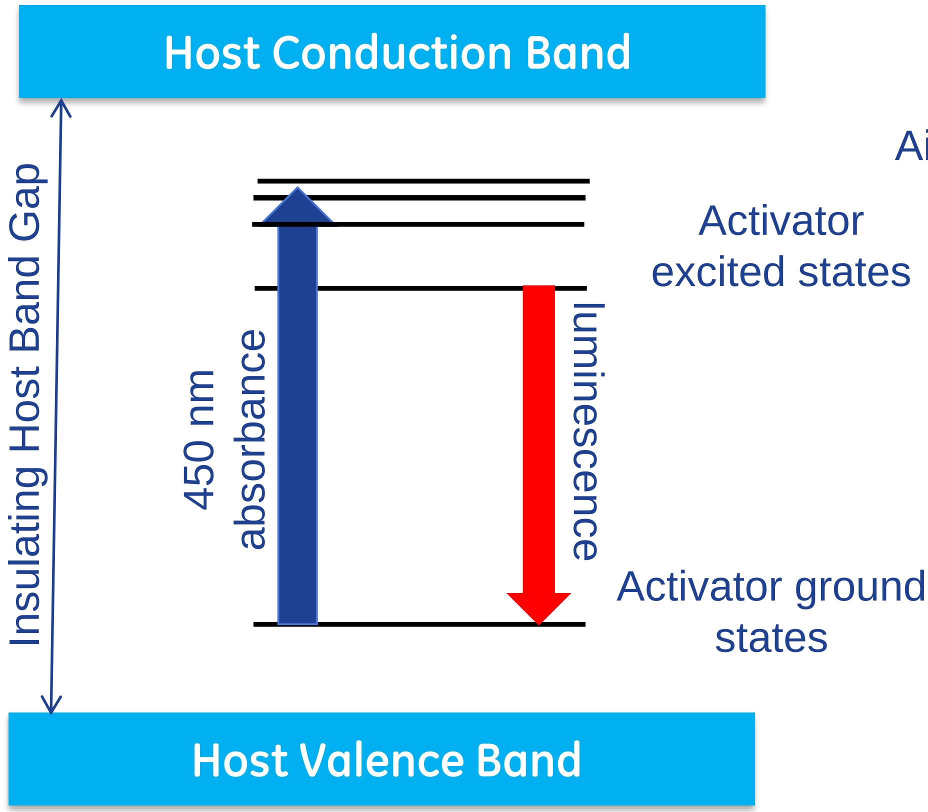
Air stable phosphor powder



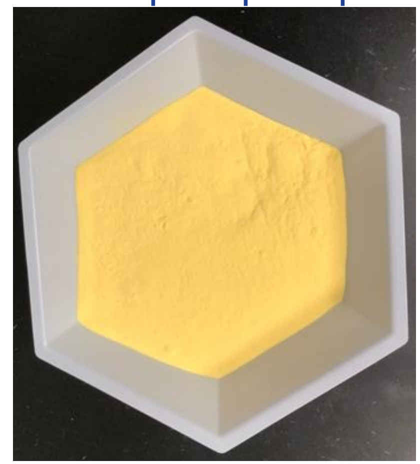
Phosphor in silicone

- **Host**: Insulator with band gap in UV = transparent
  ex. K_2SiF_6 (PFS/KSF)
- **Activator**: Dope in a few mol % of an optically active cation to enable absorbance/luminescence
  ex. Mn^{4+} to give $K_2(Si, Mn)F_6$

LED Phosphors- Host: Activator Concept

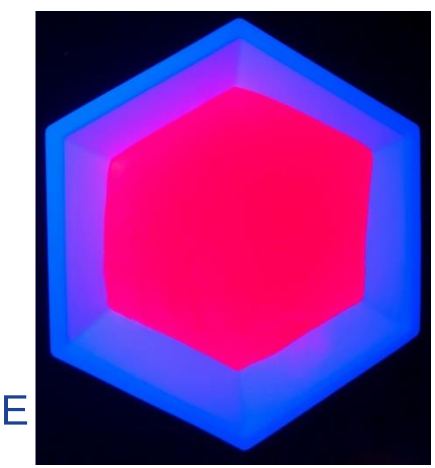


Air stable phosphor powder



Phosphor in silicone

Blue Excitation ➔ luminescence



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- Too little activator = weak absorbance, high loading
- Too much activator = concentration quenching, low QE
- Emission may be tuned via composition

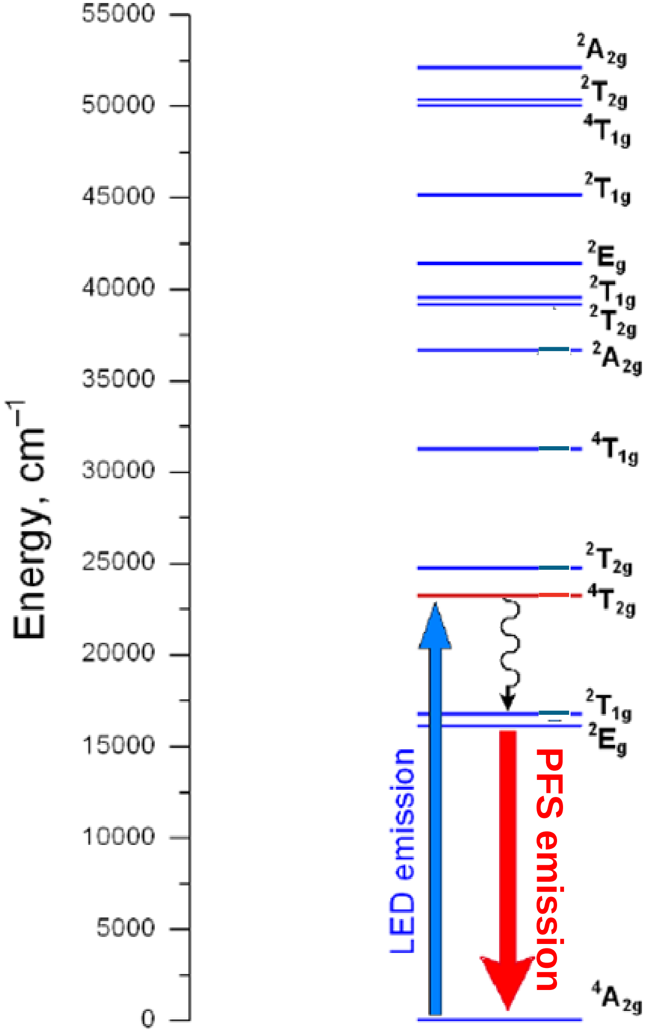
Red-Emitting Components for white pc-LEDs

