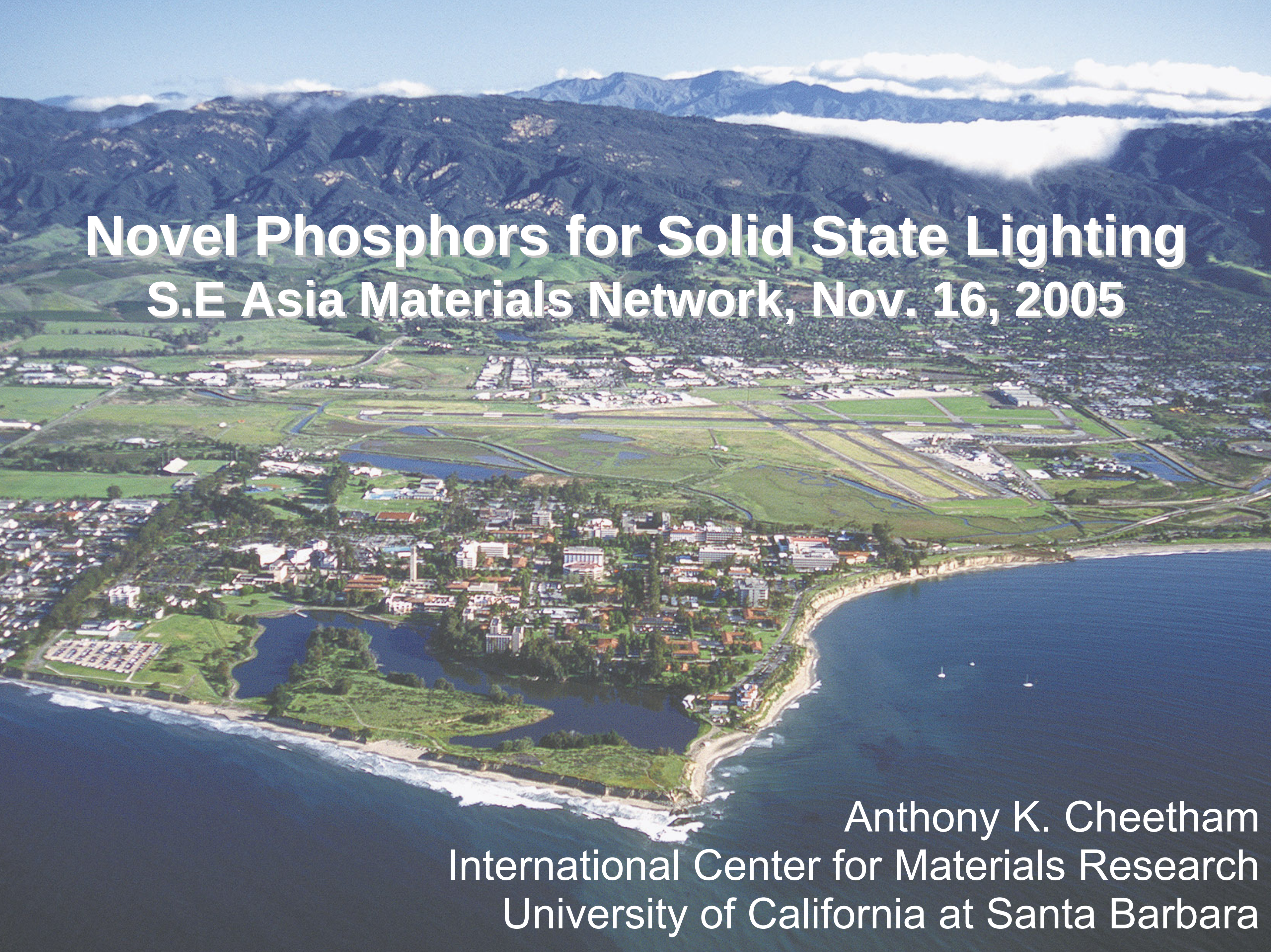
Novel Phosphors for Solid State Lighting

S.E Asia Materials Network, Nov. 16, 2005



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Overview of Cheetham Group Research
Functional Inorganic Materials

- **Open-framework materials**
  - Transition metal phosphates
    - catalysis, hydrogen storage, separation
  - Hybrid organic-inorganic materials
    - catalysis, magnetic and optical properties
- **Nanomaterials**
  - Polymer nanocomposites
    - functional nanoparticles of inorganics in polymers
  - Nanoparticle structure by PDF method
- **Biferroic and other magnetic materials**
  - e.g. ferroelectric/ferromagnetic $BiMnO_3$
- **Solid state lighting**
  - Novel phosphors for blue/near-UV down-conversion

OVERVIEW OF PHOSPHORS FOR SOLID STATE LIGHTING

- Developments in wide band gap LEDs based on GaN
- Motivation for solid state lighting
- Common strategies with blue and near-UV LEDs
- New phosphors based on cerium oxides and nitrides
- Conclusions and future developments

Two Classes of LEDs for SSL

- **Inorganic GaN and In/GaN Materials**
  - **Blue light was the missing color needed for full-color displays and white solid-state lighting**
  - **New options with near UV LEDs**
  - **Ideal for point source illumination**
  - **Recent LED efficiency improvements**
- **Organic LEDs (OLEDs)**
  - **All colors now available**
  - **Ideal for area illumination**
  - **Cheaper to manufacture**
  - **But poorer stability than inorganic LEDs**

    (20 k hours versus 100 k hours that is needed for SSL)

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LED Traffic Lights

- *85 - 90 % Electricity Savings*
- *5 + Year Life*
- *Maintenance Savings*
- *Tort Savings*

Philadelphia Replaced 14,000 Red Traffic Signals

Projected 5 Year Savings = $4.8 million

New Applications of Solid State Lighting

- Full color projection displays
- Backlighting for LCDs and cellphones
- Automotive
- Streetlighting

Off-Grid Lighting for Developing Countries by the Light Up The World Foundation (www.lutw.org)

Carl (left) , LUTW technician with his coworkers erect first demonstration lamp in one of the communities surrounding the Weichau Hippo Reserve, Ghana. 2004

Two Modular 1Watt Luxeon WLED lamps

12 Volt 7 Ah Sealed Lead Acid Battery – Rechargeable maintenance free battery

5 Watt Kyocera Solar Panel

100,000 hour lifetime

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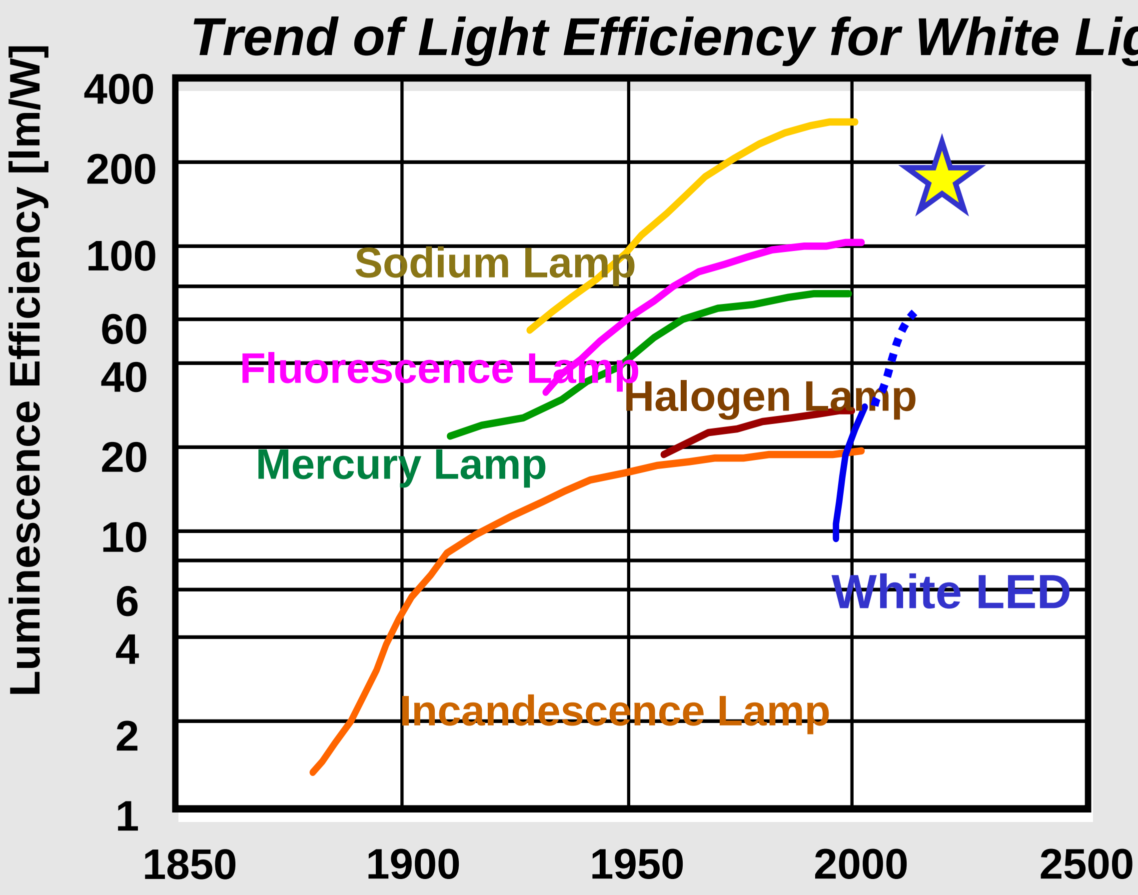
Lighting Efficiency

A key goal is to save energy by achieving greater efficiency:

Edison’s first lamp	1.4 lm/W
Incandescent lamps	15
Halogen incandescent lamps	20
Fluorescent lamps	70
Metal halide lamps	120
High Pressure sodium lamps	120
Solid State Lighting	Up to 200

Solid State Lighting



SSL Target
>200 lm/W

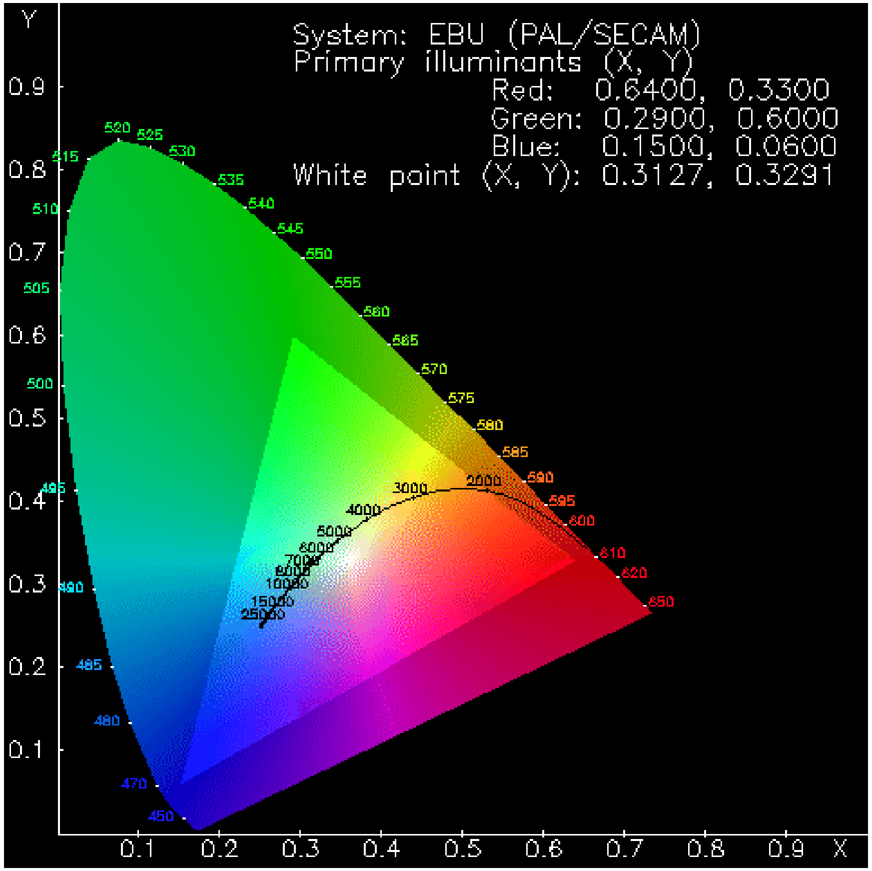
Currently
At ~100 lm/W

Solid State Lighting

Some important statistics and projections (US DOE 2004):

