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

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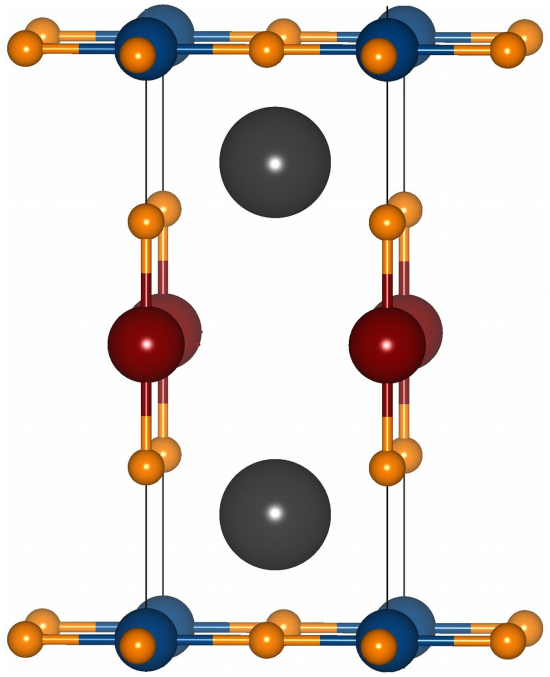
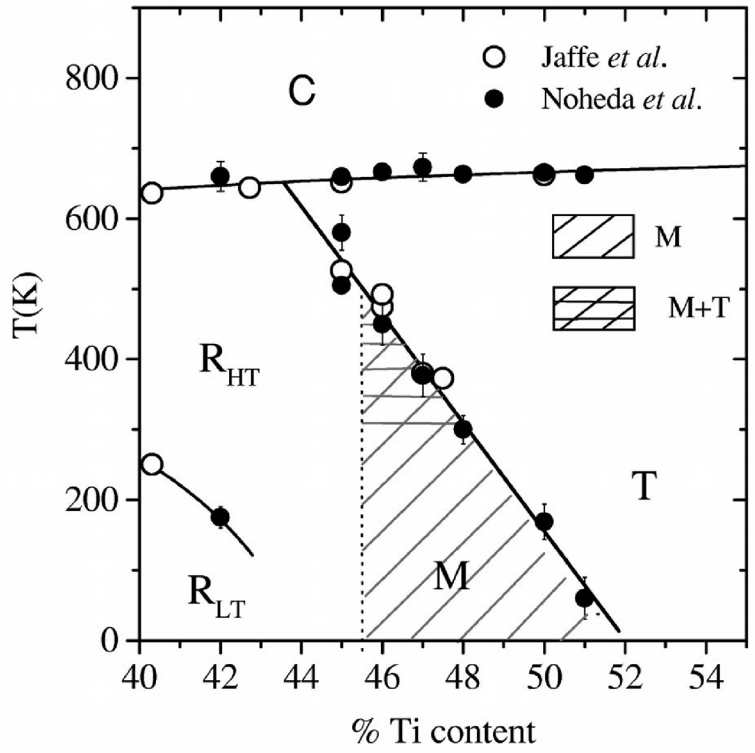
Overview: Strategies for new functional materials

1. Make a material (new structure, new composition…) that displays the function sought (*eg.* $HgBa_2CuO_{4+\delta}$, T_C = 94 K)



Putilin, Antipov, Chmaissen, Marezio, *Nature* **362** (1993) 226–228.

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



Noheda, Cox, Shirane, Guo, Jones, Cross, *Phys. Rev. B* **63** (2000) 014103(1–9).

Compositional tuning within a given structure type

$La_{1-x}Ca_xMnO_3$: Colossal magnetoresistance, charge-ordering

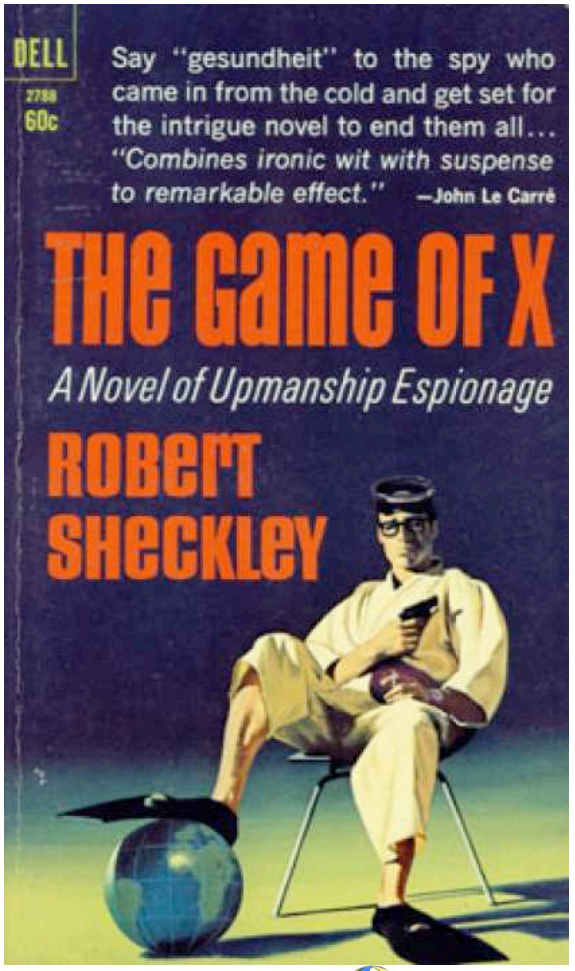
$PbZr_{1-x}Ti_xO_3$: Piezoelectric tuning