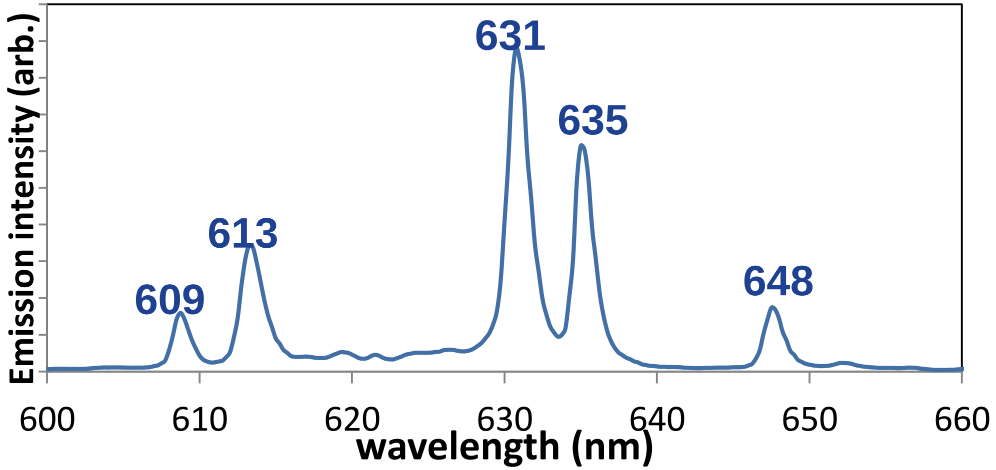
Material	Peak Emission (nm)	FWHM	Pros	Cons
$K_2SiF_6:Mn^{4+}$	631nm	5 peaks each <2nm	Narrow FWHM, best on chip LPW, minimal scattering	Long PL decay time, low abs. coefficient
$(Ba, Sr)_2Si_5N_8:Eu^{2+}$	590-625	80-100 nm	Good reliability demonstrated commercially	IR Spillover (LPW loss),
$(Ca, Sr)AlSiN_3:Eu^{2+}$	610-660	80-90 nm	Good reliability demonstrated commercially	IR Spillover (LPW loss),
$Sr[LiAl_3N_4]:Eu^{2+}$	650	50nm	4-12% higher LPW vs. other nitrides, good thermals	Self absorption, some IR Spillover (LPW loss)
$Sr[Mg_3SiN_4]:Eu^{2+}$	615	44nm	higher LPW vs. other nitrides	Self absorption, thermals
$Sr_{1-x}Ca_xS:Eu^{2+}$	615-650	60-70nm	More narrow band emission than 1st generation nitrides	Thermals, chemical interaction with package & moisture
CdSe/CdS QDs	Tunable green-red	30-50 nm	Narrow FWHM, size dependent tunable emission	Reliability, more complex architecture designs, RoHS
InP QDs	Tunable green-red	45-65 nm	Narrow FWHM, size dependent tunable emission	Reliability, more complex architecture designs
Direct Red LEDs	Tunable red	25-35nm	No stokes loss	Thermals, more complex architecture designs,

Pust, P.; Schmidt, P.; Schnick, W., A Revolution in Lighting, Nat. Mater., Vol. 14, May 2015, p. 454-458

Energy levels & Properties of K_2SiF_6:Mn^{4+} (PFS/KSF)

DOE 2025 Red Target: 615-635nm peak Emission & 30nm FWHM





Pros:

- 5 main emission peaks centered at 631 nm each with <2nm FWHM enabling energy efficient lighting & wide gamut displays
- RI ~ 1.4 for minimal scattering in silicone
- No thermal quenching up to 150 ºC
- On chip solution, RoHS compliant

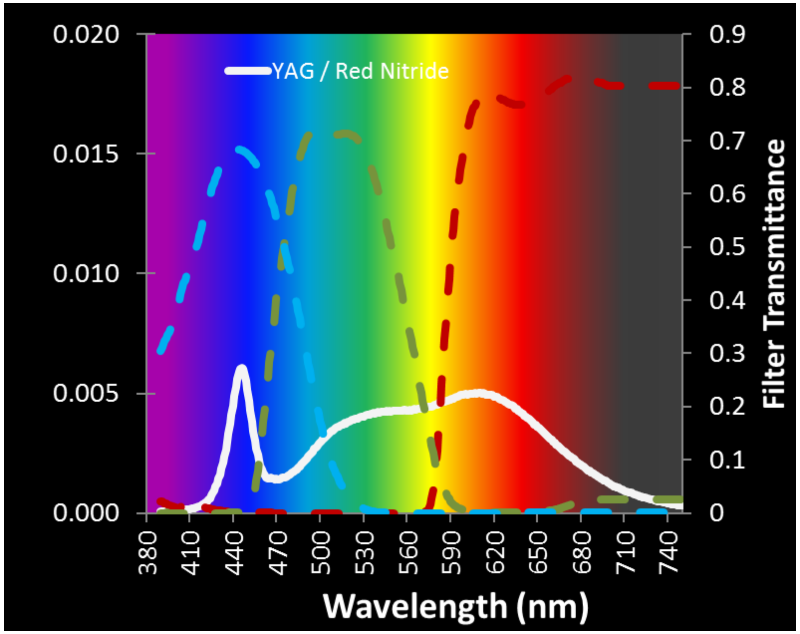
Cons:

- Emission from ^2E -> ^4A is both spin & parity forbidden resulting in PL decay time ~ 8ms
- Ground state absorption ($^4A_{2g}$ -> ^4T) is spin allowed & parity forbidden.
- Saturation effects become measurable > 25W/cm^2

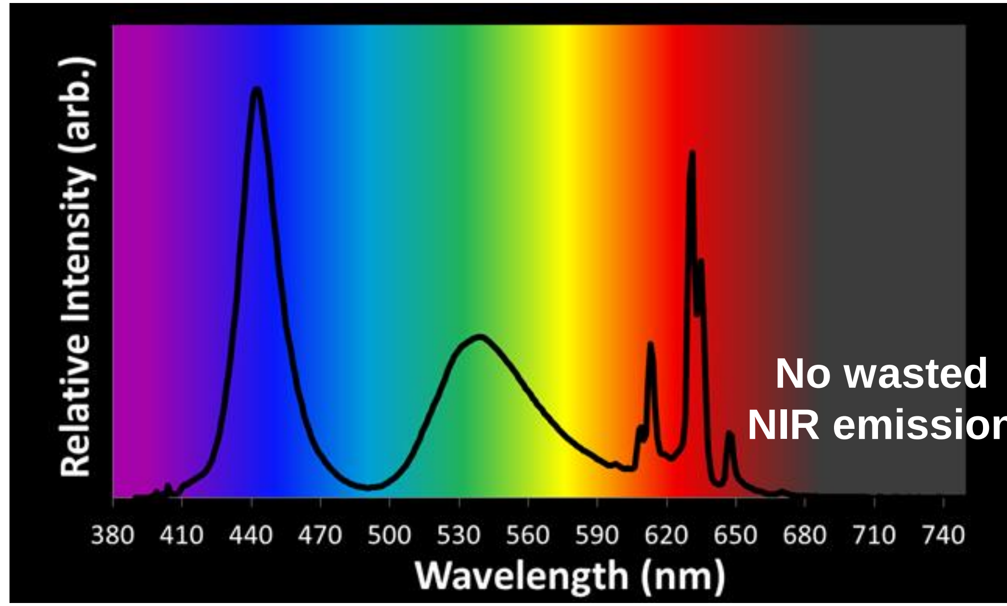
PFS can be used in typical LED packages

Major Disruption in LCD Display Phosphors
-Fueled by brightness & wider color gamut market forces

Pre 2012: Garnet:Ce^{3+} + Nitride:Eu^{2+}
FHWM >100nm FWHM > 60nm



Post 2013: oxynitride:Eu^{2+} + Fluoride:Mn^{4+}
FHWM ~55nm FWHM: 5 peaks < 2nm

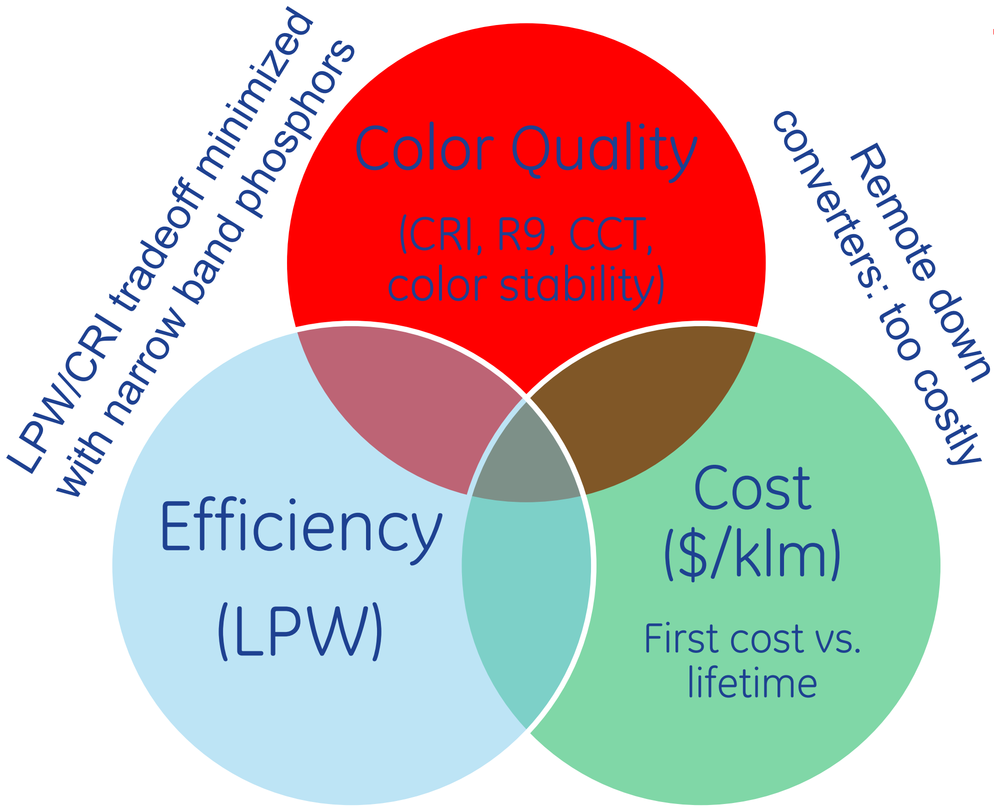


- Narrow band emitting phosphors (micron size & QDs) at correct wavelengths enable more efficient, brighter, wider color gamut displays
- GE patented Fluoride:Mn^{4+} narrow band red emitting phosphor = 19 licensees
- Estimated 30% LCD display market penetration in 2017
- U.S. Manufacturing in Cleveland, OH

