# Narrow Emitting Red Phosphors for Improving pcLED Efficacy


Principal Investigator:
Robert Nordsell, CEO
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Presenter:
Daniel Bugaris, Principal Scientist
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# Project Summary

## Timeline:

Start date: September 1, 2016

Planned end date: August 31, 2018

## Key Milestones:

1. $Eu^{3+}$-containing material (crystal) with red emission at 77 K – Completed May 2017
2. $Eu^{3+}$-containing material (crystal) with red emission at RT – Completed December 2017
3. Performance Testing – Begun January 2018
4. Commercial Characterization – Projected completion by August 2018

## Budget:

**Total Project $ to Date: $1,350,551.71**

- DOE: $1,080,441.41
- Cost Share: $270,110.30

**Total Project $: $1,860,529.00**

- DOE: $1,488,423.00
- Cost Share: $372,106.00

## Key Partners:

| |
|---|
| MaterialsQM Consulting |
| Professor James Whitten (UMass-Lowell) |
| Professor Oliver Monti (University of Arizona) |
| Stanford Synchrotron Radiation Lightsource (SLAC) |
| Advanced Photon Source (ANL) |

## Project Outcome:

The focus of this Project is the development of a narrow-band red $Eu^{3+}$-activated phosphor for blue-pumped, on-chip LED applications. The goal is to improve pcLED efficacy by up to 28%.

# Experimental Team – Lumenari, Inc.

**Robert Nordsell**
CEO & PI
MBA
U.C. Berkeley, 2013

**Daniel Bugaris**
Experimental Team Lead
PhD, Solid State Chemistry
Northwestern, 2009

**Jonathan Melman**
VP, Product
PhD, Chemistry
Rutgers, 2003

**Thomas Chasapis**
Principal Scientist
PhD, Solid State Physics
Aristotle Univ. of Thessaloniki, 2012

**Julien Makongo**
Principal Scientist
PhD, Solid State Chemistry
Max Planck, 2009

**Dino Sulejmanovic**
Scientist
PhD, Solid State Chemistry
Clemson, 2015

# Computational Team

**Shyue Ping Ong**

Professor Ong received his BA and MEng from the University of Cambridge in Electrical & Information Science Engineering, and his PhD in Materials Science & Engineering from MIT. In addition to MaterialsQM, he currently leads the Materials Virtual Lab at U.C. San Diego.

**Anubhav Jain**

Dr. Jain received his BS from Cornell University in Applied & Engineering Physics, and his PhD in Materials Science & Engineering from MIT. In addition to MaterialsQM, he currently leads the Hacking Materials group at Lawrence Berkeley National Lab.

MaterialsQM Consulting

ACCELERATED MATERIALS DISCOVERY THROUGH RAPID SIMULATION AND DATA ANALYTICS

# Spectroscopic Characterization Team

**James E. Whitten**

Dr. Whitten received his PhD in Physical Chemistry from Ohio State University. He is currently a Professor in the Department of Chemistry at the University of Massachusetts-Lowell. His research group studies the chemistry at the surfaces and interfaces of light-emitting diodes and photovoltaic devices.

**Oliver Monti**

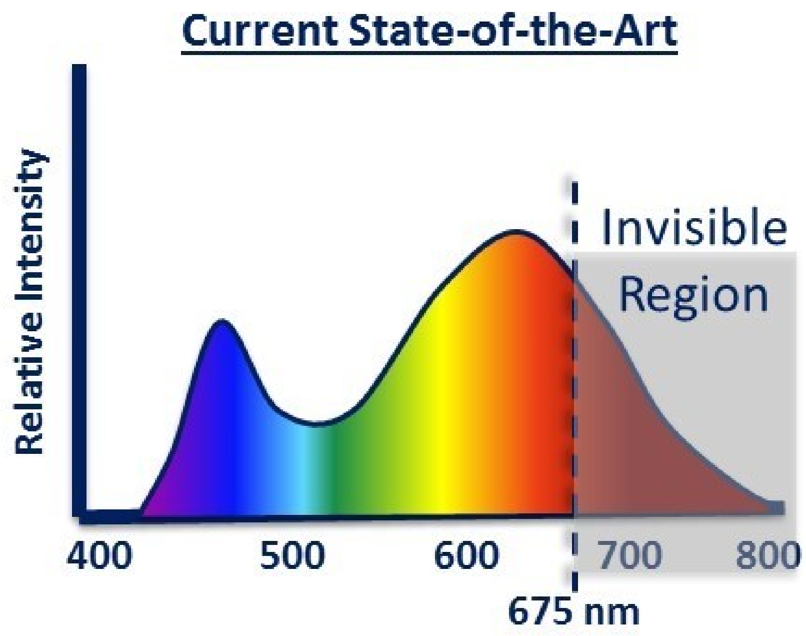
Dr. Monti received his PhD from the University of Oxford. He is currently an Associate Professor with joint appointments in the Departments of Chemistry & Biochemistry and Physics at the University of Arizona. His research group investigates the electronic structures of material interfaces with advanced steady-state and ultrafast photoelectron spectroscopies.

