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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Manager, Material Sustainability
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Niskayuna, NY

December 6, 2010
Rare Earth Based Phosphors in Fluorescent Lamps

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

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>Code</th>
<th>Color</th>
<th>Emission Wavelength</th>
<th>Nature</th>
<th>Rare Earth(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaMgAl_{10}O_{19}:Eu^{2+}</td>
<td>BAM</td>
<td>Blue</td>
<td>450 nm</td>
<td>Broad band</td>
<td>Eu</td>
</tr>
<tr>
<td>LaPO_{4}:Ce^{3+}, Tb^{3+}</td>
<td>LAP</td>
<td>Green</td>
<td>545 nm</td>
<td>Sharp line</td>
<td>La,Ce,Tb</td>
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<tr>
<td>Y_{2}O_{3}:Eu^{3+}</td>
<td>YEO</td>
<td>Red</td>
<td>610 nm</td>
<td>Sharp line</td>
<td>Y, Eu</td>
</tr>
</tbody>
</table>

Rare Earths in Fluorescent Lamps: Y, Eu, La, Ce and Tb
LED lighting & phosphor usage

Potential market for LED lighting

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

Phosphor usage

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)₅O₁₂:Ce³⁺ (1-5%)
(Ba,Sr,Ca)₂SiO₄:Eu²⁺ (1-5%)
Ca₃Sc₂Si₃O₁₂:Ce³⁺ (1-5%)
(Sr,Ca)₃(Al,Si)O₄(F,O):Ce³⁺ (0.5-2%)

Yellow-orange
(Ba,Sr,Ca)₂Si₅N₈:Eu²⁺ (1-10%)
(Li,Ca,Sr,Y)ₐ-SiAlON:Eu²⁺ (1-10%)

Red
(Ca,Sr)AlSiN₃:Eu²⁺ (1-5%)
K₂(Si,Ti)F₆:Mn⁴⁺
Mg-fluorogermanate:Mn⁴⁺
High Efficiency Phosphors with Reduced Rare Earth Content

Partha Dutta

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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
Rich History of Phosphors

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

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

Need for new blue excitable phosphors


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 °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

<table>
<thead>
<tr>
<th>Devices</th>
<th>Electrode</th>
<th></th>
<th>Phosphor</th>
<th></th>
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<tbody>
<tr>
<td>Fluorescent lamp</td>
<td>Electrode</td>
<td>W</td>
<td>Phosphor</td>
<td>Tb, Eu, Ce, Y, La, Mn</td>
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<tr>
<td>LED lighting device</td>
<td>LED</td>
<td>Ga</td>
<td>Phosphor</td>
<td>Eu, Ce, Y</td>
</tr>
<tr>
<td>Liquid Crystal</td>
<td>Electrode</td>
<td>In</td>
<td>Back light</td>
<td>Same as LED or fluorescent lamp</td>
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<tr>
<td>Plasma Display</td>
<td>Sealing glass</td>
<td>Bi</td>
<td>Electrode</td>
<td>In</td>
</tr>
<tr>
<td></td>
<td>Phosphor</td>
<td>Eu, Y, Tb, Mn</td>
<td>Phosphor</td>
<td>Eu, Y, Tb, Mn</td>
</tr>
</tbody>
</table>
• Yttrium Aluminum Garnet family: \((Y_{x}Gd_{1-x})_{3}(Al_{y}Ga_{1-y})_{5}O_{12}: Ce^{3+}, Pr^{3+}\) with \(0 < x < 1\)