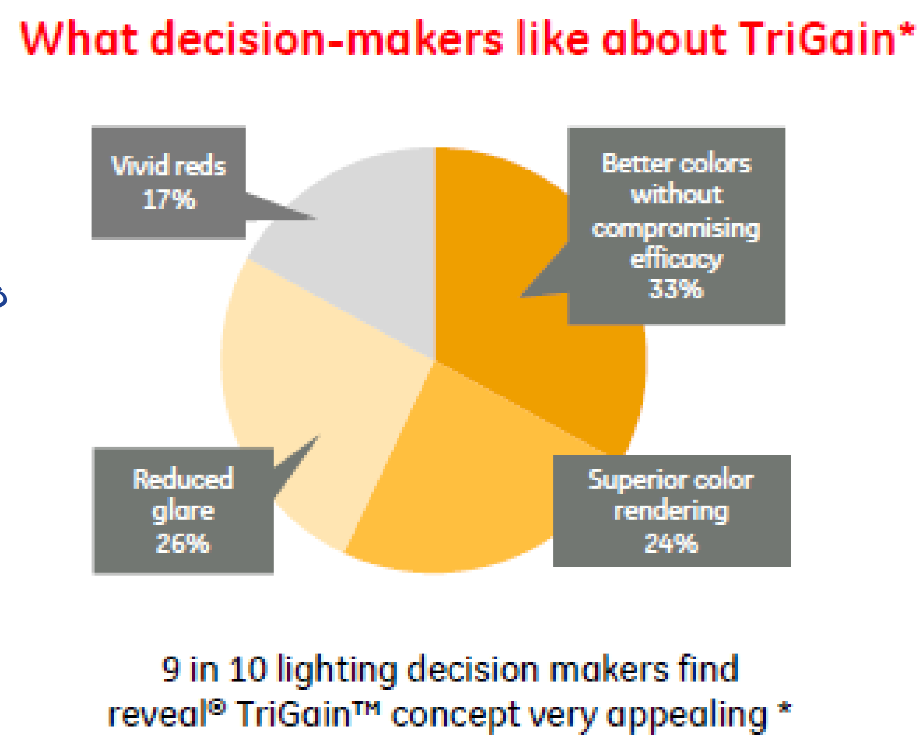
Optimization of narrow band phosphors for display may benefit SSL

DOE Goals: Efficiency First!

Higher LPW enables more light to be produced with less electrical power at lower operating temperatures = longer-lasting, quality lighting products & increased energy savings/security



Overdriving LEDS: may lower LED count but decreases LPW & product life.



Continued shift towards higher LPW mid-power packages will open the design space for downconverters = less photo/thermal stress

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GE TriGain™ Phosphor Optimization

Synthesis & Processing

Extensive Characterization

- Quantum Efficiency
- Blue light flux stability
- Temperature Stability
- Particle Size
- Photoluminescent Lifetime
- Humidity Stability: Surface chemistry
- Composition: %Mn, host
- Thermal Quenching
- Bulk Density: Agglomeration
- Particle Morphology
- Scattering

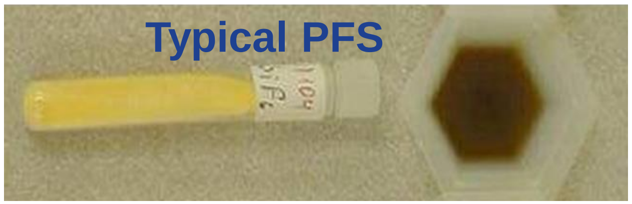
Package Performance
TriGain = high LPW

Reliability: Minimize phosphor degradation under high blue flux & high temp./humidity (HTHH)
From invention to commercialization > 3 years to optimize & pass device testing

Temperature + Humidity (HTHH) Stability

(85°C / 85% RH)

Before After 24hrs

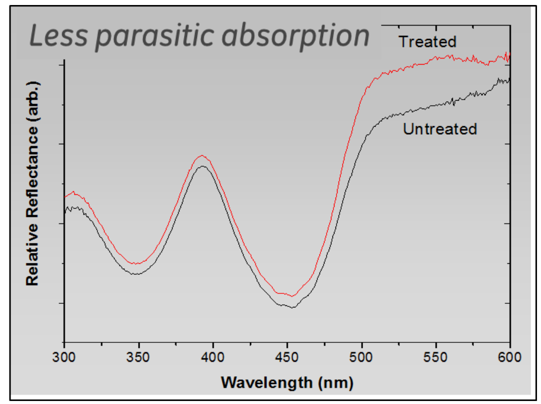


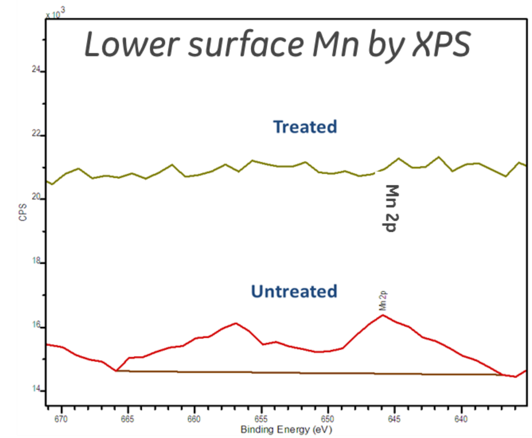
Hydrolysis of Surface Manganese

Initial K_2SiF_6:Mn particle Mn Free surface

Washing process in acidic aqueous solution improves reliability

Chemical Treatment to remove Surface Mn

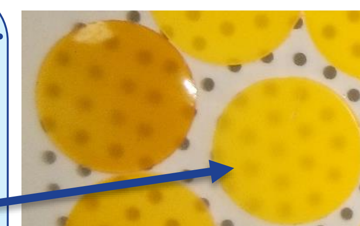




HTHH Testing: 85°C/85%RH at 150 hrs.