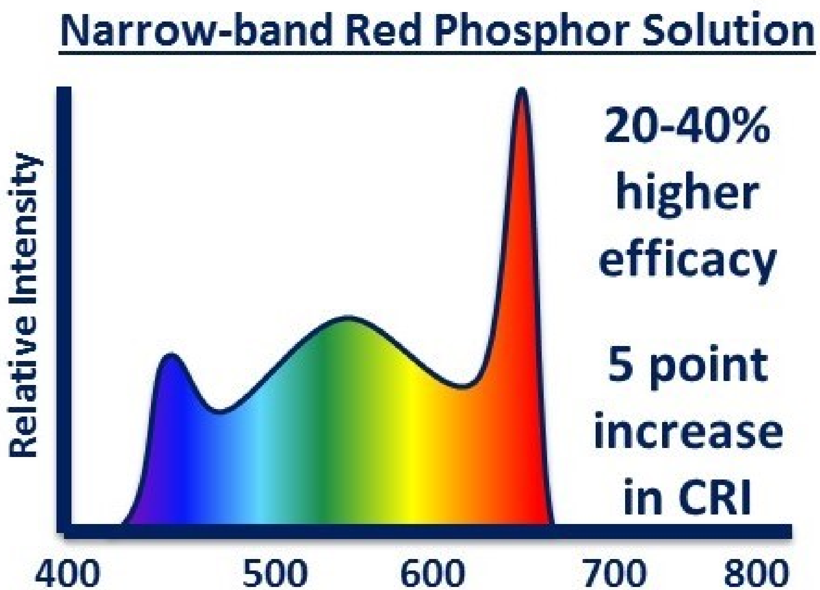
UMASS LOWELL

THE UNIVERSITY OF ARIZONA.

# Challenge: Optimization of Emission

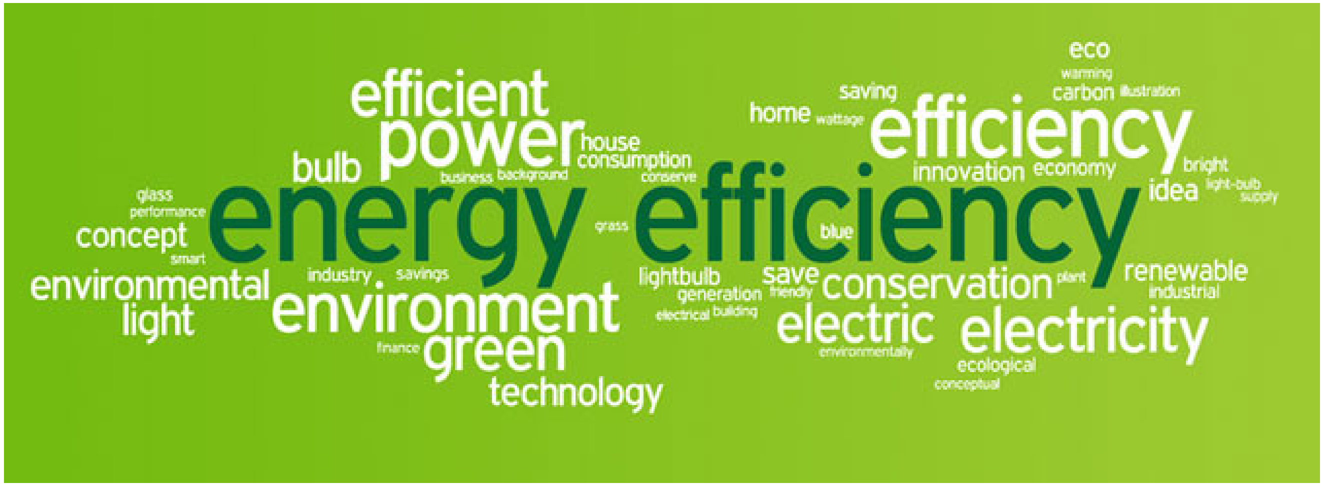
The major challenge in LED lighting is shifting light emitted by the current state-of-the-art red phosphor out of the IR and into the red region. Narrowing the red emission band improves LED efficacy 20-40% by concentrating all of the emitted light into the visible red region.



