Department of Energy
Washington, DC 20585

ARPA-E Rare Earth and Critical Materials Workshop
Breakout Session: Phosphors

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Rare Earth Needs for Phosphors

ARPA-E Workshop on Rare Earth & Critical Materials

Phosphor Breakout

Steven Duclos
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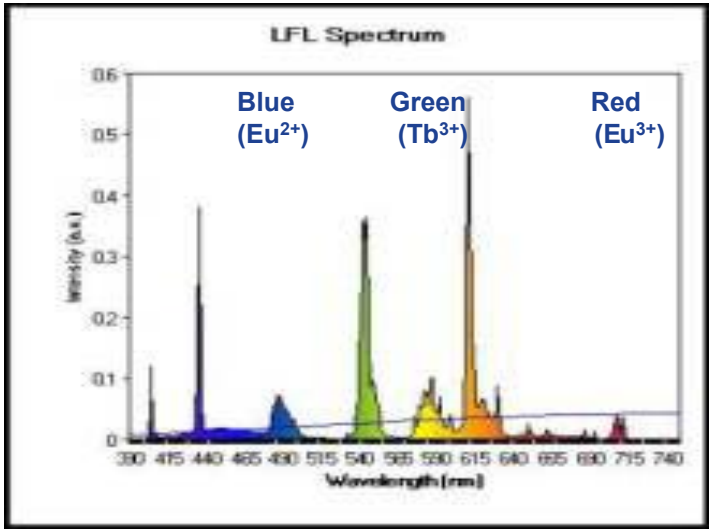
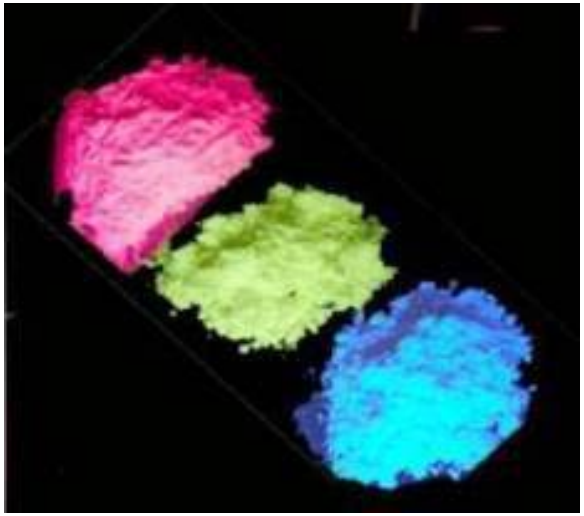
Niskayuna, NY

December 6, 2010

imagination at work

Rare Earth Based Phosphors in Fluorescent Lamps





- Efficiency
- Color
- Stability
- Cost
- Manufacturability
- Environmental

- **In fluorescent lamps, white light is generated by combining the emission of three phosphors : Blue (450 nm)+Green (545 nm)+Red (610 nm)**

Phosphor	Code	Color	Emission Wavelength	Nature	Rare Earth(s)
$BaMgAl_{10}O_{19}:Eu^{2+}$	BAM	Blue	450 nm	Broad band	Eu
$LaPO_4:Ce^{3+}, Tb^{3+}$	LAP	Green	545 nm	Sharp line	La,Ce,Tb
$Y_2O_3:Eu^{3+}$	YEO	Red	610 nm	Sharp line	Y, Eu

Rare Earths in Fluorescent Lamps: Y, Eu, La, Ce and Tb

LED lighting & phosphor usage

Potential market for LED lighting

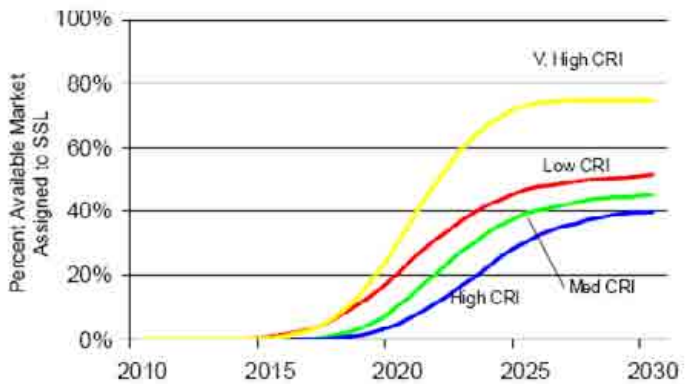
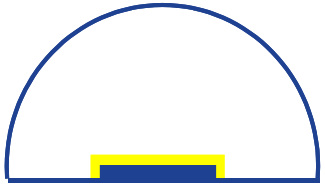


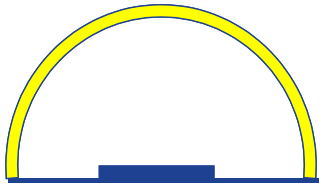
Figure 7-1. Commercial Sector Lamps Market Purchasing LED

~20% of general lighting market using LEDs with phosphors by 2020

Phosphor usage



Phosphor coated on LED chip



LED package w/ "Remote" phosphor

Current LEDs >100x reduced phosphor usage/lumen

Future phosphor use depends upon lamp form factor

Current LED phosphors

Yellow-green

$(Y,Gd,Lu,Tb)_3(Al,Ga)_5O_{12}:Ce^{3+}$ (1-5%)

$(Ba,Sr,Ca)_2SiO_4:Eu^{2+}$ (1-5%)

$Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ (1-5%)

$(Sr,Ca)_3(Al,Si)O_4(F,O):Ce^{3+}$ (0.5-2%)

Yellow-orange

$(Ba,Sr,Ca)_2Si_5N_8:Eu^{2+}$ (1-10%)

$(Li,Ca,Sr,Y)a\text{-}SiAlON:Eu^{2+}$ (1-10%)

Red

$(Ca,Sr)AlSiN_3:Eu^{2+}$ (1-5%)

$K_2(Si,Ti)F_6:Mn^{4+}$

Mg-fluorogermanate:Mn^{4+}

imagination at work

Market projections from "Energy savings potential of solid-state lighting in general illumination applications from 2010 to 2030," prepared by Navigant Consulting for DOE, 2/1010

SMART LIGHTING ENGINEERING RESEARCH CENTER

Lighting Innovation for a Smarter Tomorrow

High Efficiency Phosphors with Reduced Rare Earth Content

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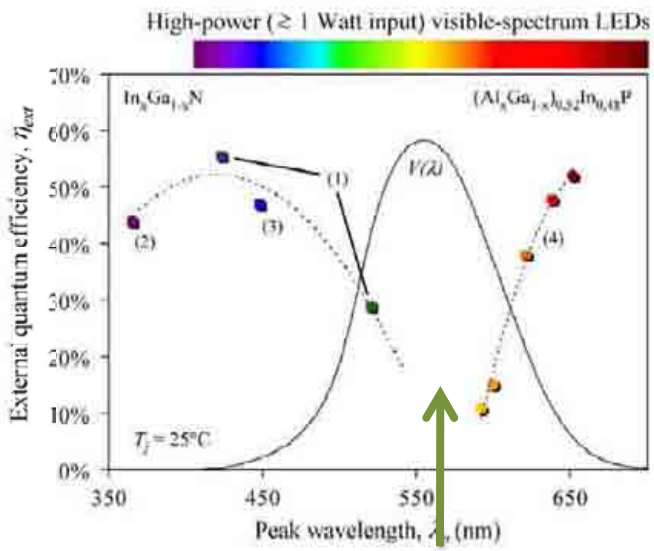
Outline

- Phosphor Requirements for Solid State Lighting
- Advanced Processes for Phosphor Synthesis*
- Rare earth reduction in Phosphors*
- Smart Lighting Systems

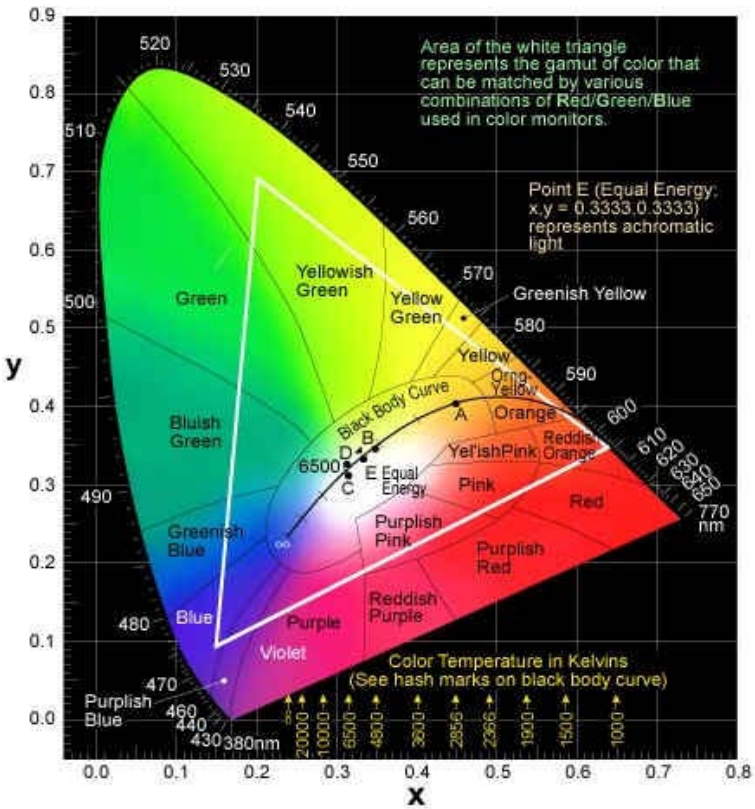
*Phosphor Safari 2010 (Nov 9-11th, Suwon, Korea)

Our Phosphor Development Motivations

- Bridge the *green gap*
- Rapid (and cost effective) development of high efficiency *illumination grade* LEDs with any primary color across the visible light spectrum
  - Leverage the high efficiency blue LED platform technology (for excitation source)
- *Full spectrum* white light sources



Green Gap



Rich History of Phosphors

- Enabled both the energy efficient light bulbs and display back lighting

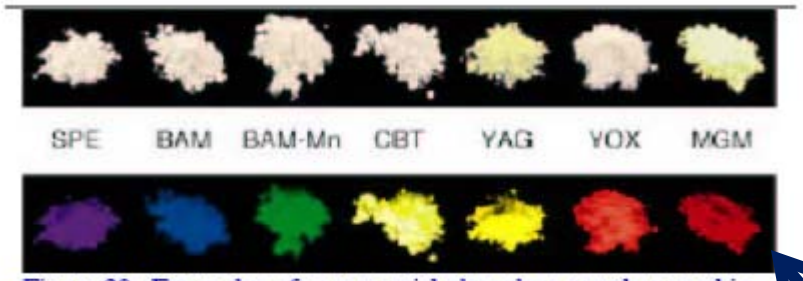


Figure 20. Examples of commercial phosphor powders used in fluorescent lamps and displays, under white light illumination (top) and under UV (254nm) illumination (bottom). The abbreviations are:

SPE	$Sr_2P_2O_7:Eu^{2+}$
BAM	$BaMgAl_{10}O_{17}:Eu^{2+}$
BAM-Mn	$BaMgAl_{10}O_{17}:Eu^{2+}, Mn^{2+}$
CBT	$(Ce^{3+}, Gd^{3+}, Tb^{3+})MgB_5O_{10}$
YAG	$Y_3Al_5O_{12}:Ce^{3+}$
YOX	$Y_2O_3:Eu^{3+}$
MGM	$Mg_4GeO_{5.5}F:Mn^{2+}$

After T. Justel, H. Nikol, and C. Ronda, "Developments in the field of luminescent materials for Lighting and Displays," Angew. Chem. Int. Ed. 37 (1998) 3084-3103.

phosphors: $LaPO_4$: Tb,Ce(green), Y_2O_3: Eu(red), and $BaMgAl_{10}O_{17}$: Eu(blue).

But these are not suitable for LED based solid state light sources

Need for new blue excitable phosphors

W.M. Yen and M.J. Weber, Inorganic Phosphors: Compositions, Preparation and Optical Properties, CRC Press (2004)

S. Shionoya and W.M. Yen, Phosphor Handbook, CRC Press (1999)

Phosphors for Illumination grade LEDs

- Excitation (absorbing) wavelength: 380-480 nm
- Emission Wavelength: 500-680 nm
- Quantum efficiency > 80%
- Optical absorption coefficient > 1000 cm^{-1}
- Optically transparent to emission wavelength
- Minimize scattering
- Low degradation over 100,000 hrs
- Low variation in efficiency & absorption up to 175 - 200 ^{o}C
- Comprised of non-toxic materials
- Can be manufactured easily and at low cost
- Easy to mix with silicones
- Provides stable light output over time (at least 90% lumen maintenance over its life)

Phosphor LED Issues

- Multi-phase phosphor particles that leads to poor conversion efficiency
- Scattering of photons from the phosphor layer with randomly distributed particles with irregular shape, size and morphology
- Opacity of the phosphor particles leading to photon trapping in the layer and re-absorption, etc.

- *Need for synthesis process development that could result in optically clear (scattering free) phosphors*
  - Flux (solution) growth of single phase crystals
  - Melt crystal growth
    - *Developed in our group*
    - Recently also started in Japan for combinatorial chemistry to identify high quantum efficiency phosphor compositions*
    - Mitsubishi Chemical alloy synthesis process*

*Phosphor Safari 2010

Rare Earth Metals for Lighting and Display

Devices		
Fluorescent lamp	Electrode	W
	Phosphor	Tb, Eu, Ce, Y , La, Mn
LED lighting device	LED	Ga
	Phosphor	Eu, Ce, Y
Liquid Crystal	Electrode	In
	Back light	Same as LED or fluorescent lamp
Plasma Display	Sealing glass	Bi
	Electrode	In
	Phosphor	Eu, Y, Tb, Mn

Primary Concerns with Eu and Tb Supply

YAG Family

- Yttrium Aluminum Garnet family: $(Y_xGd_{1-x})_3(Al_yGa_{1-y})_5O_{12}$: Ce^{3+}, Pr^{3+} with $0 < x < 1$
- Most commonly used composition (for white LEDs): $Y_3Al_5O_{12}$: Ce^{3+}
  - Excitation peaks ~ 470 nm, Broad emission with peak ~ 550 nm
- Emission peak shifts (numerous combinations):
  - 550 nm to 585 nm by replacing Y with Gd
  - 550 nm to 510 nm by replacing Y with Lu
  - 550 nm to 505 nm by replacing Al with Ga
- Sharp emission peak around 620 nm (red) by adding Pr^{3+}
- Typical quantum efficiency: 70-80%
- Luminous Efficacy:
  - Highest with 470 nm excitation
  - Maximum for synthesis temperature: 1400-1500 ^oC
  - Decreases for increasing Ce (studied for 0.1 - 5 mol% range)
  - Significant drop with Pr^{3+} doping, Gd and Ga replacements
  - Temperature effects: 2.5 % drop every 10 ^oC rise up to 200 ^oC (for 5 mol% Ce)
  - *Low Ce content requires thicker layer for wavelength conversion and higher reflectance of blue photons*

Nitrides & Oxo-Nitrides

- **Metal nitrides family**: $M_xSi_yN_z:Eu^{2+}$, Ce^{3+} ; M = Mg, Ca, Sr, Ba, Ln, Y, Yb, Al, Eu
  - Excitation: 465 nm; Emission: 580-680 nm; Quantum efficiency: 80%, Superior thermal quenching property (few % up to 150 ^oC); highly promising orange-red phosphors; high chemical stability; difficult to synthesize
  - $Sr_2Si_5N_8:Eu^{2+}$ (600-680 nm); $Ba_2Si_5N_8:Eu^{2+}$ (580-680 nm) ; $Eu_2Si_5N_8$ (640 nm)
- $CaAlSiN_3:Eu^{2+}$, (Excitation: 300-600 nm, Emission: 650 nm)
- $Ca_xAl_ySi_zN_3:Ce^{3+}$, (Emission: 585 nm)
- $CaSiN_2:Ce^{3+}$ (Emission: 630 nm)

- **Metal oxo-nitrides family**: $MSi_2O_2N_2:Eu^{2+}$ where M = Ba, Sr, Ca, etc.
  - Tunable from green to red emissions; Excitation: 300-500 nm; high thermal stability, Quantum Efficiency > 90%, Extremely difficult to manufacture
- $(SrCa)_{p/2}Al_{p+q}Si_{12-p-q}O_qN_{16-q}:Eu^{2+}$ (Emission: 575 nm)
- $(Ca_xM_y)(Si,Al)_{12}(O,N)_{16}:Eu^{2+}$ where M = Eu,Tb,Yb,Er group element
- $Li_xM_yLn_zSi_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}:Eu^{2+}$ where M = Ca, Mg, Y and Ln = Eu, Dy, Er, Tb, Yb, Ce
- $SrSiO_2N_2:Eu^{2+}$ (Emission: 538 nm); β-SiAlON:Eu^{2+} (Emission: 535 nm); Ca-α-SiAlON:Eu^{2+} (Emission: 586 nm); SrSiAlON:Eu^{2+} (Emission: 525 nm)
- *Mitsubishi Chemicals (alloy synthesis process): $Ba_3Si_6O_{12}N_2$: Eu^{2+} (Green ~ 528nm); $La_3Si_6N_{11}:Ce^{3+}$ (Yellow); $CaAlSiN_3 – Si_2N_2O$: Eu^{2+} (Red)*

Silicates

- **Alkaline earth metal silicates**:
  - $(Ba_{1-x-y}Sr_xCa_y)SiO_4:Eu^{2+}$ series $Ca_3MgSi_2O_8$: Eu^{2+}, $Sr_3MgSi_2O_8$: Eu^{2+}, $Ba_3MgSi_2O_8$: Eu^{2+}, $Ba_2MgZnSi_2O_4:Eu^{2+}$, $Li_2SrSiO_4:Eu^{2+}$, A_2SiO_4: Eu^{2+}, D (where A is elements from group II (Sr, Ba,Ca,Zn,Cd,Mg) and D is elements such as F,Cl,Br,I,N,S,P)
    - Excitation: 300 – 500 nm; Emission: 505 -575 nm
    - Quantum efficiency: 90%
    - Thermal quenching beyond 100 ^oC

- $Sr_3SiO_5:Eu^{2+}$ (Excitation: 460 nm; Emission: 570 nm)

Sulfides and Selenides

- Alkaline earth metal sulfides and selenides, MS: Eu^{2+} and MSe: Eu^{2+}. Here M is elements from group IIA (Mg, Ca, Sr, Ba)
  - $Ca_{1-x}Sr_xS:Eu^{2+}$ (Excitation: 400-580 nm; Emission: 635-655 nm); Lower quantum efficiency (80%) compared to thiogallates; highly prone to moisture
  - $Ca_{1-x}Sr_xSe:Eu^{2+}$ (Excitation: 400-500 nm; Emission: 564-608 nm); Lower quantum efficiency compared to thiogallates; prone to moisture

Other Garnets

- Silicate garnet family: $ML_2QR_4O_{12}$: Ce^{3+}, Eu^{3+}
  - M is elements from the group IIA (Mg, Ca, Sr, Ba)
  - L is rare earth elements from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu
  - Q is elements from the group IVA (Si, Ge, Sn, Pb)
  - R is elements from the group IIIA (B, Al, Ga, In, Tl)
    - $Ca_3Sc_2Si_3O_{12}$: Ce (excited ~ 450 nm, broad emission with peak ~ 570 nm)
    - $BaY_2SiAl_4O_{12}$: Ce

- Vanadate garnet family: $Ca_2NaMg_2V_3O_{12}$: Eu^{3+}
  - Better with UV-LED excitation, white light with high CRI
  - Thermal quenching above 100 ^oC

Mixed Oxide Families

- $Y_{2-x-y}Eu_xBi_yO_3$: Eu^{3+}
  - Red phosphor; Excitation 340-410 nm; Highest luminescence with x = 0.16 and y = 0.12
- $Na_2Gd_2B_2O_7$: Ce^{3+}, Tb^{3+} ,
  - Green emission; Thermal quenching above 100 ^oC
- $YCa_3M_3B_4O_{15}$: Eu^{3+} where M is elements from group IIIA (Al, Ga, In),
  - Excitation: 395 nm; Red emission: 622 nm; Better than CaS: Eu^{3+}
- $Ba_2Al_2O_4$:Eu^{2+}
  - Excitation: 380 nm; Emission: 505 nm

- **$La_{1-x}Ce_xSr_2AlO_5$:Ce^{3+}**
  - **Excitation: 450 nm; Emission ~ 556 nm; CRI: 80-85; CCT: 4000 – 5500 K (highest luminescence for x = 0.025)**

Model Material for our studies: Thiogallates

- **Metal sulfide thiogallates :** $(SrMgCaBa)(GaAlIn)_2S_4$:Eu^{2+}
  - $SrGa_2S_4$:Eu^{2+} (Excitation: 470 nm; Emission: 535 nm); Good color saturation; high efficiency > 80%; Drop in efficacy by 90% beyond 100 ^oC; proper surface coating for avoiding moisture degradation; alloying with $MgGa_2O_4$ improves efficiency
  - $CaGa_2S_4$:Eu^{2+} (Emission: 560 nm); $BaGa_2S_4$:Eu^{2+} (Emission: 540 nm)
- **Metal sulfo-selenide thiogallates:** $MA_2(S_xSe_y)_4$:B; $MA_4(S_xSe_y)_7$:B; $M_2A_4(S_xSe_y)_7$:B; (M = Be,Mg,Ca,Sr,Ba,Zn; A = Al,Ga,In,Y,La,Gd; B = Eu,Ce,Cu, Tb,Cl,Br,F,I,Mg,Pr,K,Na,Mn.
  - $SrGa_2Se_4$:Eu^{2+} (Excitation: 380-475 nm; Emission: 560 nm); Good color saturation; high efficiency > 80%; Drop in efficacy beyond 100 ^oC; proper surface coating necessary for moisture degradation

