Compositional tuning of functional inorganic materials: Examples of phosphors and catalysts

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Overview: Strategies for new functional materials

1. Make a material (new structure, new composition...) that displays the function sought (e.g. HgBa$_2$CuO$_{4+\delta}$, $T_C = 94$ K)


2. Take a known structure type and tune the composition to achieve the desired function (e.g. PZT)

Compositional tuning within a given structure type

La$_{1-x}$Ca$_x$MnO$_3$: Colossal magnetoresistance, charge-ordering
PbZr$_{1-x}$Ti$_x$O$_3$: Piezoelectric tuning
Ba$_{1-x}$Sr$_x$TiO$_3$: Capacitors
La$_{2-x}$Sr$_x$CuO$_4$: Superconductivity
V$_{2-x}$Cr$_x$O$_3$: Insulator-metal transitions
Al$_{2-x}$Cr$_x$O$_3$: Ruby
Today: Phosphors and catalysts

Ce$^{3+}$ phosphors:

Dr. Won Bin Im

Professor Steven DenBaars, Dr. Hisashi Masui, Dr. Natalie Fellows, Stuart Brinkley, Dr. Jerry Hu, Dr. Alexander Mikhailovsky

support: Solid State Lighting and Energy Center

Pd$^{2+}$ catalysts:

Dr. Jun Li, Joshua Kurzman

Professor Susannah Scott, Dr. Udayshankar Singh, Xiaoying Ouyang

support: NSF-IGERT, Department of Energy
Research group, January 2010
Ce$^{3+}$ phosphors for solid state white lighting
LEDs: Converting electricity to light (*not heat!*)

[Diagram of an LED with labels for holes and electrons.]
Solid state lighting strategies

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

Some applications of solid state lighting
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
Ce\(^{3+}\) 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 Ce\(^{3+}\) phosphors work, and develop new hosts that outperform current ones. Explore known structure types via compositional tuning.

Requires tools to understand local structure around Ce\(^{3+}\) of phosphors.

**The outcome:** Finding out that making new, efficient phosphors is very hard!
Understanding Ce$^{3+}$ phosphors

Ce is [Xe]$4f^15d^16s^2$  \hspace{1cm} Ce$^{3+}$ is [Xe]$4f^15d^06s^0$  \hspace{1cm} Ce$^{4+}$ is [Xe]$4f^05d^06s^0$

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.
The canonical material: $Y_3Al_5O_{12} \cdot Ce^{3+}$ (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: $Mg_3Al_2Si_3O_{12}$
Almandine: $Fe_3Al_2Si_3O_{12}$
Spessartine: $Mn_3Al_2Si_3O_{12}$
Andradite: $Ca_3Fe_2Si_3O_{12}$
Grossular: $Ca_3Al_2Si_3O_{12}$
Uvarovite: $Ca_3Cr_2Si_3O_{12}$
The canonical material: $Y_3Al_5O_{12}$:Ce$^{3+}$  Why?

Rigid 3D connectivity – a consequence of low charge on Al$^{3+}$ [Pauling's rules].

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 5d crystal-field splitting on Ce$^{3+}$. 
Some other phosphor hosts for Ce$^{3+}$

La$_3$Si$_6$N$_{11}$

CaAlSiN$_3$

CaSc$_2$O$_4$
The Ce$^{3+}$ phosphor periodic table palette
LaSr$_2$AlO$_5$, a new Ce$^{3+}$ phosphor host

LaSr$_2$AlO$_5$: isostructural with known tetragonal EuSr$_2$AlO$_5$ ($I_4/mcm$)
LaSr$_2$AlO$_5$:  

**Why?**  

$[\text{Sr}_3]^{6+}$ and $\text{Si}^{4+}$ in $\text{O}_5$ (known host)  

$[\text{LaSr}_2]^{7+}$ and $\text{Al}^{3+}$ in $\text{O}_5$  

**How?**  

Prepared from La$_2$O$_3$, SrCO$_3$, Al$_2$O$_3$, CeO$_2$  

1400°C to 1500°C, 5% H$_2$/N$_2$, 4 h
LaSr$_2$AlO$_5$

Appropriate absorption and emission positions for blue + yellow = white. Maximum emission intensity for 2.5 atom-% Ce$^{3+}$ substitution.
Phosphor mounted on an InGaN chip (Natalie Fellows).