# Impact

The benefits of a narrow-band red phosphor have been known to and championed by the Department of Energy. The energy savings in the U.S. in 2025 as a result of LED adoption in general lighting are expected to be 217 TW-hr, if the 2020 R&D goals from the 2014 DOE MYPP are met. The product developed as a result of this Project will be a $Eu^{3+}$-activated narrow-band red phosphor for blue pcLED applications that will improve pcLED efficacy by up to 28%, thereby further ***reducing site electricity consumption in the U.S. by 50 TW-hr, effectively displacing 10 coal plants and reducing $CO_2$ emissions by 47 million metric tons annually.***




U.S. Energy Information Administration, Electric Power Annual 2013 (2015)

# Approach

Selection criteria for red phosphor activator ions can be grouped into three categories.

| | PFS:$Mn^{4+}$ | Lumenari $Eu^{3+}$-activated phosphor target specs | CASN:$Eu^{2+}$ |
|---|---|---|---|
| **Required Properties** | | | |
| Peak Emission, $\lambda$ | 630 nm | **610-625 nm** | 623-649 nm |
| Excitation Peak/Edge | 450 nm/500 nm | **450 nm/500 nm** | 475 nm/650 nm |
| **Critical Properties** | | | |
| Absorption, $\alpha_{450}$ | < 60 $cm^{-1}$ | **> 200 $cm^{-1}$** | > 200 $cm^{-1}$ |
| PL Decay Lifetime | ~ 8.7 ms | **~ 200 μs** | < 3 μs |
| Quantum Yield at RT | ~ 90% | **> 90%** | ~ 90% |
| **Desired Properties** | | | |
| FWHM | < 10 nm | **< 10 nm** | 75-90 nm |

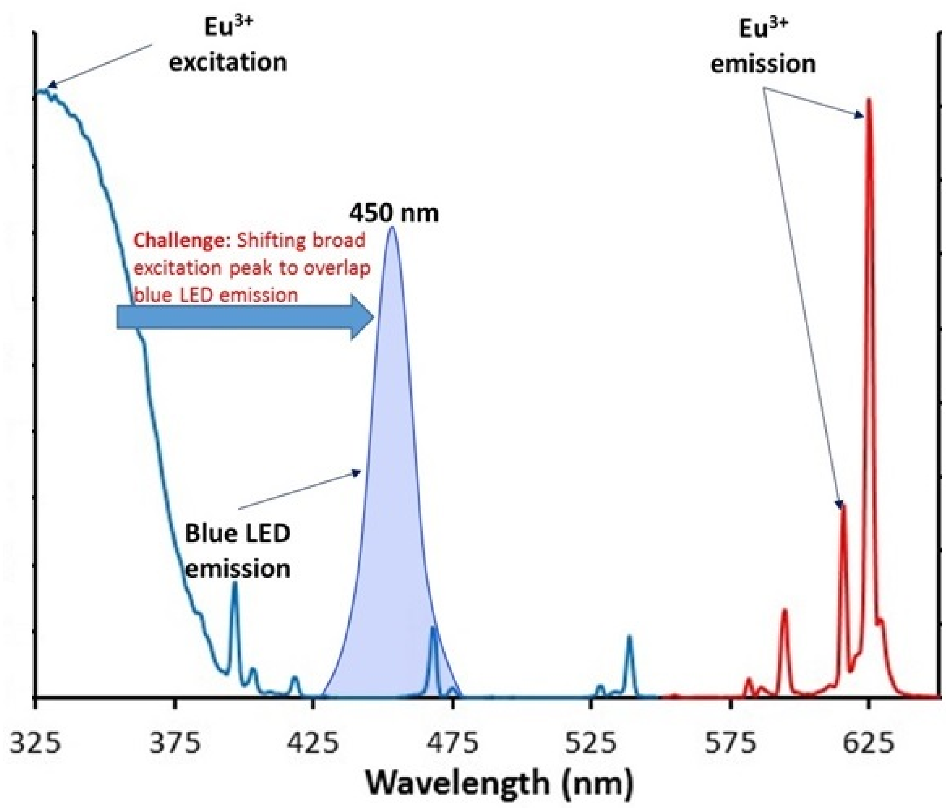
$Mn^{4+}$-activated phosphors, while having the desired narrow-band emission, exhibit low absorption and long decay lifetimes (i.e. inadequate flux density saturation) due to parity forbidden transitions, regardless of the host lattice.

$Eu^{2+}$-activated phosphors, while having strong absorption and short decay lifetime, are unlikely to achieve efficient emission when the FWHM < 50 nm because of the direct correlation between FWHM and Stokes shift.

**The limiting factors for $Mn^{4+}$ and $Eu^{2+}$ activation in LED applications are not fundamental physical limitations for $Eu^{3+}$ activation!**

# Shifting Excitation for $Eu^{3+}$-Activated Phosphor

The scientific problem for $Eu^{3+}$-activated phosphor development involves designing a host lattice that broadly absorbs blue LED emission (430-460 nm) and efficiently transfers that energy to $Eu^{3+}$.