Phosphor Powder Synthesis

- Emission wavelength tuned by chemical composition and dopant species (most common dopants: Eu and Ce)
- Most common phosphor synthesis process: high temperature solid state reaction
  - Mix ingredients, react, grind, anneal, chemical treatments, surface coating
- Conversion efficiency depends on:
  - Crystalline perfection & Surface Characteristics of phosphor particles
  - Dopant Concentration
  - Size, size distribution and morphology of particles
  - Refractive index of the matrix material
- Methods to improve phosphor conversion efficiency
  - Synthesis temperature, time, ambient, gas pressure
  - Post synthesis chemical treatments
  - Post synthesis annealing

Crystal Growth of Thiogallates

Table I. X-ray data and properties of compounds in the system $M^{II}M_2^{III}(S, Se)_4$

Compound	Pseudo-orthorhombic cell (A) a	b	c	Body color	Melting point (°C)	Resistivity 298°K (ohm-cm)
$EuAl_2S_4$	10.193	6.060	10.374	Light yellow		
$EuGa_2S_4$	10.223	6.108	10.354	Yellow	1215	$\geqq 10^8$
*$EuIn_2S_4$	10.490	6.497	10.360	Yellow		$\geqq 10^{11}$
$EuGa_2Se_4$	10.666	6.375	10.795	Yellow-orange	1093-1114	7×10^8
*$EuIn_2Se_4$	11.104	6.704	10.879	Orange	1012	$\geqq 10^{12}$
$SrAl_2S_4$	10.227	6.065	10.429	White		
$SrGa_2S_4$	10.255	6.107	10.424	White	1215	
*$SrIn_2S_4$	10.548	6.510	10.439	Pink		
$SrGa_2Se_4$	10.711	6.385	10.864	White		7×10^4
*$SrIn_2Se_4$	10.938	6.728	11.017	Orange		7×10^7
$CaGa_2S_4$	10.026	6.06	10.053	White		$\geqq 10^{10}$
*$CaGa_2Se_4$	10.506	6.319	10.662	Pink		$\geqq 10^{10}$
*$YbAl_2S_4$	10.045	6.020	10.029	Yellow		
*$YbGa_2S_4$	10.041	6.066	10.056	Red-orange		10^5
*$YbGa_2Se_4$	10.185	6.338	10.501	Red		4×10^5
*$BaGa_2Se_4$	10.605	6.408	11.321	Light orange		$\geqq 10^{10}$
*$BaIn_2S_4$	10.840	6.556	10.885	Pink		
*$BaIn_2Se_4$	11.262	6.785	11.335	Light orange		3×10^9
	Cubic cells a in A					
$BaGa_2S_4$	12.610			White	1055	$\geqq 10^{10}$
*$BaAl_2S_4$	12.588			White		

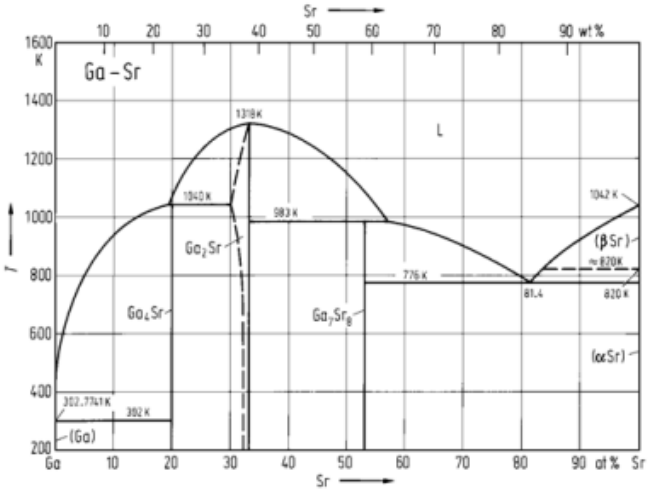
Cubic cells a in A.
* New compositions.

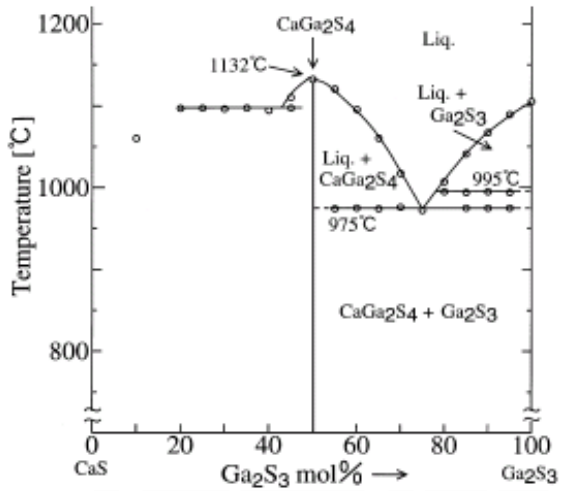
P. C. Donohue and J. E. Hanlon[1]

J. Electrochem. Soc.: SOLID-STATE SCIENCE AND TECHNOLOGY *January 1974*

Our phosphor development focus is using high temperature melt/solution crystal growth processes

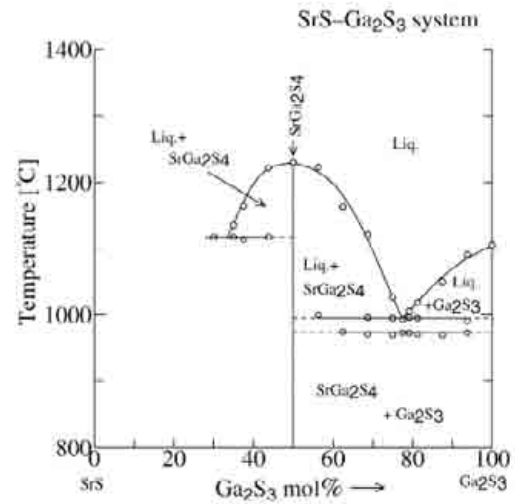
Phase Equilibria





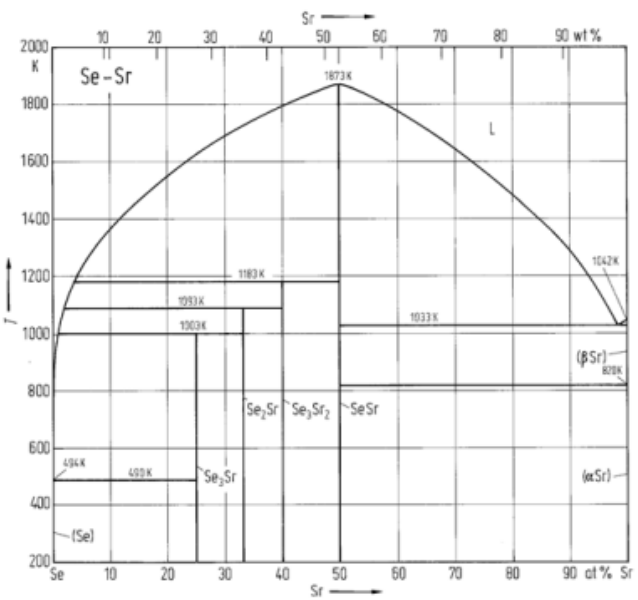
C. Komatsu-Hidaka, T. Takizawa*

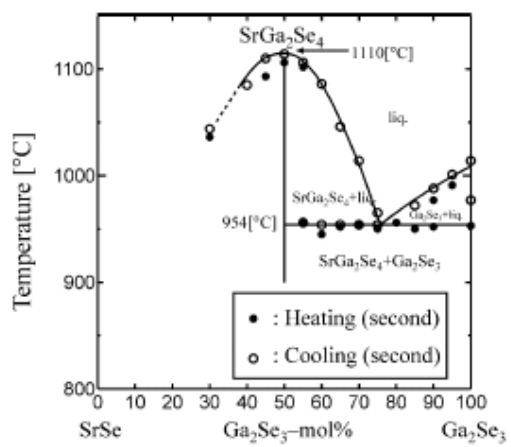
Journal of Crystal Growth 222 (2001) 574–578



C. Komatsu*, T. Takizawa

Journal of Crystal Growth 210 (2000) 677–682





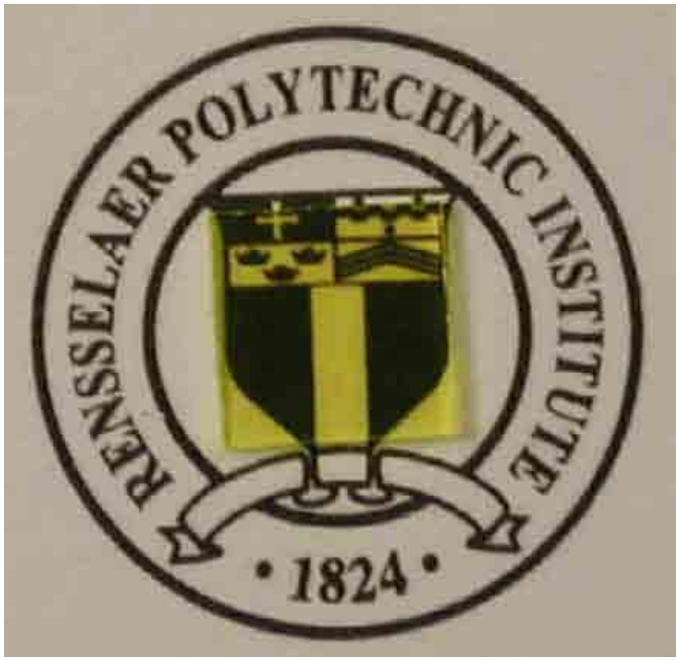
Chiharu Hidaka*, Nobuyasu Makabe, Takeo Takizawa

Journal of Physics and Chemistry of Solids 64 (2003) 1797–1800

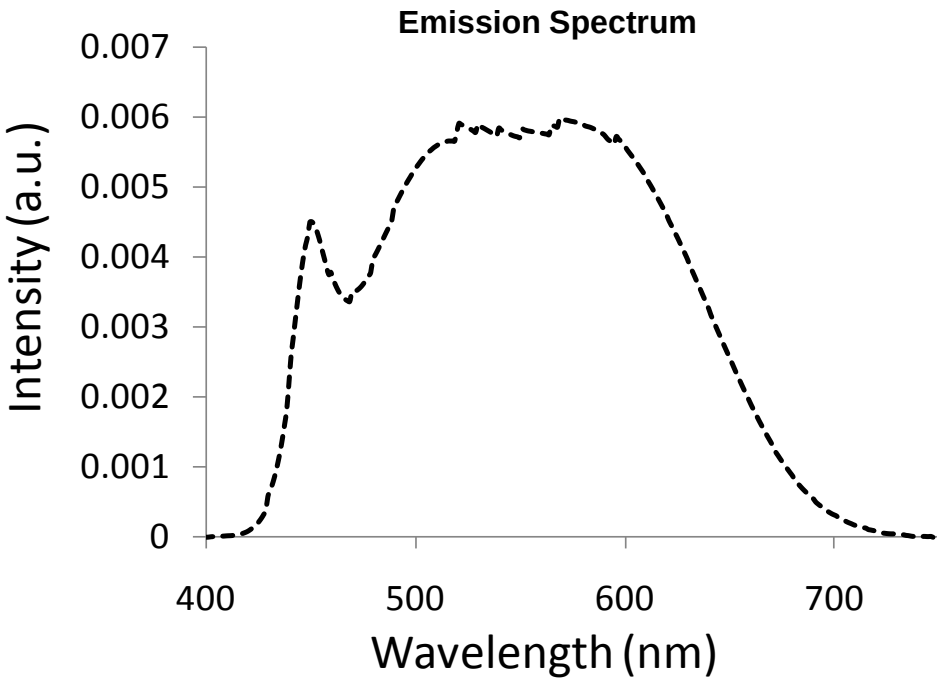
Phase diagrams crucial for crystal growth

Non-Scattering Phosphor Substrate

- Melt grown substrate with graded composition $(Sr_xCa_{1-x})(Ga_yIn_{1-y})_2S_4:Eu^{2+}$ ($0 < x < 1; 0 < y < 1$)

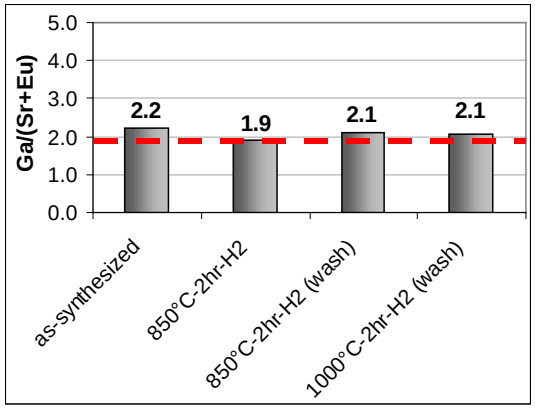


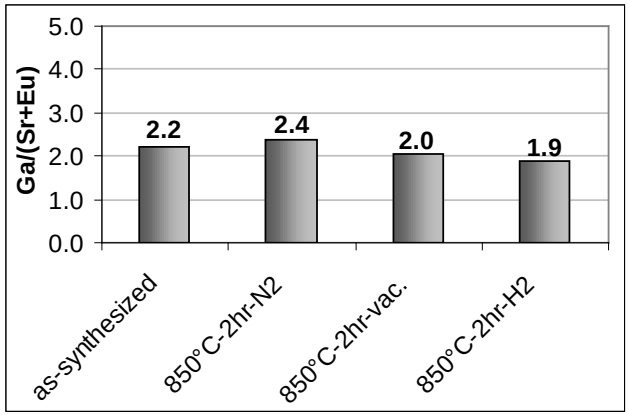
Phosphor Plate (1 sq. cm area)



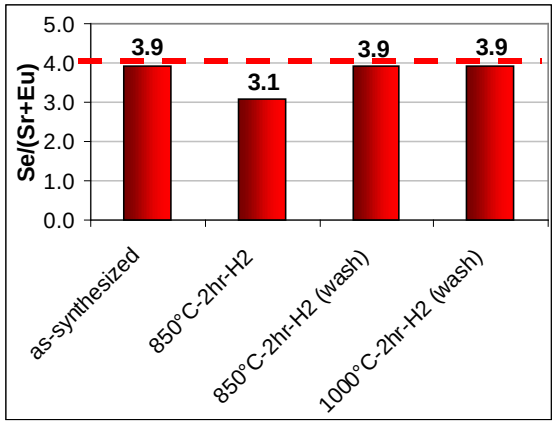
Full Spectrum White Light Source

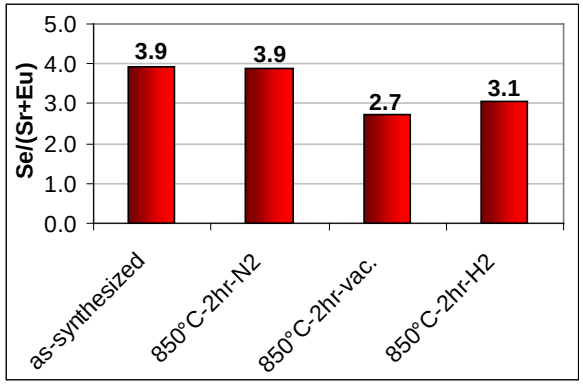
Role of Surface Composition on Luminous Efficacy



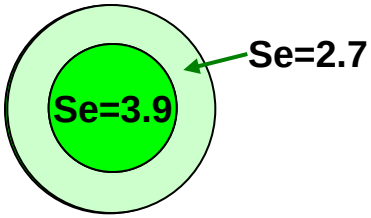


	lm/W
as-synthesized	17.0
850°C-2hr-H2	84.3
850°C-2hr-H_2 (wash)	82.7
1000°C-2hr-H_2 (wash)	43.7





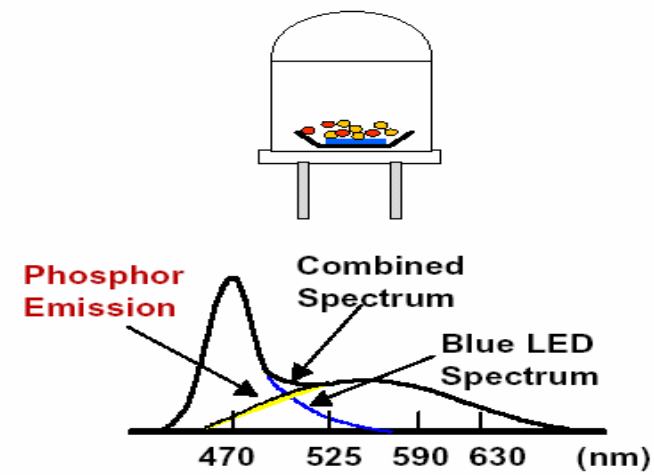
	lm/W
as-synthesized	17.0
850°C-2hr-N_2	40.1
850°C-2hr-vac.	62.8
850°C-2hr-H_2	84.3



$SrGa_2Se_4:Eu^{2+}$

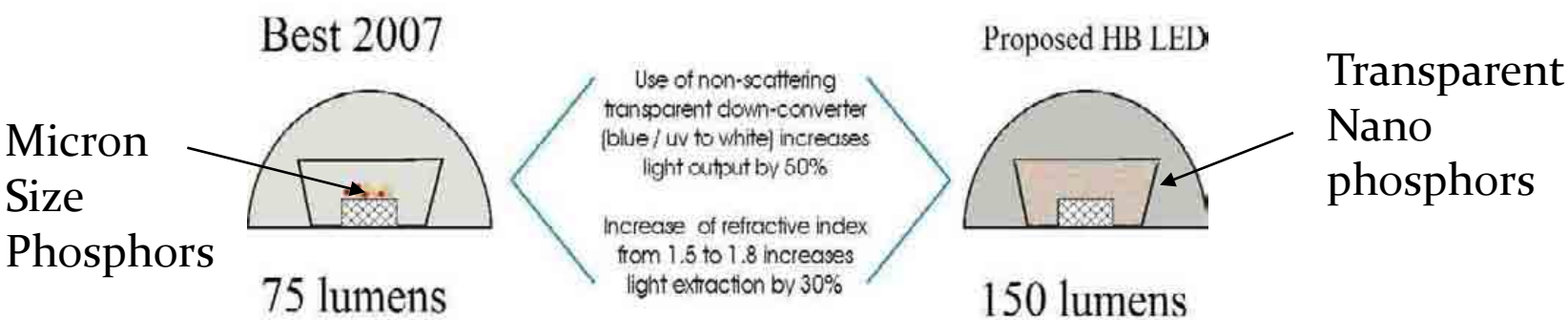
Transparent Nanophosphors

- **Replacing phosphors with non-scattering nanophosphors improves the light output by 50%**



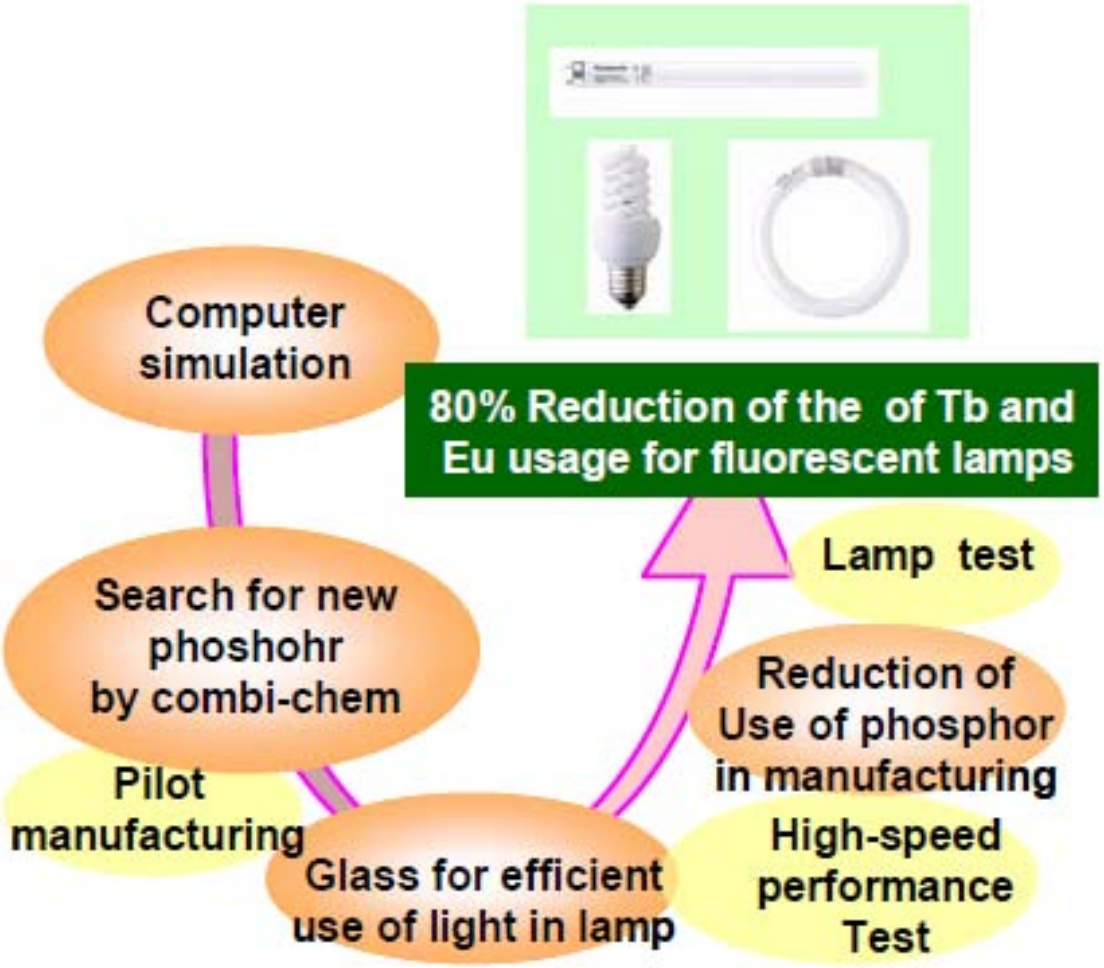
Increasing refractive index from 1.5 to 1.8 using nano-composites enhances the light output by 40%

- **High refractive nano composites**



Courtesy: Ravi Rao, Xicato Inc.