Good color rendering, but efficiency poor compared to YAG:Ce$^{3+}$.

LaSr$_2$AlO$_5$: Tunability

For most compositions, the emission peak scales with compression of the CeO$_8$ polyhedron.

Im, Fellows, DenBaars, Seshadri, Kim, Chem. Mater. 21 (2009) 2157
LaSr$_2$AlO$_5$: Local structure

Maximum entropy image restoration of the electron density from synchrotron x-ray data suggests non-spherical electron density at the mixed La/Sr site.
LaSr$_2$AlO$_5$: Local structure

(a) PDF $G(r)$ suggests local coordination of La and Sr are distinct; not well described by the average structure.

(b) Better fit using a structure that allows distinct coordination.
LaSr$_2$AlO$_5$: Local structure

PDF local coordination of La and Sr are distinct; modeled using an ordered structure.

Coordination of La/Ce more regular than suggested by average structure.

LaSr$_2$AlO$_5$-Sr$_3$SiO$_5$ solid solution

Solid solutions between two end-members with distinct crystal structures.

(a) LaSr$_2$AlO$_5$

(b) Sr$_3$SiO$_5$

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LaSr$_2$AlO$_5$-Sr$_3$SiO$_5$ solid solution

Emission intensity in the solid solution goes through a maximum.

Absorption and emission features remain appropriate for white lighting.

Much more efficient phosphor than the LSA end-member.

Oxyfluorides: $\text{Sr}_{3-x}\text{AlO}_4\text{F}:\text{Ce}^{3+}_x$

Compound, with (suggested) well ordered fluorine layers

Modification of the LSA phosphor

La$\text{Sr}_2\text{AlO}_5 \leftrightarrow \text{Sr}_3\text{AlO}_4\text{F}$

La$^{3+}$ changed to Sr$^{2+}$
Fluoride for charge compensation

Two Sr sites for Ce$^{3+}$ with distinct environment of O/F

Sr<sub>3-x</sub>Ba<sub>x</sub>AlO<sub>4</sub>F:Ce<sup>3+</sup>, an efficient green phosphor:

\[ a = b = 6.9189(6) \, \text{Å}, \quad c = 11.2071(7) \, \text{Å} \]

Ba addition into SAF:Ce<sup>3+</sup> stabilizes the host

<table>
<thead>
<tr>
<th>atoms</th>
<th>site</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>8h</td>
<td>1.99</td>
</tr>
<tr>
<td>Ba</td>
<td>4a</td>
<td>1.93</td>
</tr>
</tbody>
</table>
Locating F in the structure is key since optical properties depend on the nature of the Ce$^{3+}$O$_x$F$_y$ coordination.

BABA (back-to-back) 2D MAS NMR, of $^{19}$F, following the single-quantum/double-quantum correlations allows a picture of F positions to emerge.

3 is impurity.

2—2 correlations are important, 1—2 correlations are important, 1—1 are not.

Dr. Jerry Hu, UCSB MRL
Sr$_{3-x}$Ba$_x$AlO$_4$F:Ce$^{3+}$, an efficient green phosphor:

Quantum efficiency (QE) data

<table>
<thead>
<tr>
<th>Sample</th>
<th>QE (%)</th>
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</thead>
<tbody>
<tr>
<td>SAF:Ce$^{3+}$</td>
<td>83</td>
</tr>
<tr>
<td>SBAF:Ce$^{3+}$</td>
<td>95</td>
</tr>
<tr>
<td>YAG:Ce$^{3+}$</td>
<td>81</td>
</tr>
</tbody>
</table>

30 lm/W at 20 mA ($\lambda_{\text{max}}=405$ nm chip)

Prototype LED image

Im, Fourré, Brinkley, Sonoda, Nakamura, DenBaars, Seshadri, Optics Express 17 (2009) 22673; Im, Brinkley, Mikhailovsky, Hu, DenBaars, Seshadri, Chem. Mater. (ASAP).