• Most commonly used composition (for white LEDs): \(Y_{3}Al_{5}O_{12}: Ce^{3+}\)
  – Excitation peaks \(\sim 470\) nm, Broad emission with peak \(\sim 550\) 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: \(1400-1500\) °C
  – 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 °C rise up to \(200\) °C (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**: $M_xS_i_yN_z:Eu^{2+}, Ce^{3+}$; $M = Mg, Ca, Sr, Ba, Ln, Y, Yb, Al, Eu$
  - Excitation: 465 nm; Emission: 580-680 nm; Quantum efficiency: 80%, Superior thermal quenching property (few % up to 150 °C); 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
  - $(SrCa)_p/2Al_p+qSi_{12-p-q}O_qN_{16-q}:Eu^{2+}$ (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); $\beta$-SiAlON:$Eu^{2+}$ (Emission: 535 nm); $Ca\alpha$-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)
• **Alkaline earth metal silicates:**
  – $(\text{Ba}_{1-x-y}\text{Sr}_x\text{Ca}_y)\text{SiO}_4:\text{Eu}^{2+}$ series  \(\text{Ca}_3\text{MgSi}_2\text{O}_8: \text{Eu}^{2+}\),  
   \(\text{Sr}_3\text{MgSi}_2\text{O}_8: \text{Eu}^{2+}\),  
   \(\text{Ba}_3\text{MgSi}_2\text{O}_8: \text{Eu}^{2+}\),  
   \(\text{Ba}_2\text{MgZnSi}_2\text{O}_4: \text{Eu}^{2+}\),  
   \(\text{Li}_2\text{SrSiO}_4: \text{Eu}^{2+}\),  
   \(\text{A}_2\text{SiO}_4: \text{Eu}^{2+}\),  
   \(\text{D}\)  
   (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 °C

• **Sr$_3$SiO$_5$: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)
  - $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}^{2+}$ (Excitation: 400-580 nm; Emission: 635-655 nm); Lower quantum efficiency (80%) compared to thiogallates; highly prone to moisture
  - $\text{Ca}_{1-x}\text{Sr}_x\text{Se}:\text{Eu}^{2+}$ (Excitation: 400-500 nm; Emission: 564-608 nm); Lower quantum efficiency compared to thiogallates; prone to moisture
Other Garnets

- **Silicate garnet family:** $\text{M}_2\text{Q}_4\text{R}_4\text{O}_{12}: \text{Ce}^{3+}, \text{Eu}^{3+}$
  - 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)
    - $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}: \text{Ce}$ (excited $\sim 450$ nm, broad emission with peak $\sim 570$ nm)
    - $\text{BaY}_2\text{SiAl}_4\text{O}_{12}: \text{Ce}$

- **Vanadate garnet family:** $\text{Ca}_2\text{NaMg}_2\text{V}_3\text{O}_{12}: \text{Eu}^{3+}$
  - Better with UV-LED excitation, white light with high CRI
  - Thermal quenching above 100 °C
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 °C
- $YCa_3M_3B_4O_{15}$: $Eu^{3+}$ 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**: $(\text{SrMgCaBa})(\text{GaAlln})_2\text{S}_4 :\text{Eu}^{2+}$
  - $\text{SrGa}_2\text{S}_4 :\text{Eu}^{2+}$ (Excitation: 470 nm; Emission: 535 nm); Good color saturation; high efficiency $>$ 80%; Drop in efficacy by 90% beyond 100 °C; proper surface coating for avoiding moisture degradation; alloying with $\text{MgGa}_2\text{O}_4$ improves efficiency
  - $\text{CaGa}_2\text{S}_4 :\text{Eu}^{2+}$ (Emission: 560 nm); $\text{BaGa}_2\text{S}_4 :\text{Eu}^{2+}$ (Emission: 540 nm)

- **Metal sulfo-selenide thiogallates**: $\text{MA}_2(\text{S}_x\text{Se}_y)_4 :\text{B}$; $\text{MA}_4(\text{S}_x\text{Se}_y)_7 :\text{B}$; $\text{M}_2\text{A}_4(\text{S}_x\text{Se}_y)_7 :\text{B}$; (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.
  - $\text{SrGa}_2\text{Se}_4 :\text{Eu}^{2+}$ (Excitation: 380-475 nm; Emission: 560 nm); Good color saturation; high efficiency $>$ 80%; Drop in efficacy beyond 100 °C; 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
Our phosphor development focus is using high temperature melt/solution crystal growth processes.
Phase diagrams crucial for crystal growth
Non-Scattering Phosphor Substrate

- Melt grown substrate with graded composition \((\text{Sr}_x\text{Ca}_{1-x})\text{(Ga}_y\text{In}_{1-y})_2\text{S}_4:\text{Eu}^{2+}\) \((0 < x < 1; 0 < y < 1)\)

![Emission Spectrum](image)
Phosphor Plate (1 sq. cm area)