Sample	Initial QE/Abs	Δ(QE*ABS)
Typical PFS	95/72	-14%
TriGain™	**100/70**	**-2%**

Higher QE & less HTHH degradation



TriGain™ phosphors are moisture resistant & require no encapsulation

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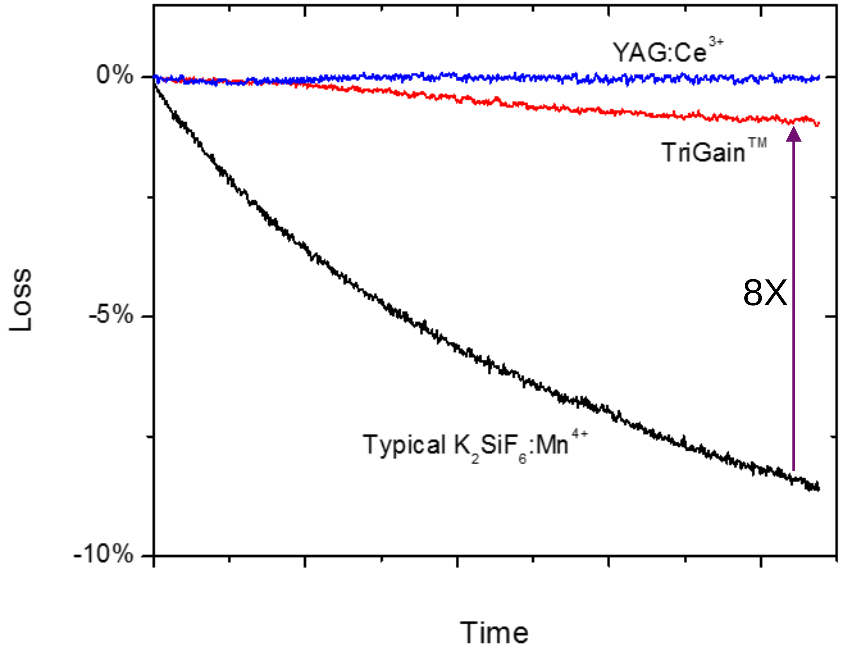
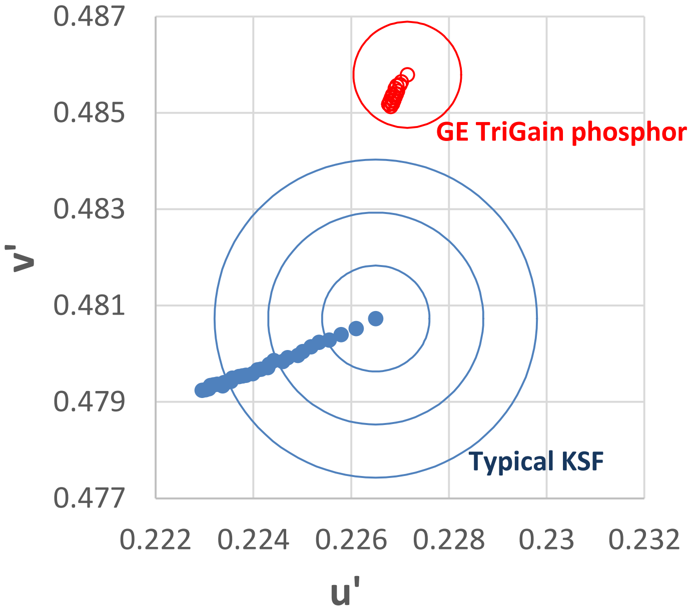
Included in US8057706, US8252613 and other global patents.

Partially supported by the U.S. DOE through contract#DE-EE0003251

GE TriGain™ Improved Reliability Under High Blue Flux

Accelerated Light damage testing





Reduced damaged under high flux

Improved color shift in LED packages (under highly stressed conditions)