- Lighting consumes about 20% of the USA's electricity
- Solid state lighting has the potential to reduce energy consumption from lighting by ~30% by 2025
- That equates to ~6% of the nation's electricity consumption
- It would eliminate the need to build ~40 1000 MW power plants
- Most of the cost savings are in the Commercial sector, followed by Residential
- Savings should begin in ~2010
- The cost savings are approx. $15 billion per year by 2025
- The SSL market revenues are ~$10 billion per year by 2025

Chromaticity Diagram showing how white light can be obtained

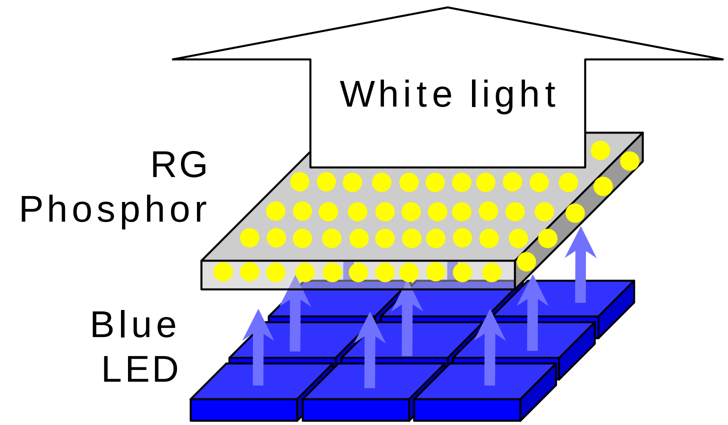


- Combination of red, green and blue phosphors can give good quality white light
- Combination of only two colors limits the possibilities
- The color rendering depends not only on the coordinates in the CIE diagram but also on the spectrum itself

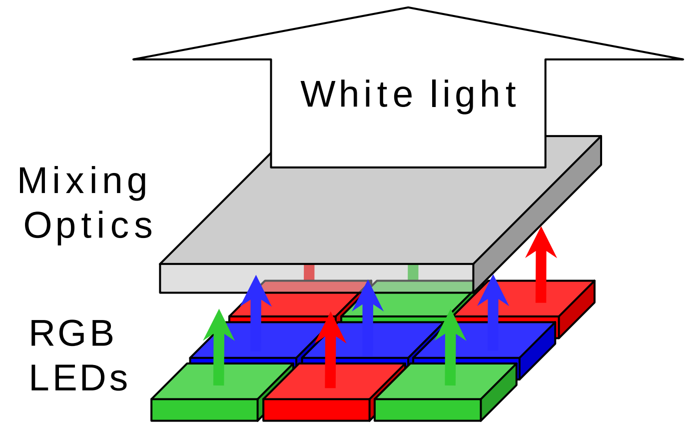
Common Strategies for Solid State Lighting

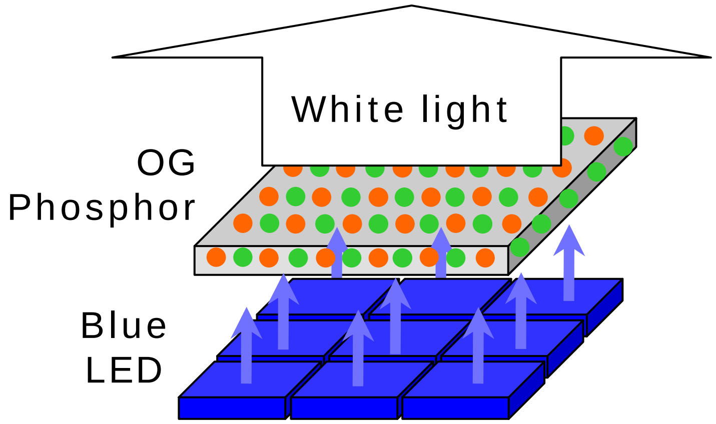
- Combination of red, green and blue LEDs
  - relatively expensive, but continuously tunable
- Blue LEDs plus yellow phosphor
  - already available, but modest color quality
- Blue LEDs plus red and green phosphors
  - better, but there are no good red phosphors
- Near UV LED plus red, green and blue phosphors
  - attractive, but needs new generation of phosphors

How to get white light with Blue/UV LEDs ?

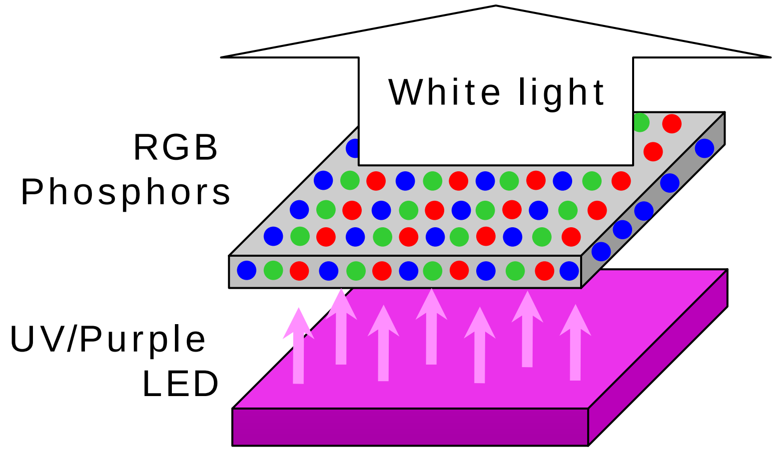


1st generation





2nd generation

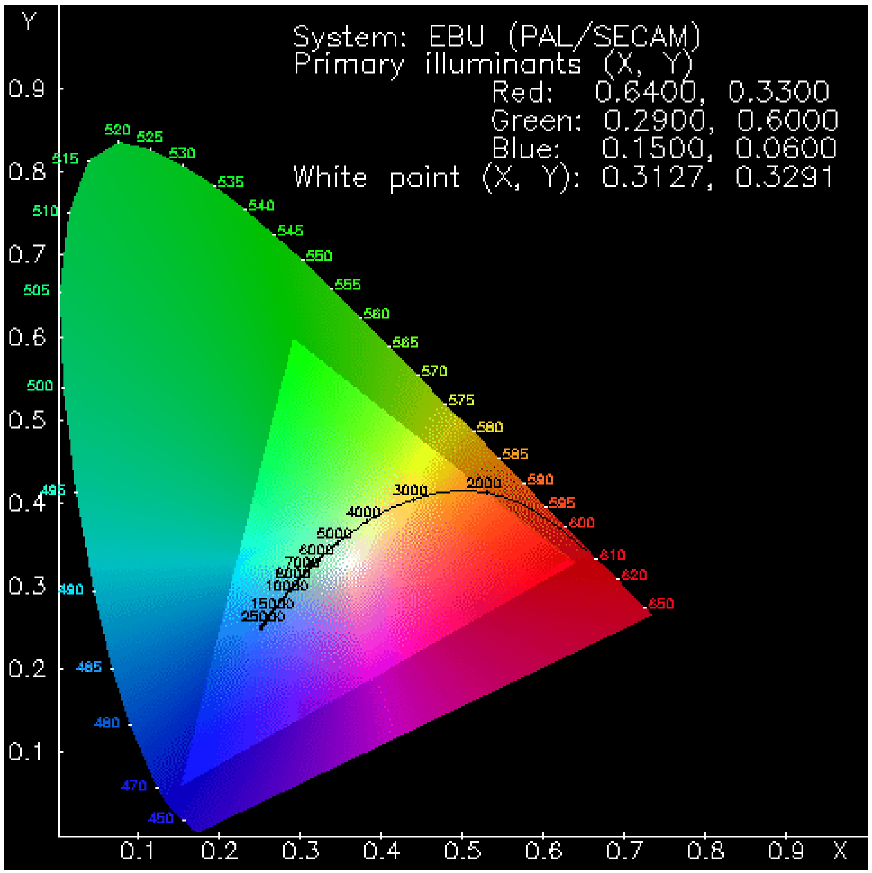


3rd generation

The blue LED plus YAG yellow phosphor strategy

- Systems of this type are already available and give a bluish-white light
- (In/Ga)N-based blue LEDs emit at ~465 nm
- A garnet phosphor containing Ce^{3+} (f^1) absorbs part of the blue through a broad $f^1 \rightarrow d^1$ transition at ~460 nm
- This decays by emitting a broad line in the yellow at ~540 nm
- The wavelength of this emission can be fine-tuned by appropriate substitutions in the garnet: $Ln_3M_5O_{12}$ (Ln=Y,Gd; M=Al,Ga)
- It cannot be tuned as far as the red
- We have studied the mechanism of this fine-tuning in a wide range of garnet phosphor compositions