$Ba_{1-x}Sr_xTiO_3$: Capacitors

$La_{2-x}Sr_xCuO_4$: Superconductivity

$V_{2-x}Cr_xO_3$: Insulator-metal transitions

$Al_{2-x}Cr_xO_3$: 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**

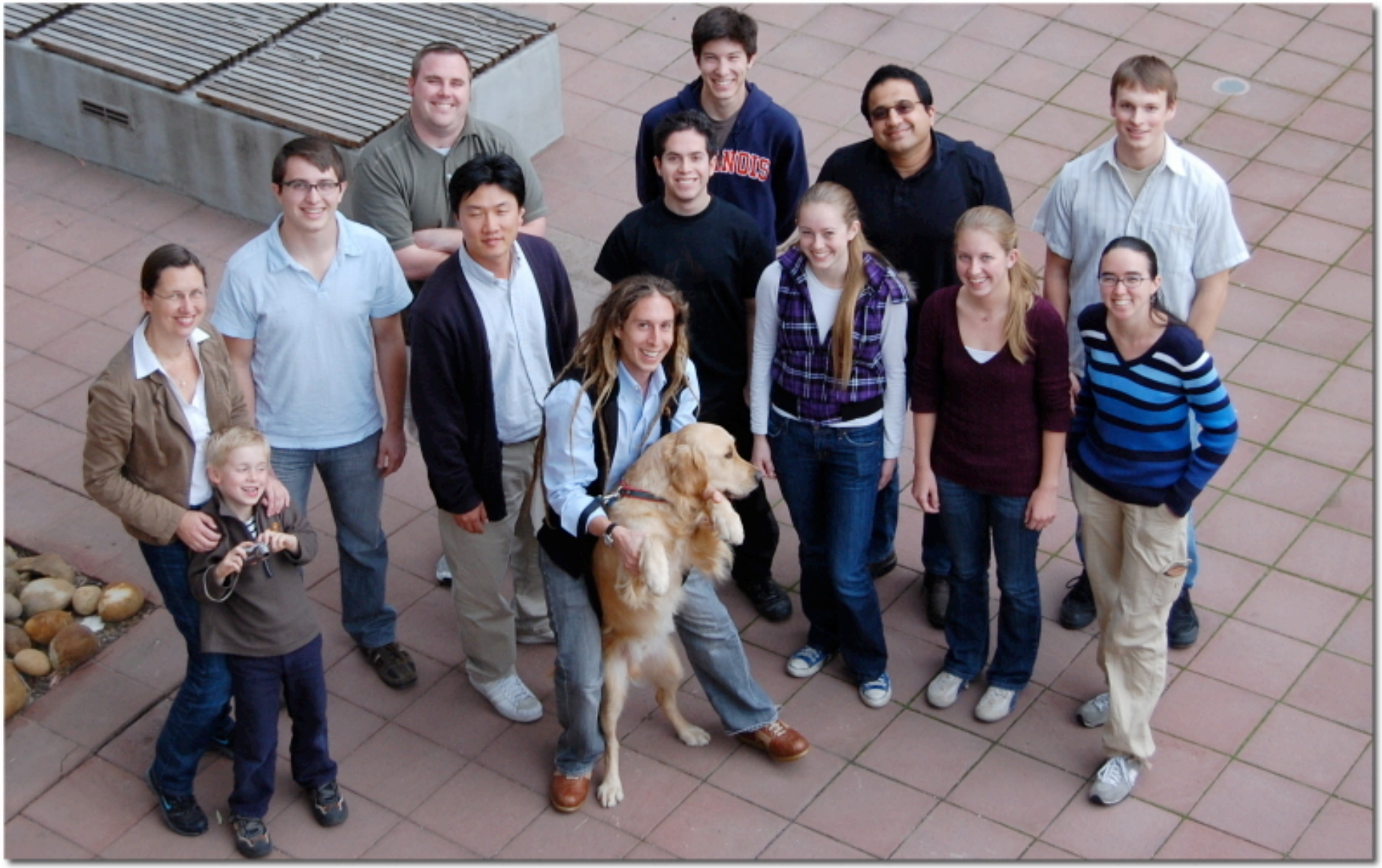
Pd^{2+} catalysts:

Dr. Jun Li, Joshua Kurzman

Professor Susannah Scott, Dr. Udayshankar Singh, Xiaoying Ouyang

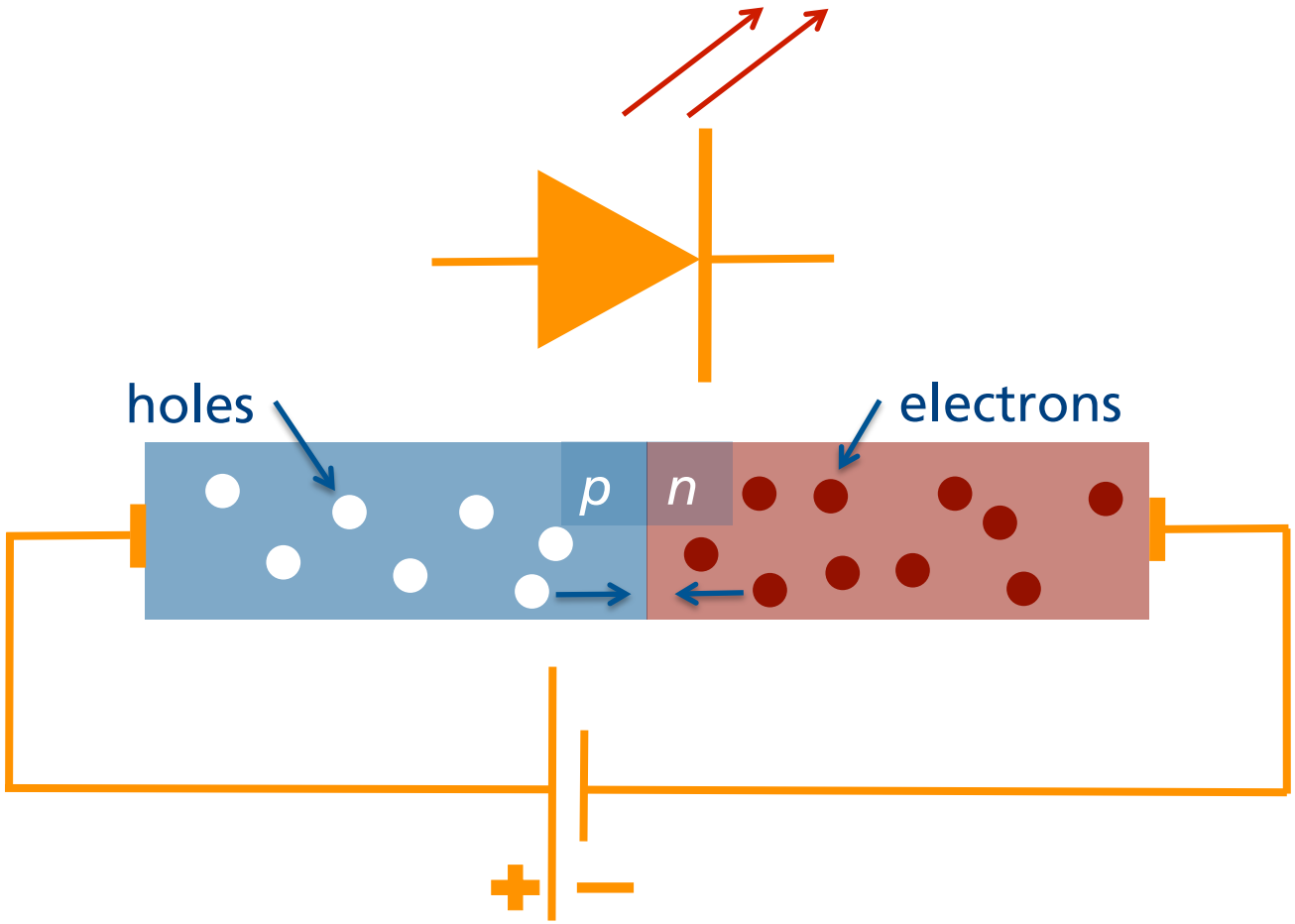
support: **NSF-IGERT, Department of Energy**