Full Spectrum White Light Source
Role of Surface Composition on Luminous Efficacy

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<th>Condition</th>
<th>Im/W</th>
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<td>850°C-2hr-H2</td>
<td>84.3</td>
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<tr>
<td>850°C-2hr-H2 (wash)</td>
<td>82.7</td>
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<tr>
<td>1000°C-2hr-H2 (wash)</td>
<td>43.7</td>
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<th>Condition</th>
<th>Ga/(Sr+Eu)</th>
<th>Se/(Sr+Eu)</th>
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<td>850°C-2hr-H2 (wash)</td>
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<tr>
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<td>850°C-2hr-H2</td>
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<td>850°C-2hr-H2 (wash)</td>
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<td>3.1</td>
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SrGa$_2$Se$_4$:Eu$^{2+}$
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

Micron Size Phosphors

Best 2007

75 lumens

Proposed HB LED

150 lumens

Transparent Nano phosphors

Courtesy: Ravi Rao, Xicato Inc.
Research in Japan on Reduction of Rare Earth Phosphor Usage in Lamps

80% Reduction of the usage of Tb and Eu for fluorescent lamps

Computer simulation
Search for new phosphors by combi-chem
Pilot manufacturing
Glass for efficient use of light in lamp

Lamp test
Reduction of use of phosphor in manufacturing
High-speed performance test

Courtesy: Dr. Tomoko Akai, AIST
Possible Ways to reduce Rare Earth Content in Phosphors

- Non-scattering Phosphor Matrix
- Transparent Y(V,P)O₄: Eu nano-films for plasma display panels
- Doped Quantum dots/nanoparticles (Mn doped ZnS, ZnSe, etc.)
- I-III-VI QDs (CuInS₂/ZnS)
- Co-doping with non rare earth metals for enhancing luminescence efficiency (Mg²⁺ doped SrSi₂O₂N₂:Eu²⁺)
- New rare-earth free phosphors (blue excitable, red emission La₂MgGeO₆:Mn⁴⁺; SiP₂O₇:Mn²⁺)
- 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

HOME and OFFICE
Adaptive Lighting

HEALTH
Personal Lighting

SENSING
Information

COMMUNICATIONS
Dual-Use

APPLICATIONS AND IMPACTS

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

Photonic Sources

Communications Control and External Interfaces

- Ubiquitous
- Self Adaptive
- Dynamic
- Reconfigurable
- Secured

Photonic Sensors

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

Photonic Sources

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Smart Lighting ERC Research

Stakeholders
- Lighting Industry
- Health Care Industry
- Transportation Industry
- Datacomm Industry

- Prototypes
- Design Standards
- Integration Protocols

Requirements
Products & Outcomes

Efficient Full Spectrum Lighting
Display Illumination Fusion System

Adaptive Lighting Systems
Healthy Lighting
Lighting for Data Communication

Human Factors
Adaptive Sampling & Control Model Theory

Light Flow Modeling

Communications Test Bed
Smart Space Test Bed
Biochemical Sensing Test Bed

Opto Electronic Device Design
Phosphor Crystal Optics
Nanotechnology LED Technology
Color-Selective Sensors

III-Nitride Epitaxy
High Efficiency Phosphors
Plasmonic Structures

BARRELS
- System Cost
- Lighting Designer Acceptance
- Light/RF Wireless Standards Integration
- Clinical Impacts

- Color and intensity uniformity maintenance
- Stray light impact on sensor SNR
- Lack of source/sensor communications protocols
- Biochmol-identification & discrimination

- Inefficient LEDs (except blue)
- Limited bandwidth of sources
- Lack of color discriminating sensors
- Lack of monolithic optoelectronic integration
Three Ways To Produce Warm White Light with LEDs

### RGB (Red, Green, Blue)
- **Pros:**
  - Tunable CCT, colors
  - Any color possible
- **Cons:**
  - Difficult to control
  - Low CRI (<70)
  - Lowest LPW efficacy (<40LPW*)

**CRI ~ 70**

### Blue + Yellow Phosphor
- **Pros:**
  - Single LED type
  - Easy to control
  - Easy secondary optics
- **Cons:**
  - OK CRI (~82)
  - OK efficacy (~40–50LPW*)