Current Versions use a Blue InGaN LED combined with a YAG Phosphor



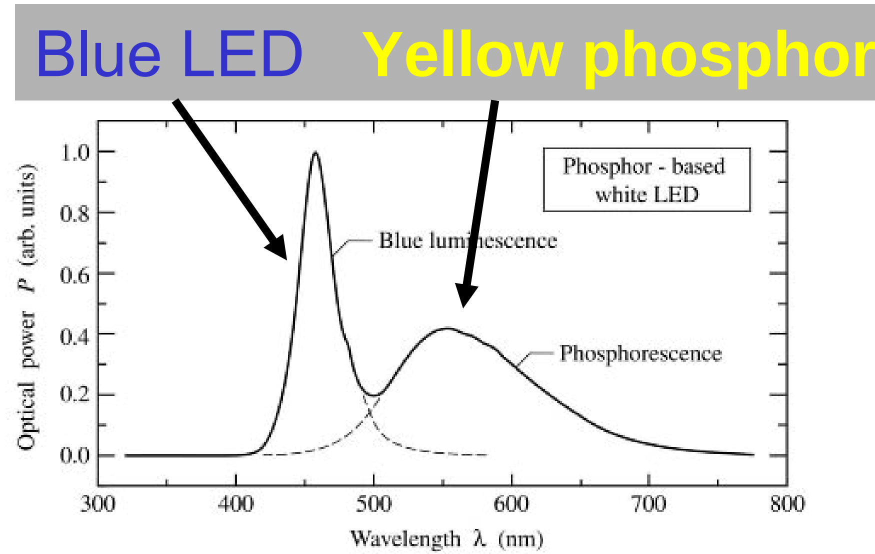
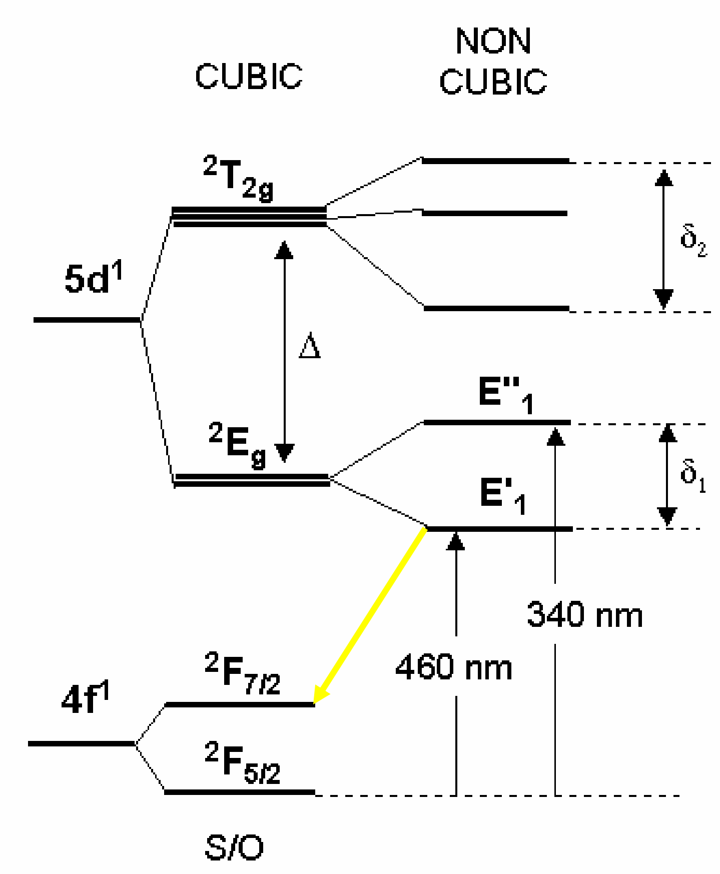


Fig. 11.6. Emission spectrum of a commercial phophor-based white LED manufactured by the Nichia Chemical Industries Corporation (Anan, Tokushima, Japan).

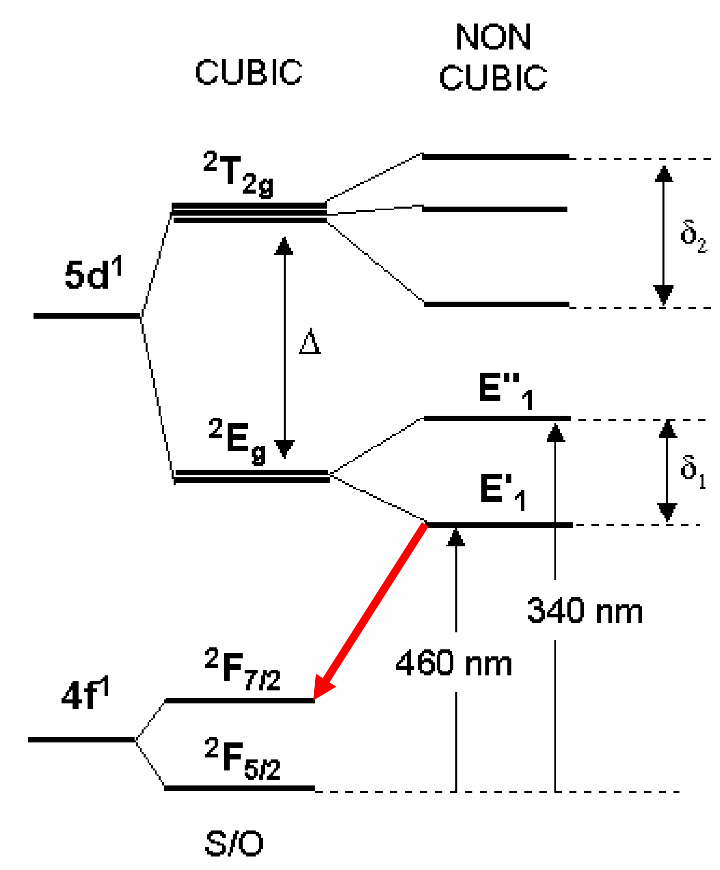
The yellow phosphor is based upon Ce^{3+}-YAG

How can we control the ligand field splitting?



By controlling the ligand field splitting in the excited state, we should be able to control the color of the emission....

Emission can be tuned towards the red if we increase the ligand field strength



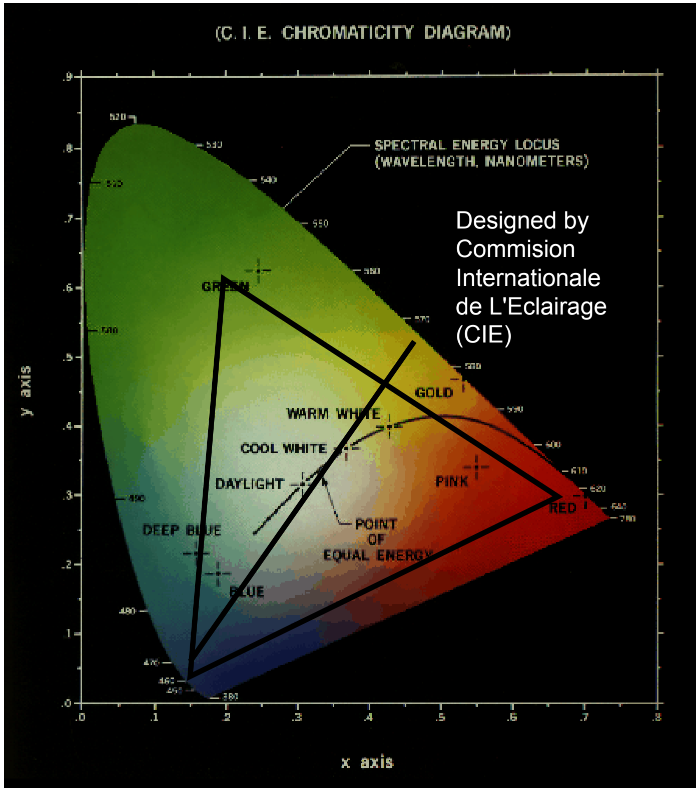
This can be achieved in a number of ways, e.g. by changing the symmetry or by using nitrides rather than oxides

The near-UV LED plus RGB phosphor strategy

- Systems of this type should give better quality white light
- Uses GaN-based LEDs that emit at ~380-400 nm
- New phosphors are required to down-convert this excitation into red, green and blue
- Optimum systems at present are:
  - $Y_2O_2S:Eu^{3+}$ for red
  - $ZnS:(Cu^{+}, Al^{3+})$ for green
  - $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) for blue
- The green and blue phosphors are about 8x more efficient than the red!
- The red phosphor has poor thermal and optical stability

Phosphors: Technical Requirements

- ✓ **High Quantum Efficiency (QE)**
  - **Optimize grain size for scattering**
  - **Composition and crystallinity**
- ✓ **Well matched to LED emission**
- ✓ **Appropriate PL lifetimes**
- ✓ **Good CRI indices (warmer light)**
- ✓ **Stability: water, UV (360 nm) and heat (200C), time**
- ✓ **Non toxic**
- ✓ **Low production cost**
- ✓ **IP protectable**



New Phosphor Options for Solid State Lighting

- Better yellow phosphors for blue LEDs
  - Garnets of type $Ln_3M_5O_{12}$ (Ln=Y,Gd; M=Al,Ga)
  - New systems based upon Ce^{3+} and Eu^{2+}
    - Eu;$Sr_2Si_5N_8$ from Schnick et al.
- New green and red phosphors for blue LEDs
  - Nitride phosphors containing upon Ce^{3+} and Eu^{2+}
- New red, green and blue phosphors for near UV systems
  - Quantum dots based upon CdSe
  - Mixed metal molybdates, tungstates and vanadates
  - Nitrides

Quantum Dots based on CdSe give Fluorescence under UV Excitation

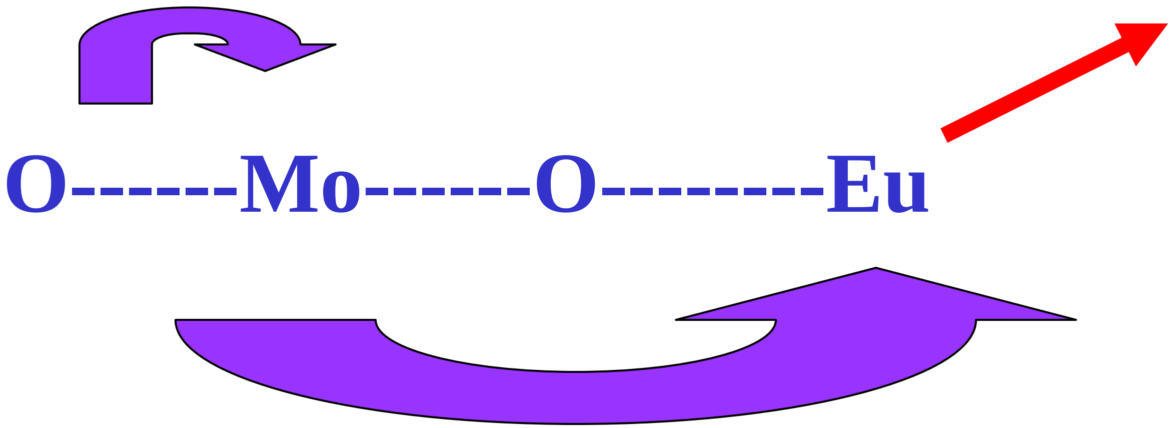
Color changes with the size of particles, but toxocity and stability issues make these undesirable

Reproduced From http://www.qdots.com/new/technology/what.html

Strategy for New Red Phosphors Excited in Near UV

- We have explored Eu^{3+}-doped materials with broad and intense charge-transfer (C-T) absorption bands in the near UV to capture the excitation from the GaN. Examples include vanadates, molybdates, tungstates.
- The C-T absorption bands can be further shifted to the near-UV and the visible by choice of materials, e.g. partial replacement of oxygen by sulfur or nitrogen, or rare–earth by bismuth
- We have studied new host candidates involving the rare earth elements as well as main group elements