Research in Japan on Reduction of Rare Earth Phosphor Usage in Lamps



Courtesy: Dr. Tomoko Akai, AIST

Possible Ways to reduce Rare Earth Content in Phosphors

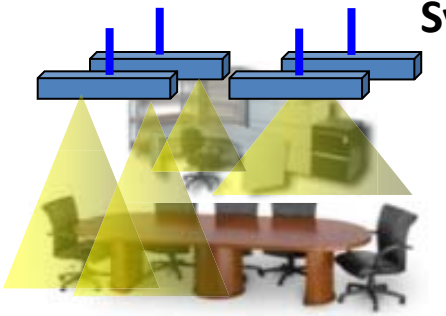
- Non-scattering Phosphor Matrix
- Transparent $Y(V,P)O_4$: Eu nano-films for plasma display panels
- Doped Quantum dots/nanoparticles (Mn doped ZnS, ZnSe, etc.)
- I-III-VI QDs ($CuInS_2/ZnS$)
- Co-doping with non rare earth metals for enhancing luminescence efficiency (Mg^{2+} doped $SrSi_2O_2N_2:Eu^{2+}$)
- New rare-earth free phosphors (blue excitable, red emission $La_2MgGeO_6:Mn^{4+}$; $SiP_2O_7:Mn^{2+}$)
- Exfoliation of Layered Compounds (e.g. GaSe)
- Multi-facetted or multiphase GaInN crystallites for white light emission

SSL: *an expanding platform*

Conventional Lighting:
Limited Controllability
Limited Efficiency

Solid-State Lighting:
Controllability
Efficiency

Smart Lighting Systems:
Adaptibility
Awareness



APPLICATIONS AND IMPACTS

HOME and OFFICE
[Adaptive Lighting]

HEALTH
[Personal Lighting]

SENSING
[Information]

COMMUNICATIONS
[Dual-Use]

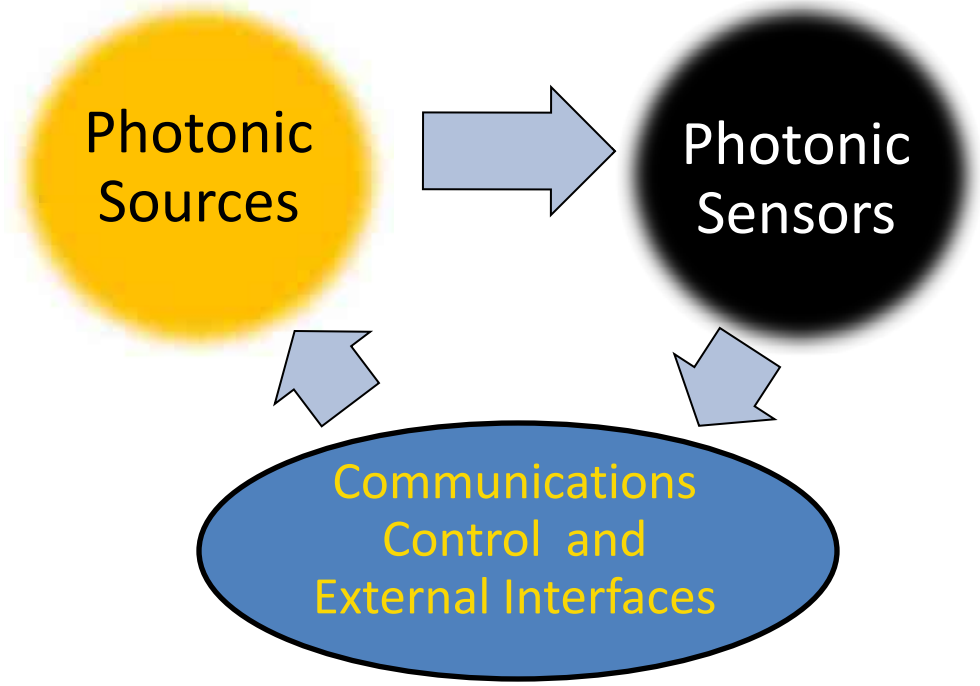
ENERGY EFFICIENCY
[Infrastructure]

Urban Agriculture

Full Spectrum Solid State Light Sources for Numerous Applications beyond Illumination and Display

Smart Lighting: Holistic View

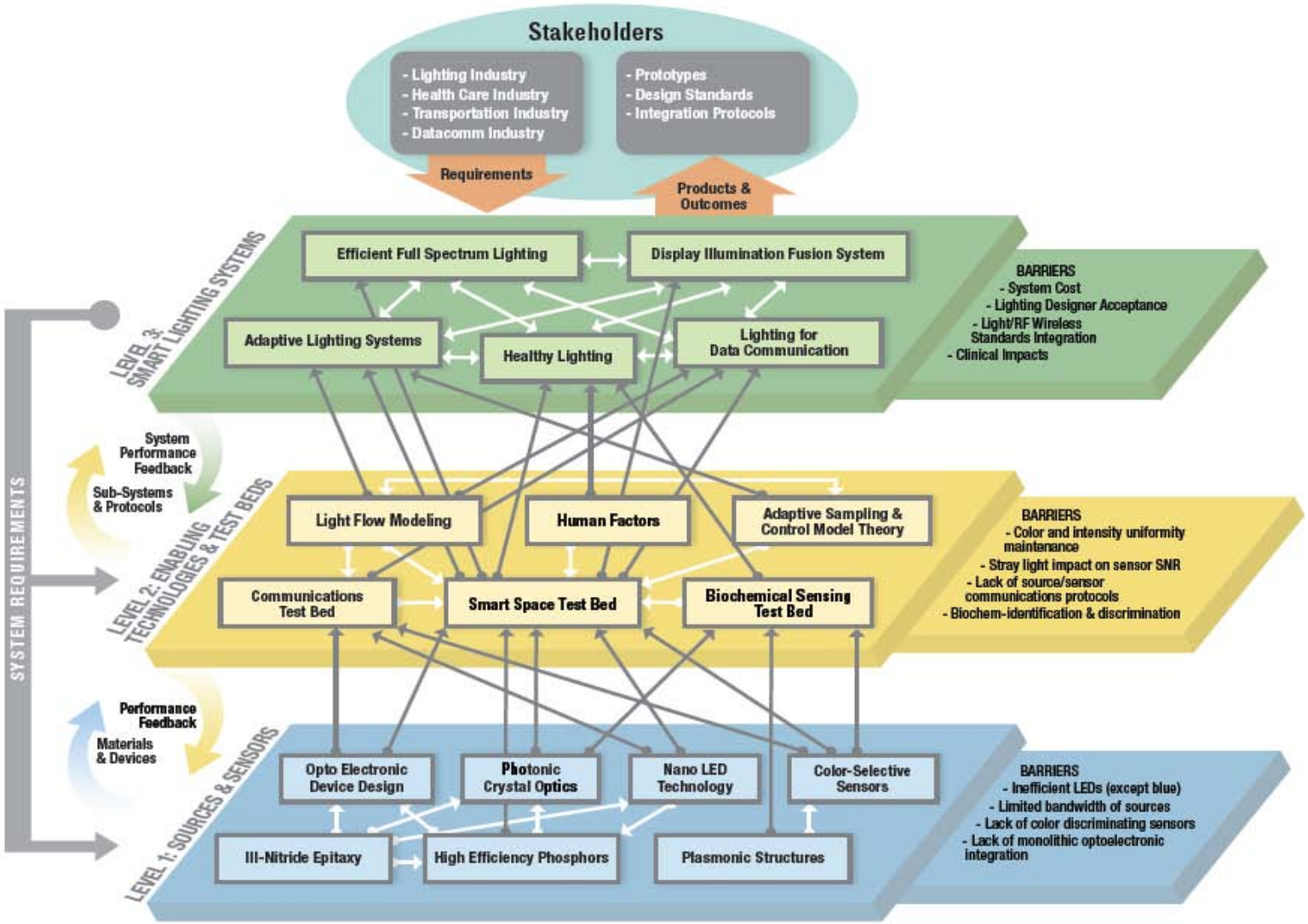
- Color Tunable
- Polarization Controlled
- Directional
- Variable Intensity (over a wide range)
- Information Coding (modulator) & Transmitter



- Color Resolution
- Polarization Sensitive
- Illuminance Range
- Information Receiver & Demodulation

- Ubiquitous
- Self Adaptive
- Dynamic
- Reconfigurable
- Secured

Smart Lighting ERC Research



Rare Earth and Critical Materials ARPA-E Workshop

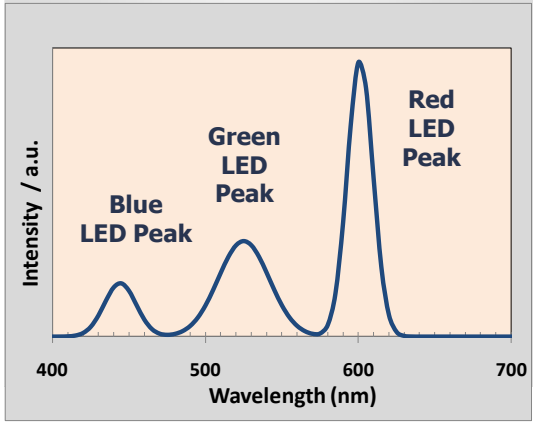
Monica Hansen

December 6, 2010

CREE®

Three Ways To Produce Warm White Light with LEDs

RGB (Red, Green, Blue)

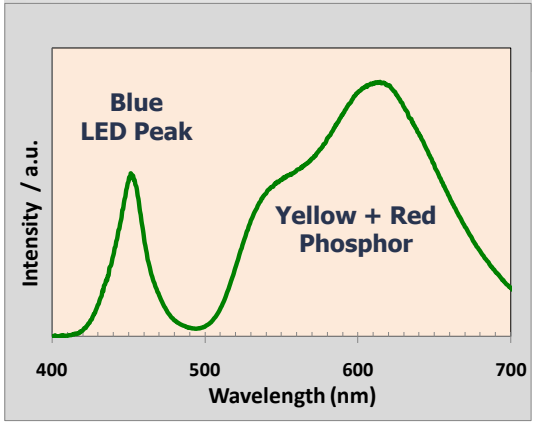


RGB LED
CRI ~ 70

Pros:
- Tunable CCT, colors
- Any color possible

Cons:
- Difficult to control
- Low CRI (<70)
- Lowest LPW efficacy (<40LPW*)

Blue + Yellow Phosphor



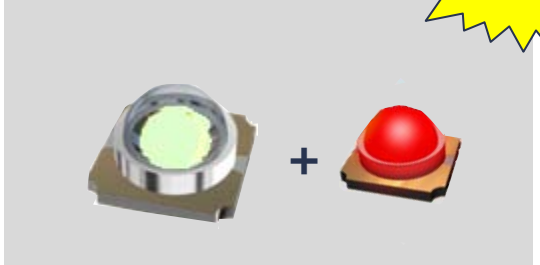
White Phosphor LED
CRI ~ 80

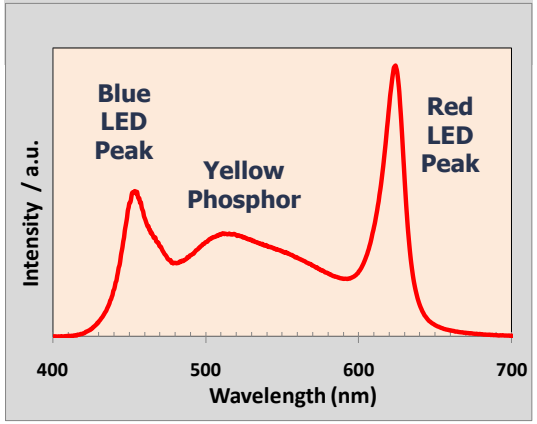
Pros:
- Single LED type
- Easy to control
- Easy secondary optics

Cons:
- OK CRI (~82)
- OK efficacy (~40– 50LPW*)

BSY + Red

NEW!!





Cree TrueWhite™
CRI = 92

Pros:
- Highest CRI (>90)
- Highest efficacy (60-100LPW*)

Cons:
- Very complicated to control (proprietary technology)

Down Converters for LED Lighting

- **Benefits of LED lighting**
  - **Low rare-earth content in phosphors (e.g. 3-5% Eu in red phosphors)**
    - **10^3 -10^4 less phosphor volume in LED system vs. fluorescent tube**
    - **Lumens / RE-oz.**

- **Requirements for LED lighting applications:**
  1. **Quantum efficiency stability up to ~ 150-200°C**
  2. **25,000 hour reliability in air (humidity exposure) and operating temperatures**
     - **Minimum efficiency degradation with time**
  3. **Cost – reduce from $10,000+/kg to $50-100/kg**

A Suggested Path Forward…

- Drive the cost down for LED phosphors to fluorescent levels
  - Very limited research in US
- Deficit: Narrow emission (< 50nm) RE-free red phosphors that are…
  - Reliable in air
  - Temperature stable
  - Withstand high excitation density
  - Low cost
- Possible solutions
  - Quantum dots?
  - OLED-Inorganic hybrids?
  - New phosphor systems?

cree.com

PORTABLE | RESIDENTIAL | OFFICE | RETAIL | ARCHITECTURAL | OUTDOOR

LED lighting: Energy efficient & planet friendly.

Cree. Leading the LED lighting revolution.

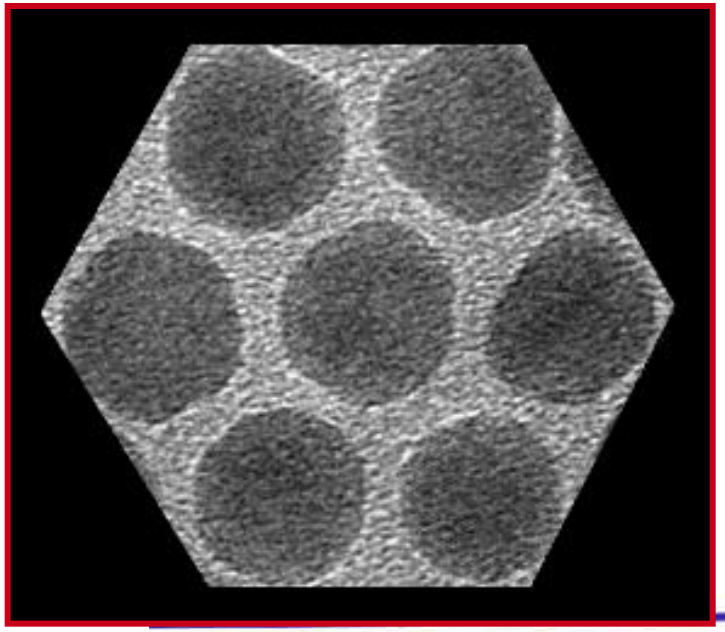
Join Cree's LED lighting revolution. We invite you to see how our high-performance, high-efficiency LEDs are lighting up the world.

CREE®

“Giant” Nanocrystal Quantum Dots: Disruptive Technology for Efficient and Robust Light-Emission

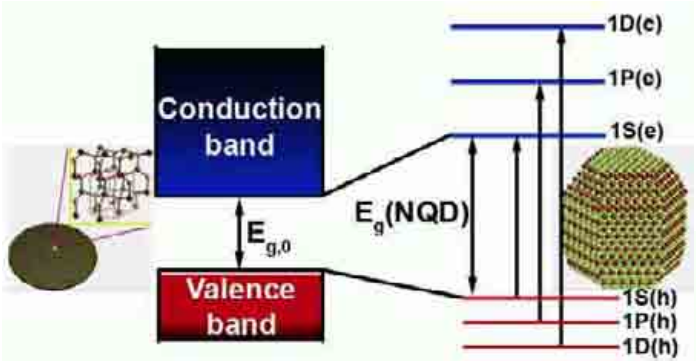
Jennifer A. Hollingsworth
Los Alamos National Laboratory
Chemistry Division and The Center for Integrated Nanotechnologies

- **DOE-BES SISGR Project (J. Hollingsworth/H. Htoon): Fundamental studies provide advances in controlling properties through physical- and electronic-structure manipulation**



Semiconductor Nanocrystal Quantum Dots (NQDs): "Nearly ideal" light emitters

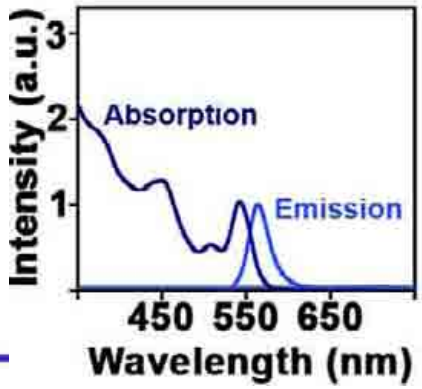
- **Quantum-confinement effects**



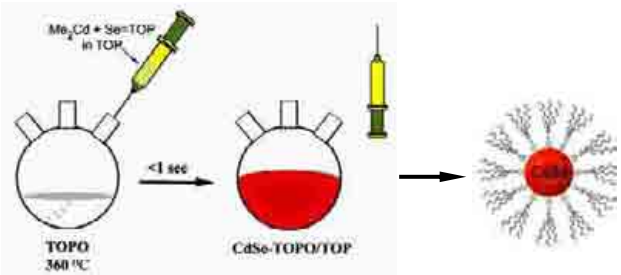
"Quantum box" model:

$$E_g(NQD) \approx E_{g,0} + \frac{\hbar^2\pi^2}{2m_{eh}R^2}$$

- Tunable bandgap = tunable colors
- Narrow bandwidth emission = pure colors
- Bright emission
- Broadband & efficient absorption
- Nanosize limits light scattering

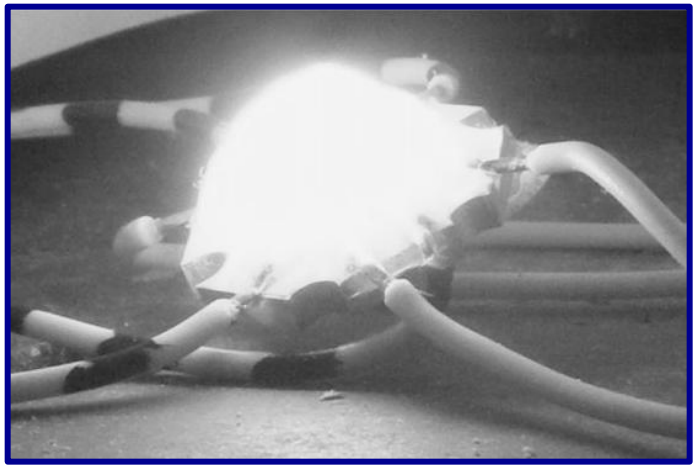


- Chemically processible/all-solution-phase options
- Flexible composition options (II-VI, III-V, IV-VI, etc.)
- Low polydispersity (+/- 4%)
- Single-crystalline



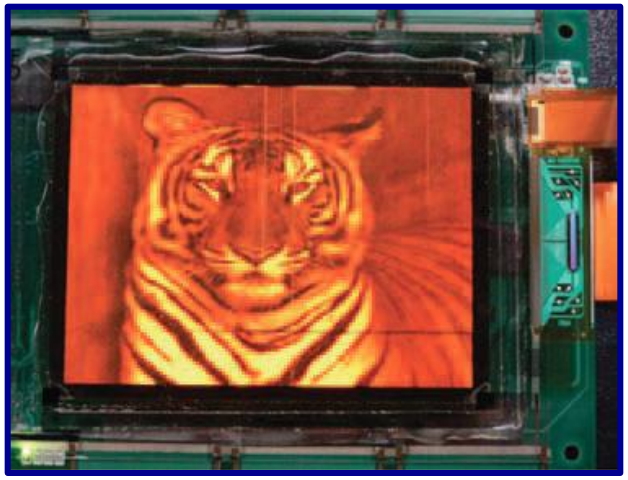
NQDs as emitters for solid-state lighting: Two applications

- **Optical excited down converters for traditional blue LEDs**



- Example from Ziegler et al. Adv. Mater

- **Charge-injected active layers for "QD-LEDs"**



- Example from Cho et al. Nature Photonics 2009 (Samsung)

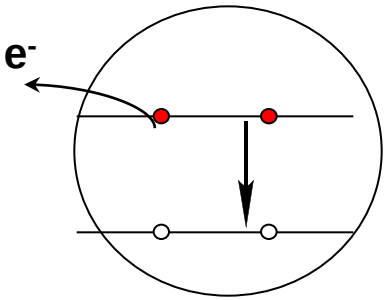
The darker side of NQDs:
"Blinking" behavior and nonradiative Auger recombination