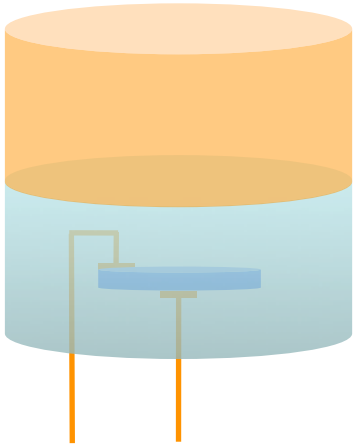
Research group, January 2010



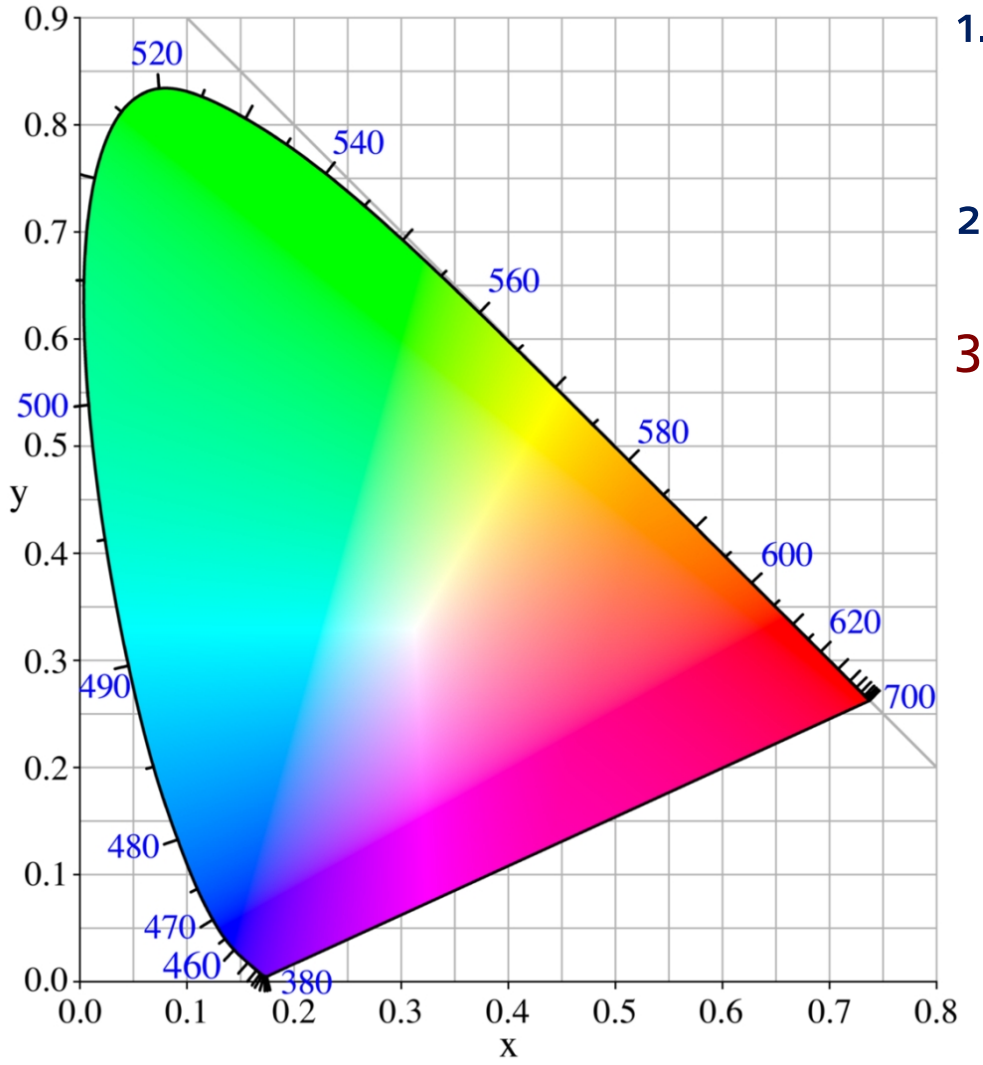
Ce^{3+} phosphors for solid state white lighting

LEDs: Converting electricity to light (*not heat !*)