Schematic Mechanism for Charge Transfer Phosphors



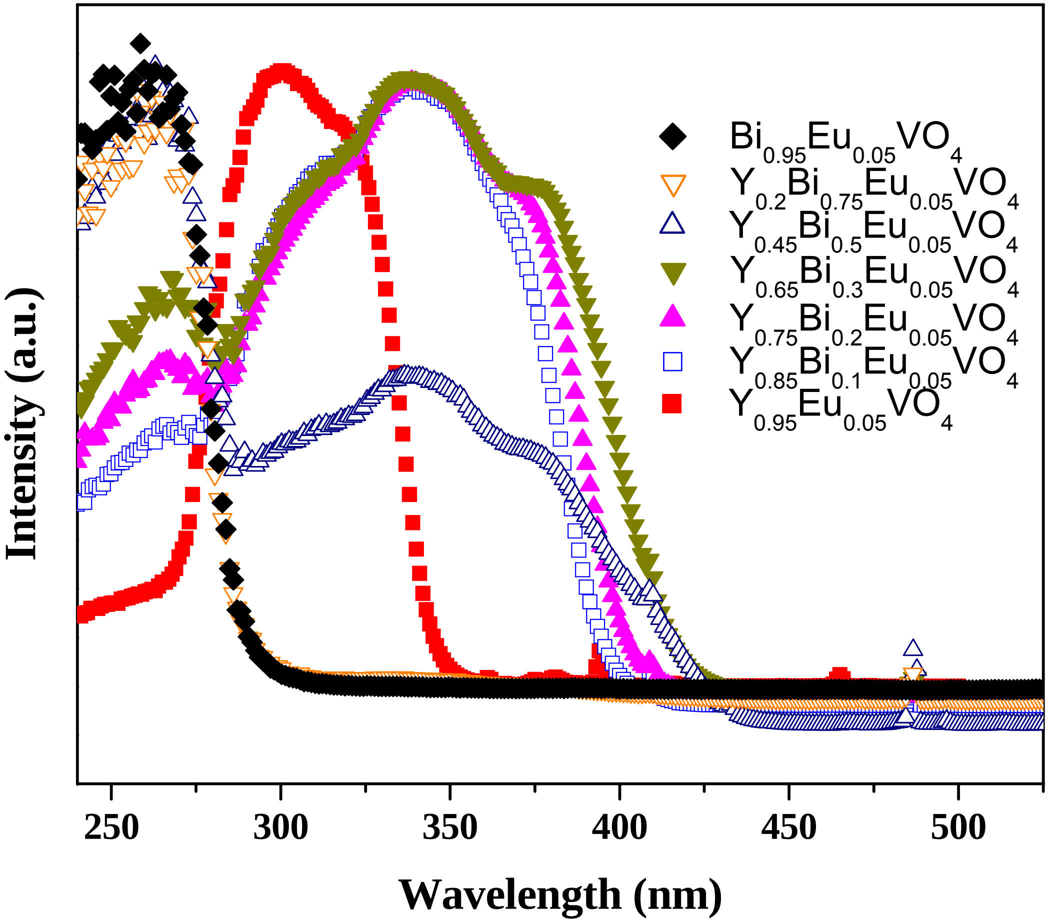
(1) Oxygen to Mo charge transfer in near UV

(2) Energy transfer from Mo to Eu *

(3) Internal transitions on Eu^{3+}

(4) Red emission from Eu^{3+}

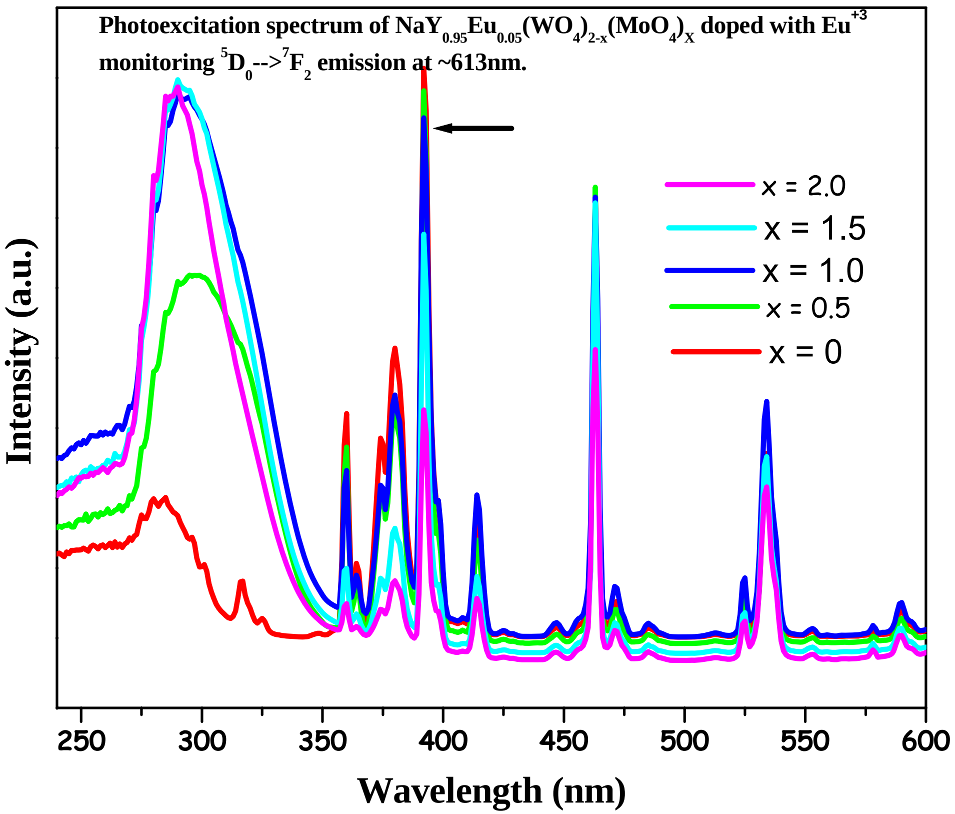
Photoexcitation Spectra of $Y_{1-x}Bi_xVO_4$ doped with Eu(III)



Composition	Emission Intensity λ_{exc} = 400nm
Y_2O_2S:Eu (standard)	1.0
$Y_{0.95}Eu_{0.05}VO_4$	0.13
$Y_{0.90}Bi_{0.05}Eu_{0.05}VO_4$	0.15
$Y_{0.85}Bi_{0.10}Eu_{0.05}VO_4$	0.12
$Y_{0.75}Bi_{0.20}Eu_{0.05}VO_4$	0.72
$Y_{0.70}Bi_{0.25}Eu_{0.05}VO_4$	0.77
$Y_{0.65}Bi_{0.30}Eu_{0.05}VO_4$	1.2
$Y_{0.60}Bi_{0.35}Eu_{0.05}VO_4$	0.81
$Y_{0.55}Bi_{0.40}Eu_{0.05}VO_4$	0.97
$Y_{0.50}Bi_{0.45}Eu_{0.05}VO_4$	0.71

Neeraj, Kijima & Cheetham, Solid State Comm. 131, 65 (2004)

Excitation Spectra of Eu^{+3} doped $NaY(WO_4)_{2-x}(MoO_4)_x$

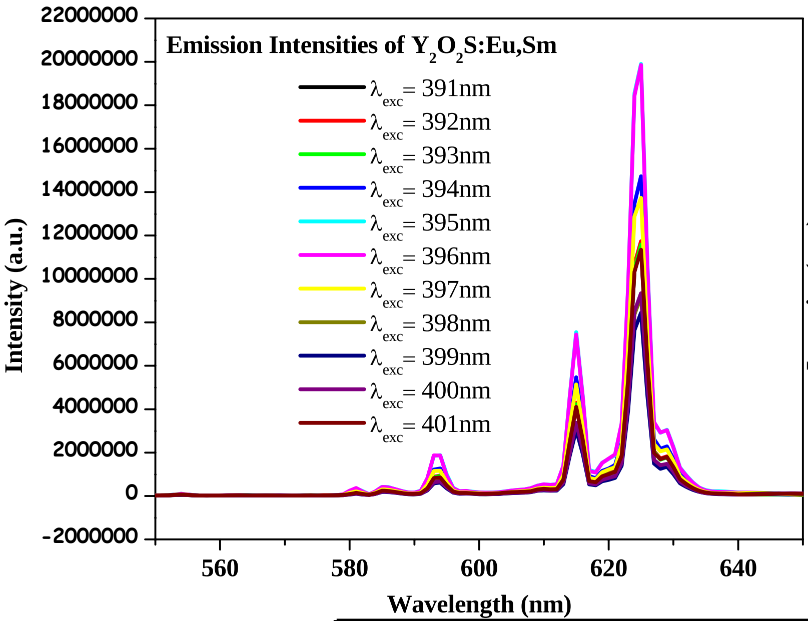


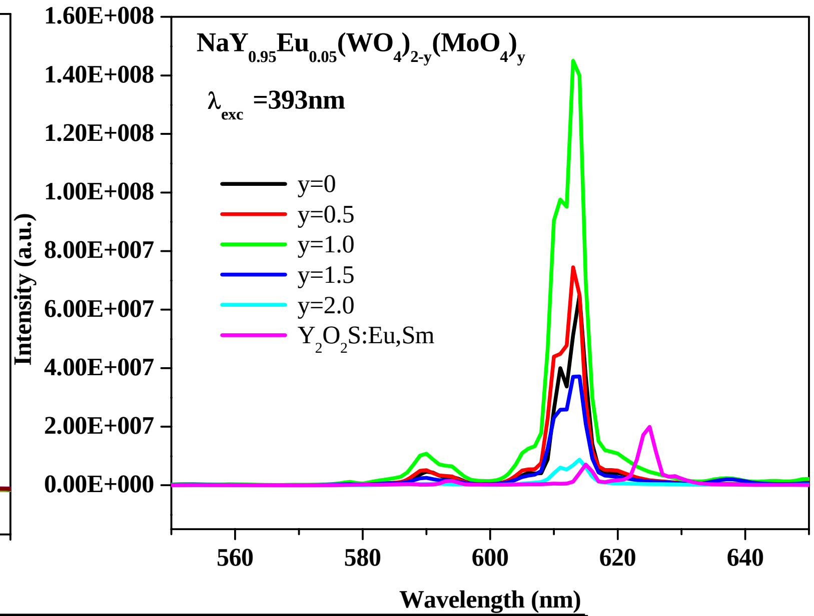
Composition	Emission Intensity, 400nm
Y_2O_2S:Eu (standard)	1.0
$NaY_{0.95}Eu_{0.05}(WO_4)_2$	0.65
$NaY_{0.95}Eu_{0.05}(WO_4)_{1.75}(MoO_4)_{0.25}$	0.65
$NaY_{0.95}Eu_{0.05}(WO_4)_{1.50}(MoO_4)_{0.50}$	0.59
$NaY_{0.95}Eu_{0.05}(WO_4)_{1.25}(MoO_4)_{0.75}$	0.78
$NaY_{0.95}Eu_{0.05}(WO_4)(MoO_4)$	0.74
$NaY_{0.95}Eu_{0.05}(WO_4)_{0.75}(MoO_4)_{1.25}$	0.67
$NaY_{0.95}Eu_{0.05}(WO_4)_{0.50}(MoO_4)_{1.50}$	0.68
$NaY_{0.95}Eu_{0.05}(WO_4)_{0.25}(MoO_4)_{1.75}$	0.76
$NaY_{0.95}Eu_{0.05}(MoO_4)_2$	0.63

The excitation spectrum shows a strong $^7F_0 \rightarrow {}^5L_6$ band at 394nm, which has comparable intensity to that of O→ Mo LMCT bands

Neeraj, Kijima & Cheetham, Chem. Phys. Lett. 387, 2-6 (2004)