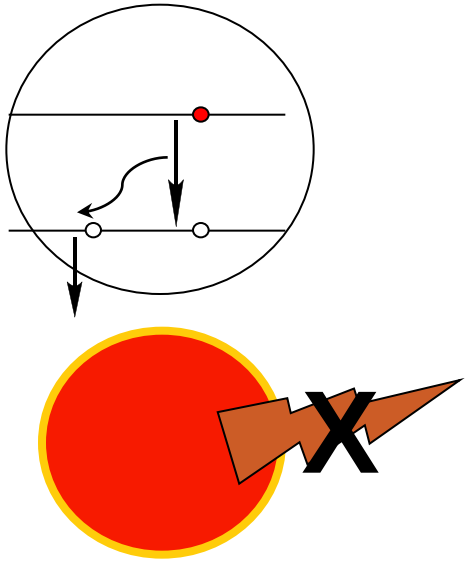
- **Quantum dot fluorescence intermittency**

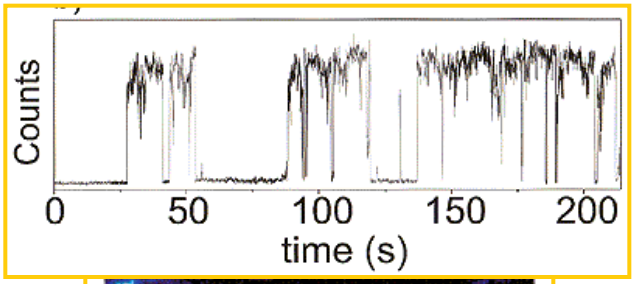
(I) Continuous illumination or chemical red-ox stress leads to charged NQD

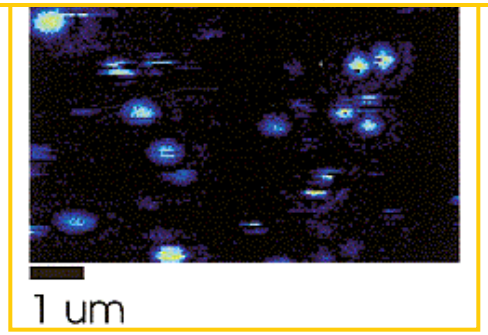
(II) Photo-excited electron-hole recombination in charged NQDs dominated by efficient Auger non-radiative decay

(III) Random cycle of charging/ discharging events leads to blinking or fluorescence intermittency







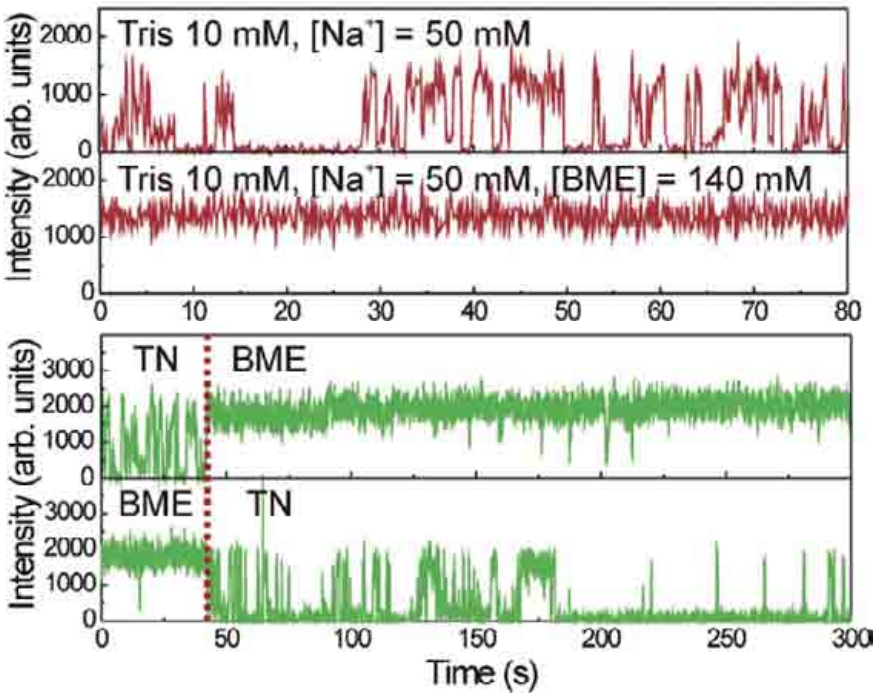


- Nirmal, Dabbousi, Bawendi, Macklin, Trautman, Harris & Brus *Nature* 1996, *383*, 802-804
- Efros *Nature Mater.* 2008, *7*, 612-613

Attempts to address the NQD blinking problem: „Antiblinking reagents'

- **Charge mediators / compensators**
  - Short-chain thiols
  - Organic conjugated ligands
  - Propyl gallate ("antioxidant")

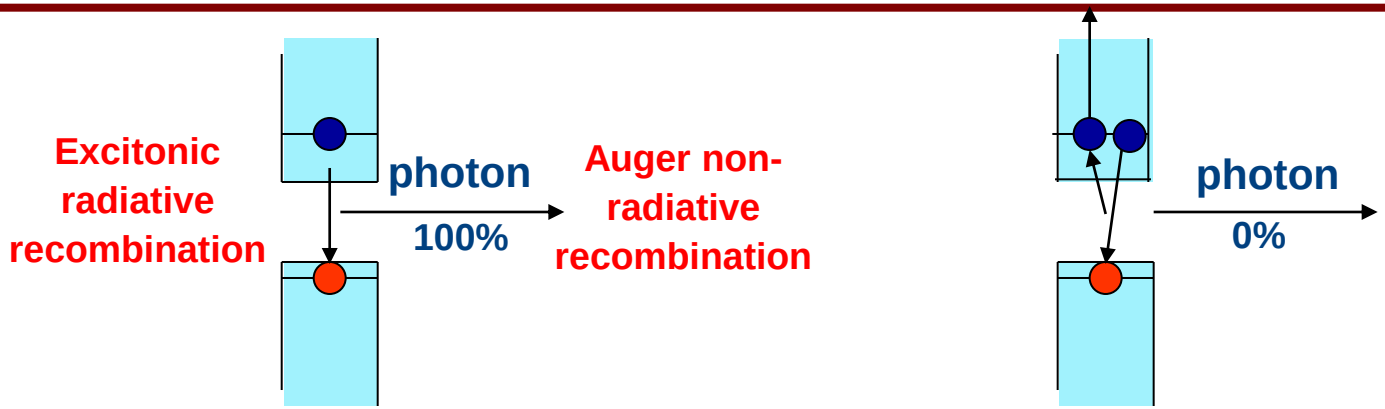
Hohng & Ha *J. Am. Chem. Soc*. 2004, *126*, 1324-1325
Hammer et al. *J. Phys. Chem. B* 2006, *110*, 14167-71
Fomenko & Nesbitt *Nano Lett.* 2008, *8*, 287-293



- **Often very challenging to reproduce**
- **Strongly dependent on approach and environmental conditions**
- **Does not address Auger nonradiative recombination!**

Auger recombination limits NQD performance potential

- **Efficient Auger recombination (sub-nanosecond timescales)**
  - Leads to non-radiative losses in LEDs (via charge build-up)
  - Limits efficiency of multiexcitonic/charged emission
  - Reduces optical gain lifetimes
  - Reduces optical gain bandwidth
  - Limits ability to reliably extract single photons

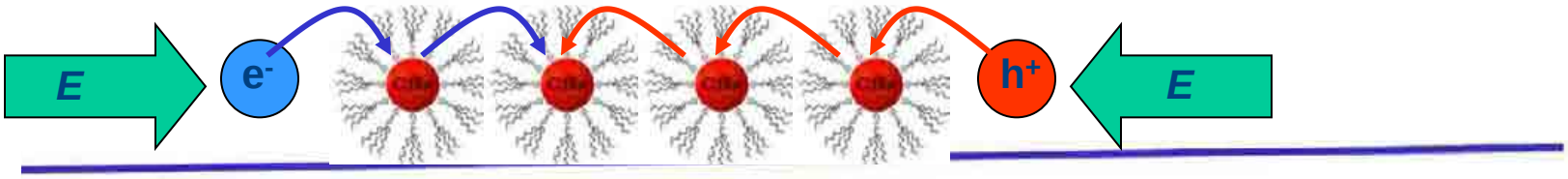


Additional barriers for the application of NQDs in solid-state light-emitting devices

- **Dependence of NQD optical properties on organic ligand surface layers**
  - Emission efficiency in the solid-state typically 10-fold less than solution phase
  - Ligands create an insulating barrier that blocks efficient injection of electrical charges into NQDs

- **"Intrinsic" NQD semiconductor properties, including large band offsets with traditional carrier transport layers**

- ***Together, imply non-optimized carrier injection and contact resistance, a tendency for charge-imbalance, and related electron-hole recombination issues***

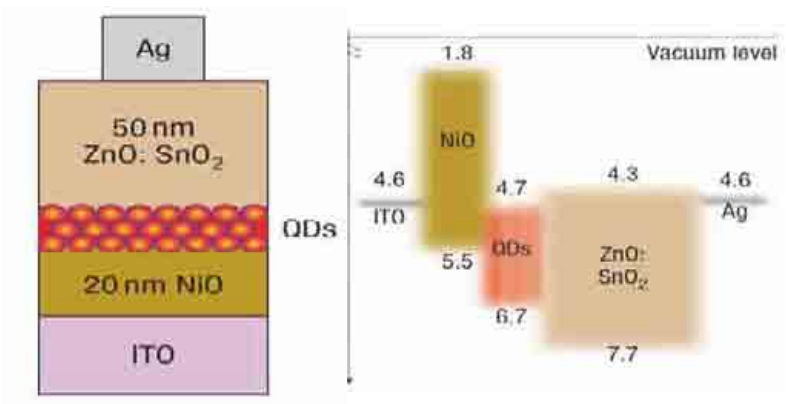


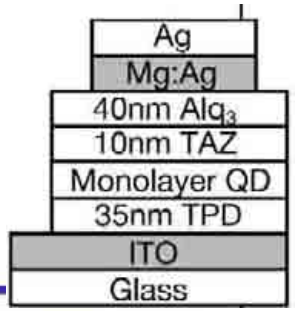
NQD-LEDs to date: Efficiencies limited

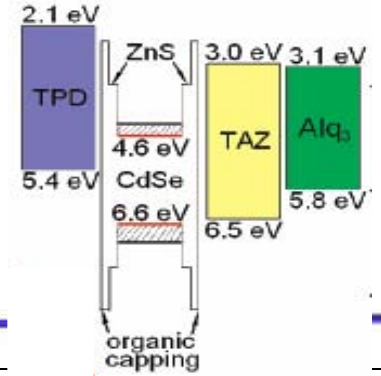
"Inorganic" and "organic-hybrid" NQD LEDs

Reference	EQE %
R. A. M. Hikmet et al J. Appl. Phys. 93, 3509 (2003) **(UCB)**	**0.001 %**
H. Muller et al., Nano Lett. 5, 1039 **(2005)** **(LANL)**	**0.01%**
J.-M Caruge et al Nat. Photon. 2, 247 **(2008)** **(MIT)**	**0.1%**

Reference	EQE %
B. O. Dabbousi et al Appl. Phys. Letts 66, 1316, **(1995)**	**0.0005%**
S. Core et al., Nature 420, 800 **(2002)** **(MIT)**	**0.6%**
S. Core et al., Adv. Funct. Mater.15, 1117 **(2005)**	**2.0%**
P. O. Anikeeva et al., Nano Lett. 7, 2196 **(2007)** **(MIT)** (red) (green) (blue)	**2.0%** **0.5%** **0.2%**
P. O. Anikeeva et al., Phys. Rev. B 78 085434 **(2008)**	**2.0%**
Cho et al. Nature Photonics 3, 341 **(2009)**	**2.5%**







NQDs as "phosphors" with or without traditional phosphors for white-light emission: Not yet optimized

- **Optically excited down converters for traditional blue LEDs**

light source	(correl.) color temperature [K]	CRI	lum. efficacy [lm W^{-1}]	lifetime [h]
Sunlight	5600	100	93	billions
tungsten light bulb	2790	100	<18	1000
fluorescent lamp	3000–5000	50-80	50–100	10000
com.(prot) white-LED	3200–6500	70 (90)	30–70 (100)	50000
White-OLED (prot.)	no data	no data	(8)	(5000)
our white-LED with InP NCs	3200–6500	86	10–20	no data

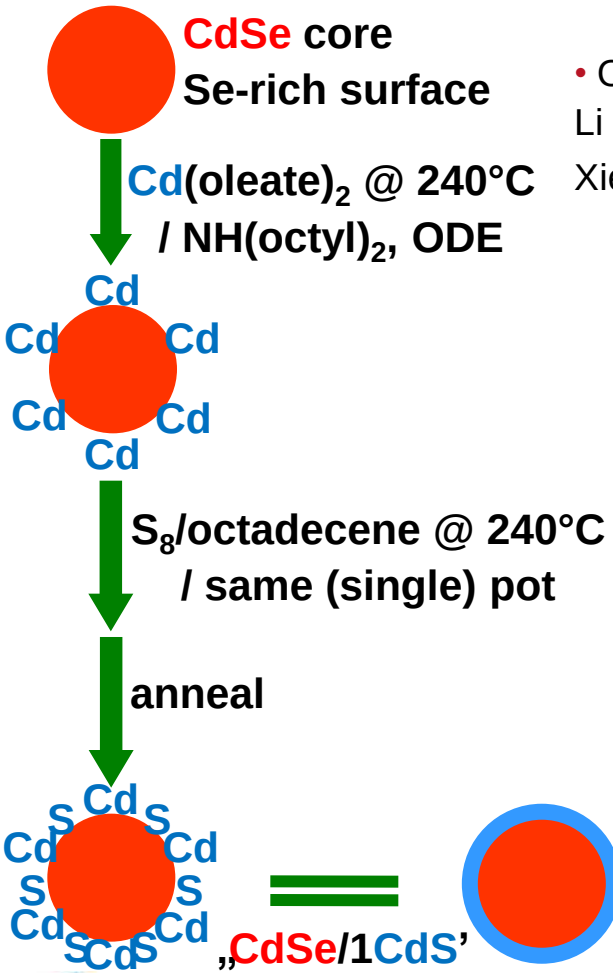
- Also from Ziegler et al. Adv. Mater. 20, 4068, (2008)

- Jang et al. Adv. Mater. 20, 2696 (2008) achieved similar excellent color-rendering and lum. eff.
- Lim et al. Adv. Mater. 19, 1927 (2007) and Nizamoglu APL 92, 031102 (2008) achieved white-light LED without using conventional phosphors.
- Woo et al. Nanotechnology 21, 495704 (2010) achieved combined high CRI (83) and lum. Eff. (to 66 lm W^{-1}) in a mixed system.

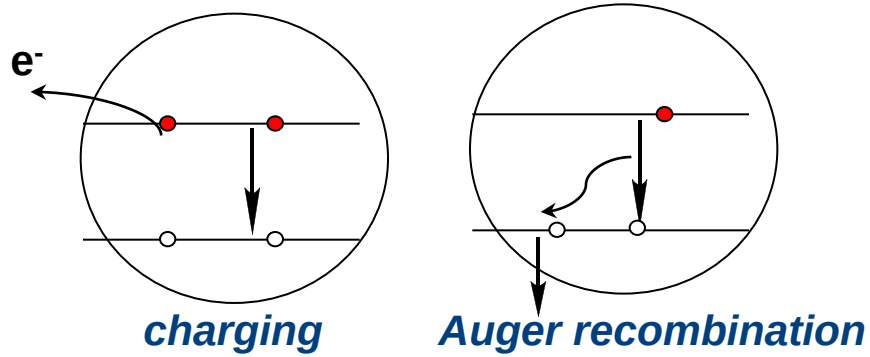
• Excellent color-rendering possible, but…
• Optical performance (luminous efficacy) reasonable though not optimized
• ~~Lifetime not yet well understood and highly NQD dependent~~

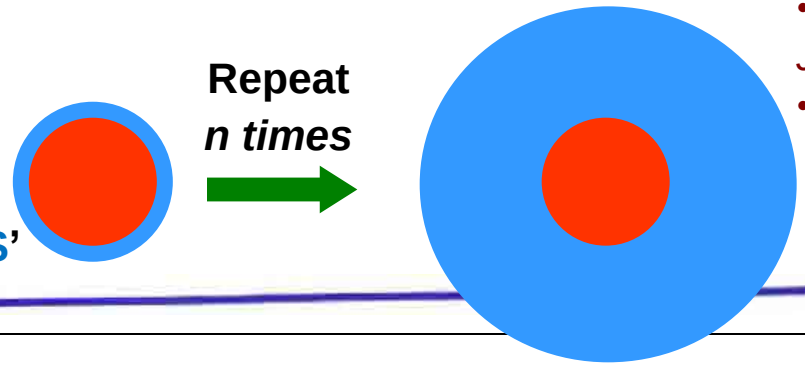
Our approach to eliminating the issues of charging effects, Auger recombination, and the organic ligand layer: "Epitaxial QDs in a flask"

- **Controlled growth of ultra-thick inorganic shells**



- Original thin-shell systems via SILAR:
Li & Peng et al. *J. Am. Chem. Soc.* 2003
Xie, Kolb, Li, Basche & Mews *J. Am. Chem. Soc.* 2005

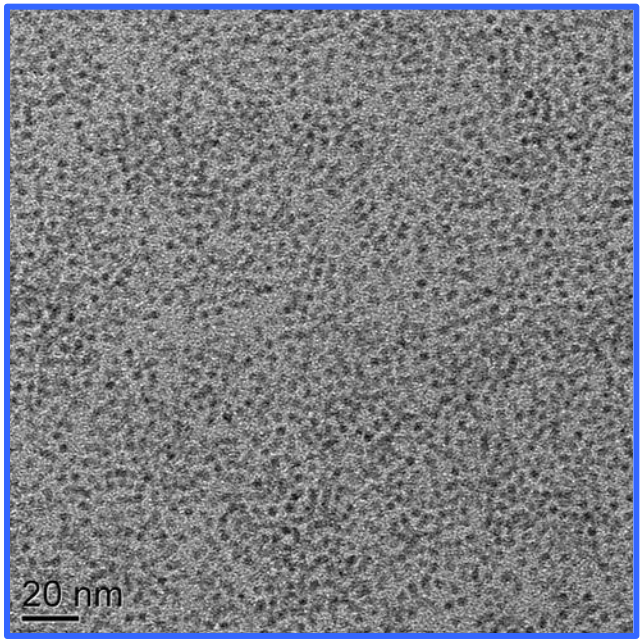


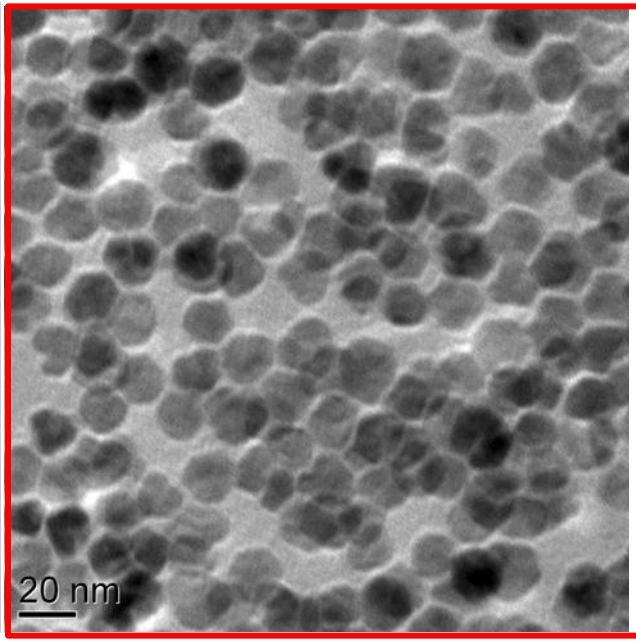


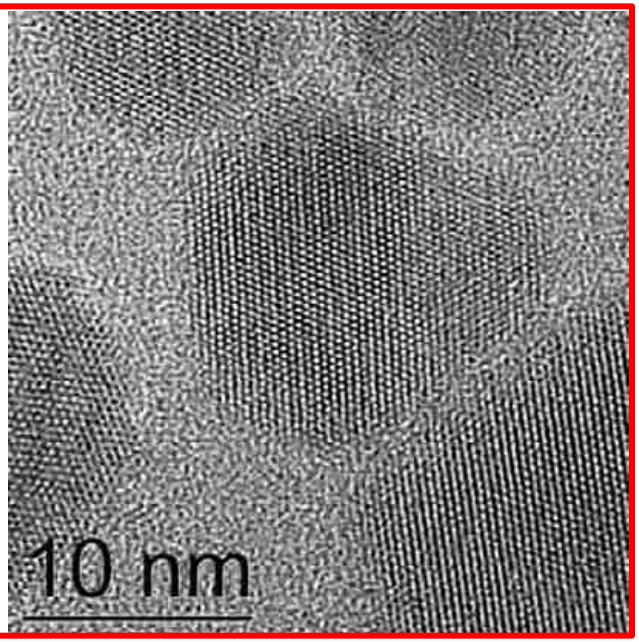
- Chen, Vela, & Hollingsworth et al. *J. Am. Chem. Soc.* 2008 (n<20
- Mahler, et al. *Nat. Mater.* 2008 (n<10)