Solid state lighting strategies



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

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

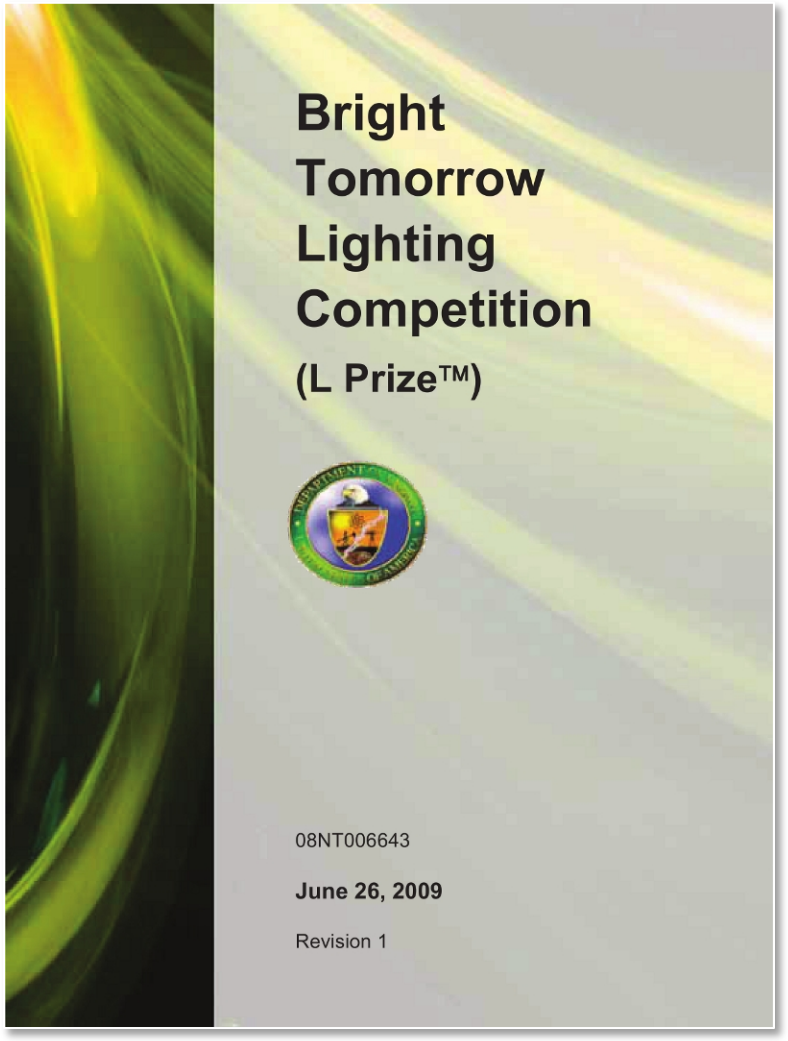
Cut Your Electricity Bill

High Times Magazine

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.

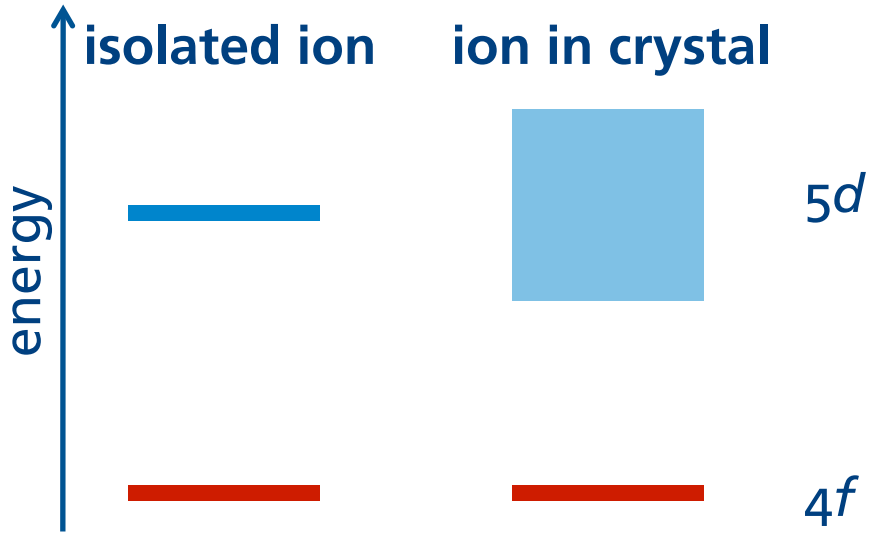
The outcome: Finding out that making new, efficient phosphors is very hard !

Understanding Ce^{3+} phosphors

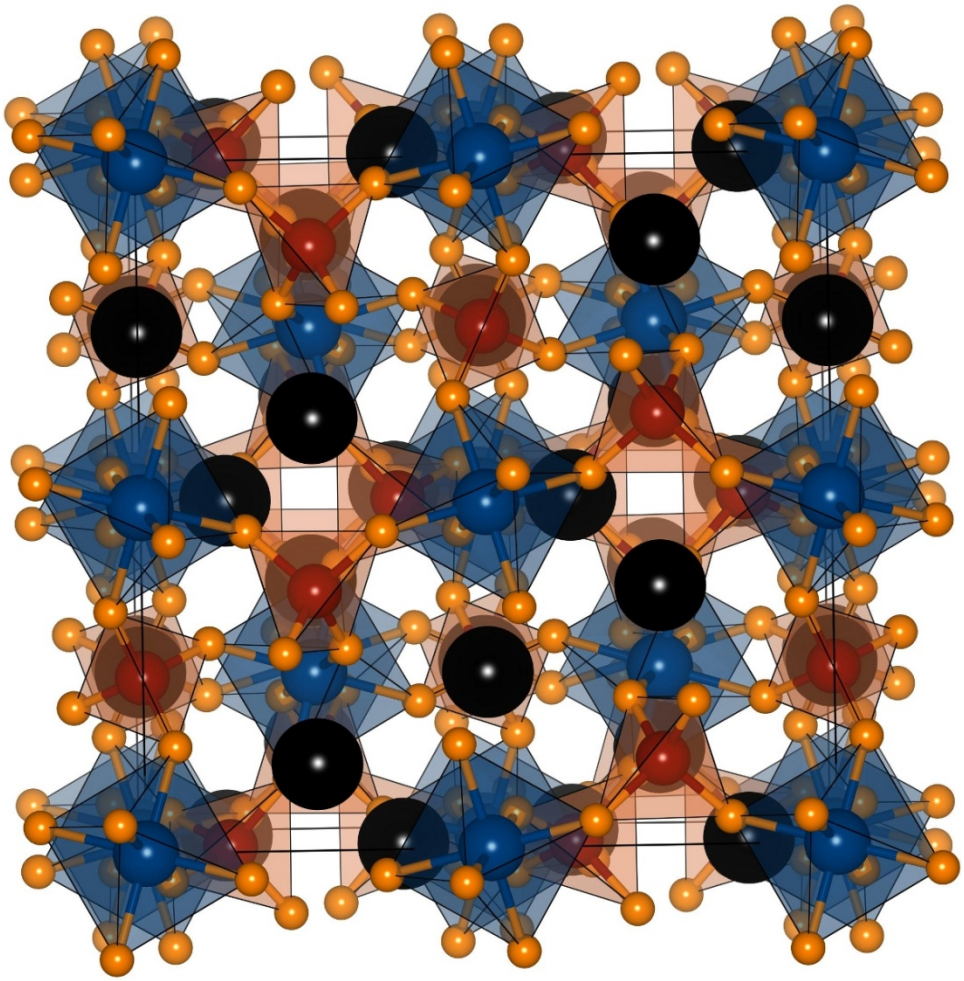
Ce is $[Xe]4f^{1}5d^{1}6s^{2}$ Ce^{3+} is $[Xe]4f^{1}5d^{0}6s^{0}$ Ce^{4+} is $[Xe]4f^{0}5d^{0}6s^{0}$