PL with Excitation at 393 nm of Eu^{+3} doped $NaY(WO_4)_{2-x}(MoO_4)_x$





Composition	Emission Intensity λ_{exc} = 393nm
Y_2O_2S:Eu,Sm (standard)	1
$NaY_{0.95}Eu_{0.05}(WO_4)_2$	3.25
$NaY_{0.95}Eu_{0.05}(WO_4)_{1.50}(MoO_4)_{0.50}$	3.74
$NaY_{0.95}Eu_{0.05}(WO_4)(MoO_4)$	7.28
$NaY_{0.95}Eu_{0.05}(WO_4)_{0.50}(MoO_4)_{1.50}$	1.87
$NaY_{0.95}Eu_{0.05}(MoO_4)_2$	0.44

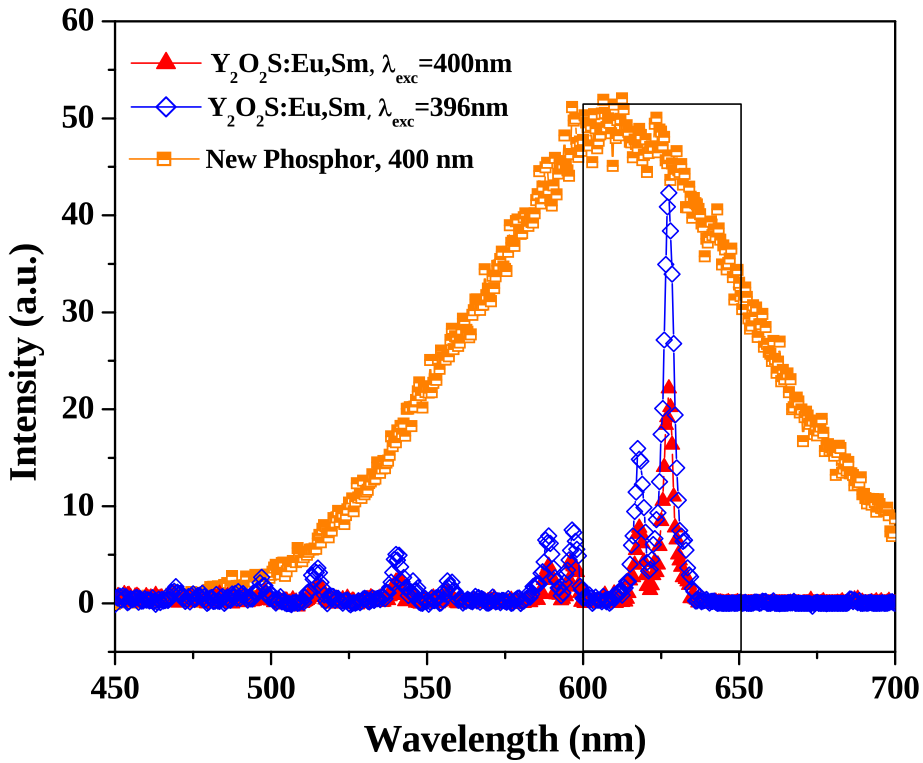
PL with Excitation at 394 nm of Eu^{+3} doped $NaY(WO_4)_{2-x}(MoO_4)_x$

- Excitation via the <u>sharp</u> Eu^{3+} $^7F_0 \rightarrow {}^5L_6$ line at 394 nm increases the efficiency by eliminating the energy transfer process from the molybdate to the rare-earth.
- All the action takes place on the Eu^{3+} ion.
- Since the excitation is very sharp, this is good with laser diodes but not with LEDs which have broad emission

Composition	Emission Intensity λ_{exc} = 393nm
Y_2O_2S:Eu,Sm (standard)	1
$NaY_{0.95}Eu_{0.05}(WO_4)_2$	3.25
$NaY_{0.95}Eu_{0.05}(WO_4)_{1.50}(MoO_4)_{0.50}$	3.74
$NaY_{0.95}Eu_{0.05}(WO_4)(MoO_4)$	7.28
$NaY_{0.95}Eu_{0.05}(WO_4)_{0.50}(MoO_4)_{1.50}$	1.87
$NaY_{0.95}Eu_{0.05}(MoO_4)_2$	0.44

Advantages of Ce^{3+} (and Eu^{2+}) compared with the charge transfer systems

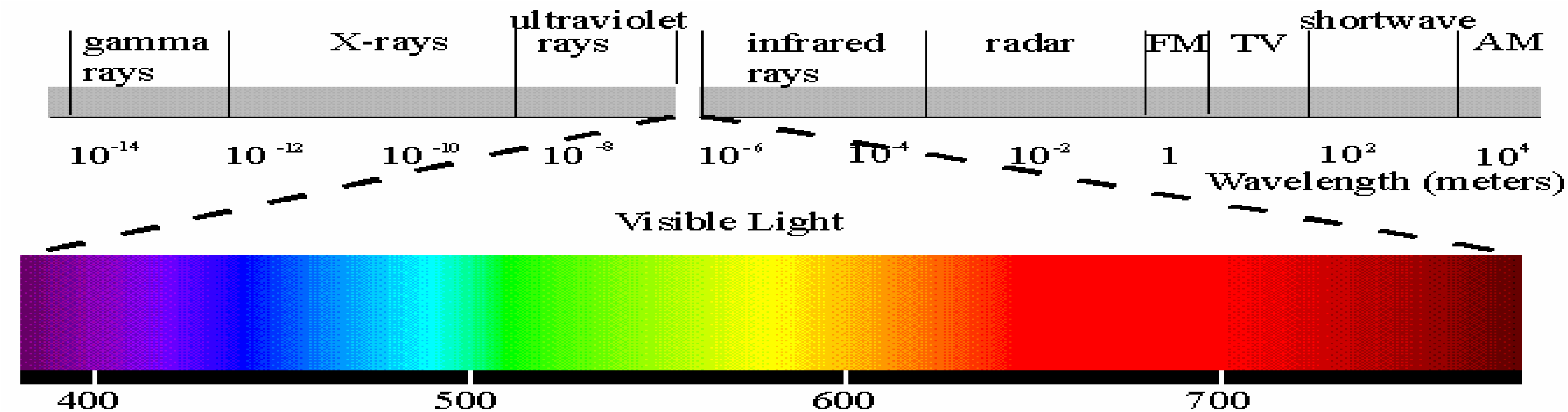
- The ions have f -> d rather than f -> f transitions.
- These are broader than f->f transitions
- They are more intense than f->f transitions
- They are more tunable than f->f transitions
- They are more efficient because excitation and emission is on the same ion



TERNARY NITRIDE PHOSPHORS FOR SOLID STATE LIGHTING

M-Si-N [M=(Mg, Ca, Sr, Ba, Ln, Y)]		M-Al-N [M=(Mg, Ca, Sr, Ba)]	
M_4SiN_4 $M_5Si_2N_6$ **$MSiN_2$** MSi_7N_{10} **$M_2Si_5N_8$** $SrSi_7N_{10}$ $M_3Si_6N_{11}$	$M_4Si_6N_{11}$ $Y_6Si_3N_{10}$ $Y_2Si_3N_6$ MSi_3N_5 $M_9Si_{11}N_{23}$ $M_2Si_4N_7$	**$MAlSiN_3$** α-$Ca_3Al_2N_4$ β-$Ca_3Al_2N_4$	$Sr_3Al_2N_4$ $Ca_6Al_2N_6$
M-Ge-N **[M=(Ca, Sr)]**		**M-Ga-N** **[M=(Mg, Ca, Sr)]**	
Ca_2GeN_2 Ca_4GeN_4 $Ca_5Ge_2N_6$	$Sr_{11}Ge_4N_6$ Sr_3GeMgN_4 $Li_4Sr_3Ge_2N_6$	**$Sr_3Ga_2N_4$** **$Sr_3Ga_3N_5$** Sr_3GaN_3 Sr_6GaN_5 $(Sr_6N)[Ga_5]$	$LiSrGaN_2$ $Ca_3Ga_2N_4$ α-$Ca_3Ga_2N_4$ $Ba_6N)[Ga_5]$

Eu^{2+}- based phosphors



Nitrides

- $M_xSi_yN_z$ M= Ca,Sr,Ba
- $Sr_3Al_2N_4$ orthorhombic
- $Sr_3B_2N_4$ cubic
- $CaSi_{10}Al_2N_{16}$ 560-580 nm
- $Sr_3Ga_2N_4$ monoclinic

Oxy-nitrides

- $MSi_2O_{2-x}N_{2+2/3x}$ monoclinic
  Ba: 490-500 nm,
  Ca: 560 nm,
  Sr: 530-570 nm

Oxides

- Sr_2SiO_4 orthorhombic 550 nm
- $SrGa_2O_4$ Monoclinic 400 nm
- $SrAl_2O_4$ Monoclinic 540 nm

Sulfides

- $SrGa_2S_4$ orthorhombic 540 nm

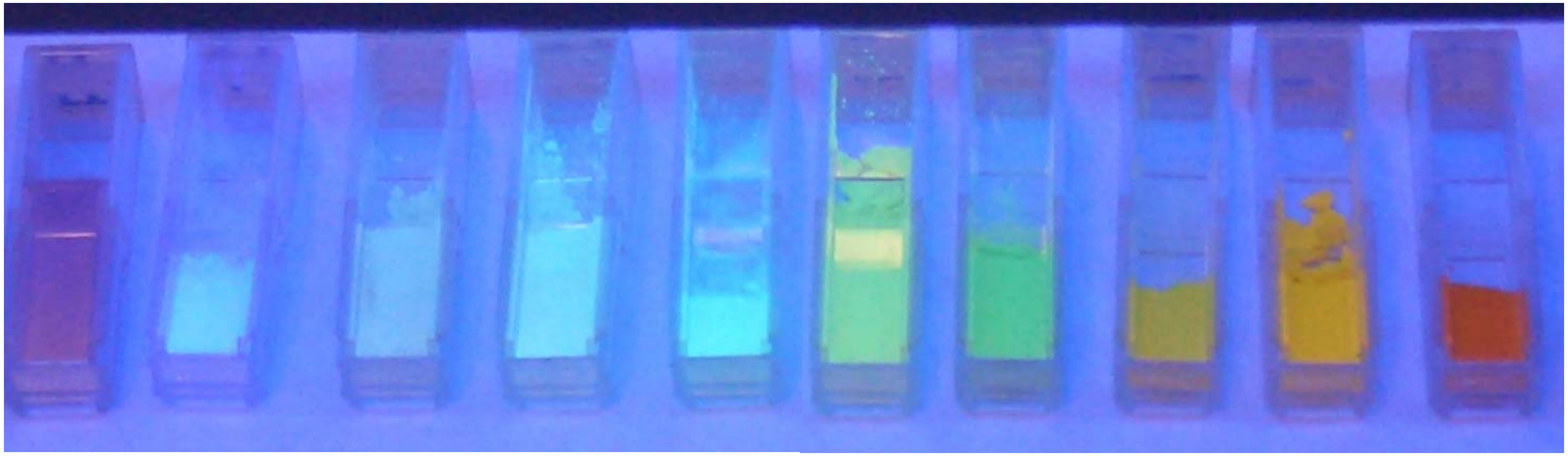
New Nitride Phosphor Materials from UCSB

New Cerium based phosphor materials IP protected:

- New Blue-Green phosphor for excitation in the near UV
- New Green phosphor for excitation in the Blue
- New Yellow phosphor for excitation in the near UV or Blue
- New Orange phosphor for excitation in the Blue
- New Red phosphor for excitation in the Green