„CdSe/*n*CdS', n>7

Giant NQDs:
From CdSe to 19 layers of CdS shell (CdSe/19CdS)







TEM
CdSe cores
1S ≈ 540 nm

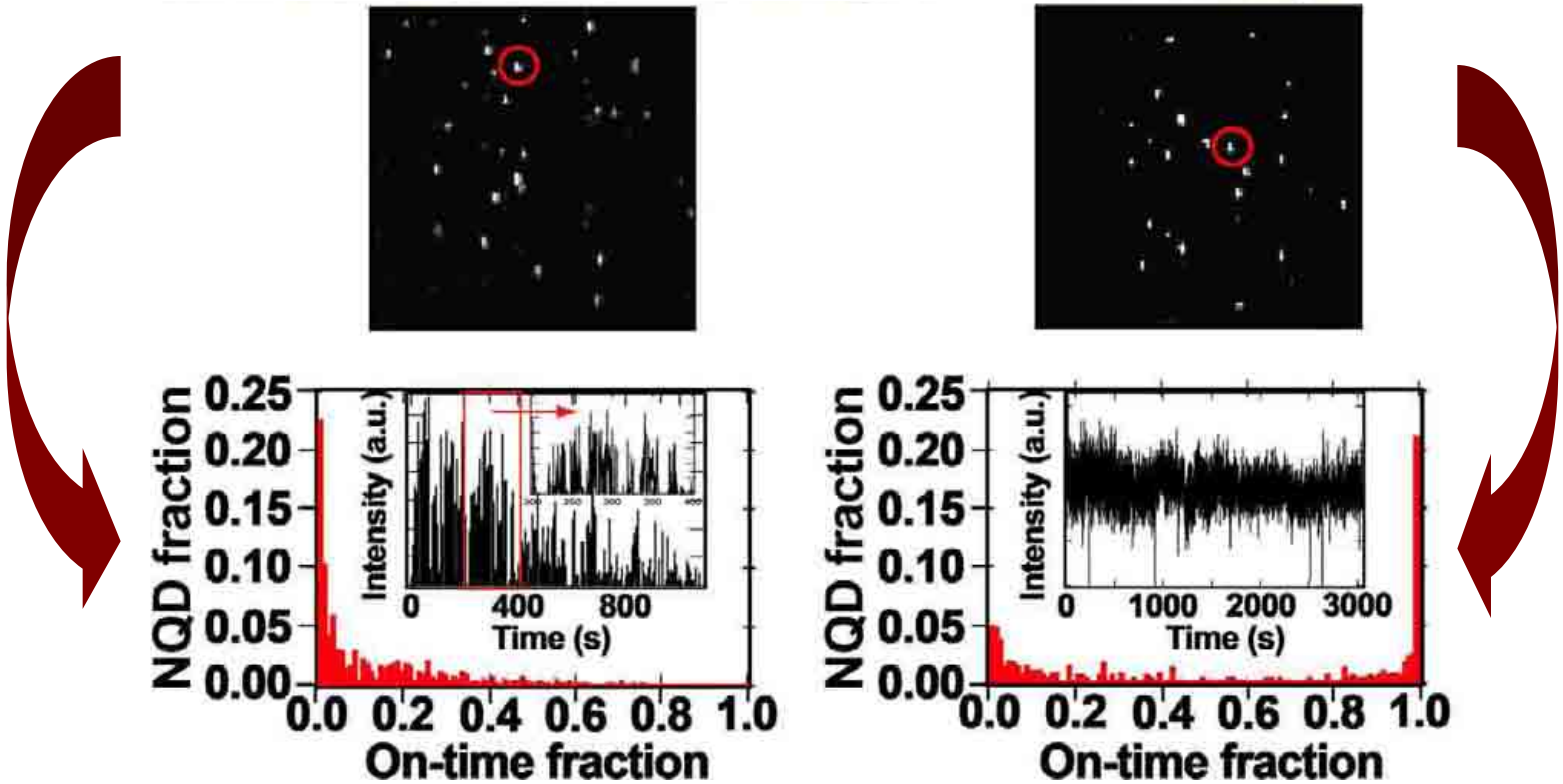
TEM
CdSe/19CdS
15.5 ± 3.1 nm

Hi-Res TEM
CdSe/19CdS
faceted

– Chen *et al. J. Am. Chem. Soc.* 2008

Results immediately promising: Blinking significantly suppressed

- Commercial core/shell NQDs
- g-NQDs

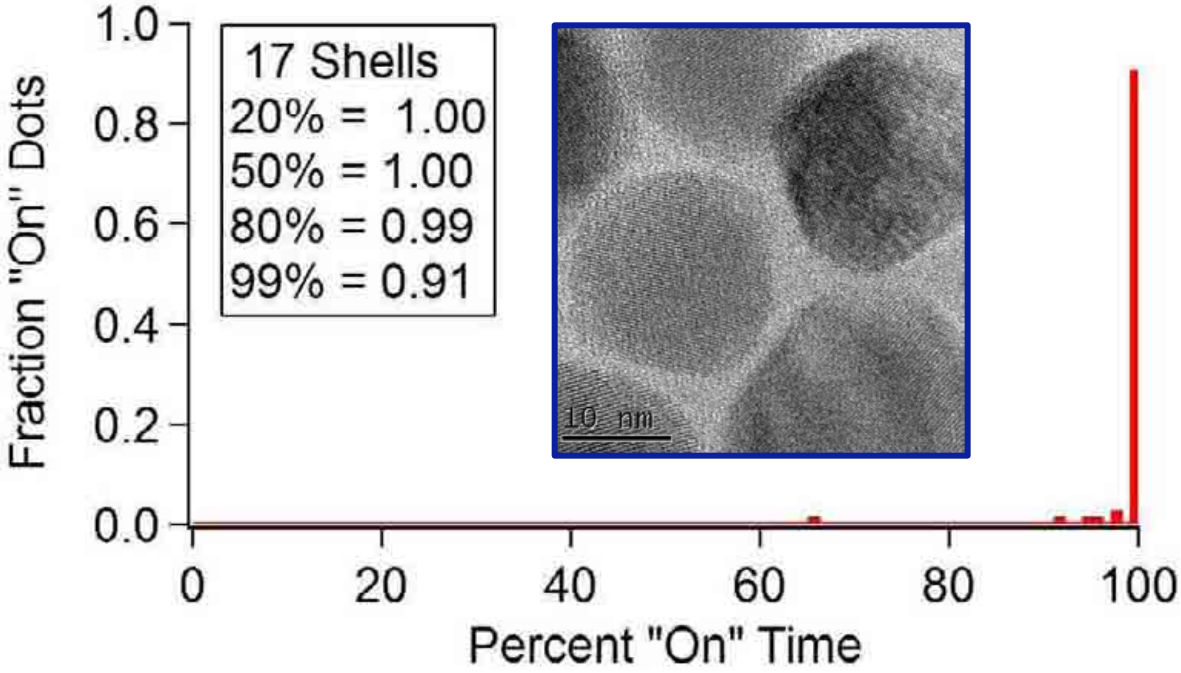


- Single-NQD time-dependent photoluminescence imaging: track 100's of NQDs in parallel
- Long interrogation time: 54 minute

– Chen *et al. J. Am. Chem. Soc.* 2008

Optimized g-NQD growth: Blinking essentially eliminated

- g-NQDs

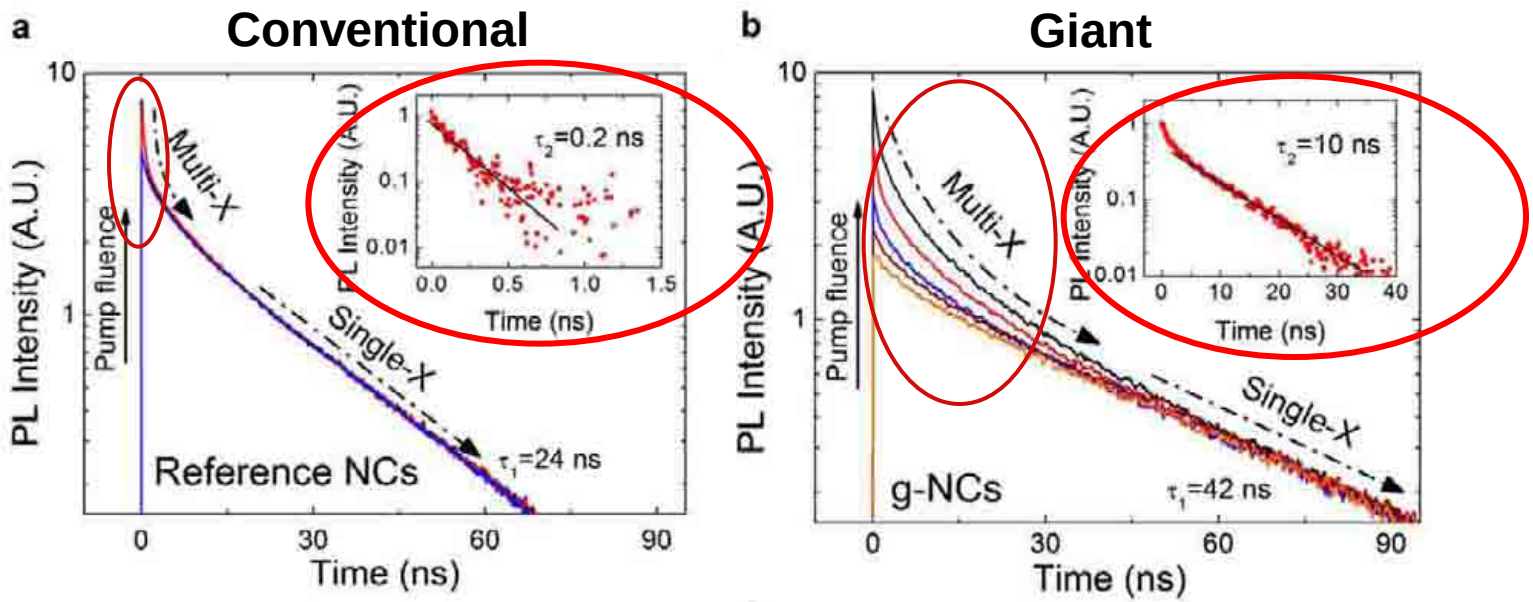


- **Single-NQD time-dependent photoluminescence imaging: track 100's of NQDs in parallel**
- **Long interrogation time: 54 minute**

– Chen *et al. J. Am. Chem. Soc.* 2008

And, dramatically suppressed Auger recombination: >50-fold increase in "biexciton" lifetime

- **Pump-intensity-dependent time-resolved photoluminescence**
  - Conventional − Multiexcitonic component is sub-ns due to Auger decay
  - Giant − Multiexcitonic component extends to 30 ns

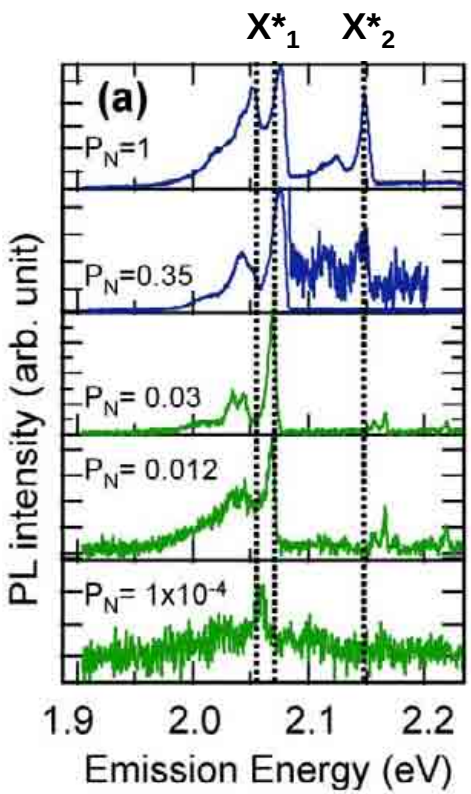


- **Insets: *50-fold increase* g-NQD derived biexciton lifetime**

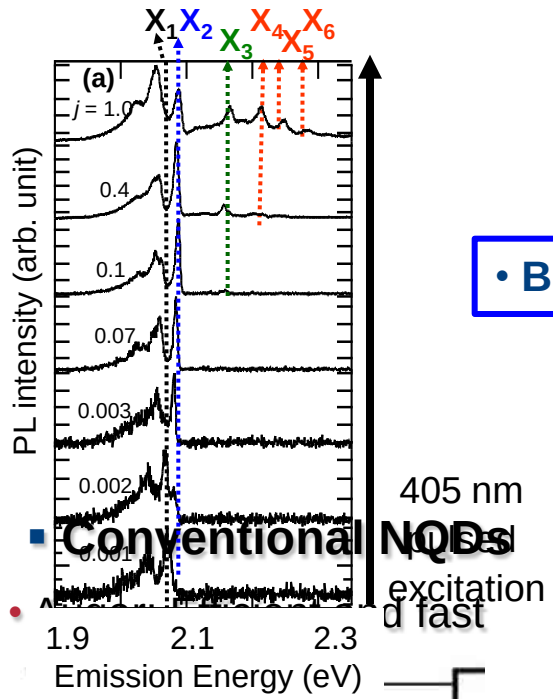
– Garcia-Santamaria et al. Nano Lett., 2009

Beyond blinking suppression: Transformational new physics from novel chemistry

- **New pathways for electron→photon conversion**
  - Efficient emission from charged and multiexcitonic states in low-T, steady-state, single-NQD PL



– Htoon et al., Nano Lett. 2010, 10, 2401-07

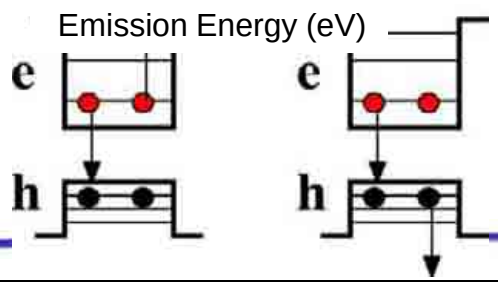


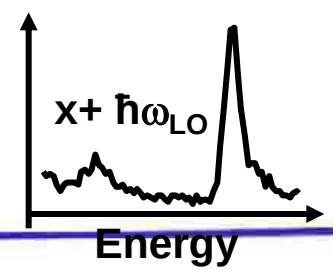
405 nm excitation

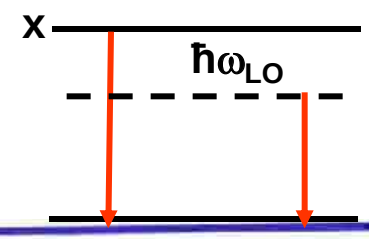
- **Conventional NQDs**
- d fast

- **Biexciton quantum yields of 90%!**

- Low-T photoluminescence: Lowest exciton state emission

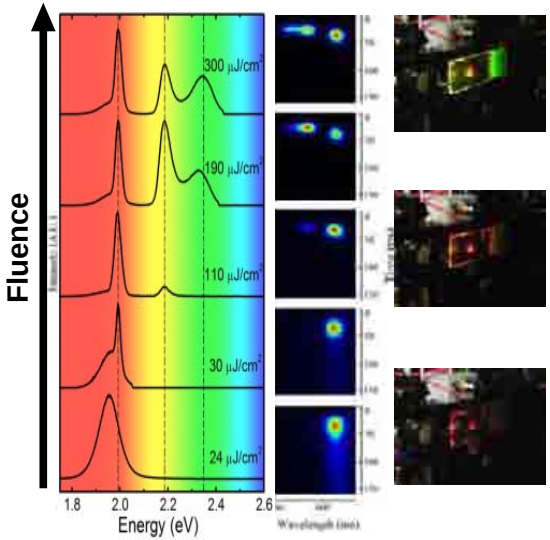






Beyond blinking suppression: Transformational new physics from novel chemistry

- **New pathways for electron→photon conversion**
  - Low-threshold, multi-color Amplified Spontaneous Emission (ASE)



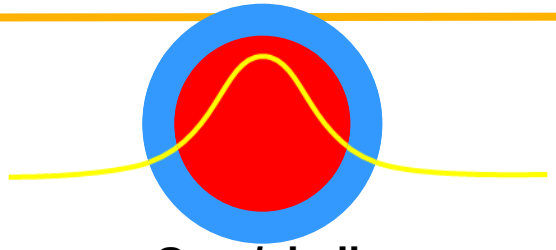
✓ Optical gain over unprecedented bandwidth (>500 meV)

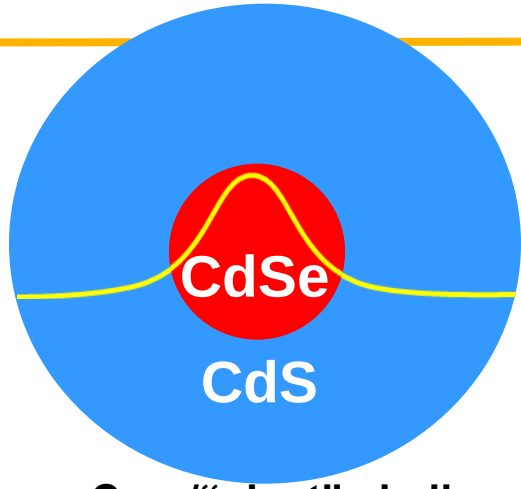
✓ Low thresholds due to large cross sections and long-lived multiexcitons

– García-Santamaría et al., Nano Lett. 2009 9, 3482

- **Biexciton quantum yields of 90%!**
- **Low-threshold, multicolor amplified spontaneous emission**

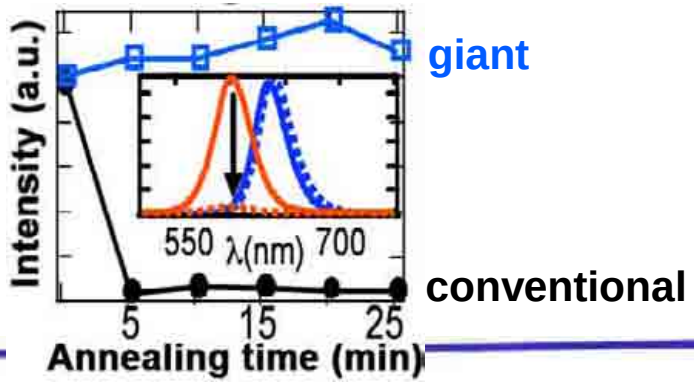
What does a thick/ultra-thick shell do?: Wavefunction confinement





Core/"giant" shell

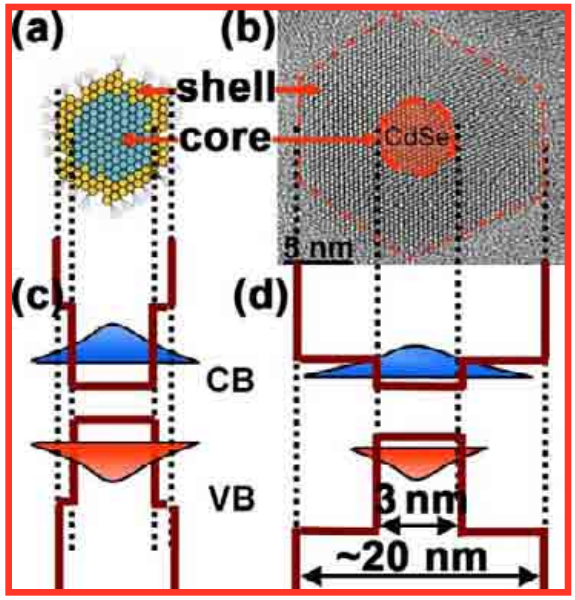
- **Thick shell isolates excitonic wavefunction to core**
  - Charging minimized
  - *Blinking, photobleaching, and quantum yield* rendered <u>independent of NQD surface chemistry/chemical environment</u>



Also suppression of non-radiative Auger recombination?

- **Auger recombination is suppressed by:**
  - Decreasing exciton-exciton Coulomb coupling
  - Separating electrons from holes
  - Smoothing the interfacial confinement potential

- **All modes active in giant NQDs:**
  - Volume effect
  - „Quasi-Type-II' electronic structure



- Nanda et al. *J. Appl. Phys.* 2006
- García-Santamaría et al. *Nano Lett.* 2009
- Htoon, Hollingsworth, & Klimov et al. *Phys. Rev. Lett.* 2003
- Supporting theory: Efros, A. L., in *Semiconductor Nanocrystals, 2003*

Also suppression of non-radiative Auger recombination?