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: $Y_3Al_5O_{12}:Ce^{3+}$ (Blasse)

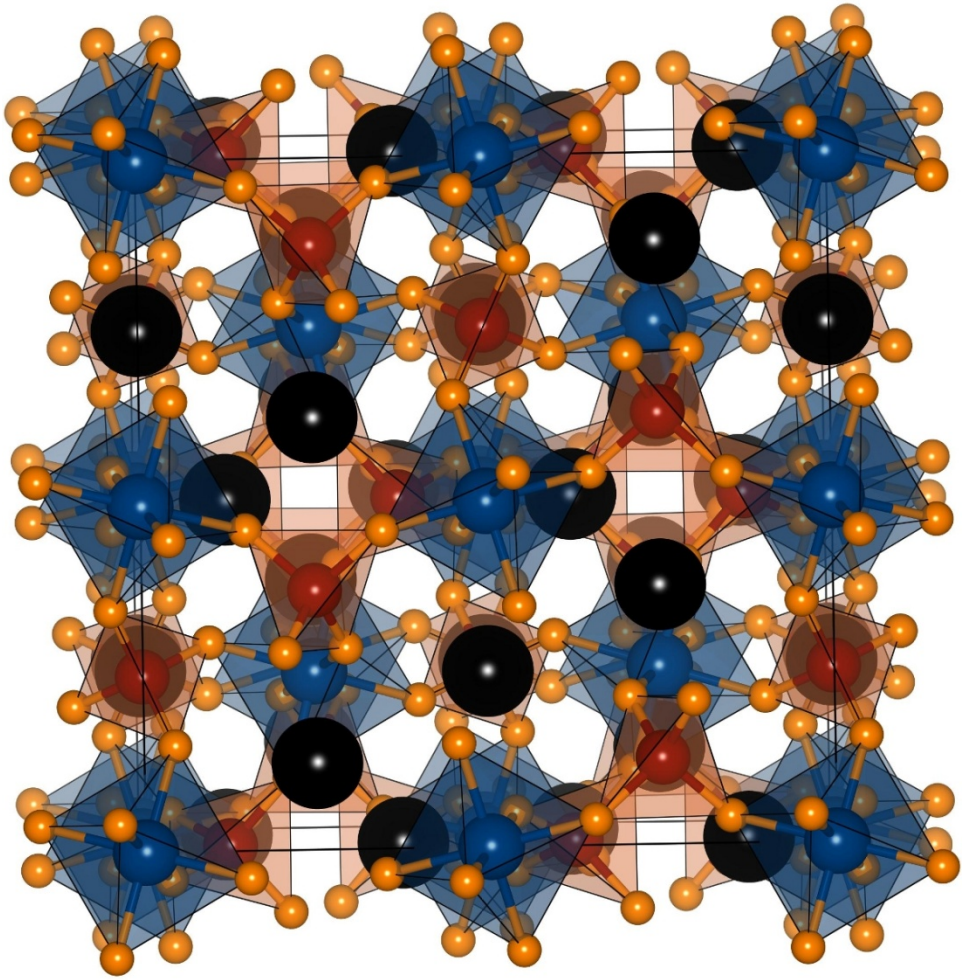


Garnet crystal structure: AlO_4 tetrahedra and AlO_6 octahedra, all completely corner-connected.

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].

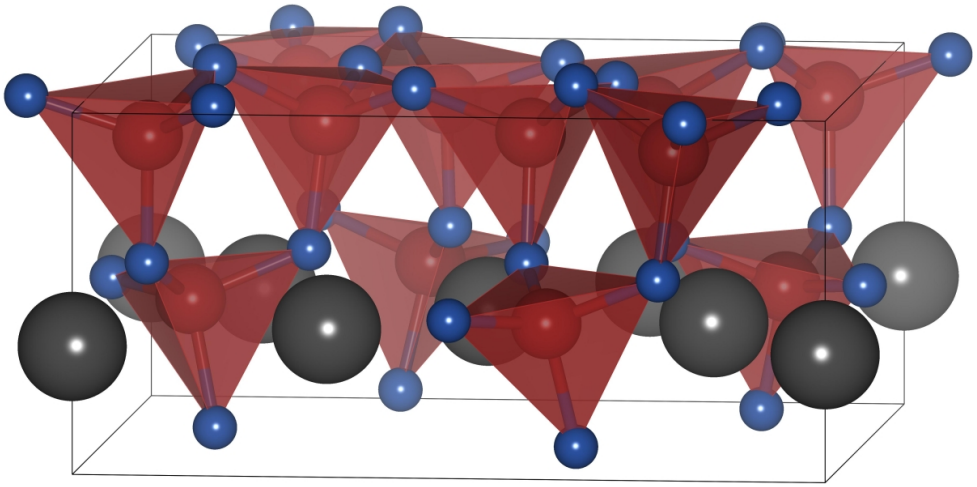
Large band gap because of Al, and connectivity.