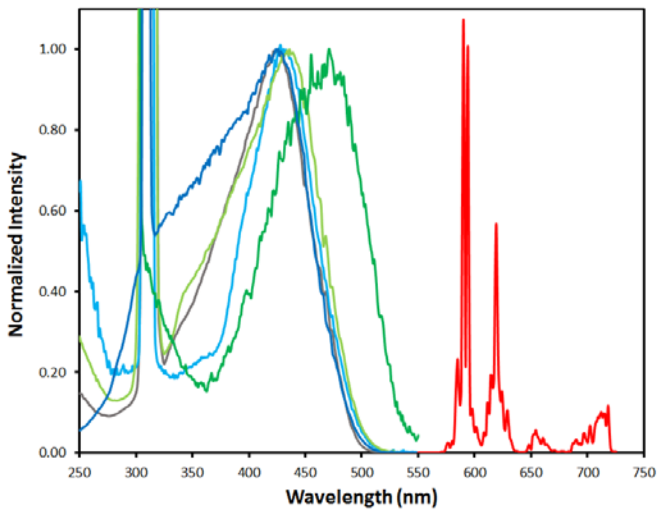

*Previous approaches:*

1) Utilize as a UV-pumped phosphor due to coverage in the 360-400 nm region

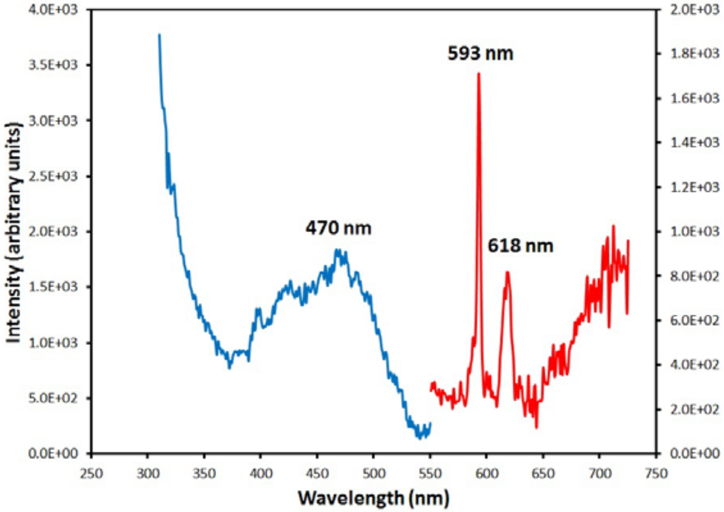
2) Sensitize the narrow ${}^7F_0 \rightarrow {}^5D_2$ absorption at 465 nm

# Computationally Guided Materials Design

1) Computational screening of a large database (Inorganic Crystal Structure Database) of known materials by calculating parameters of interest (band gap, relaxation energy)



