Phosphors for solid state lighting (SSL)

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Research on functional inorganic materials

Batteries
Heterogeneous catalysts
Lone-pair effects and polar materials
Magnetism and M–I Transitions
Phosphors for white solid state lighting
Semiconductors
Thermoelectric oxides and intermetallics

Photo by Tony Mastres
Tutorial on LED Lighting

History of Lighting — Major Innovations

| BC Oil lamps | 1900 Incandescent | 1936 Fluorescent | 2010 Incandescent replacement LED bulbs |
| 1962 GaAs/GaP LEDs | 1996 White LEDs | 2002 Higher Power White LEDs |
LED Color Timeline

1962 GaAs IR diodes
non-visible infrared — for sensors and remote controls

1965-1975 GaP LEDs
red, amber, or green — for indicator lamps

1970 IR to visible up-conversion
red, green, or blue — for indicator lamps

1970
Partial conversion patents
white and colors — for, e.g., display backlight and general lighting

1993 Bright GaN blue LED

1996

Comparison to Other Types of Lighting

Incandescent Light Bulb

Only 15 lm/W

LED

> 70 lm/W

Lumens per Watt (lm/W) measures efficiency
Comparison to Other Types of Lighting

**Incandescent Light Bulb**
- Change light bulb every 850 hours

**LED**
- Only change LED every 10,000-50,000 hours

**Comparison to Other Types of Lighting**

**Small Size/Miniature Lamps**
- Medical Applications
- LCD TVs
- Decorative Lighting
How do LEDs work?

- Semiconductor $p$-$n$ junction
- Subject to forward bias, which creates pairs of electrons and holes (excitons)
- Delocalized excitons recombine to emit light
White light

- White light does not exist as a spectral color
- Polychromatic light, \textit{e.g.}, white light, can be created by mixing colors
- The mixed color produced depends on the ratio of the source color

3-LED solution

\textbf{What is holding this back?}
- Needs 3 power supplies
- Expensive
- LED intensities need to be readjusted for temperature changes and burning time
Full conversion

LED with red, green, and blue phosphors

Fluorescent lamp

Partial conversion: The solution of choice

BLUE LIGHT

PHOSPHOR
Luminescence Conversion Material

YELLOW LIGHT

FILTER
Light Filtering Material
Partial conversion: The solution of choice

Peak from a typical blue LED

Partial conversion: The solution of choice

Broad yellow emission from a phosphor
Partial conversion: The solution of choice

- Some of the blue light from the LED is converted
- Some of the blue light is scattered
- The two combine to create a third color (e.g., white light)
How is partial conversion achieved: Phosphors

- Electrons in the activator ion absorb incident light and re-emit at longer wavelengths.

The workings of a phosphor

- Excited state 1 to excited state 2, non-radiative transition.
- Ground electronic state.

Dopant activator ion (e.g. Ce³⁺ or Eu²⁺) in a host matrix.
The workings of a phosphor (roles as scatterer)

Inorganic phosphors

Advantages:

• Does not degrade
• Light scattering by inorganic powders greatly reduces light trapping
• Much better performance at elevated temperatures
The CIE Diagram

- Shows all light colors in an x, y coordinate system
- Pure spectral colors lie along the border
- Polychromatic light lies within the interior
  - a mixture of spectral colors

Obtaining the CIE coordinates

- Experimental spectrum is fit to tristimulus function displayed below on the right
- Three values obtained, of x, y, and z, that are constrained according to \( x + y + z = 1 \)
• Planckian radiators define polychromatic light in certain areas of the CIE diagram
Warm White
LEDs: Converting electricity to light (not heat !)
LEDs: Converting electricity to (white) light

A history closely allied with two UCSB researchers:

Herb Kroemer (2000 Nobel) Heterostructures, laser diodes ...