Stiff lattice because of connectivity and light elements: Also low quenching (incl. thermal).

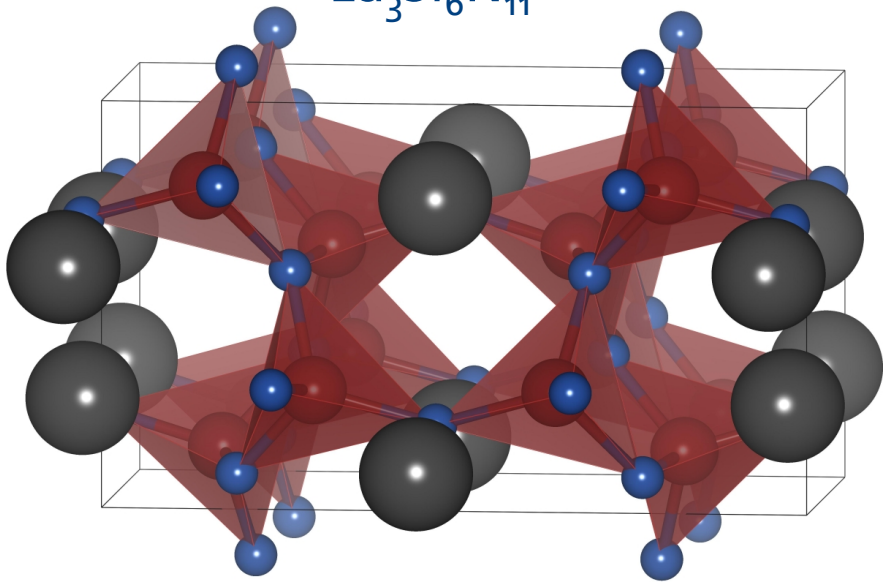
Single site for Ce^{3+}: Low disorder, and hence fewer non-radiative pathways.

Ce^{3+} substitutes smaller Y^{3+}: larger 5*d* crystal-field splitting on Ce^{3+}.