TriGain™ phosphor = better reliability for display & lighting LEDs

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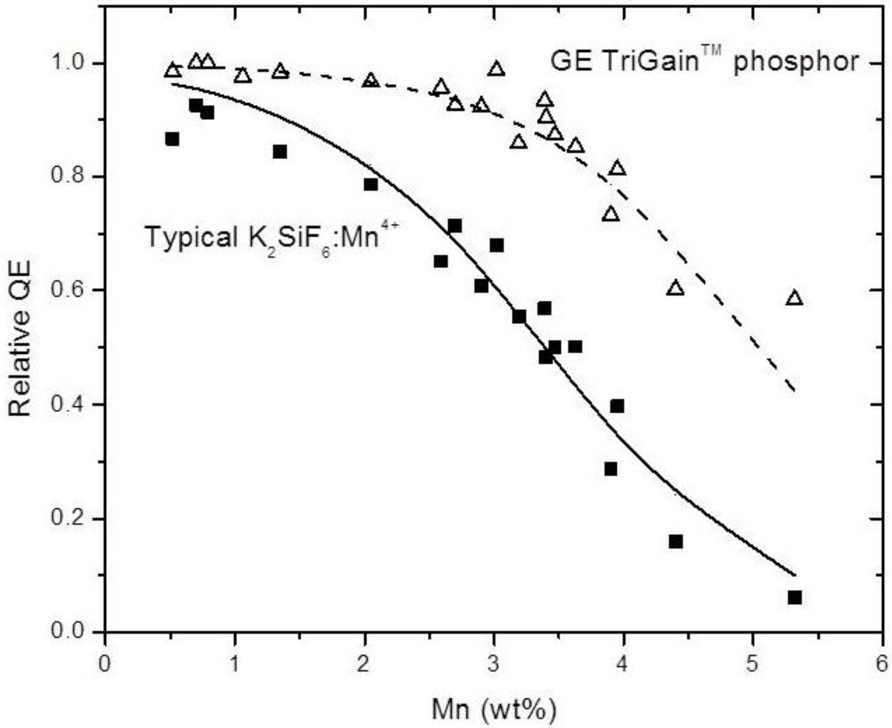
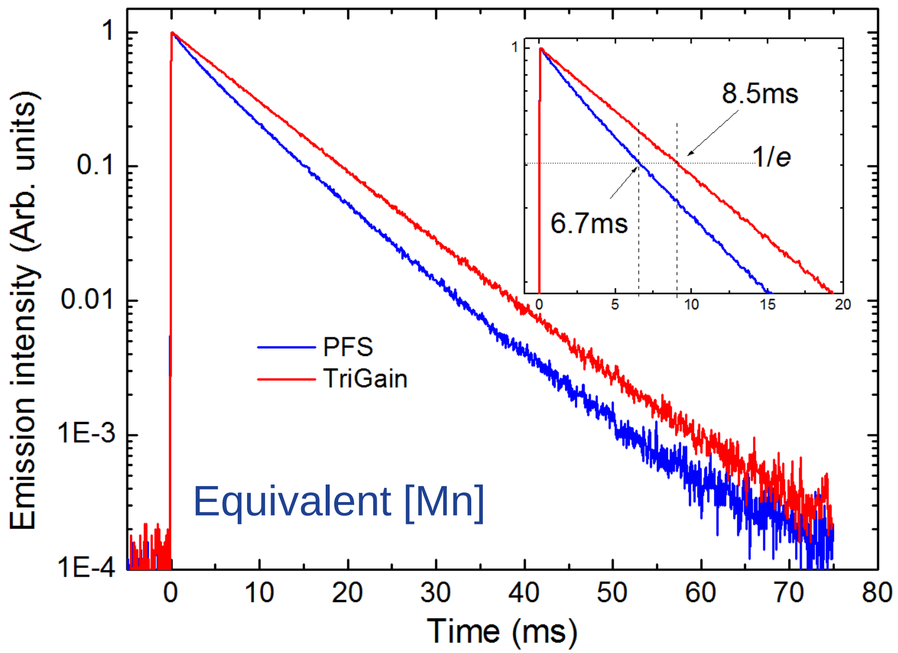
Overcoming quenching in TriGain™ phosphors

Modified synthesis/composition = less defects & higher Mn concentration#

- Energy migration & quenching models* estimate >5x defect reduction
- Methods developed to detect synthesis/composition in powder/package





Can use much less TriGain™ phosphor vs. typical KSF/PFS for same color point to enable low CCT Lighting Products

TriGain™ phosphor = higher Mn^{4+} level & lower loading/usage

#US2015/0361337A1

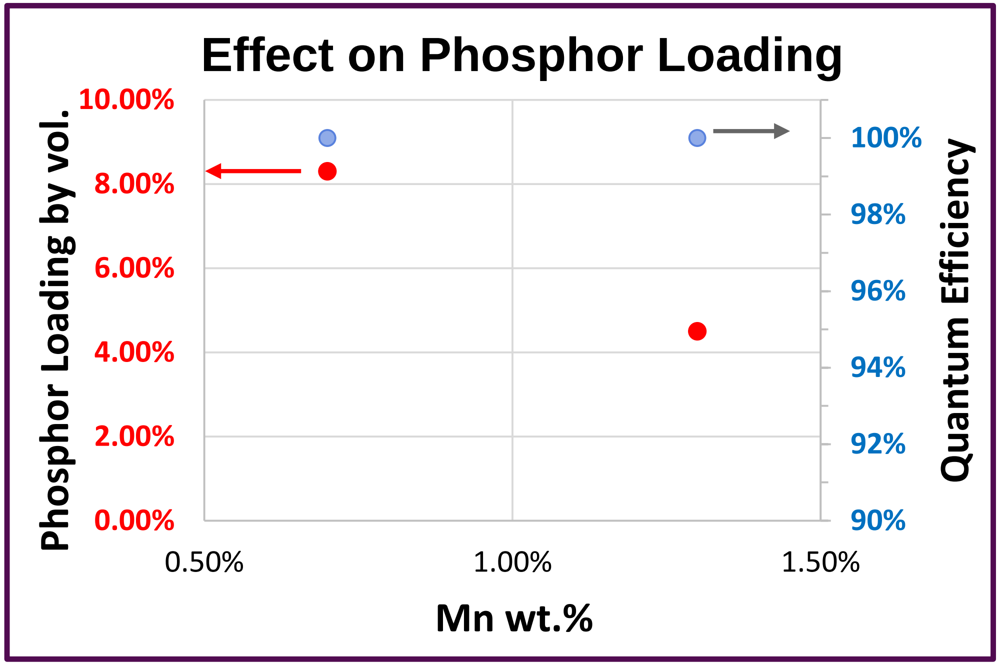
*Blumen, A. & Sibley, R. *J. Chem. Phys.* **70**, 3707-3714 (1979).