New phosphor materials from UCSB

phosphor materials under normal light



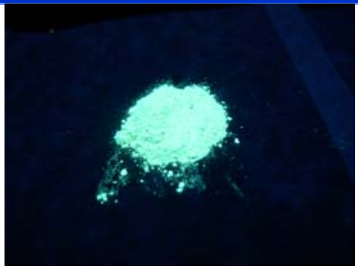
phosphor materials under UV light 360 nm

UV LED (380 nm) + phosphors

Next steps: Optimization of doping concentration, layer thickness, phosphor proportion

New Blue-green Phosphor for Excitation In The Near UV

Ce doped Sr-Si-O-N



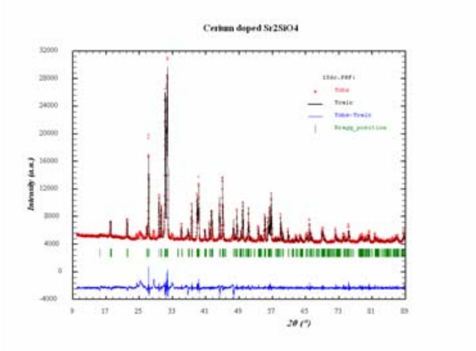
1st step: formation of reactive SrO powder

$$Sr(NO_3)_2 + \varepsilon\, Ce(NO_3)_3 + (NH_4)_2C_2O_4 \rightarrow SrC_2O_4 + \varepsilon Ce_2(C_2O_4)_3$$

$$SrC_2O_4 + \varepsilon\, Ce_2(C_2O_4)_3 \rightarrow Sr_{1-\varepsilon}Ce_\varepsilon O$$

2nd step: High temperature synthesis 1400˚C under N_2

$$2\, Sr_{1-\varepsilon}Ce_\varepsilon O + TEOS + Si_3N_4 \rightarrow Sr_{2-2\varepsilon}Ce_{2\varepsilon}SiO_{4-\delta}N_\delta$$



X-ray powder diffraction

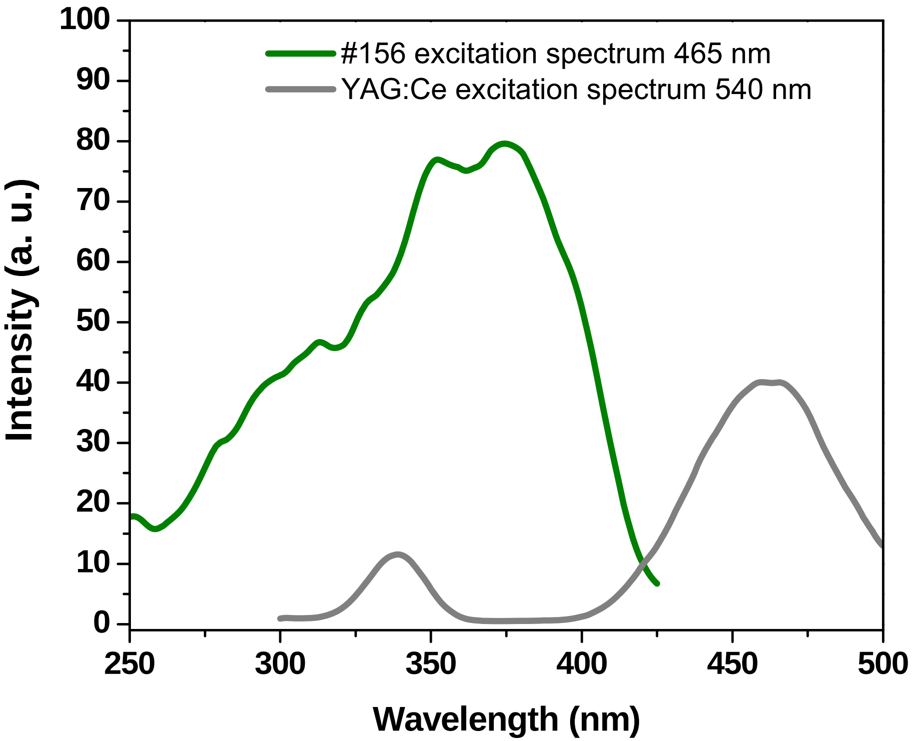
orthorhombic structure

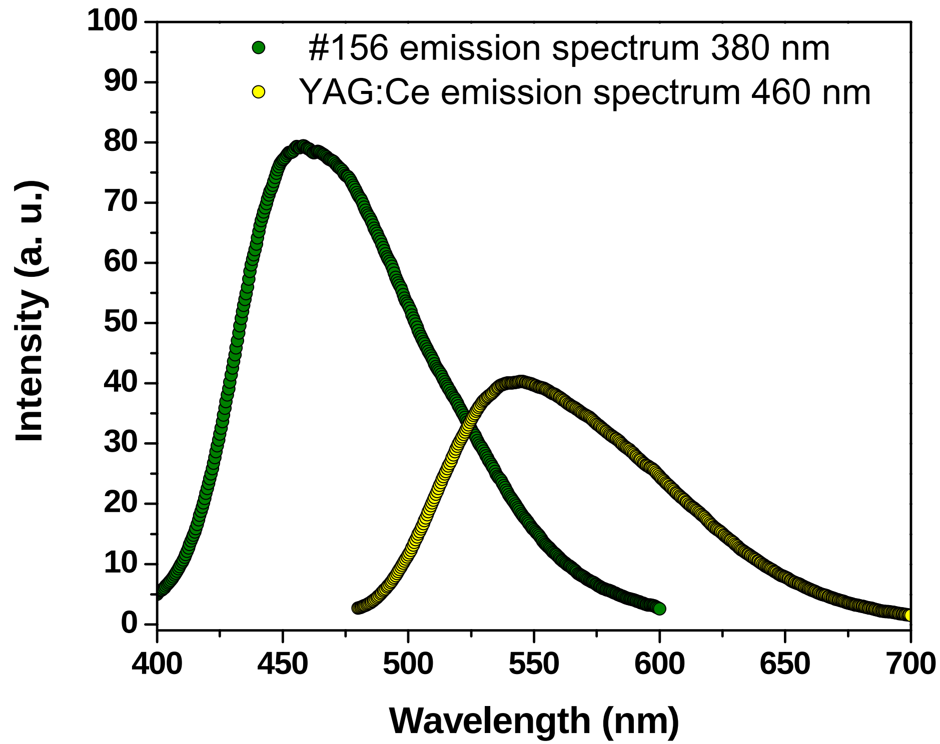
space group Pmnb unit cell parameters

a= 5.667(1) Å, b=7.074(1) Å, c=9.736 (2) Å

New Blue-green Phosphor For Excitation In The Near UV

Ce doped Sr-Si-O-N

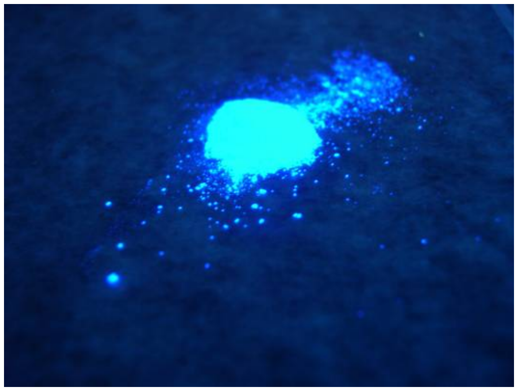




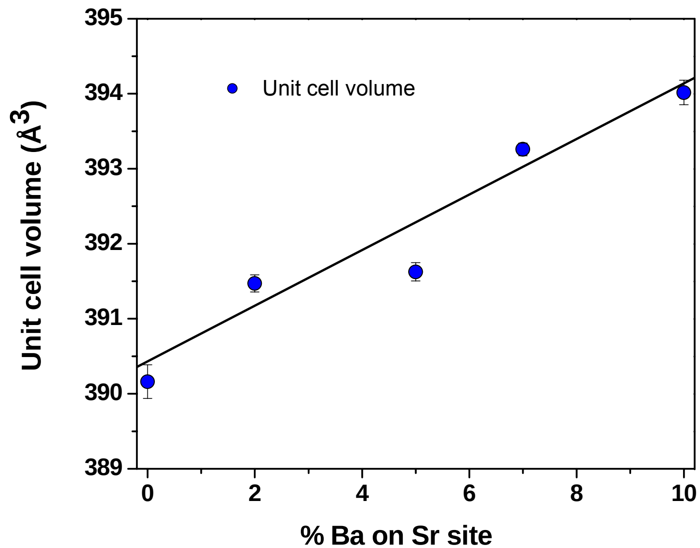
Excitation at 380 nm and emission at 470 nm

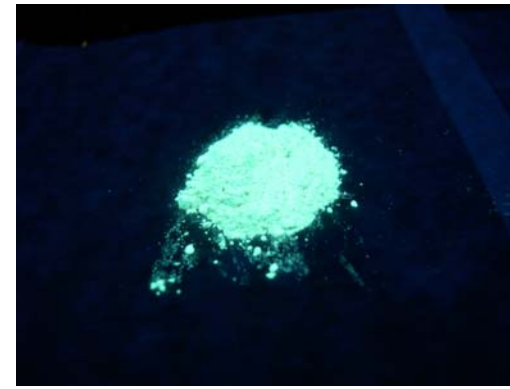
Intensity much larger than YAG:Ce at its best

New Blue-green Phosphor For Excitation In The Near UV



Phosphor under 360 nm UV light
Pure Sr sample





Phosphor under 360 nm UV light
10% of Ba on Sr site

Radius:

r_{Sr2+}=1.26 Å

r_{Ba2+}=1.48 Å

	Emission λ (nm)
ED-3 (1% Ba substitution)	482
ED-19 (5% Ba substitution)	505
ED- 51 (10% Ba substitution)	525

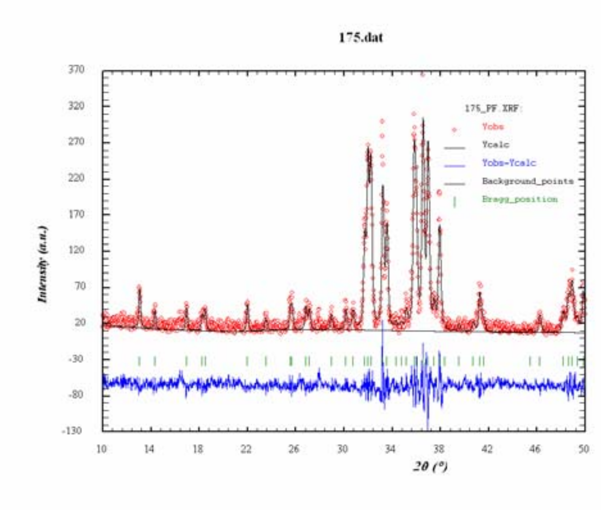
New Yellow Phosphor Material For Excitation In The Near UV