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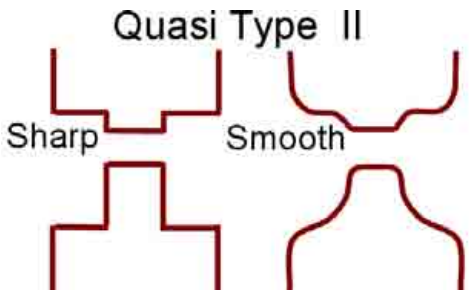

- **All modes active in giant NQDs:**
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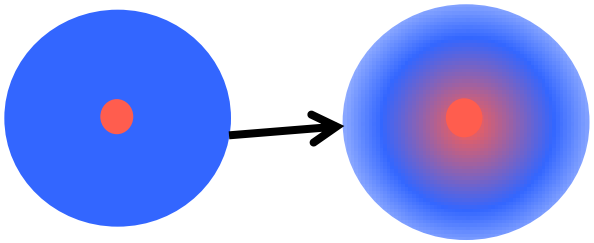

- Nanda et al. *J. Appl. Phys.* 2006
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- Htoon, Hollingsworth, & Klimov et al. *Phys. Rev. Lett.* 2003
- Supporting theory: Efros, A. L., in *Semiconductor Nanocrystals, 2003*

NQDs are an obvious choice as active layers in LEDs or to replace/assist conventional RE phosphors

- **Must address NQD-specific technical barriers to optimized efficiencies (e.g., 0.1-2% LED EQEs) and operation lifetimes (>300 hrs):**

  - ✓ **Exciton management for radiative conversion: Eliminate non-radiative pathways, especially "intrinsic" Auger**
  - ✓ **Dependence of inorganic emission properties on organic ligand layers**
  - ✓ **Stability in the face of harsh processing or operation conditions**
  - ✓ **Characteristic small Stokes shift: reabsorption**
  - **Compatibility with relevant processing methods**
  - **Compatibility with relevant ETLs and HTLs: Band level matching**
  - **Dependence on "rare" or toxic elements**
  - **Large-scale production with retention of properties (optical/structural)**
  - **Charge management in devices: (engineering) e.g., optimization of emitting/ HTL/ETL layers; NQD matrix encapsulation,…**
  - **Take advantage of plasmonic-coupling enhancements**
  - **Take advantage of rare-earth/NQD coupling: NQDs as "antennas"**

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U.S. DEPARTMENT OF ENERGY

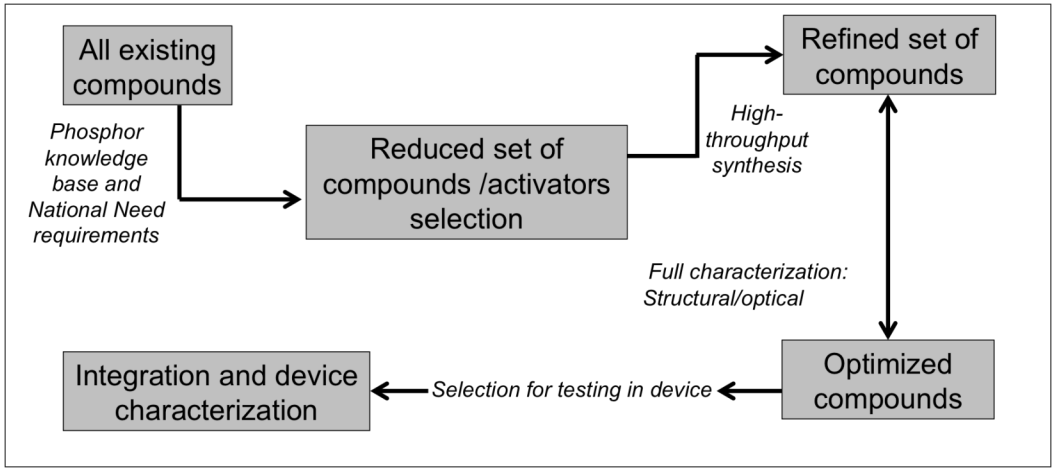
Phosphors Breakout Session

David K. Shuh
Senior Scientist, Actinide Chemistry Group, Chemical Sciences Division
Associate Director, The Glenn T. Seaborg Center
Lawrence Berkeley National Laboratory, Berkeley, CA 94720 USA

ARPA E Workshop
Arlington, VA
6 Dec. 2010

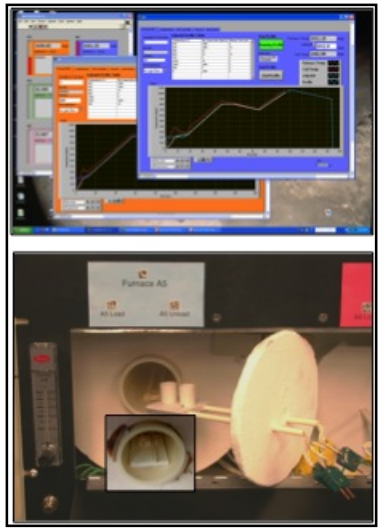
UNIVERSITY OF CALIFORNIA

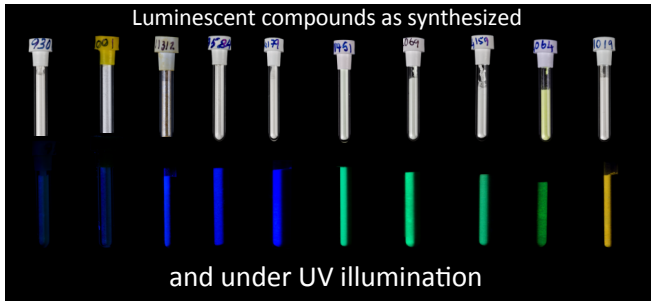
Combinatorial Approach to Phosphor Synthesis



HIGH-THROUGHPUT SOLID-STATE SYNTHESIS:

- 30 furnaces 1200°C
- 12 furnaces 1700°C
- PID controllers
- Different atmospheres (N_2, Ar, H_2/Ar, O_2/Ar)
- Labview control / interface to master database for data collection and analysis.





E. Bourret, EDBourret@lbl.gov

High-throughput Characterization of Phosphors

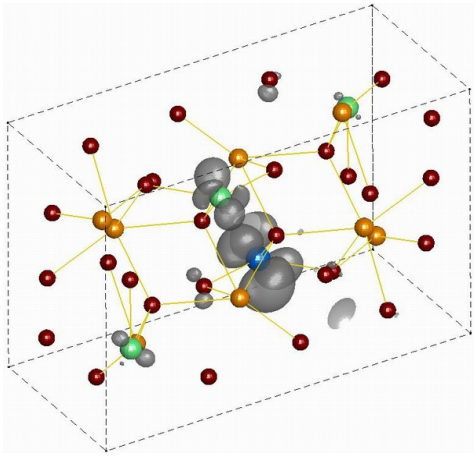
- **X-ray diffraction**
- **X-ray luminescence**
- **Optical excitation and emission spectra**
- **Band gap measurement (reflection)**
- *All with computer-controlled sample changers, bar code readers, and automatic data upload to a real-time database*

E. Bourret, EDBourret@lbl.gov

Research Possibility - Combine Theory Plus Experiment

Theory for new materials - predictive and for understanding

Example - DFT electronic structure calculations to determine the position and character of the Ce 4f and 5d states to relate to luminescence for new scintillator detectors (Canning, et al. Phys. Rev. B, accepted)



(Ce3+)* electron state (5d)

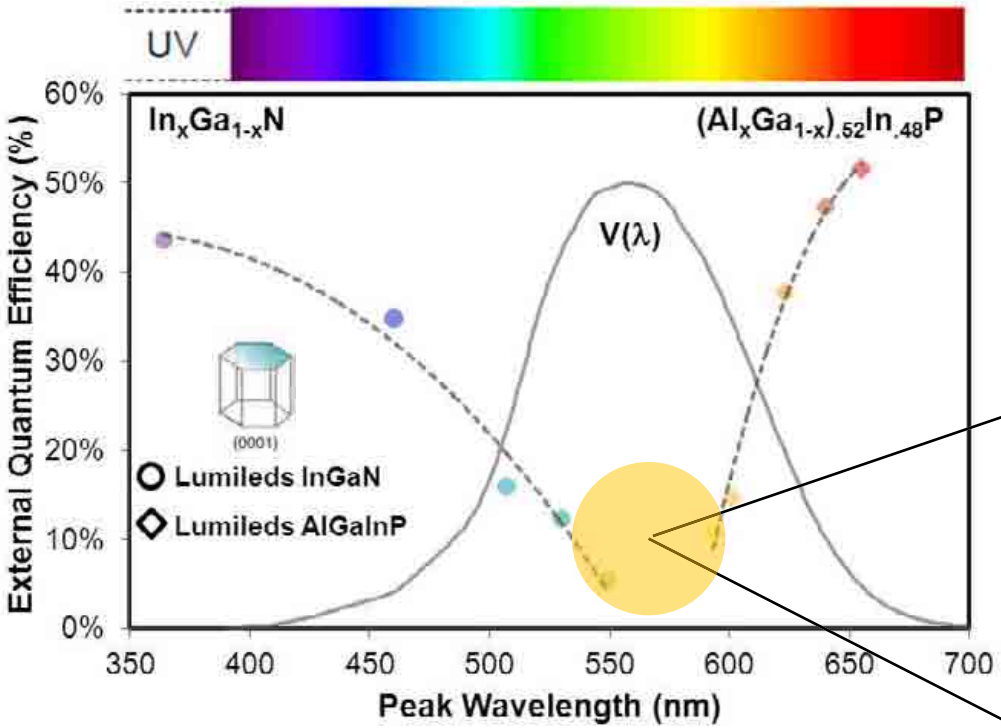
Material synthesis and characterization → Applications

Rapid discovery of new composition
Rapid evaluation of new activators and related optimization
Rapid evaluation of new RGB mixtures
Color rendition vs. composition and activators
Rapid synthesis for UV and thermal resistance of phosphors

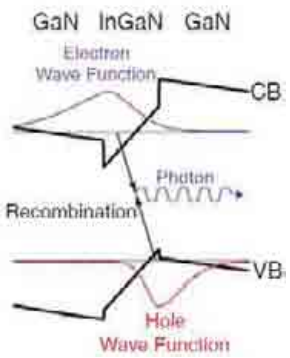
CFLs: RE free phosphors
LEDs: Blue-base; RE-free
LEDs: UV-base; RE-free

A. Canning, ACanning@lbl.gov

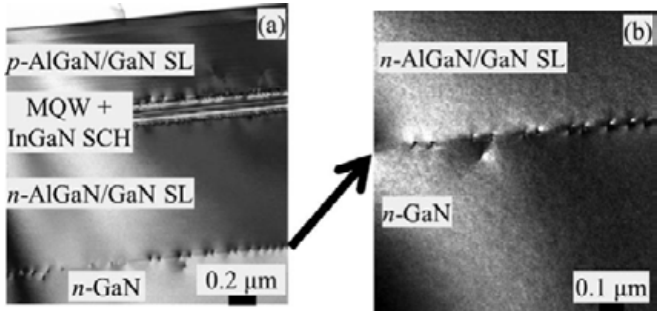
LED Efficiency Limitation: "The Green Gap"



Polarization-induced electric fields



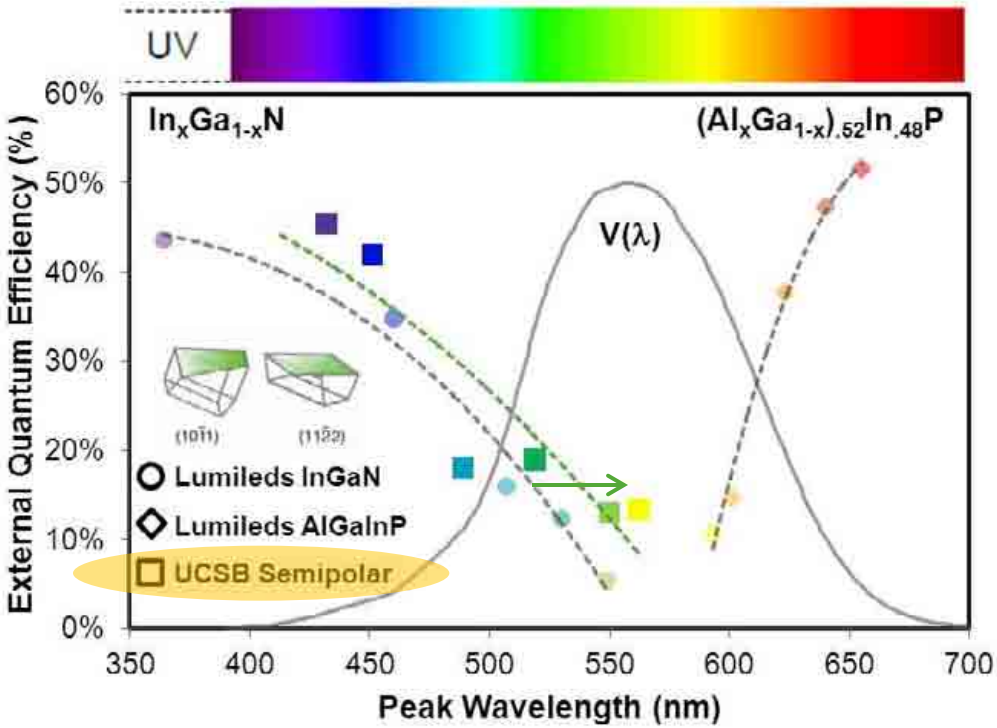
Strain-induced misfit dislocations



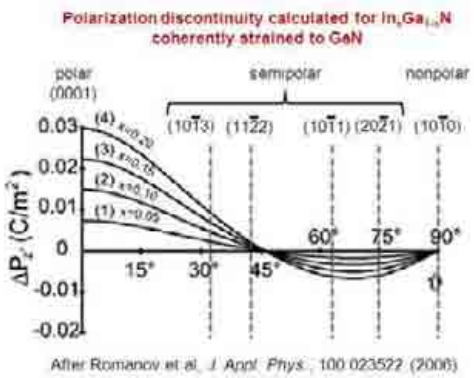
A. Tyagi et al, *Appl. Phys. Lett.* 95 251905 (2009)

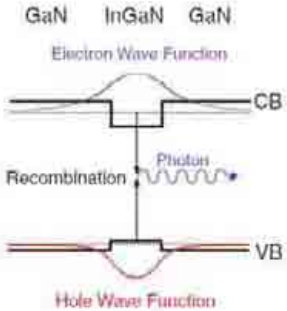
Semipolar III-Nitrides offer a solution to these issues

Semipolar III-Nitrides



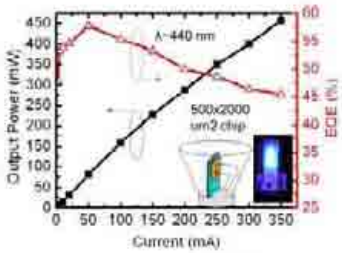
Reduced polarization-related electric fields
⇒ increased optical efficiency

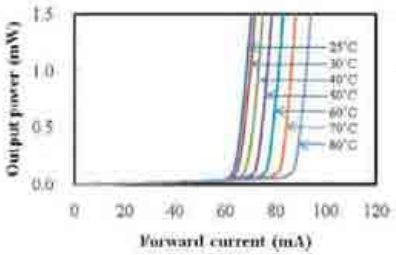




UCSBs semipolar InGaN LEDs show improved efficiency in the green/yellow

Low threshold semipolar (20$\bar{2}$1) green lasers demonstrated (J_{th} = 4.3 kA/cm^2)

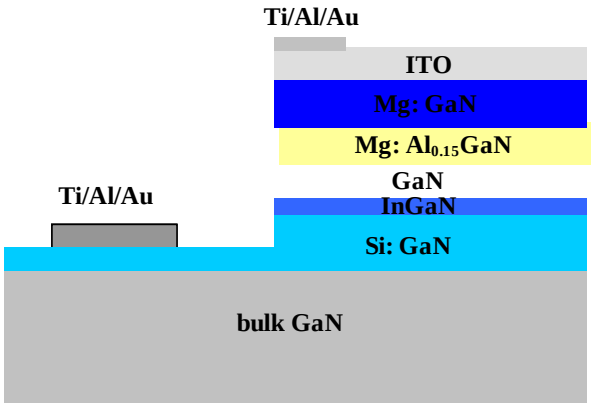




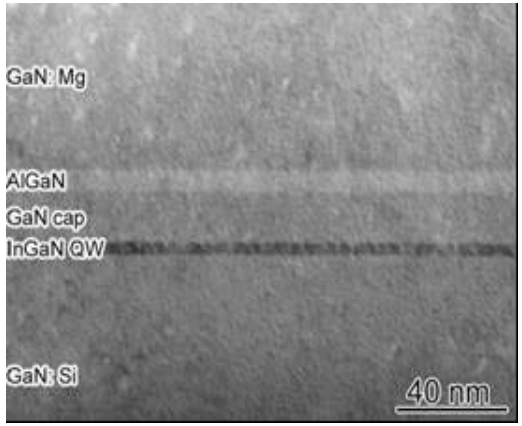
M. Adachi et al, *Appl. Phys. Exp.* 3 121001 (2010)

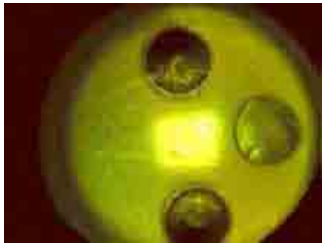
Semipolar (11$\underline{2}$2) Yellow LEDs

SQW based LED Structure

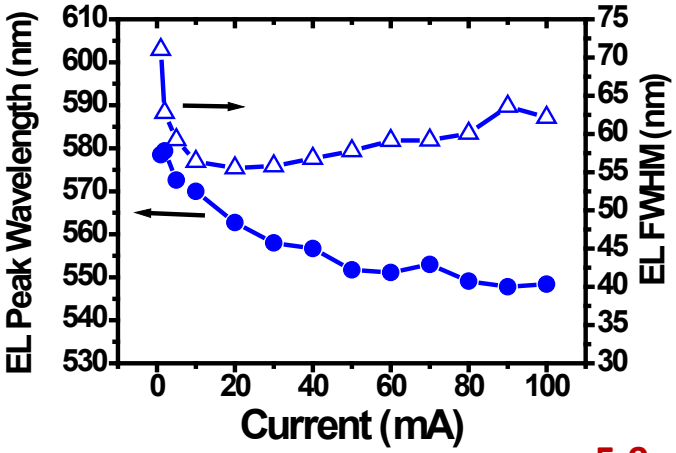


TEM micrograph

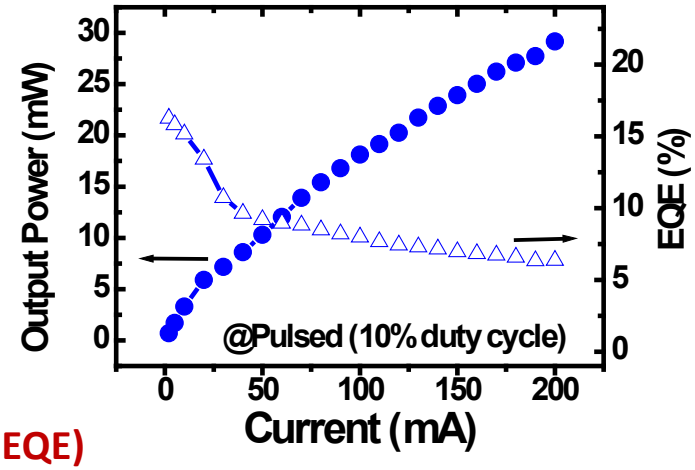




EL Characteristics



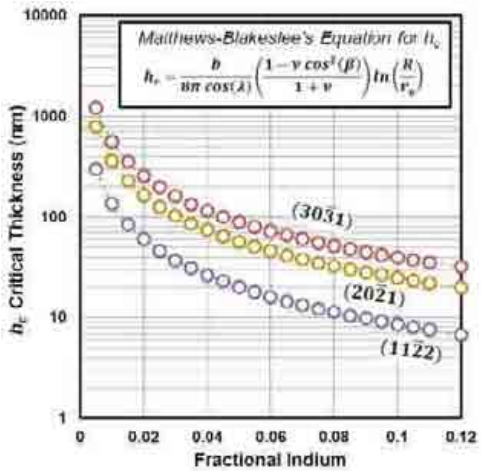
Power and EQE

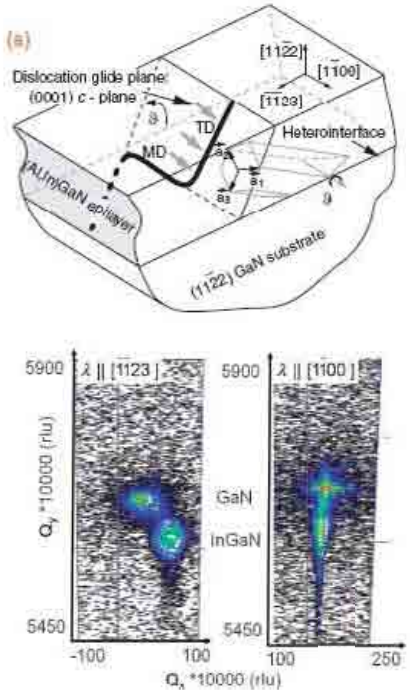


5.9 mW @ 20 mA (13.4% EQE)

H. Sato *et al.* APL **92**, 221110 (2008)

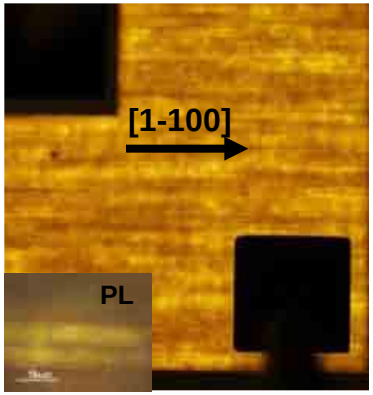
Strain Relaxation in Semipolar III-Nitrides



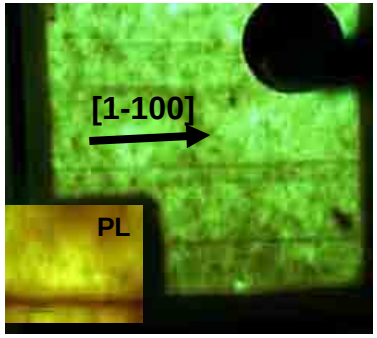


1st LED results on strain-relaxed buffer layers

without buffer layer:
P_o = 0.22 mW, λ = 550nm

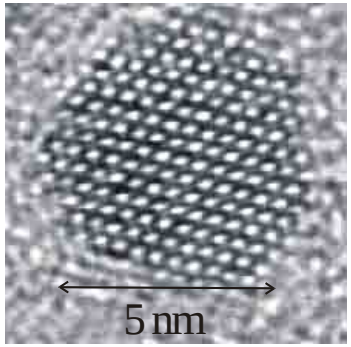


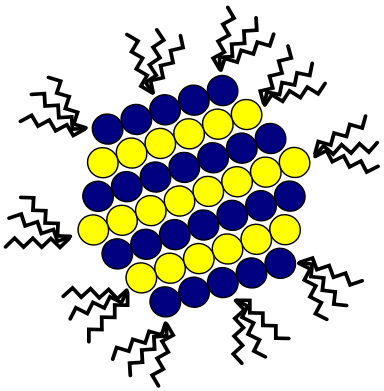
with buffer layer:
P_o = 1.6 mW, λ = 529nm

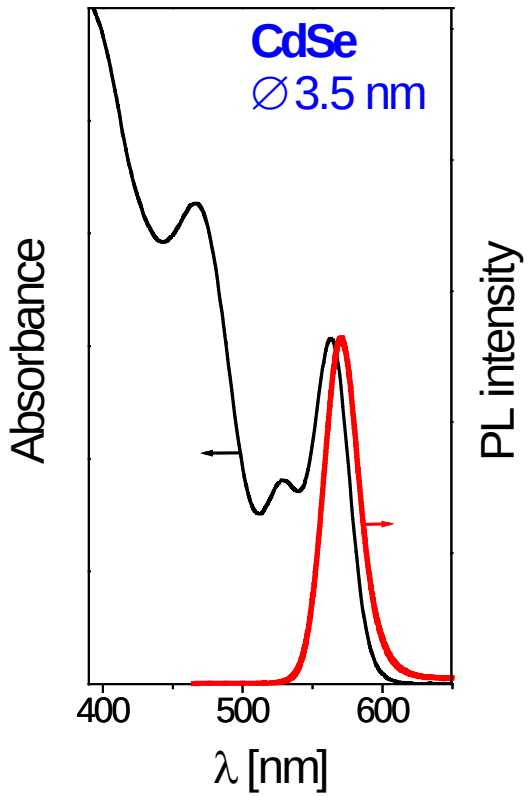


- Stress relaxation via misfit dislocation formation via glide in lattice mismatched semipolar III-nitrides observed
- Early results for high-indium-content LEDs grown on strain-relaxed buffer layers demonstrate improved optical efficiency

Quantum dots as an alternative for rare-earth phosphors?