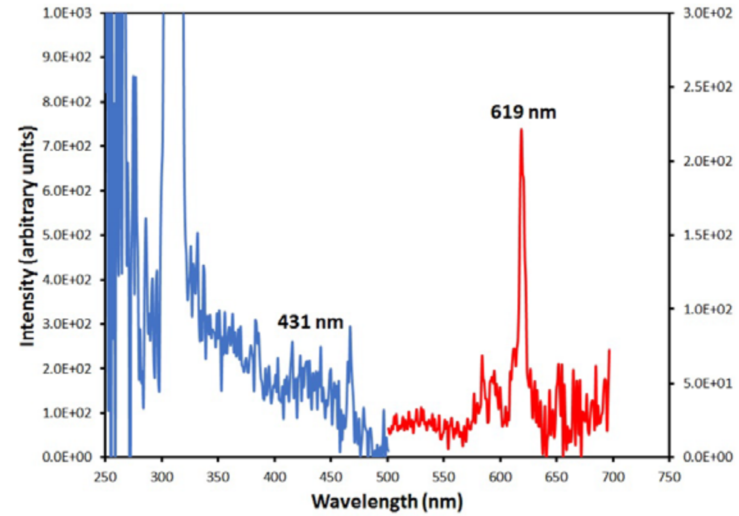

2) Synthesize powders of $Eu^{3+}$-doped materials and analyze PL at 77 K

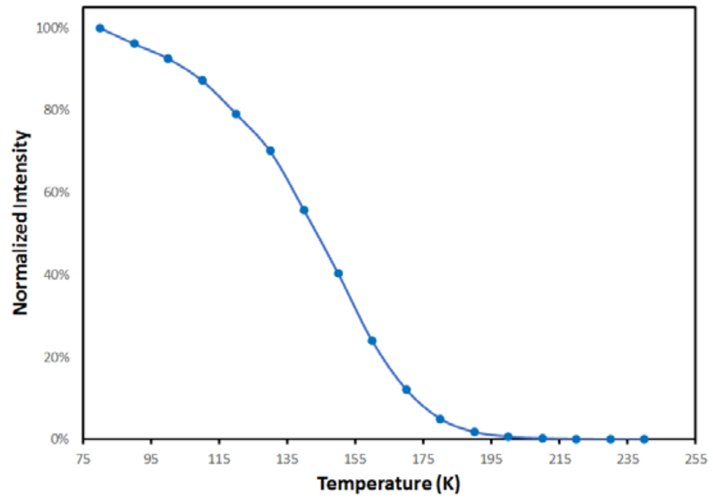

3) Synthesize crystals of $Eu^{3+}$-doped materials and analyze PL at 77 K

# Computationally Guided Materials Design

4) Synthesize powders of $Eu^{3+}$-doped materials and analyze PL at 298 K

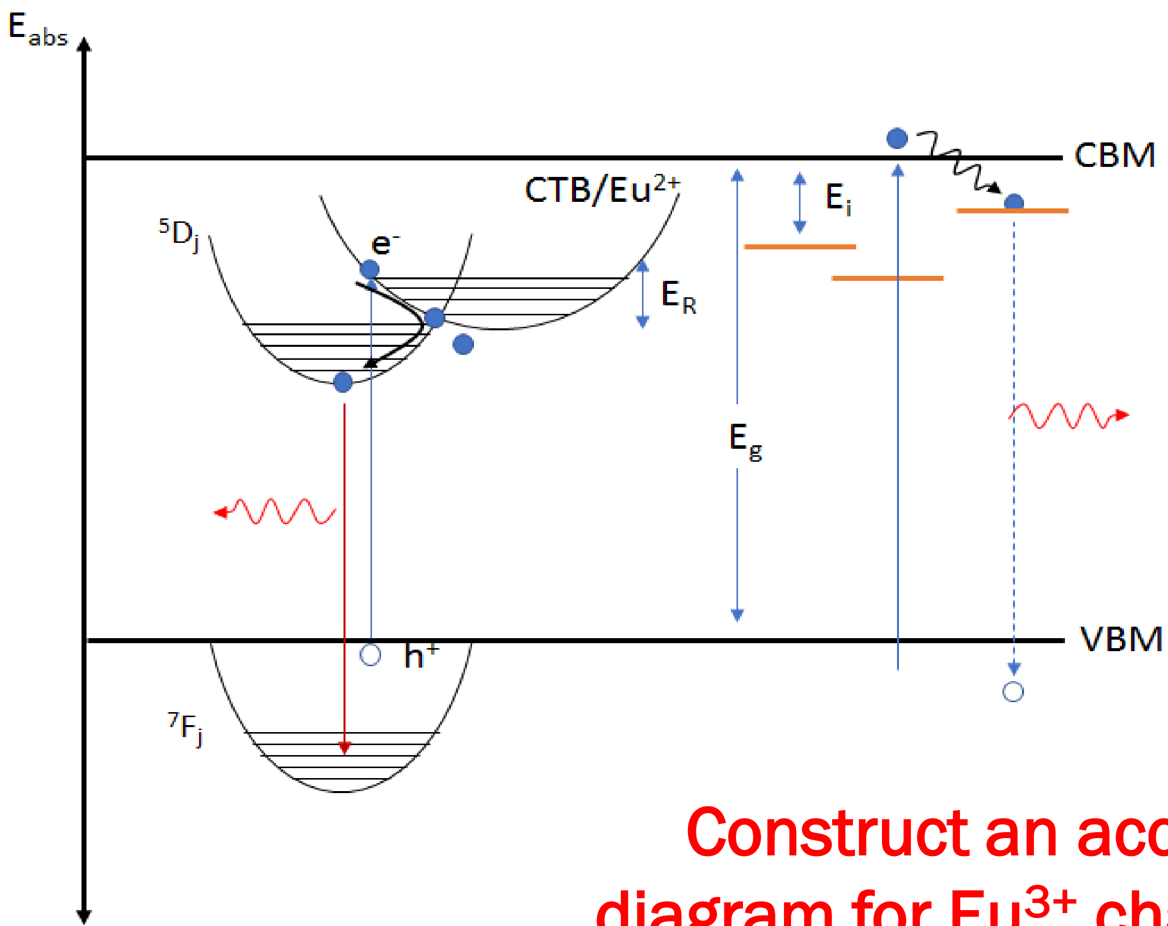



5) Synthesize crystals of $Eu^{3+}$-doped materials and analyze PL at 298 K


Materials are quenched at RT, indicating inefficient charge transfer mechanism and/or non-radiative relaxation