Shuji Nakamura (2011 Emmy) GaN lighting (blue LEDs), blue laser diodes ... materials chemistry of GaN

Solid state lighting strategies

1. Tricolor LEDs with no need for phosphors
2. UV LED + RGB phosphors
3. Blue LED + yellow/orange phosphors

Blue LED (450 nm)
The L Prize

60 W Incandescent Replacement Lamp
- More than 90 lm/W
- Less than 10 watts
- More than 900 lumens
- More than 25,000 hour life
- More than 90 CRI
- Between 2700 K – 3000 K CCT

Some applications of solid state lighting

Audi A4

The LS 600h L is the world’s first vehicle to be equipped with Light-Emitting Diode (LED) headlamps for low-beam use…a subtle blue tint, giving this LS a more modern appearance.
Some applications of solid state lighting

The Chanel Building in Osaka (Peter Marino Architect).

LED lamps for indoor cultivation

90% Less Heat
50,000 Hour Rated
LEDs Made in USA
No Heat Signature
Cut Your Electricity Bill

High Times Magazine

Ce³⁺ phosphors for solid state white lighting

**The need:** A means of efficiently converting blue light from InGaN LEDs to white light with high color rendition.

**The task:** Understand how known Ce³⁺ phosphors work, and develop new hosts that outperform current ones. Explore known structure types via compositional tuning.

Requires tools to understand local structure around Ce³⁺ of phosphors.

**People involved:**

Professor Steve DenBaars, Solid State Lighting and Energy Center
Dr. Won Bin Im (Chonnam National University, Korea)
Nathan George, Kristin Denault, Dr. Alex Birkel, Dr. Jakoah Brgoch, Michael Cantore, Leah Kuritzky, Stuart Brinkley
Dr. Alexander Mikhailovsky

Dr. Kate Page, Anna Llobet (Los Alamos, LANSCE)
Dr. Mahal Balasubramanian (APS, Argonne)
Understanding Ce$^{3+}$ phosphors (similar in Eu$^{2+}$)

Ce is [Xe]$4f^85d^16s^2$  Ce$^{3+}$ is [Xe]$4f^75d^66s^2$  Ce$^{4+}$ is [Xe]$4f^65d^66s^0$

The transition from $4f$ to $5d$ in Ce$^{3+}$ is spin allowed – it is narrow and takes place in the UV in isolated Ce$^{3+}$ atoms.

In solids, the crystal field broadening of the $5d$ states allows absorption in the near-UV/blue, and emission in the visible.

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Solid state lighting: Near-UV or blue LED + yellow phosphor

- InGaN LED $\lambda=405$ nm
- GaN LED $\lambda=450$ nm
- $\text{Ba}_2\text{SiO}_4\cdot\text{Eu}^{2+}$
- $\text{Sr}_2\text{BaAlO}_4\cdot\text{Ce}^{3+}$
- $\text{SrSiO}_4\cdot\text{Eu}^{2+}$
- $\text{Sr}_2\text{Si}_2\text{O}_7\cdot\text{Eu}^{2+}$, CaAlSiN$_3\cdot\text{Eu}^{2+}$
- $\text{Y}_2\text{Al}_5\text{O}_{12}\cdot\text{Ce}^{3+}$
Understanding Ce$^{3+}$ phosphors (similar in Eu$^{2+}$)

Ce is [Xe]$4f^65d^16s^2$  \quad Ce$^{3+}$ is [Xe]$4f^55d^06s^0$  \quad Ce$^{4+}$ is [Xe]$4f^45d^06s^0$

The transition from $4f$ to $5d$ in Ce$^{3+}$ is spin allowed – it is narrow and takes place in the UV in isolated Ce$^{3+}$ atoms.

In solids, the crystal field broadening of the $5d$ states allows absorption in the near-UV/blue, and emission in the visible.