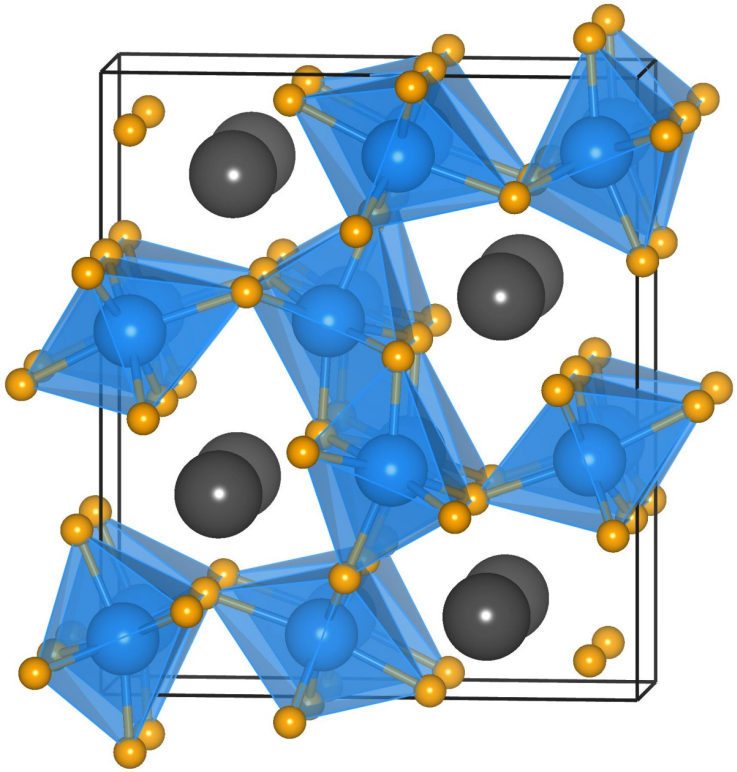
Some other phosphor hosts for Ce^{3+}



$La_3Si_6N_{11}$

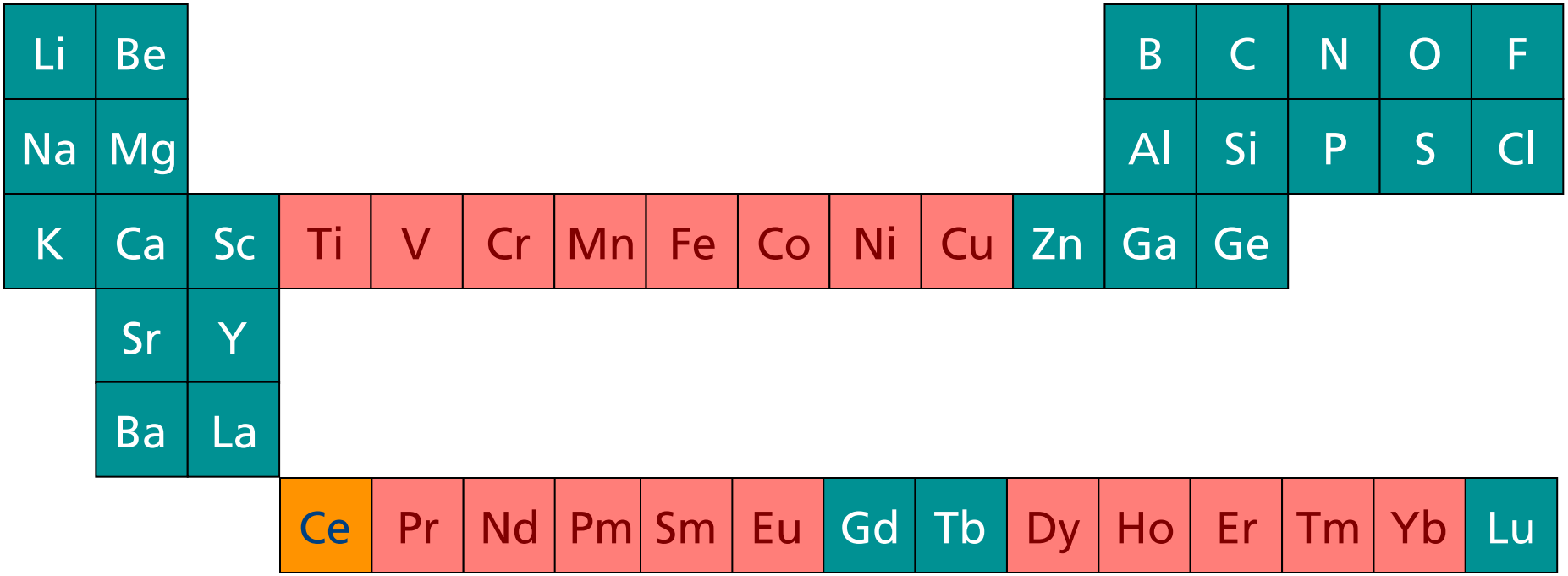


$CaAlSiN_3$

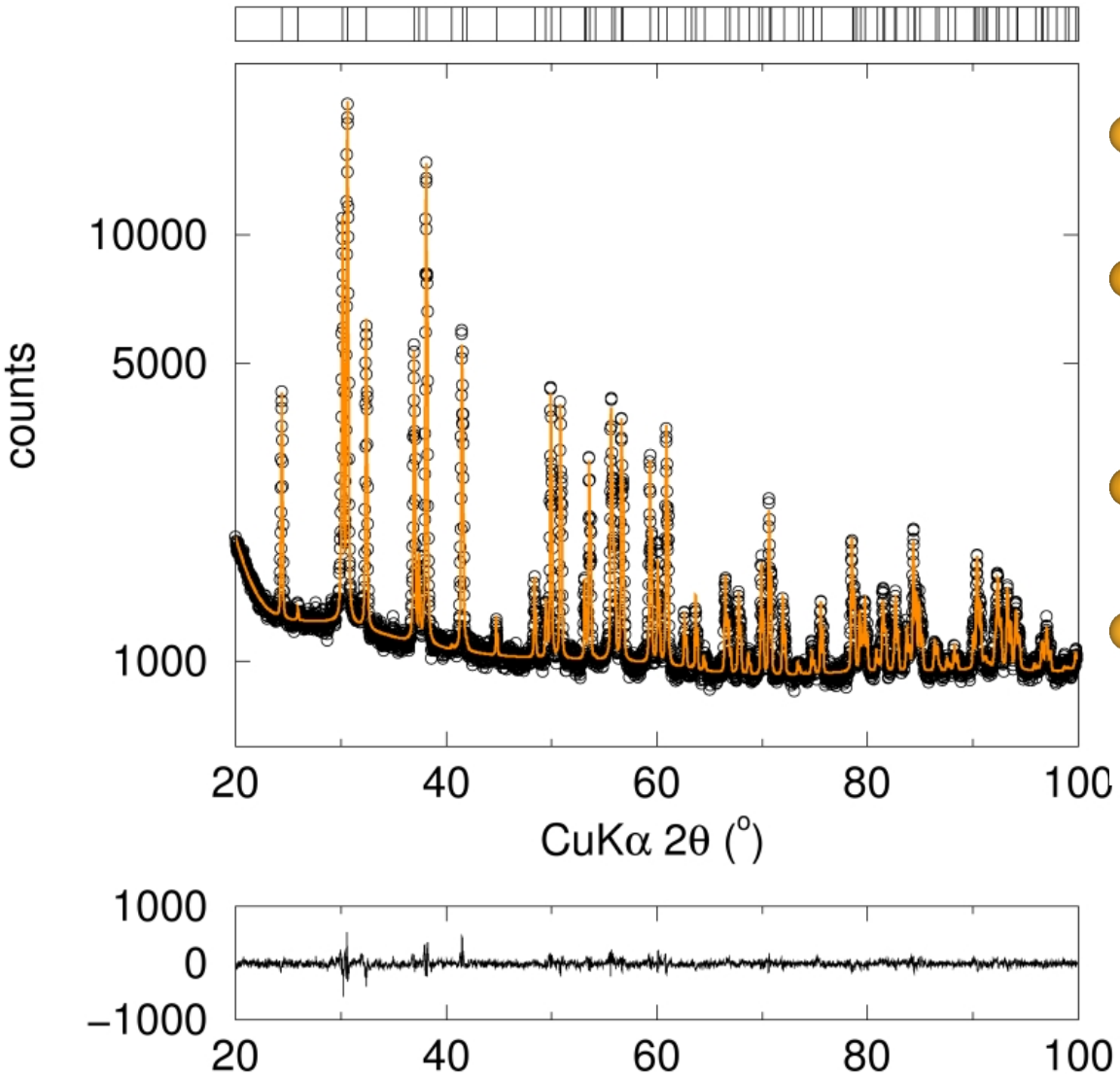


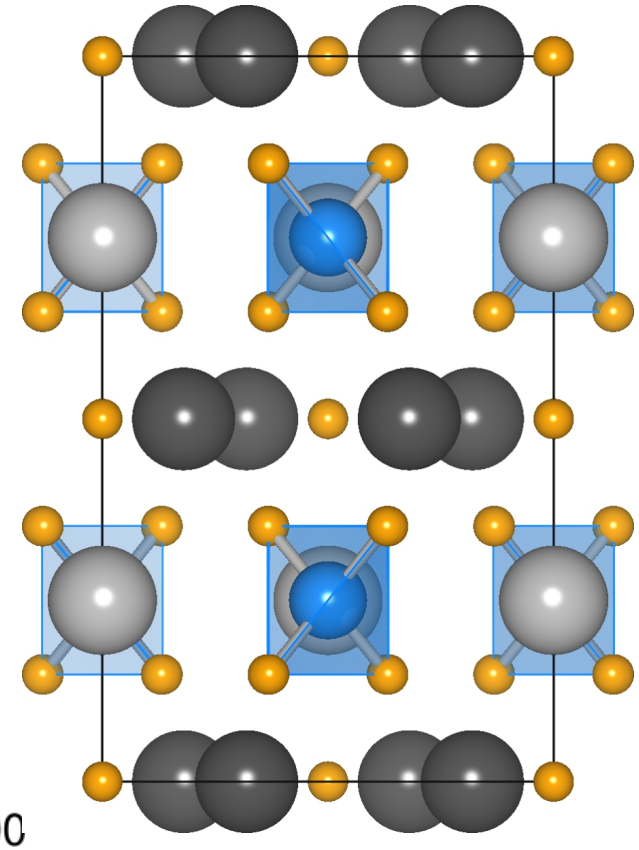
$CaSc_2O_4$