# Photoelectron Spectroscopy (PES)




*Experimental Techniques:*

XPS

UPS

IPES

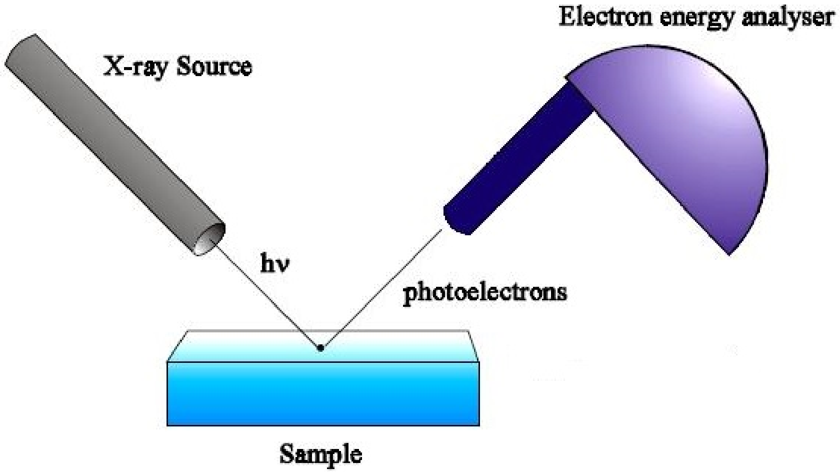
2PPE

**Construct an accurate energy level diagram for $Eu^{3+}$ charge transfer process**

In collaboration with Professors Whitten (UMass-Lowell) and Monti (UArizona)

# PES Experimental Challenge

Insulating (i.e. poorly conducting) samples present a significant hurdle for PES experimental techniques. As photoelectrons are lost during the photoemission process, a positive charge will build up on the sample. As this occurs, the kinetic energy of the emitted photoelectrons will decrease resulting in a shift to higher binding energy of the observed peaks in the spectrum.



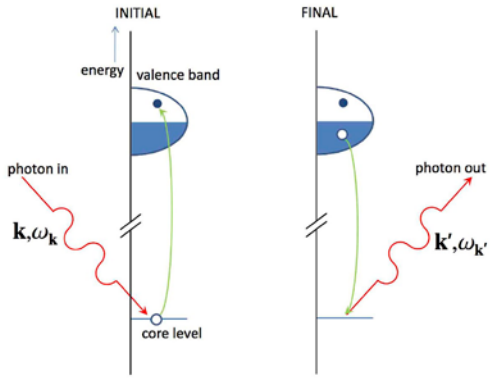

Attempted routes to compensate for sample charging included: different chemical compositions, doping to increase charge carrier concentration, different sample morphologies (powders, pellets, crystals), and different sample stages.

# Synchrotron X-Ray Spectroscopy

For synchrotron X-ray spectroscopic experiments, because the incident photon energy is much higher than in PES, sample charging is not a concern.

*X-ray absorption spectroscopy (XAS)*

- Evaluate the valence and conduction band compositions of the host materials
- Beamtime is scheduled at SSRL on May 7-9, 2018




*X-ray emission spectroscopy (XES)*

- Probe the density of states (DOS) for the excited state
- Proposal accepted, but beamtime not yet awarded

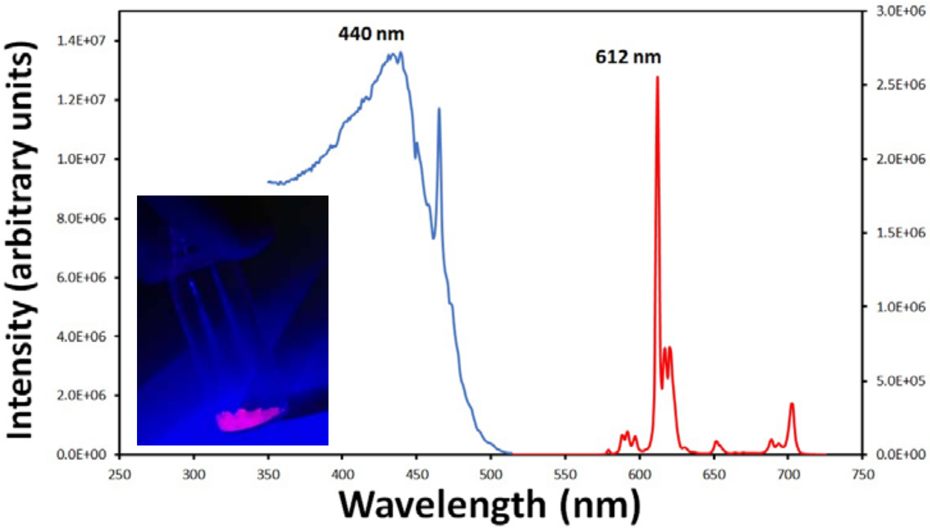
*Resonant inelastic X-ray scattering (RIXS)*