1. New oxyfluoride phosphors
2. Are there better, quicker ways of making known phosphors?
3. What makes some phosphors efficient and others not: Hints from thermal quenching behavior, and displacement ellipsoids.
4. Probing the local structure around the activator.
Other research: New oxide and oxyfluoride phosphors

*\textit{i4/mcm} structure of LaSr$_2$AlO$_5$ and Sr$_2$AlO$_4$F*

LaSr$_2$AlO$_5$ ↔ Sr$_2$AlO$_4$F


New oxyfluoride phosphors

Thermal quenching properties are greatly improved over our old phosphor, LaSr$_2$AlO$_5$: comparable with YAG:Ce$^{3+}$

*So what is the problem?*

Stability to water is poor!
New oxyfluoride phosphors

Solid solution between $\text{Sr}_3\text{AlO}_4\text{F}$ and $\text{Sr}_3\text{SiO}_5$: $(\text{SAF})_{1-x}(\text{SSO})_x:\text{Ce}^{3+}$

XRD and $^{19}\text{F}$ NMR confirm the solid solution.
The solid solution ensures more stable compounds as well as more red-shifted absorption and emission.

X-ray pair distribution functions (APS 11-ID-B) allow some understanding of local structural changes. The highest quantum yields are near $x = 0.5$. 

New oxyfluoride phosphors

$\text{(SAF)}_{1-x} \text{(SSO)}_x : \text{Ce}^{3+}$
New oxyfluoride phosphors

(SAF)$_{1-x}$(SSO)$_x$:Ce$^{3+}$

Color and efficiency are good. "Phosphor cap" strategy helps increase efficacy greatly.

A quicker route to phosphors: The use of microwaves

Rapid Microwave Preparation of Highly Efficient Ce$^{3+}$-Substituted Garnet Phosphors for Solid State White Lighting

With Byung-Chul Hong, Mitsubishi Chemicals.

No coupling when cold. Carbon susceptor ensures initial coupling, and reducing conditions.
A quicker route to phosphors: The use of microwaves

Synchrotron x-ray studies establish completely clean phases. Optical properties similar to furnace prepared samples (using 95% less time).


A quicker route to phosphors: The use of microwaves

$T$-dependence of emission show similar stability for conventionally-prepared and MW samples.

The canonical material: Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$ (Blasse)

Garnet crystal structure: AlO$_4$ tetrahedra and AlO$_6$ octahedra, all completely corner-connected.

Y occupies 8-coordinate voids formed by AlO$_n$ polyhedra.

Pyrope \[ \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} \]
Almandine \[ \text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} \]
Spessartine \[ \text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12} \]
Andradite \[ \text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} \]
Grossular \[ \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} \]
Uvarovite \[ \text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12} \]

The canonical material: Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$

Excitation and emission of YAG:Ce$^{3+}$ are well-suited to creation of white.

The high refractive index helps with scattering.

The large Stokes shift prevents re-absorption.
Understanding the canonical phosphor: YAG:Ce$^{3+}$

All the action is around the very small amount of Ce$^{3+}$ in the lattice: 2% substitution for Y$^{3+}$. How do we probe this?

Understanding Ce$^{3+}$ in YAG:Ce$^{3+}$

Synchrotron X-ray Rietveld refinement (11-BM, Argonne) reveals lattice expansion upon substitution of Y$^{3+}$ by the slightly larger Ce$^{3+}$.

In $Y_{3-x}Ce_xAl_5O_{12}$, for $x = 0.06$ (optimal), the cell expands by ≈ 300 ppm compared to $x = 0$. 

![Graph showing lattice expansion and Ce$^{3+}$ substitution](Image)
Understanding Ce$^{3+}$ in YAG:Ce$^{3+}$: Small ADPs stiffness lattice

Rietveld refinement of synchrotron X-ray and neutron (HIPD, Los Alamos) data at room temperature and neutron (NPDF, Los Alamos) at 15 K. *Unusually small ADPs!*

Small Debye-Waller factors confirmed by Ce-K-edge EXAFS.


Ce$^{3+}$ coordination relaxes to average by the fifth coordination shell.
Understanding Ce\(^{3+}\) in YAG:Ce\(^{3+}\): Total scattering analysis

**RMC analysis of the total neutron scattering (NPDF, Los Alamos) allows the local structure around Ce\(^{3+}\) to be independently probed of Y\(^{3+}\). Neutrons are more sensitive to oxygen, and in principle, provide better metal-oxygen distances.**

Within the resolution of total scattering and RMC, the Ce—O distances are indistinguishable from Y—O distances. Suggests a highly rigid lattice (as do the small ADPs) and Ce\(^{3+}\) under high compression.
Understanding Ce\textsuperscript{3+} in YAG:Ce\textsuperscript{3+}: \textsuperscript{27}Al MAS NMR

New features in the \textsuperscript{27}Al NMR upon Ce\textsuperscript{3+} substitution: Ce\textsuperscript{3+} as an internal contrast reagent.