Ca-Al-Si-N system

Weighting and Grinding in glove box

Heating in N_2 between 1250 to 1450°C
CeN as cerium source

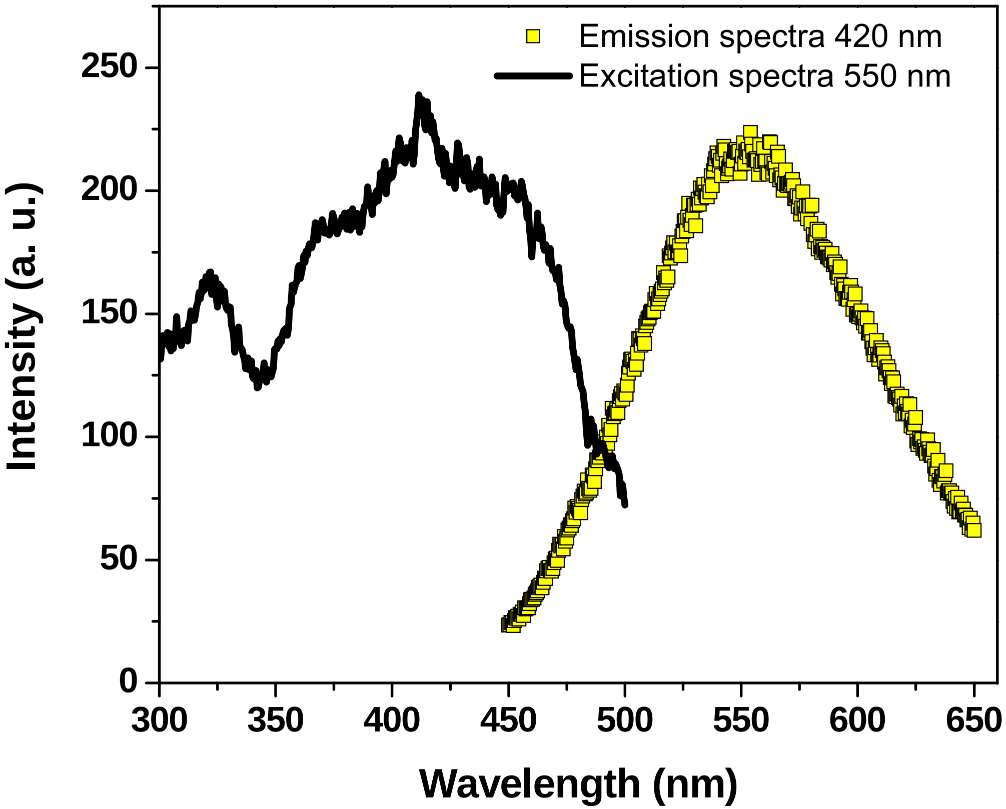
$$Ca_3N_2 + Si_3N_4 + 3\,AlN \rightarrow 3\,CaAlSiN_3$$



Phase reported as $CaAlSiN_3$
X-ray powder diffraction
orthorhombic structure
space group C222
unit cell parameters
a= 5.63 Å, b=9.58 Å, c=4.98 Å

New Yellow Phosphor Material For Excitation In The Near UV

Ca-Al-Si-N system



- ✓ Excitation band from 370 to 430 nm
- ✓ Maximum emission for λ=420 nm
- ✓ Emission peak at 550 nm

New Yellow Phosphor Material For Excitation In The Blue

New phase in the Ca-Al-Si-N system

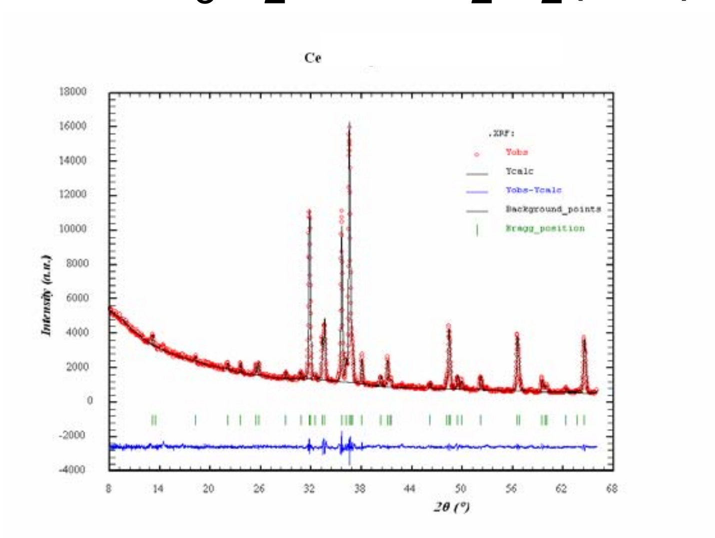
Weighting and Grinding in glove box

Heating in H_2/N_2 (5%/95%) between 1250 to 1600°C

CeN as a cerium source

$$2\ Ca_3N_2 + 3\ Si_2N_2(NH) + AlN \rightarrow 6\ Ca_xAl_ySi_zN_3 + NH3$$

with x≈y≈z≈1



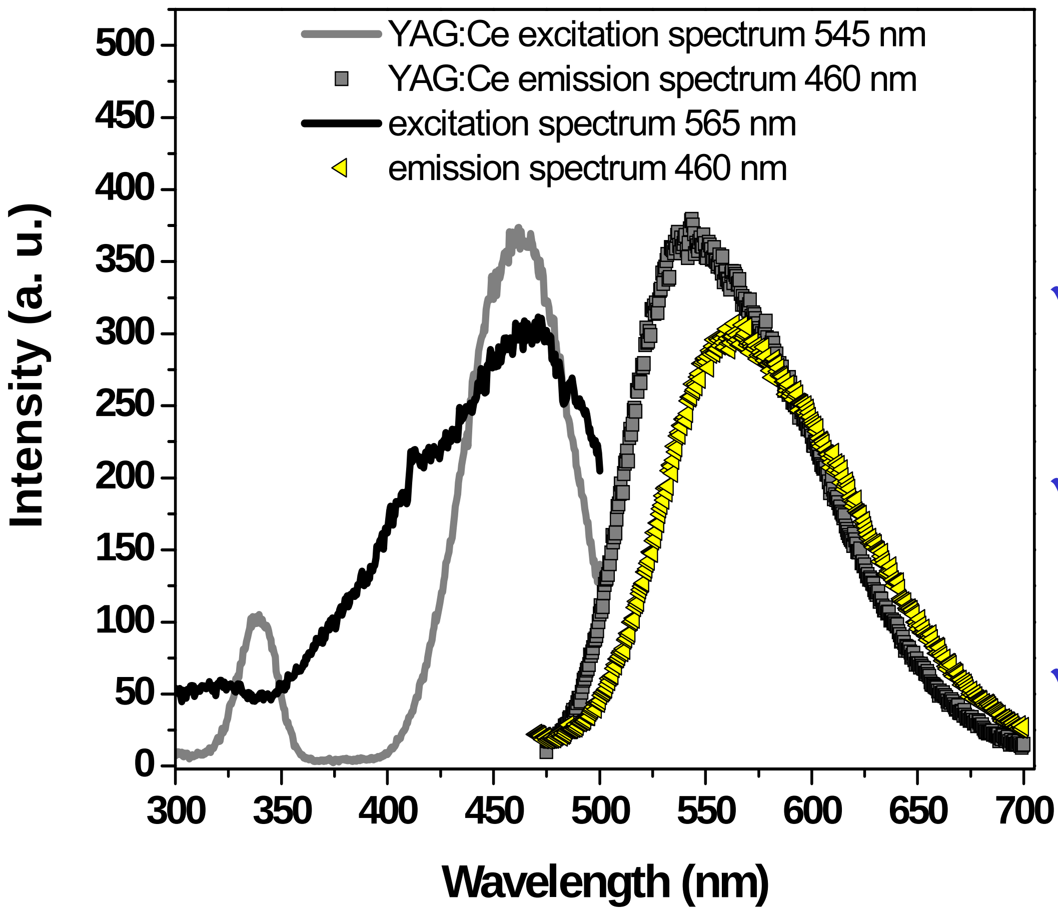
X-ray powder diffraction

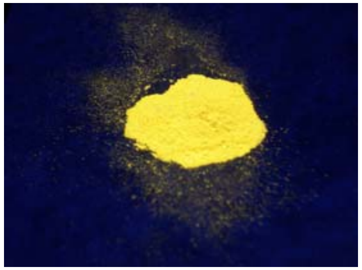
orthorhombic structure

unit cell parameters

a= 9.92 Å, b=9.11 Å, c=7.33Å

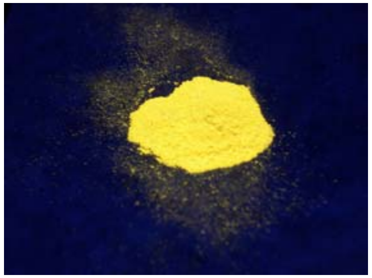
New Yellow Phosphor Material For Excitation In The Blue



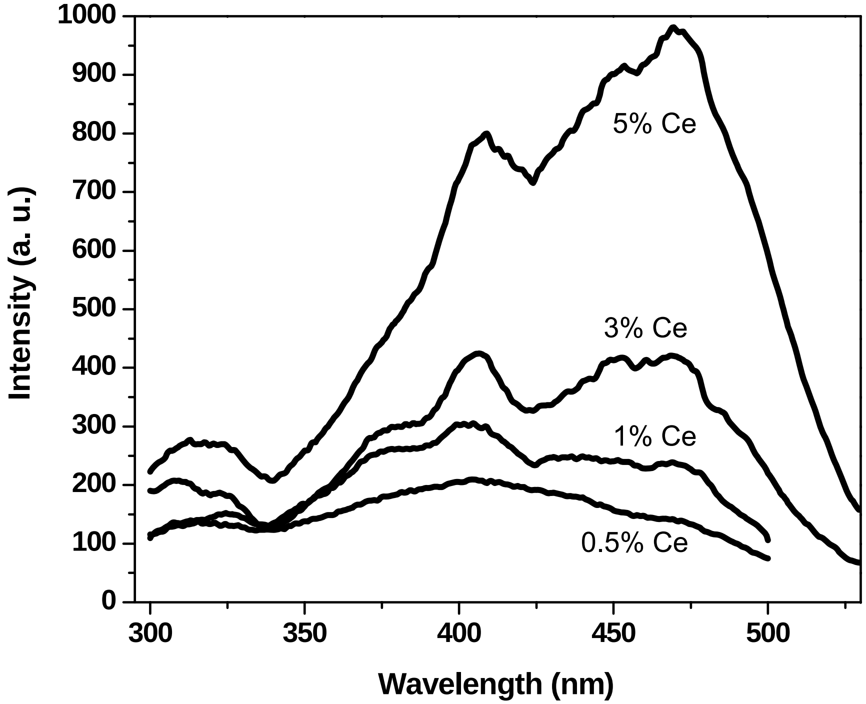


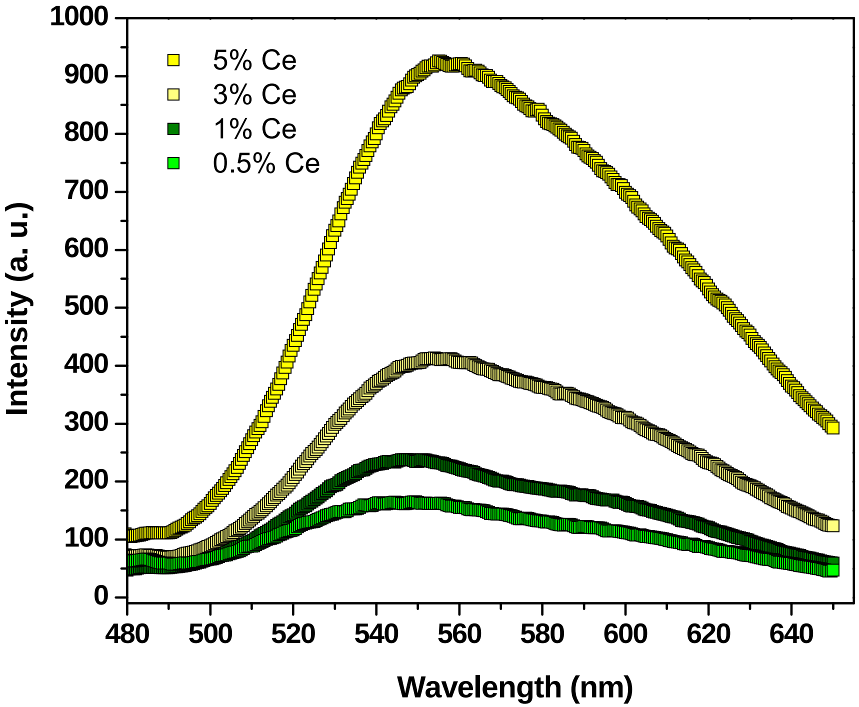
- ✓ Excitation band from 400 to 475 nm
- ✓ Maximum emission for λ=460 nm
- ✓ Emission peak at 565 nm