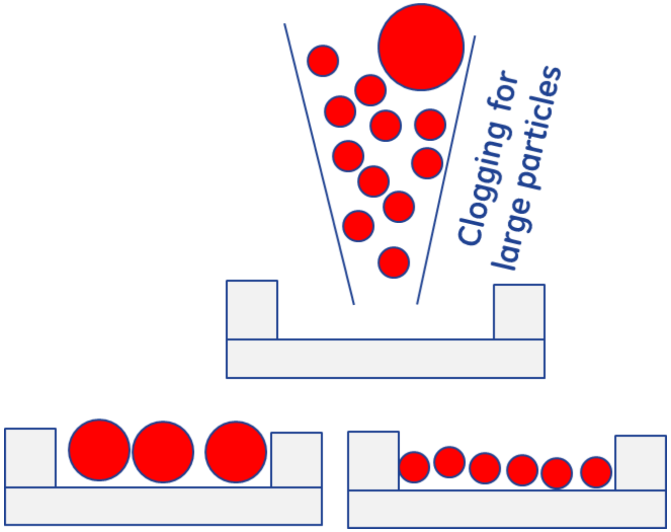
Improved & Flexible Manufacturability

TriGain™ Phosphor:

1. **Fewer defects -> Higher QE & Light Stability**
2. **Higher Mn doping -> higher absorbance**
3. **"Pop in" LED replacement = no encapsulation**

d_{50} particle size	Internal QE
40 µm	>90%
20-30 µm	>90%
<15 µm	>90%





Modifying phosphor size changes package properties

TriGain™ phosphor can be tuned for specific packaging needs

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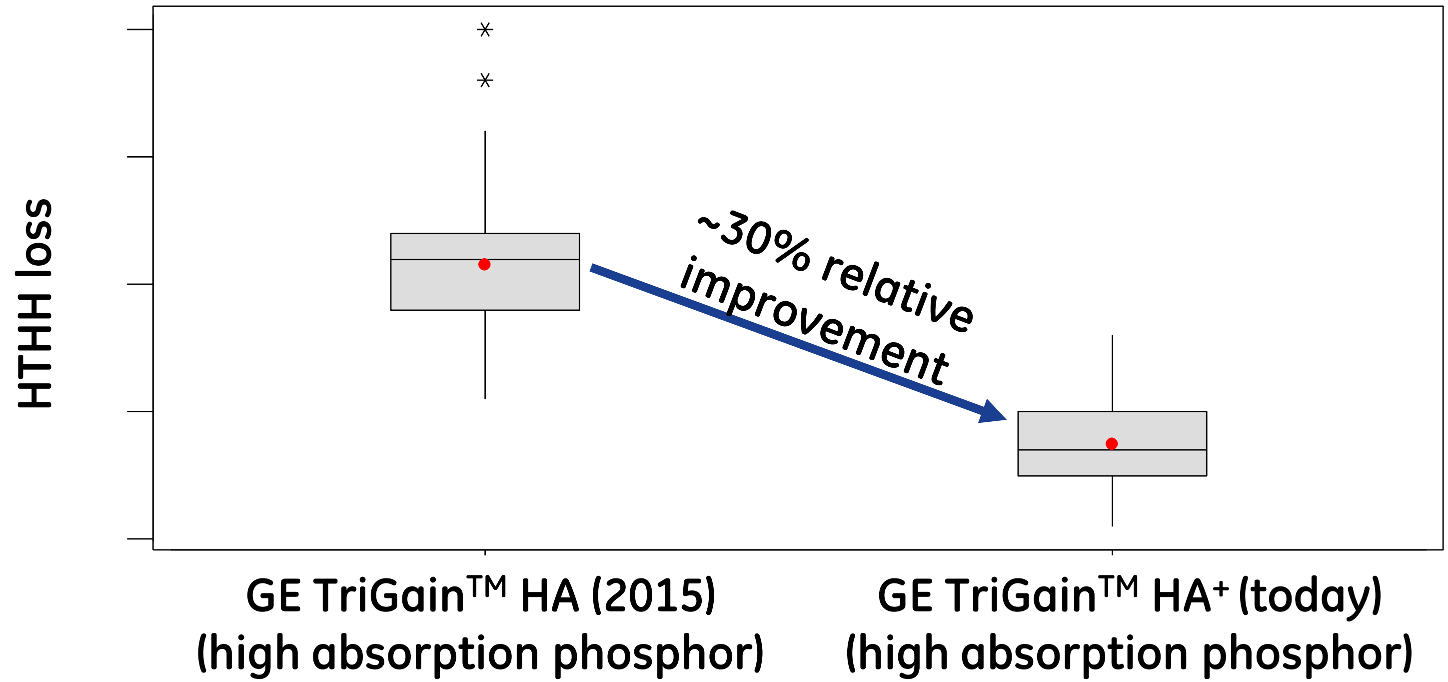
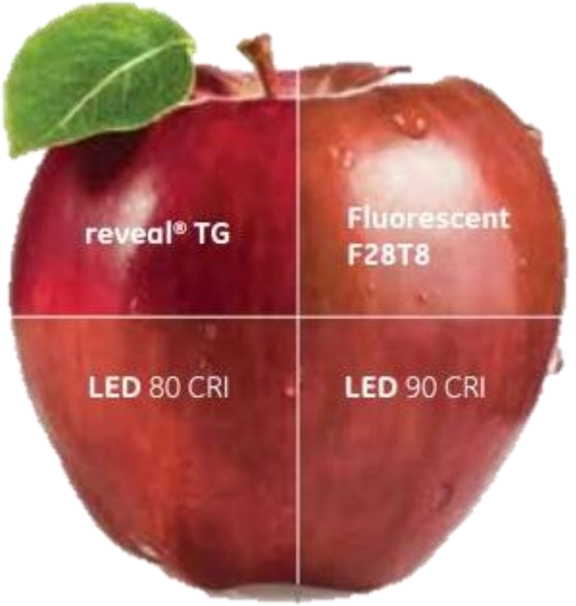
Higher reliability GE TriGain^{TM} phosphors