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Pd$^{2+}$-substituted oxides for catalysis
Motivation: Reducing PGM use in catalysts

PGM = Platinum Group Metal

Data from kitco.com
More than 50% of Pt use is in automotive catalysis: 3-way converters.

Price today (kitco):

Pd: $529/Troy oz.
Pt: $1692/Troy oz.

Data from kitco.com and google finance
PGMs: A dwindling resource


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Three-way catalytic convertors

hydrocarbons + CO + NO\(_x\)  

Catalyst: Oxide-supported PGM nanoparticles dispersed on ceramic honeycombs

The conversion should (in principle) leave the catalyst unchanged

N\(_2\) + CO\(_2\) + H\(_2\)O
**The need:** Make better use of PGMs in catalysis, especially 3-way.

**The task:** Verify that catalysts can be "intelligent" look for new hosts, new mechanisms ...

Requires close collaboration between people working in heterogeneous catalysis and in inorganic materials.

**The outcome:** A new paradigm for catalysis: Catalysis by PGM ions?
Perovskite BaCeO$_3$ as a host:

Ba$^{2+}$ creates an oxide lattice that is highly oxidizing; Ce$^{4+}$/Ce$^{3+}$ are large and somewhat forgiving in terms of coordination.

BaCe$_{1-x}$Pd$_x$O$_{3-\delta}$ with $x = 0, 0.05,$ and 0.10

Samples prepared by solid state routes in O$_2$, between 800$^\circ$C and 1000$^\circ$C.

Neutron refinements [NPDF, Los Alamos] $\Rightarrow \delta \sim x$ so Pd in lattice is Pd$^{2+}$
BaCeO$_3$:Pd: Modeling the substitution

DFT optimized structure of 2x2x2 perovskite cell with one Pd$^{2+}$ substituting Ce$^{4+}$ and one oxygen vacancy: $x = 12.5$ [Bennett and Rappe, Penn]

The oxygen vacancy prefers to be proximal to Pd$^{2+}$ and leaves it nearly square planar.
The (PDF) for the $x = 0.10$ sample is well-modeled by the DFT structure, but not by the average structure.

Magnetic measurements suggest a diamagnetic system.
BaCeO$_3$·Pd: Intelligent?

Egress of Pd as fcc-Pd upon H$_2$ reduction of $x = 0.10$ at different temperatures [5%-H$_2$/95%-N$_2$]
Ingress of Pd into the perovskite on heating the reduced two-phase sample in O\textsubscript{2} at different temperatures.
BaCeO$_3$:Pd: Intelligent?

Pd core levels of the oxidized and reduced samples.

$\chi = 0.10$

Ce is always Ce$^{4+}$

YFeO$_3$ exists as a stable perovskite or a metastable (sol-gel prep.) hexagonal compound with the YAIO$_3$ structure. 5-coordinate Fe$^{3+}$ in the hexagonal structure.
Neutron diffraction [NIST, BT-1] confirms substitution up to 8%.
YFeO$_3$:Pd – Ingress and egress of Pd

Fe core levels unchanged with oxidation/reduction.

Pd core levels suggest ingress and egress under redox. Not all Pd$^{2+}$ reduced.
YFeO$_3$\[10\%Pd\] - Ingress and egress of Pd

Pd nanoparticles seen after reduction in backscattering SEM and in TEM

YFeO$_3$ [10\%Pd] as-prepared

after 1$^{st}$ reduction [also (c) and (d)]
Good CO oxidation catalyst despite low surface area. The best catalyst is actually the as-prepared or re-oxidized sample with Pd\textsuperscript{2+}

Activity is attributed to the presence of cationic Pd\textsuperscript{2+} in the perovskite lattice

Y(Fe/Mn)O$_3$:Pd: The catalytically active species

Again, the oxidized compound with Pd$^{2+}$ is the better catalyst

Y$_{0.5}$Mn$_{0.45}$Fe$_{0.05}$O$_3$, 1000 ppm CO + 9.5%O$_2$/Ar

Low light-off temperature. Effective catalyst despite low surface areas.

Summary:

\textbf{Ce}^{3+} \textbf{phosphors:}

New phosphor materials, better understanding ...

\textbf{Pd}^{2+} \textbf{catalysts:}

A new catalyst paradigm, better catalysts ...