New Yellow Phosphor Material For Excitation In The Blue

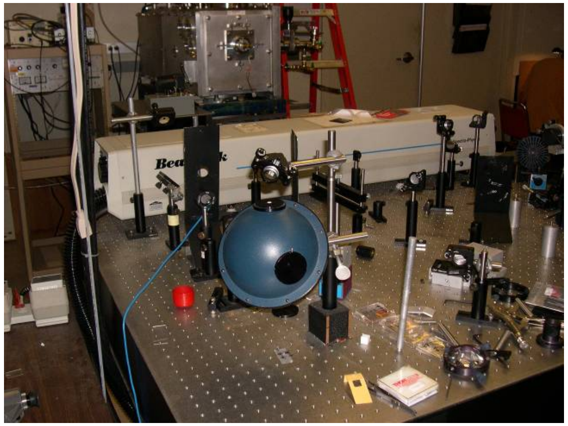


Evolution of the emission/excitation intensity with Ce^{3+} concentration



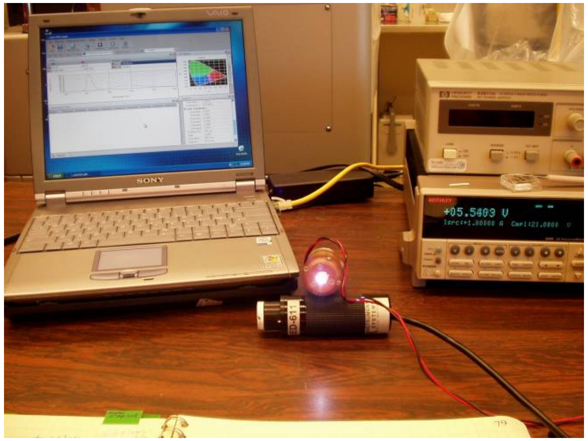


UCSB-made White LEDs



✓ **Quantum efficiency measurement mix of phosphor with silicone resin**

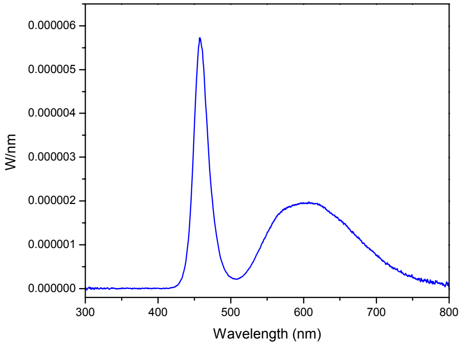
external QE is already ~50%



✓ **White LED**

first results confirm the potential of the yellow phosphors

White LED lamp ~0.4 lm @20 mA



Collaboration with H. Masui, N. Fellows from DenBaars group

New Orange-red Phosphor For Excitation In The Blue/Green

Cerium doped $CaSiN_{2-\delta}O_{\delta}$

Weighting and Grinding in glove box

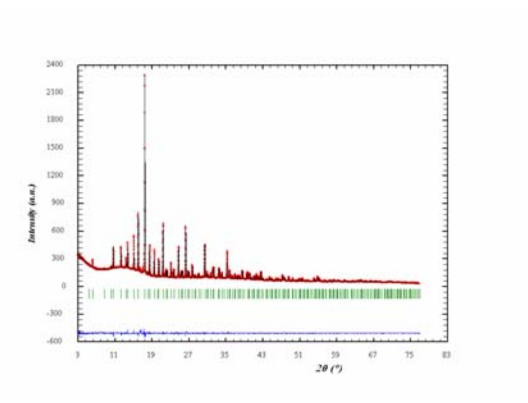
Heating in N_2 between 1250 to 1450°C

CeO_2 as a cerium source

$$2\ Ca_3N_2 + 3\ Si_2N_2(NH) \rightarrow 6\ Ca_xSi_yN_{2-\delta}O_{\delta} + NH3$$

$$Ca_3N_2 + Si_3N_4 \rightarrow 3\ Ca_xSi_yN_{2-\delta}O_{\delta}$$

with $x \approx y \approx 1$

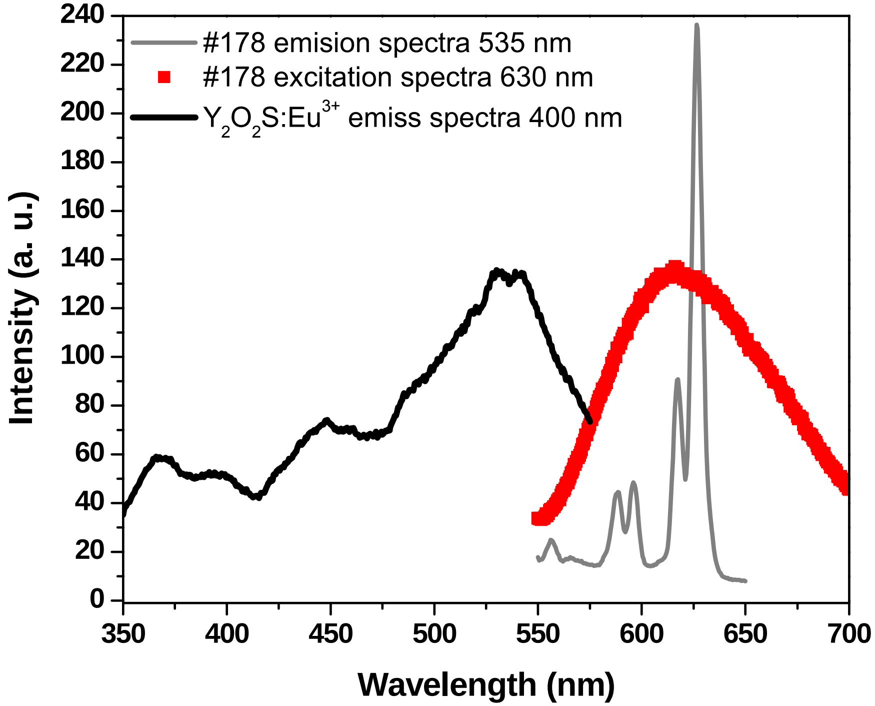


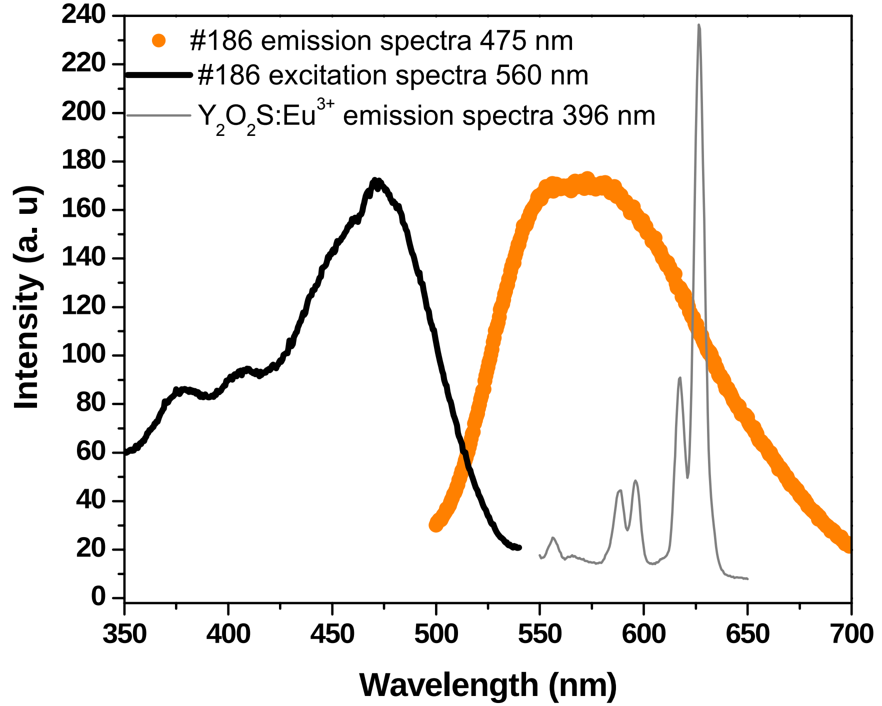
Synchrotron X-ray powder diffraction

space group F23

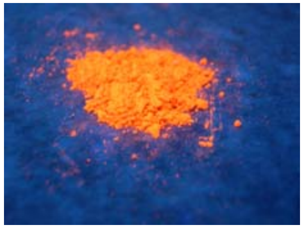
unit cell parameter a=14.882 Å

New Orange-red Phosphor For Excitation In The Blue/Green



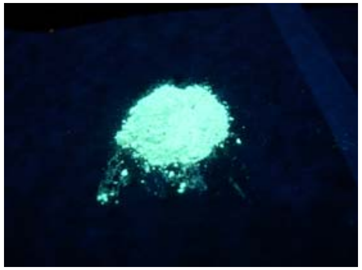


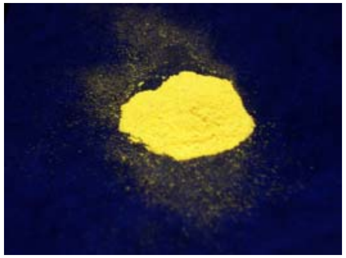
Red Phosphor	#178 535 nm	$Y_2O_2S:Eu^{3+}$ 396 nm
Integrated Intensity	12065	2148
Ratio	5.5	1



Orange Phosphor	#186 475 nm	$Y_2O_2S:Eu^{3+}$ 396 nm
Integrated Intensity	17343	2148
Ratio	8	1

Conclusions





- ✓ Use chemistry to adjust and optimize the optical properties of the phosphors
- ✓ New cerium based nitride phosphor materials covering the whole visible spectrum
- ✓ Two patent applications
- ✓ First UCSB-made white LED prototype

Acknowledgements

<u>SSLDC</u>

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Eric Drafahl


THE END!