**CRI ~ 80**

### BSY + Red
- **Pros:**
  - Highest CRI (>90)
  - Highest efficacy (60-100LPW*)
- **Cons:**
  - Very complicated to control (proprietary technology)

**CRI = 92**
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?
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.
“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

  - 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
- Charge-injected active layers for “QD-LEDs”

- Example from Ziegler et al. Adv. Mater
- 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


Attempts to address the NQD blinking problem: ‘Antiblinking reagents’

**Charge mediators / compensators**

- Short-chain thiols
- Organic conjugated ligands
- Propyl gallate (‘antioxidant’)

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

<table>
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<th>Reference</th>
<th>EQE %</th>
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<td>R. A. M. Hikmet et al. J. Appl. Phys. 93, 3509 (2003) (UCB)</td>
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<td>H. Muller et al., Nano Lett. 5, 1039 (2005) (LANL)</td>
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<td>J.-M Caruge et al. Nat. Photon. 2, 247 (2008) (MIT)</td>
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<tr>
<th>Reference</th>
<th>EQE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>S. Core et al., Nature 420, 800 (2002) (MIT)</td>
<td>0.6%</td>
</tr>
<tr>
<td>S. Core et al., Adv. Funct. Mater. 15, 1117 (2005)</td>
<td>2.0%</td>
</tr>
<tr>
<td>P. O. Anikeeva et al., Nano Lett. 7, 2196 (2007) (MIT) (red)</td>
<td>2.0%</td>
</tr>
<tr>
<td>P. O. Anikeeva et al., Nano Lett. 7, 2196 (2007) (MIT) (green)</td>
<td>0.5%</td>
</tr>
<tr>
<td>P. O. Anikeeva et al., Nano Lett. 7, 2196 (2007) (MIT) (blue)</td>
<td>0.2%</td>
</tr>
<tr>
<td>Cho et al. Nature Photonics 3, 341 (2009)</td>
<td>2.5%</td>
</tr>
</tbody>
</table>
NQDs as “phosphors” with or without traditional phosphors for white-light emission: Not yet optimized

- Optically excited down converters for traditional blue LEDs

<table>
<thead>
<tr>
<th>Light source</th>
<th>(corr.) color temperature [K]</th>
<th>CRI</th>
<th>lum. efficacy [lm W⁻¹]</th>
<th>lifetime [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sunlight</td>
<td>5600</td>
<td>100</td>
<td>93</td>
<td>billions</td>
</tr>
<tr>
<td>tungsten light bulb</td>
<td>2790</td>
<td>100</td>
<td>&lt;18</td>
<td>1000</td>
</tr>
<tr>
<td>fluorescent lamp</td>
<td>3000–5000</td>
<td>50–80</td>
<td>50–100</td>
<td>10000</td>
</tr>
<tr>
<td>com. (prot) white-LED</td>
<td>3200–6500</td>
<td>70 (90)</td>
<td>30–70 (100)</td>
<td>50000</td>
</tr>
<tr>
<td>White-OLED (prot.)</td>
<td>no data</td>
<td>no data</td>
<td>(8)</td>
<td>(5000)</td>
</tr>
<tr>
<td>our white-LED with InP NCs</td>
<td>3200–6500</td>
<td>86</td>
<td>10–20</td>
<td>no data</td>
</tr>
</tbody>
</table>

- 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**

- **CdSe core**
- **Se-rich surface**

• **Cd(oleate)$_2$ @ 240°C**
  
  / NH(octyl)$_2$, ODE

• **S$_8$/octadecene @ 240°C**
  
  / same (single) pot

• **anneal**

• **Repeat n times**

- **Chen, Vela, & Hollingsworth et al. J. Am. Chem. Soc. 2008 (n<20)**
- **Mahler, et al. Nat. Mater. 2008 (n<10)**
  
  "CdSe/nCdS’, n>7

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

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

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

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**

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

\[ \begin{align*}
X_1^* & \quad X_2^* \\
X_3 & \quad X_4 \quad X_5 \quad X_6
\end{align*} \]

- Auger: Efficient and fast

- Conventional NQDs

- Low-T photoluminescence: Lowest exciton state emission

- Biexciton quantum yields of 90%!
Beyond blinking suppression: Transformational new physics from novel chemistry