After 15 years of active research and development

Pro's:

- PL quantum efficiency 80-95%
- Stability: red emission >10^{10} photons/dot
  green emission ~10^{8} photons/dot
- Color rendering and purity: unsurpassed
- Continuous absorption spectrum ideal for excitation
- Can be produced on large scale

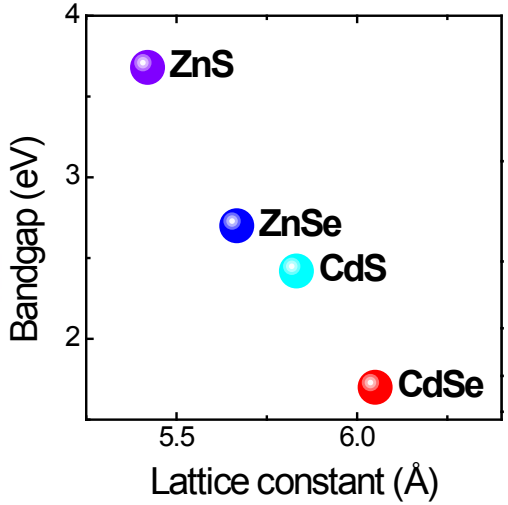
Challenges:

- Long-term stability for blue and green emitting QDs
- Direct electrical excitation
- Best emitters use cadmium (in small quantities, non-Cd emitters under development)

Dmitri Talapin, University of Chicago

Quantum dots in down-conversion LEDs

Problem: long term emission stability

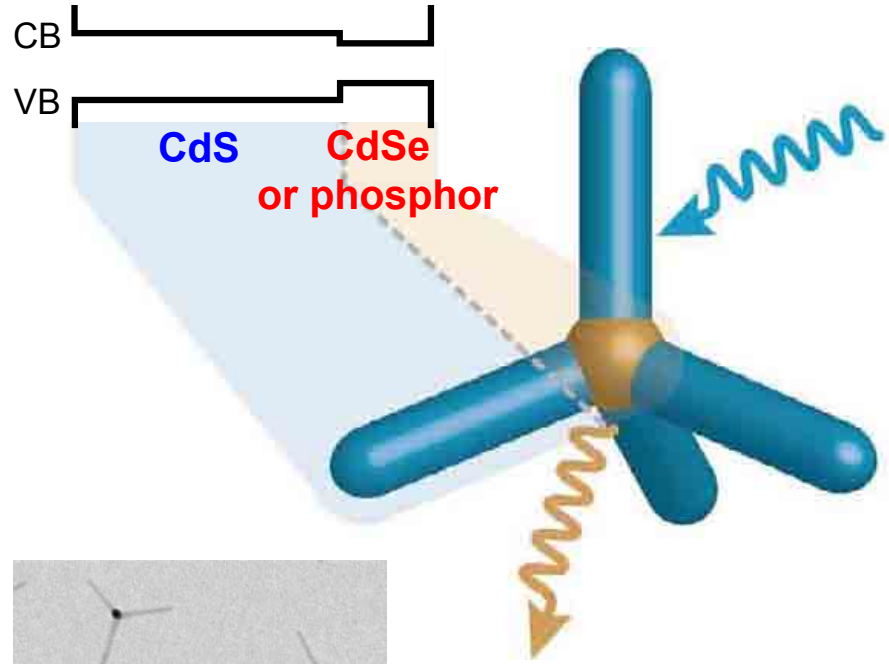


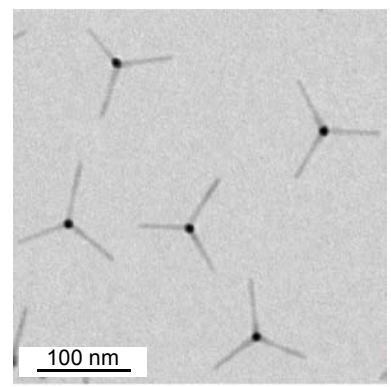
- *ZnS is viewed as only option for the outer shell*
- *ZnS band gap is not wide enough to confine both electrons and holes, especially in blue-green emitters*

Possible solution: Increase the band gap of the outer shell, e.g., by doping Mg, Ca into ZnS and by introducing materials that *were ignored* before. **Why ignored?**

Most of research on luminescent QDs was carried out with bio-labeling in mind

Another approach: excitation routing



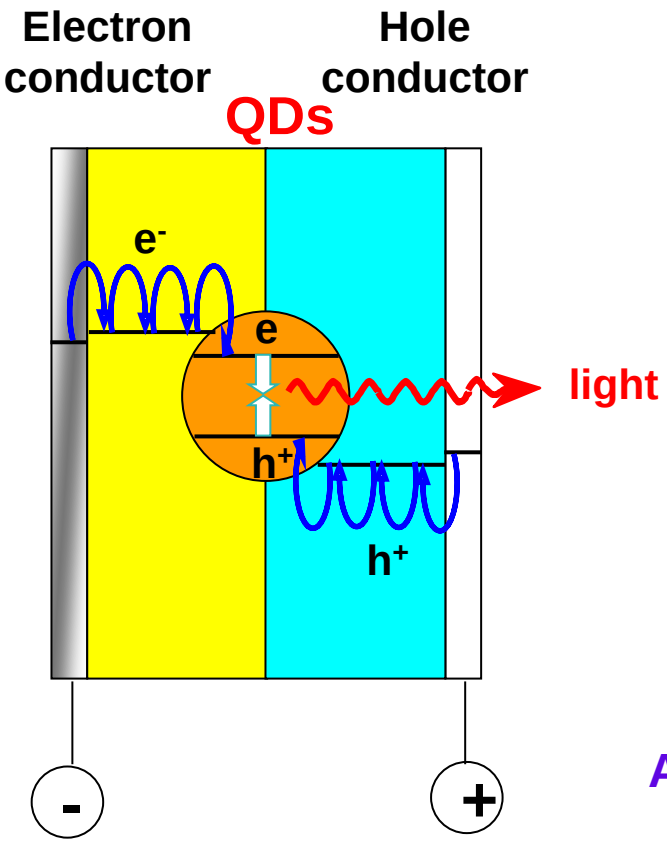


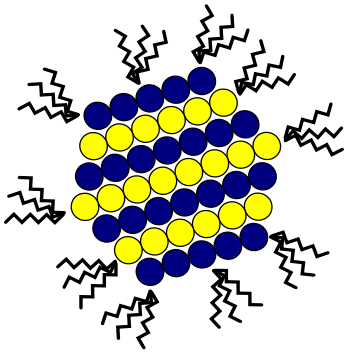
Nano Lett. **7**, 2951 (2007)
Science **330**, 1371 (2010)

Charge carrier routing will minimize the use of emitting material (phosphor)

Dmitri Talapin, University of Chicago

Quantum dots in electrically pumped LEDs



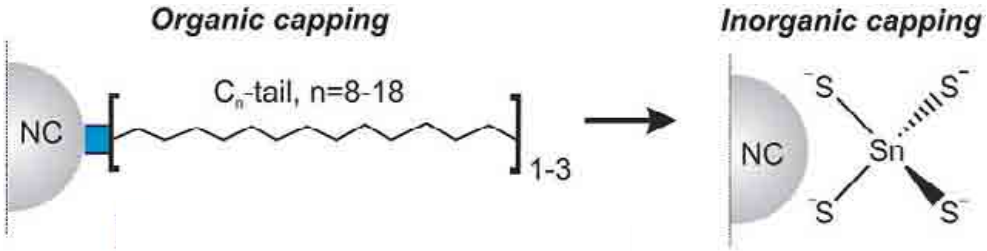


Problem: control over injection of charge carriers into the quantum dots

Why? We poorly understand the interface between QDs and organic and inorganic materials

Solution: Need systematic studies of the interfaces and novel approaches to surface chemistry of colloidal quantum dots.

An example:



Science **324**, 1417 (2009)

Dmitri Talapin, University of Chicago

Gallium Indium Nitride for Full Visible Spectrum Emitters

Christian Wetzel and Theeradetch Detchprohm

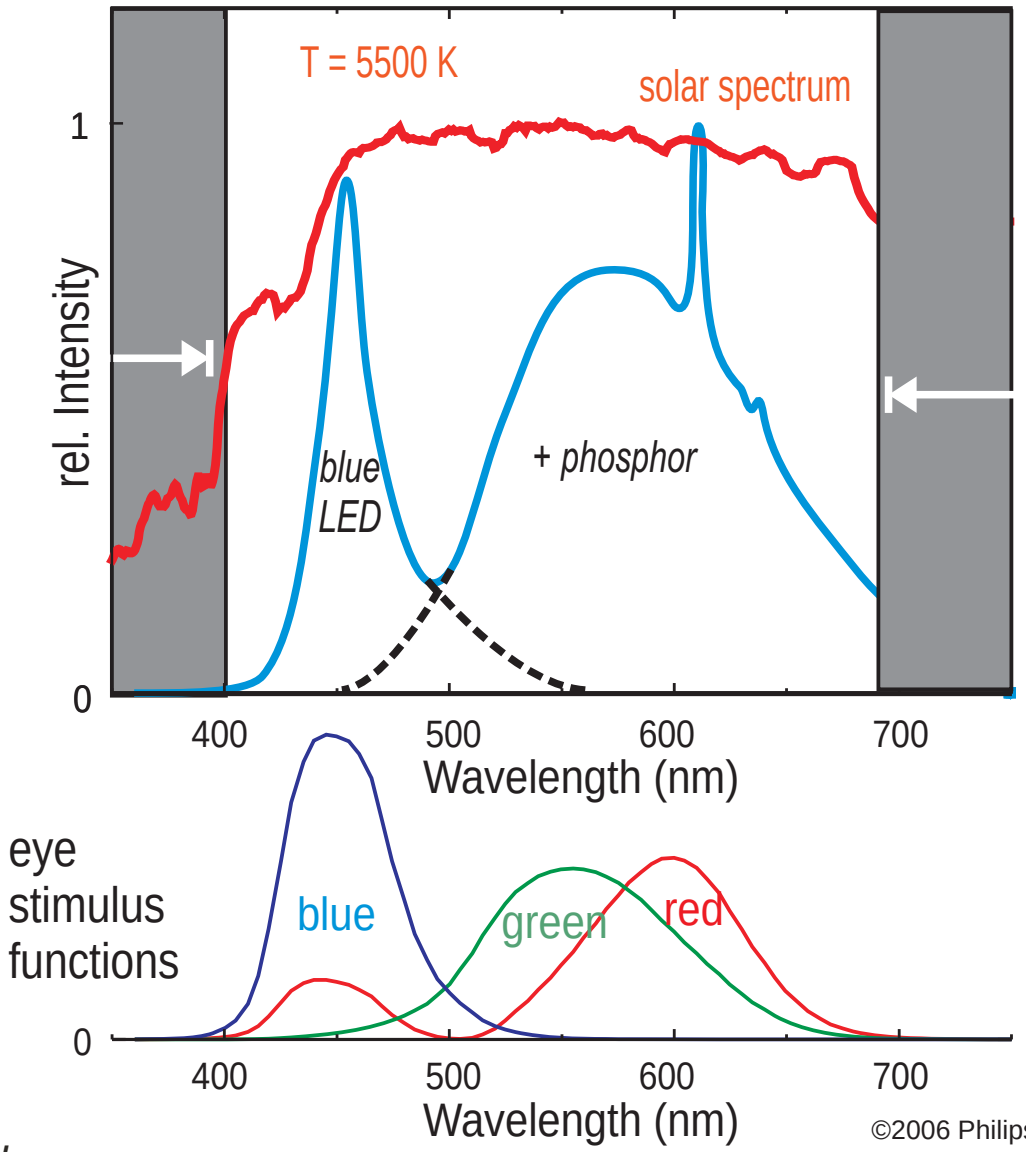
Future Chips Constellation,
Smart Lighting Engineering Research Center,
Department of Physics, Applied Physics and Astronomy
Rensselaer Polytechnic Institute, Troy, NY

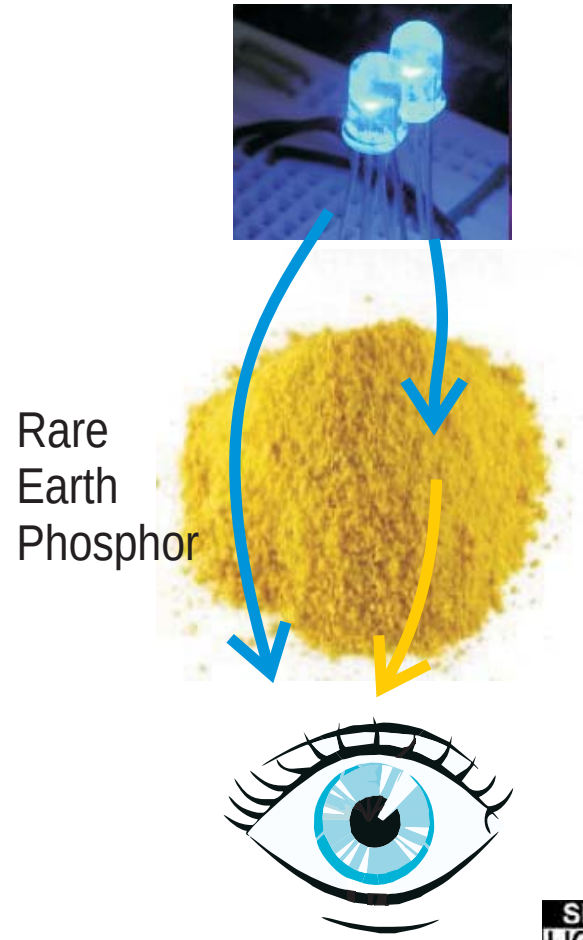
Rare Earth and Critical Materials
ARPA-e Workshop
Arlington, VA

Dec 6, 2010

Composite White Light Emitting Diode

blue plus rare earth phosphor





fox consulting ClipArtOf.com

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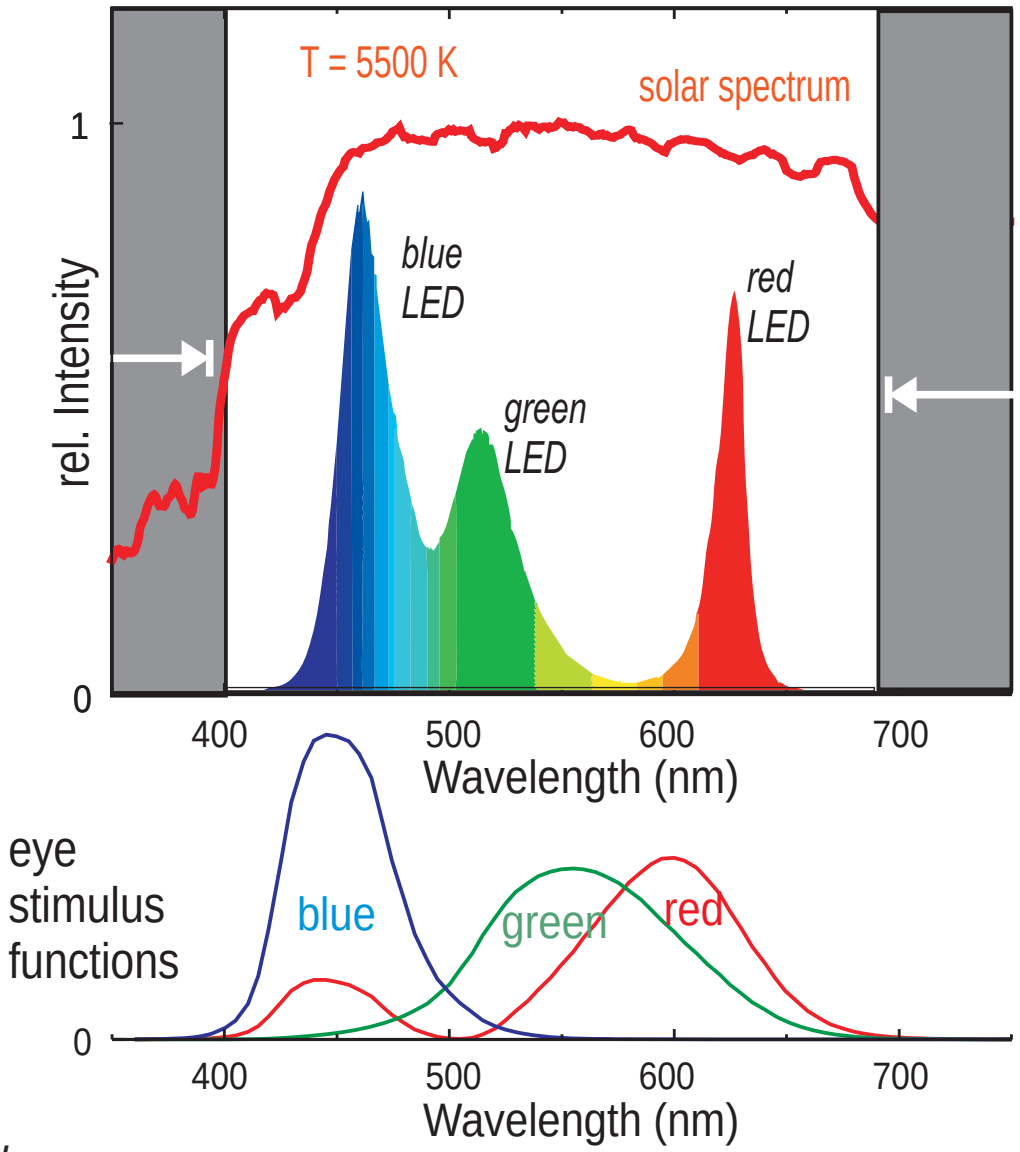
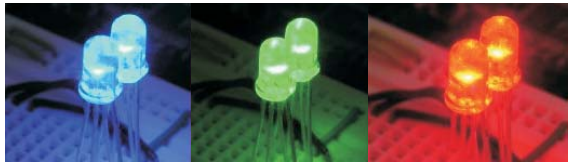
Composite White Light Emitting Diode

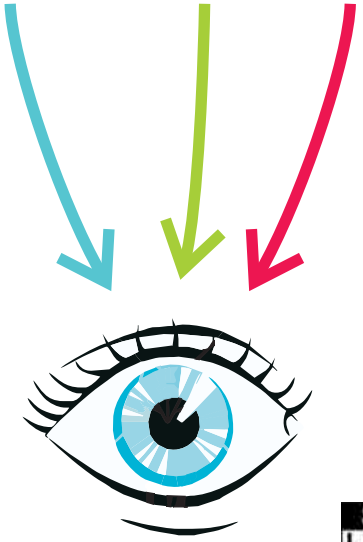
red-green-blue emitter



just add Indium!