Saturation recovery experiments confirm that the new features correspond to \textsuperscript{27}Al proximal to paramagnetic Ce\textsuperscript{3+}.

800 MHz (19.6 T) NMR spectrometer at UCSB.

The new features can be quantitatively fit to different shells around the small amounts of Ce\textsuperscript{3+} substituents.
Understanding Ce$^{3+}$ in YAG:Ce$^{3+}$: $^{27}$Al MAS NMR

$^{89}$Y NMR similarly displays new features upon Ce$^{3+}$ substitution, that can also be accounted for by the paramagnetism of Ce$^{3+}$

ESR at 4.2 K directly probes the Ce$^{3+}$. The ESR spectra can be modeled with some antisite disorder, ($Y^{3+}$ in octahedral Al$^{3+}$ site) of the order of 2%, that is confirmed by the neutron refinement.
Understanding Ce$^{3+}$ in YAG:Ce$^{3+}$: Findings

YAG unit cell expands slightly with increasing amounts of Ce (about a 300 ppm increase from $x = 0$ to $x = 0.06$).

Ce K-edge XANES and $^{27}$Al NMR results show that all the Ce is reduced to Ce$^{3+}$. 

Ce K-edge EXAFS reveals a 3% expansion in Ce-O bond distance compared to the average Y-O distance, that relaxes by the 5th coordination shell (3.7 Å). RMC/total neutron scattering simulations in agreement.

Analysis of ADPs and calculation of $\Theta_D$ confirms that the YAG lattice is very rigid, with few accessible phonons available at LED operating temperatures.

$^{27}$Al and $^{89}$Y NMR experiments also show that the unpaired 4$f$ electron in Ce$^{3+}$ causes a displacement in the NMR signal of nearby nuclei, as well as a greatly shortened $T_1$ relaxation time of nearby nuclei.

EPR spectra of the YAG:Ce phosphor show small satellite signals around the main absorption signal, corresponding to Y-Al(oct.) antisite defects in YAG:Ce of around 2 mol % of octahedral Al sites.

Understanding Ce$^{3+}$ in YAG:Ce$^{3+}$: Why is it canonical?

- Rigid 3D connectivity – a consequence of low charge on Al$^{3+}$ [Pauling's rules of crystal chemistry].
- Large band gap because of Al, and connectivity.
- Stiff lattice because of connectivity and light elements: Also low quenching (incl. thermal).
- Single site for Ce$^{3+}$: Low disorder, and hence fewer non-radiative pathways.
- Ce$^{3+}$ substitutes smaller Y$^{3+}$: larger 5$d$ crystal-field splitting on Ce$^{3+}$. 


What have we learned? The example of Sr$_2$Si$_5$N$_8$

Fully 3-connected tetrahedra, implies stiff lattice. At the heart of the great thermal stability?


Other research: Efficient nanoscale-YAG:Ce$^{3+}$

**The problem:** Solution-prepared YAG:Ce$^{3+}$ nanoparticles (≈30 nm) tend to have significantly suppressed quantum yields. **The solution:** Wrap the nanoparticles in mesoporous SiO$_2$, anneal, and then dissolve the wrapping.

Synchrotron X-ray (left) and $^{27}$Al MAS-NMR (right) of the nanoparticles, before and after annealing.
The quantum yield increases from around 30% to around 60% after annealing. The luminescence is stable.

Optical properties and transmission electron microscopy.

The pores in the final product suggest dehydration.


Other research: Efficient nanoscale-YAG:Ce\textsuperscript{3+}

Denault et al. (unpublished)
Thank you

Photo by Tony Mastres