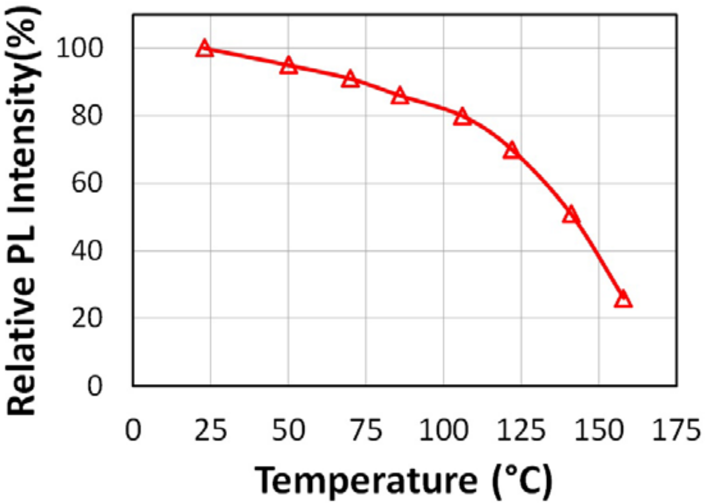
- Provide direct observation of low-lying excitations with Eu-character, such as CTS
- Proposal accepted, but beamtime not yet awarded

In collaboration with Professor Monti (UArizona)

# Highly Promising $Eu^{3+}$ Material

This $Eu^{3+}$ containing material exhibits very strong red emission with efficient blue light excitation at RT




The thermal quenching is also quite robust, retaining > 80% PL intensity (compared to RT) at 100°C

# Performance Testing

Particle Size ($d_{50}$)

- Light scattering and brightness can be impacted by particle size and morphology
- Target $d_{50}$ is ~ 10 μm
- Current $d_{50}$ is ~ 22 μm (only sieve/elutriation, and not ball-milling)
- Reported $d_{50}$ is ~ 20-30 μm for commercial PFS:$Mn^{4+}$ material

PL Decay Lifetime ($\tau$)

- Decay lifetimes longer than the human eye response decrease the efficiency
- Target $\tau$ is ~ 200 μs
- Current $\tau$ has been measured at 230-270 μs (data from Texas A&M user facility)
- Reported $\tau$ is 8.7 ms for commercial PFS:$Mn^{4+}$ material

Absorption ($\alpha_{450}$)

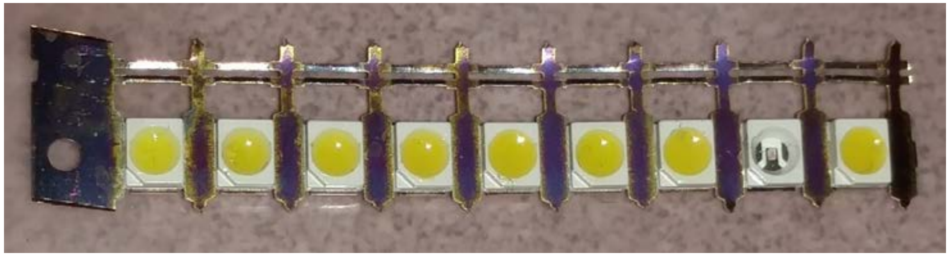
- Lower absorption values increase the difficulty of achieving warm white LEDs
- Target $\alpha_{450}$ is > 200 $cm^{-1}$

Quantum Yield (QY)

- QY provides an assessment of the phosphor's performance
- Target QY is > 90%

# Remaining Commercial Characterization

*Our $Eu^{3+}$ containing phosphor will be packaged on an LED for on-chip testing*



Thermal Quenching

- Measure of how well the phosphor will perform at elevated LED junction temperatures
- Target thermal quenching is ≥ 90% PL intensity at 150°C relative to RT
- Minimum thermal quenching is ≥ 80% PL intensity to be on-par with CASN:$Eu^{2+}$

Relative Efficacy

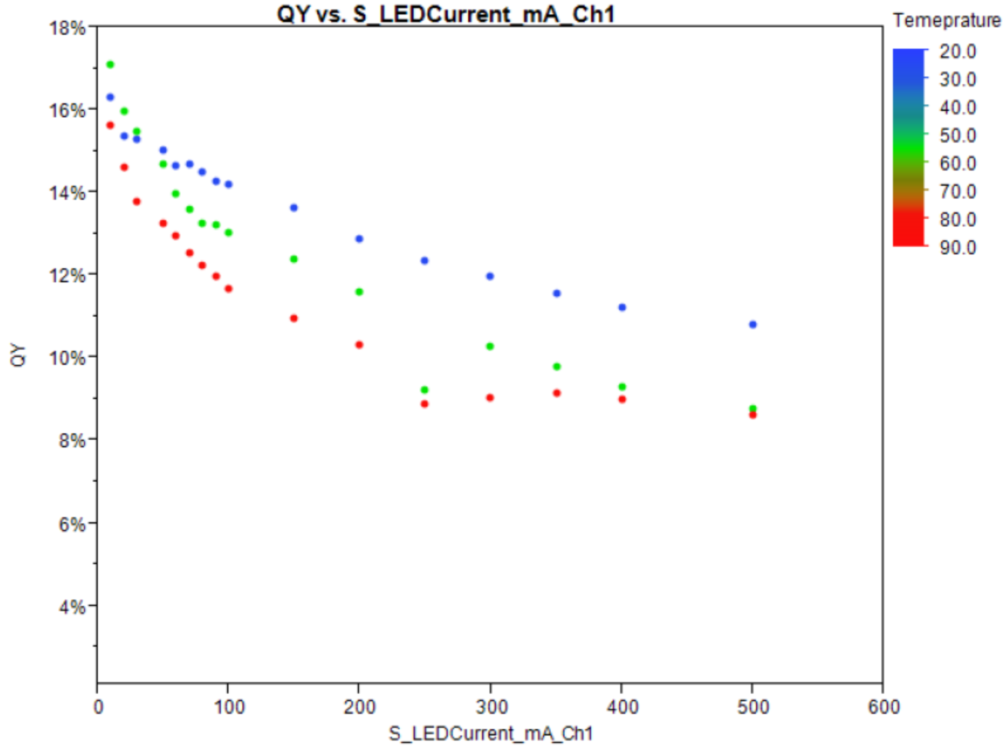
- Assuming equivalent absorption and quantum yield, the narrow-band red emission of $Eu^{3+}$ versus the broad-band red emission of $Eu^{2+}$ should greatly increase efficacy
- Target on-chip efficacy improvement is 28% relative to that of CASN:$Eu^{2+}$