GaInN/GaN alloy quantum wells





fox consulting ClipArtOf.com
ledmuseum.candlepower.us

SMART LIGHTING

Rensselaer
Future Chips Constellation

Composite White Light Emitting Diode

red-green-blue emitter

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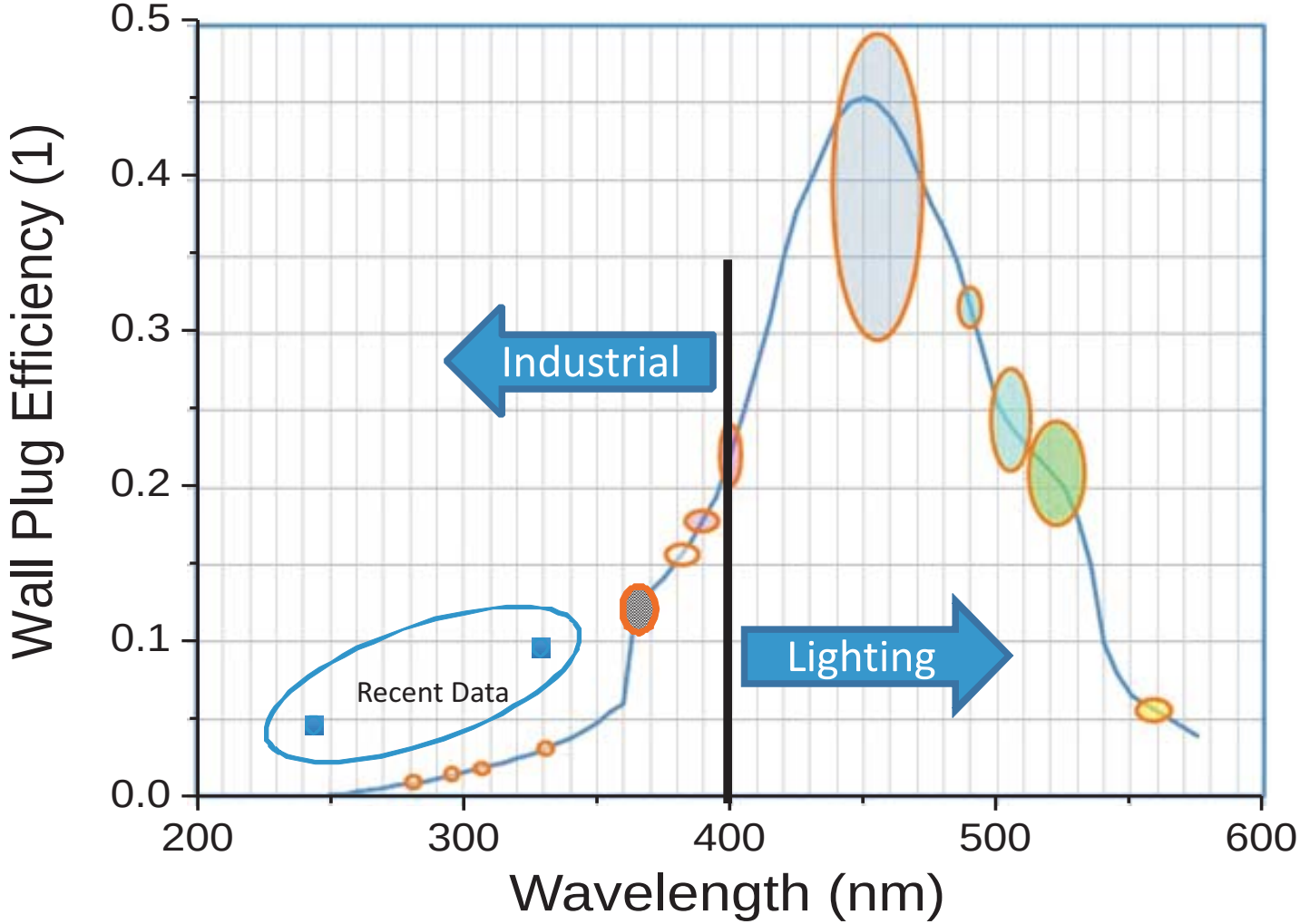
Wall Plug Efficiency

ranges of achievement



Definition:

Wall Plug Efficiency

$$= \frac{P_{\text{Light out}}}{P_{\text{El. in}}}$$

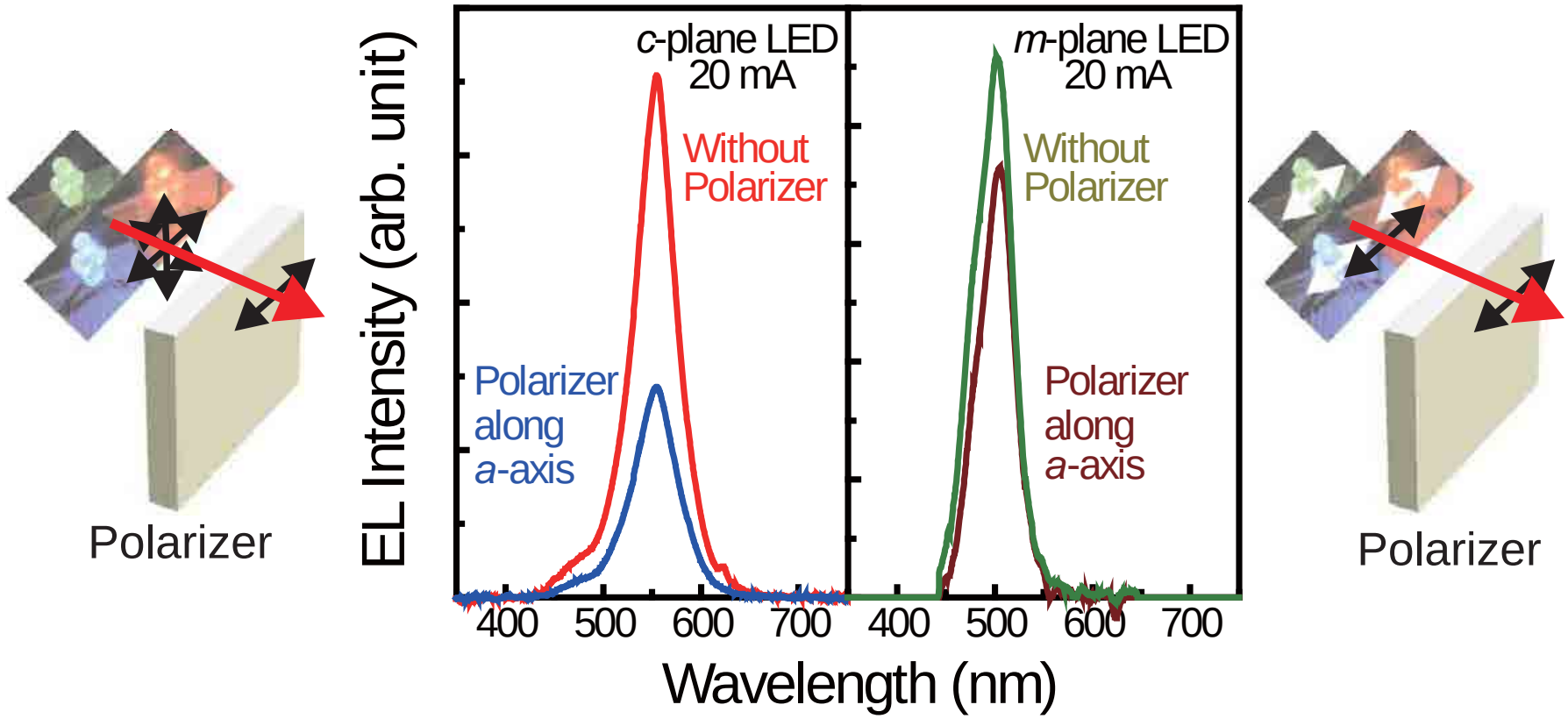
III-Nitride Based LEDs

mainly AlGaN-based alloys | mainly GaInN-based alloys

after R. Karlicek *et al.*

Polarized Light Emission

minimal losses when analyzed

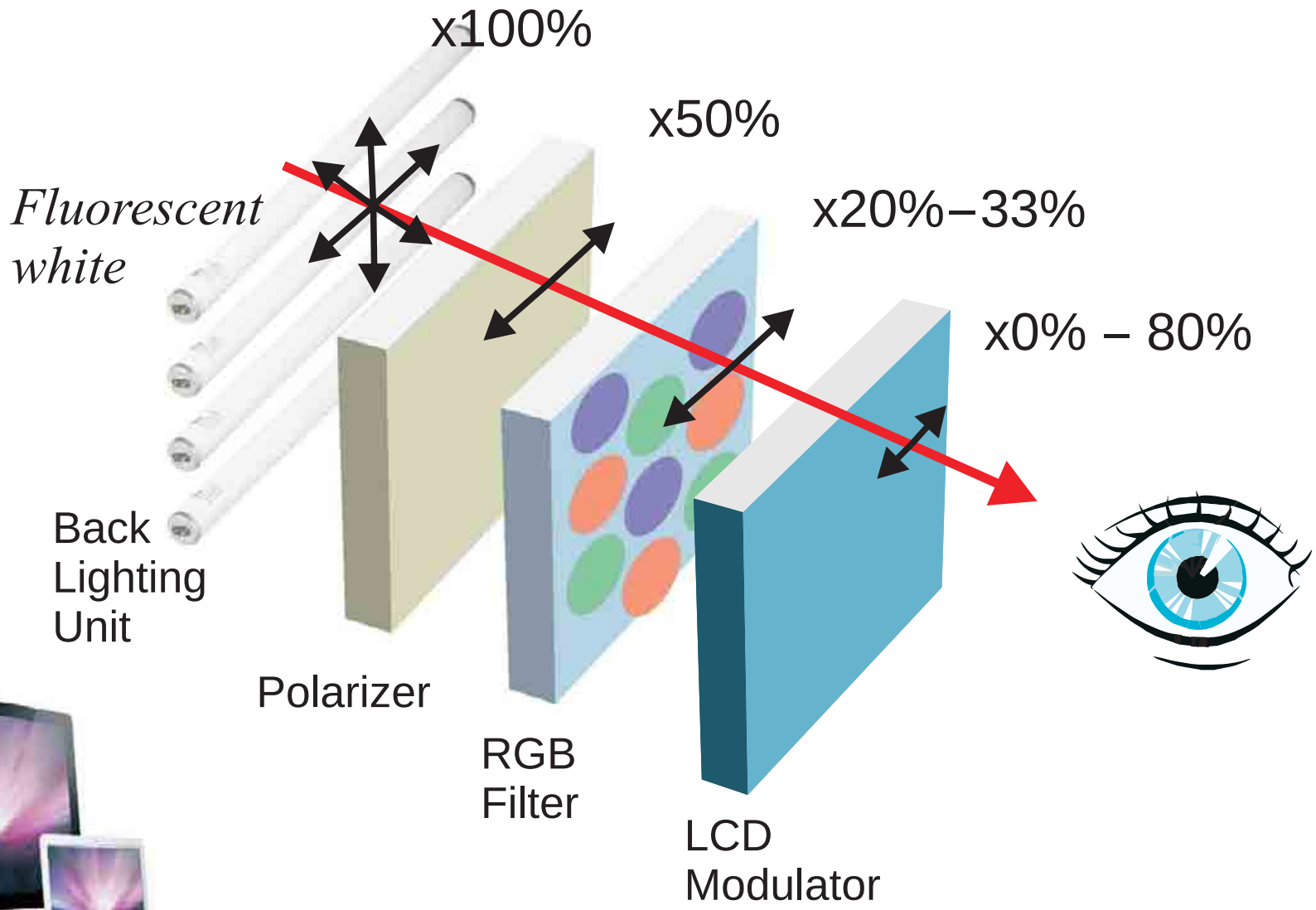


Shi You, *et al.*,
Applied Physics Express **3**, 102103 (2010)

only minimal losses in linear polarizer

LCD Display Backlighting

polarization matters



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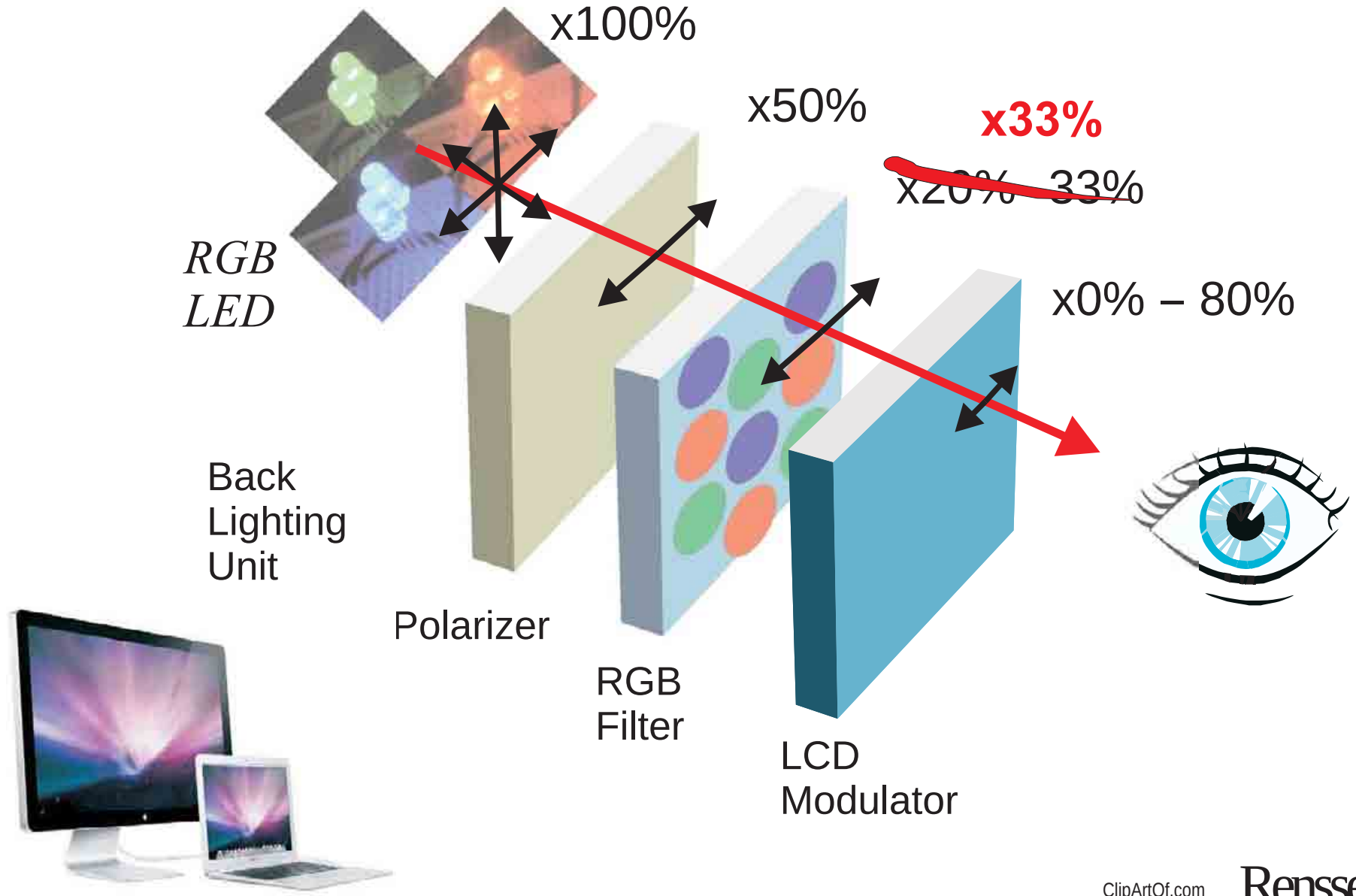
LCD Display Backlighting

polarization matters



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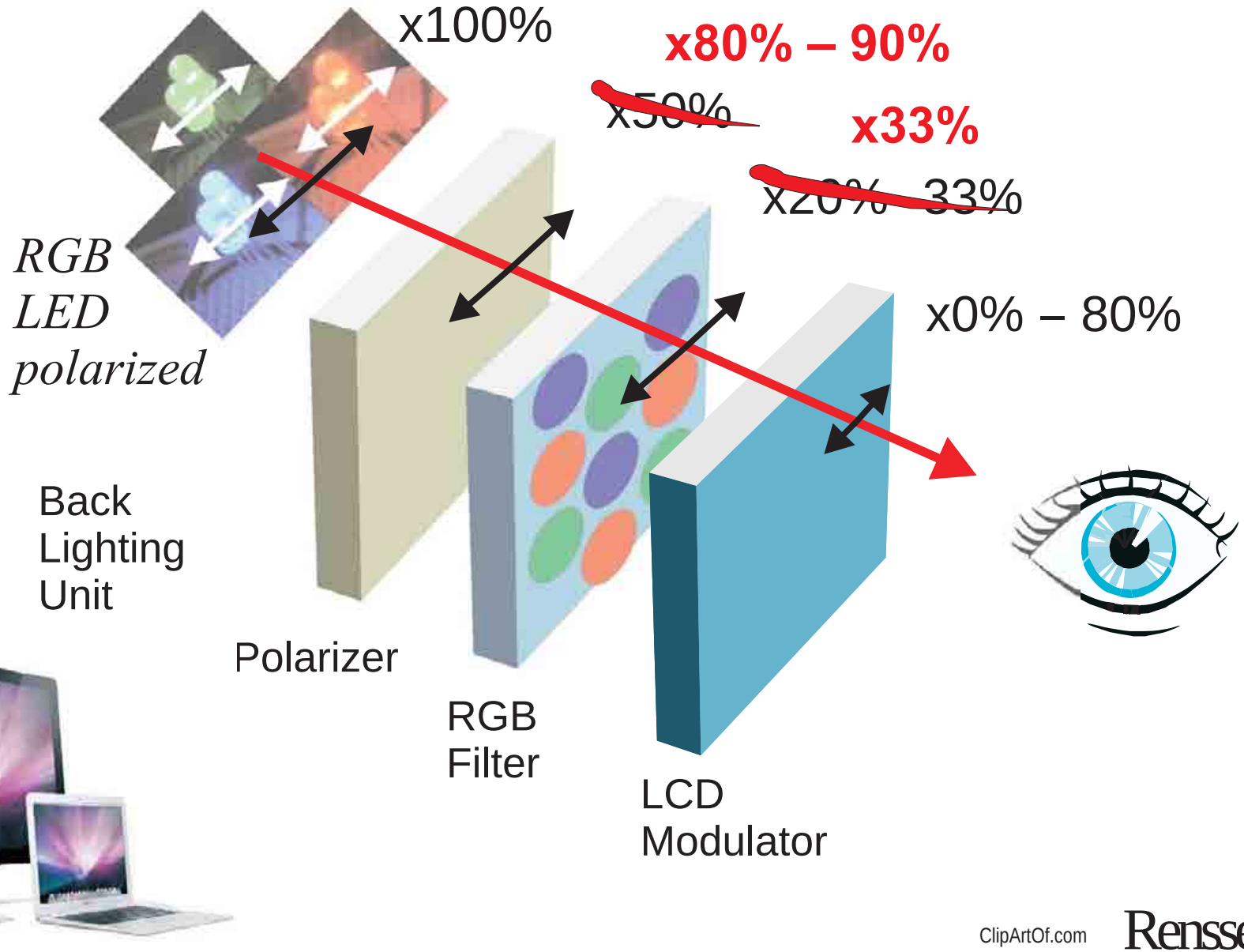
LCD Display Backlighting

polarization matters



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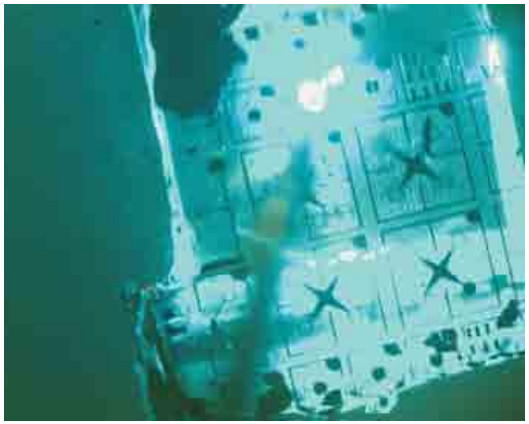
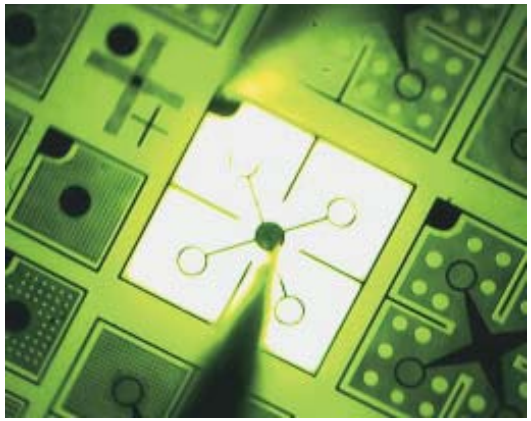
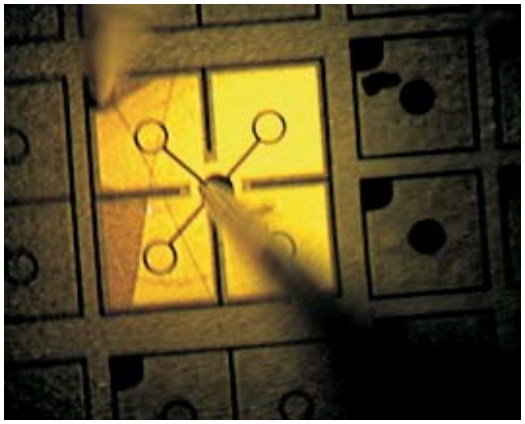
Bridging The Green Gap in LED Technology

GaInN/GaN alloy quantum wells

just add Indium!