- New pathways for electron $\rightarrow$ 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

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

![Diagram showing different core-shell configurations](image)

- Core-only
- Core/shell
- CdSe/CdS (Core/“giant” shell)

![Images of samples in hexane and water](image)

- Hexane 4CdS 12CdS
- Water 4CdS 12CdS

![Graph showing intensity and annealing time](image)

- Intensity (a.u.)
  - 550 λ(nm)
  - 700
  - 5 15 25 (min)

Operated by Los Alamos National Security, LLC for NNSA
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

Also suppression of non-radiative Auger recombination?

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All modes active in giant NQDs:

- Volume effect
- „Quasi-Type-II’ electronic structure
- Smooth interfacial confinement potential

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”
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
Combinatorial Approach to Phosphor Synthesis

HIGH-THROUGHPUT SOLID-STATE SYNTHESIS:
- 30 furnaces 1200°C
- 12 furnaces 1700°C
- PID controllers
- Different atmospheres (N₂, Ar, H₂/Ar, O₂/Ar)
- Labview control / interface to master database for data collection and analysis.

Luminescent compounds as synthesized and under UV illumination

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)

Material synthesis and characterization

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

Applications

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

(Ce3+)* electron state (5d)
LED Efficiency Limitation: “The Green Gap”

Strain-induced misfit dislocations

Polarization-induced electric fields

Semipolar III-Nitrides offer a solution to these issues

Semipolar III-Nitrides

Reduced polarization-related electric fields $\Rightarrow$ increased optical efficiency

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

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

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

- 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

1st LED results on strain-relaxed buffer layers
- without buffer layer: \( P_0 = 0.22 \text{ mW}, \lambda = 550\text{nm} \)
- with buffer layer: \( P_0 = 1.6 \text{ mW}, \lambda = 529\text{nm} \)
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 $\sim10^8$ 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
Most of research on luminescent QDs was carried out with bio-labeling in mind.

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?

Another approach: excitation routing

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

Dmitri Talapin, University of Chicago

*Science* 324, 1417 (2009)
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*

![Graph showing wavelength, relative intensity, and eye stimulus functions for blue, green, and red light.](image)

©2006 Philips Lumileds Lighting Company. AB08
Composite White Light Emitting Diode

*red-green-blue emitter*

![Graph showing relative intensity of red, green, and blue LED emitters compared to the solar spectrum and eye stimulus functions.](image)

- **T = 5500 K**
- **GaInN/GaN alloy quantum wells**
- **just add Indium!**

T = 5500 K

descriptor of solar spectrum

green LED

red LED

eye stimulus functions

blue

green

red

Wavelength (nm)

rel. Intensity

Fox Consulting

just add Indium!

GaInN/GaN alloy quantum wells

Future Chips Constellation

C. Wetzel

ledmuseum.candlepower.us

SMART LIGHTING
Composite White Light Emitting Diode

*red-green-blue emitter*
Wall Plug Efficiency

ranges of achievement

Wall Plug Efficiency (1)

Definition:

\[ \text{Wall Plug Efficiency} = \frac{P_{\text{Light out}}}{P_{\text{El. in}}} \]

III-Nitride Based LEDs

after R. Karlicek et al.
Polarized Light Emission

minimal losses when analyzed

Shi You, et al.,
LCD Display Backlighting

*polarization matters*

- **Fluorescent white**
  - x100%
  - x50%
  - x20%–33%
  - x0% – 80%

- **Back Lighting Unit**
- **Polarizer**
- **RGB Filter**
- **LCD Modulator**

C. Wetzel
LCD Display Backlighting

*polarization matters*

RGB LED

Back Lighting Unit

Polarizer

RGB Filter

LCD Modulator

x100%

x50%

x33%

x20% - 33%

x0% - 80%
LCD Display Backlighting

*polarization matters*

- RGB LED polarized
- Backlighting Unit
- Polarizer
- RGB Filter
- LCD Modulator

- x100%
- x80% – 90%
- x50%
- x33%
- x20% – 33%
- x0% – 80%
Bridging The Green Gap in LED Technology

GaInN/GaN alloy quantum wells

just add Indium!