Process/composition modification = better phosphor reliability



Continual reliability improvements = larger design windows

GE Reveal® TriGain™ Technology for Lighting



Color without Compromise

Performance of reveal® TriGain™ technology

Fluorescent F28T8	LED	LED	reveal® TriGain™ Technology
85 CRI	80 CRI	90 CRI	90 CRI
100 LPW	160 LPW	127 LPW	168 LPW
R9 < 15	R9 < 30	R9 < 45	**R9>90**

Industry standard 3030 LED measured at the same operating conditions

32% INCREASE in LPW

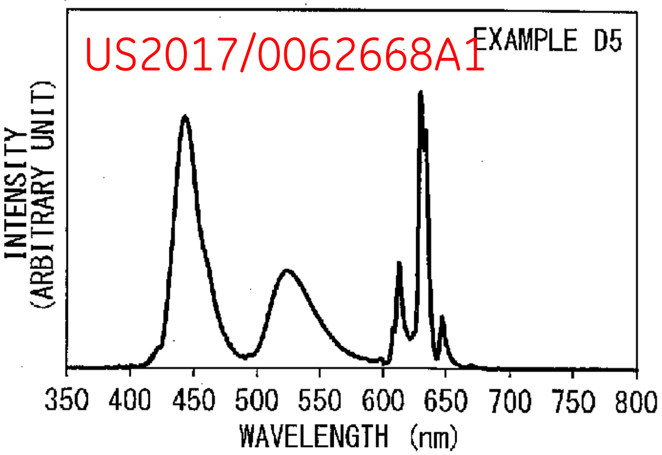
Key elements of reveal TriGain:

- GE has developed a narrow-band red phosphor that increases both CRI & R9
- Improves LED and system efficacy significantly at 90 CRI
- Best cost/efficacy from GE/Current
- Available in 20 LED Indoor product families: down lights, recessed troffers, suspended fixtures

Scoping for Narrow Green Emitting LED Phosphor Powders

Potential for display phosphors to be used for SSL?

Commercialized Today (Sharp at IDW 2016)	NTSC ratio (CIE1931)	NTSC ratio (CIE1976)	Brightness
β-sialon + CASN	86%	96%	100
β-sialon + TriGain™	96%	107%	**114**
AlON: Mn^{2+} + TriGain™	102%	111%	



Step 1: Phosphor Discovery: Blue Absorption, peak Emission, FWHM

Excitation (400/450nm)	Emission Peak (nm)	FWHM (nm)	NTSC ratio (1931) *	Rec.2020 (x,y) (%) *
+/-	558	30	63	47
+/-	522	60	96	72
+/+	530	60	99	74
+/-	530	34	102	76
-/-	530	25	107	80
+/+	520	33	108	82

Step 2: Down select/optimize the many other critical to quality requirements!

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Summary

- Less blue flux + less heat = Longer lasting LED products & expand design space for new narrow band phosphor compositions
- Continued trend towards mid-power LEDs along with improved LED efficiencies will result in less photo/thermal degradation of downconverter materials.
- Near term DOE warm white LPW goals of pc-LEDs are met with TriGain™ narrow band red emitting phosphors.
- To reach DOE goal of >240 LPW, reliable, on chip, new red and green phosphor discovery will be required.
    1. New Narrow band Green Emitters from the display industry?
    2. Hybrid solution of TriGain™ + Cd free green QDs to minimize green emission reabsorption if QDs can meet on chip reliability requirements.
    3. Basic Research Funding on understanding core shell interactions and how to increase Stokes shift of reliable Cd free QDs.

Recommendations/Comments

Table 5 Downconverters

Downconverters			
Description: Explore new, high-efficiency wavelength conversion materials for the purposes of creating warm white LEDs, with a particular emphasis on improving spectral efficiency with high color quality and improved thermal stability and longevity to enable use of materials in high-brightness LED packages. Downconverters that are non-toxic and do not contain scarce materials are encouraged.			
Metrics	**2016 Status**	**Interim 2020 Targets**	**2025 Targets**
1. Quantum yield (QY) at 25°C across the visible spectrum	98% (Green) 90% (Red)	99% (Green) 95% (Red)	99% (Green) 95% (Red)
2. Thermal stability – Relative QY at 150°C vs. 25°C	90%	95%	96%
3. Spectral FWHM	100 nm (Red/Green)	30 nm (Red) 70 nm (Green)	30 nm (across visible spectrum)
4. Color shift over time (when integrated into pc-LED)	$\Delta u'v' < 0.007$ at 6,000 hours	$\Delta u'v' < 0.002$ over life	$\Delta u'v' < 0.002$ over life
5. Flux density saturation – Relative QY at 1 W/mm^2 (optical flux) vs. peak QY	-	95%	96%

1. QY should be measured in a cured part, not a suspension QY (QDs). Understand defect chemistry
2. Thermal stability should mean both thermal quenching(reversible & instantaneous) & thermally activated damage (hysteresis, occurs over time, usually accelerated with flux & moisture).
3. Red FWHM 2025 Target already commercialized with TriGain for mid power packages. Computational modeling may offer additional insight into new material systems. Continued incentives/certifications around high LPW products may expand design space for phosphors. Hybrid concepts: on chip TriGain red + Cd free green QDs = no reabsorption of green emission.
4. Shift towards mid power packages, phosphor coatings, focus on reliability
5. This is only necessary for HPLEDs. Lower phosphor activator concentrations, ceramics & adhesives, packaging interactions, faster PL decay time narrow band red phosphors.