Operating Lifetime

- We will conduct wet high temperature operation life (WHTOL) testing to expose compositional susceptibility to performance lifetime problems
- Any target values are beyond the scope of this Project
- It should be noted that our material appears to be stable in water at RT and elevated temperatures, in the short term

# Stakeholder Engagement

An early, non-optimized, sample of our $Eu^{3+}$ containing phosphor was given to *Customer A* for evaluation




Maximum QY was approximately 20%, but phosphor underwent partial decomposition

Current challenge is to encapsulate the phosphor so that it cures in silicone for LED packaging

# Thank You

Principal Investigator:
Robert Nordsell, CEO
rob@lumenariinc.com

Presenter:
Daniel Bugaris, Principal Scientist
dan@lumenariinc.com

# REFERENCE SLIDES

# Project Budget

**Project Budget**: $1,860,529

**Variances**: There was a 6-month delay hiring a Principal Scientist due to immigration paperwork delays. These unspent funds are being used for the $Eu^{3+}$ electronic structure mapping by PES.

**Cost to Date**: $1,350,551.71

**Additional Funding**: None

| Budget History | | | | | |
|---|---|---|---|---|---|
| 9/1/2016 – 12/31/2017 (past) | | FY 2018 (current) | | 4/1/2018 – 8/31/2018 (planned) | |
| DOE | Cost-share | DOE | Cost-share | DOE | Cost-share |
| $896,650 | $224,163 | $183,791 | $45,948 | $407,982 | $101,995 |

# Project Plan and Schedule

| Project Start Date: September 1, 2016 | FY 2017 | | | | FY 2018 | | | |
|---|---|---|---|---|---|---|---|---|
| Project End Date: August 31, 2018 | Q1 (Oct-Dec) | Q2 (Jan-Mar) | Q3 (Apr-Jun) | Q4 (Jul-Sep) | Q1 (Oct-Dec) | Q2 (Jan-Mar) | Q3 (Apr-Jun) | Q4 (Jul-Sep) |
| *Milestone #1*: Computational identification of 5 compounds whose excitation peak wavelengths are calculated to be 430 nm ≤ $\lambda_{ex}$ ≤ 495 nm | | | | | | | | |
| *Milestone #2*: Powder synthesis/analysis of one computationally identified $Eu^{3+}$-doped compound with 430 nm ≤ $\lambda_{ex}$ ≤ 495 nm and 610 nm ≤ $\lambda_{em}$ ≤ 630 nm at 77 K | | | | | | | | |
| *Milestone #3*: Single crystal synthesis/analysis of one computationally identified $Eu^{3+}$-doped compound with 430 nm ≤ $\lambda_{ex}$ ≤ 495 nm and 610 nm ≤ $\lambda_{em}$ ≤ 630 nm at 77 K | | | | | | | | |
| *Milestone #4*: Powder synthesis/analysis of one computationally identified $Eu^{3+}$-doped compound with 430 nm ≤ $\lambda_{ex}$ ≤ 495 nm and 610 nm ≤ $\lambda_{em}$ ≤ 630 nm at 298 K | | | | | | | | |
| *Milestone #5*: Single crystal synthesis/analysis of one computationally identified $Eu^{3+}$-doped compound with 430 nm ≤ $\lambda_{ex}$ ≤ 495 nm and 610 nm ≤ $\lambda_{em}$ ≤ 630 nm at 298 K | | | | | | | | |
| *Milestone #6*: Completed performance testing of crystals exhibiting excitation and emission at 298 K | | | | | | | | |
| *Milestone #7*: Completed performance testing of crystals with QY ≥ 55% | | | | | | | | |
| *Milestone #8*: Completed commercial characterization | | | | | | | | |

| | | |
|---|---|---|
| Completed on time | Completed | In progress |