The Ce^{3+} phosphor periodic table palette



$LaSr_2AlO_5$, a new Ce^{3+} phosphor host

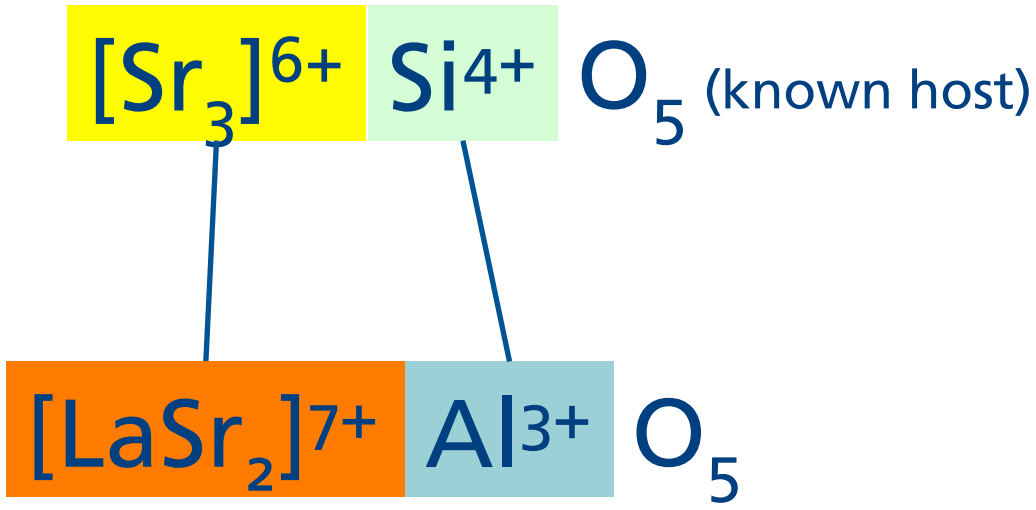




$LaSr_2AlO_5$: isostructural with known tetragonal $EuSr_2AlO_5$ (I_4/mcm)

$LaSr_2AlO_5$:

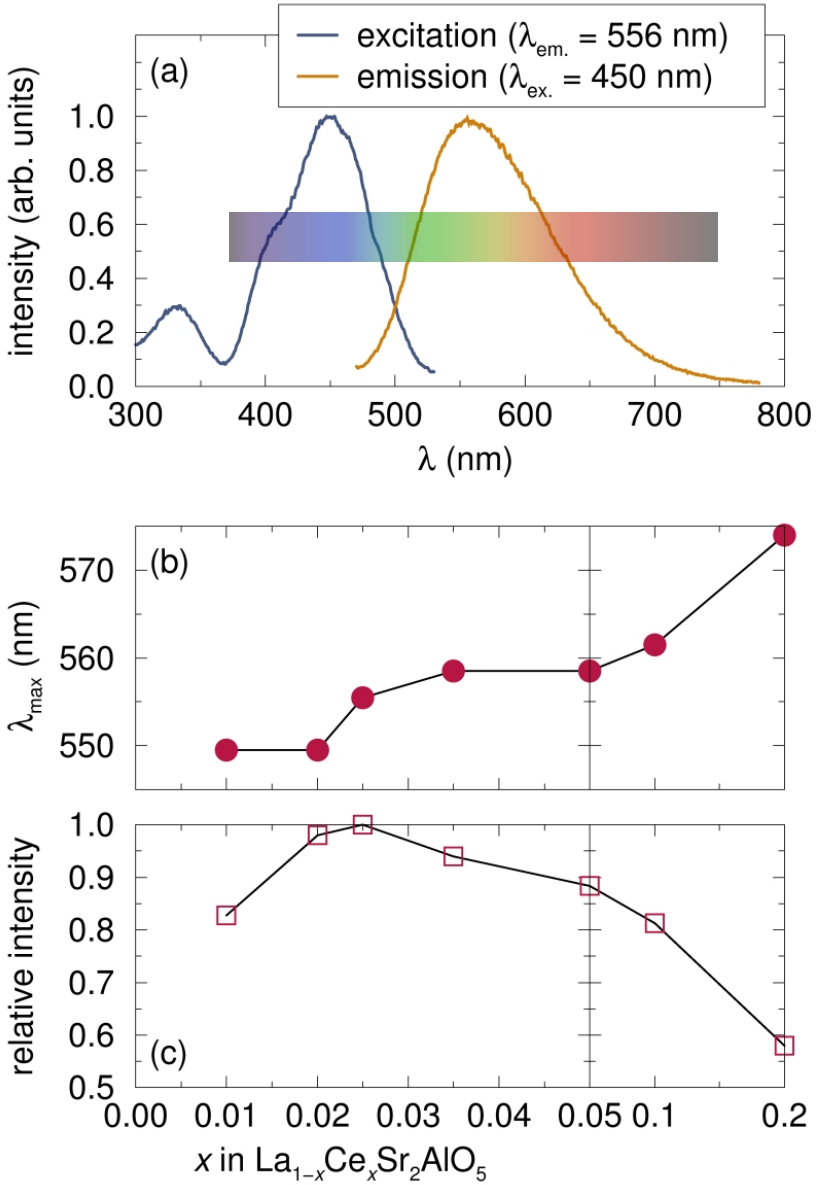
Why?



How?

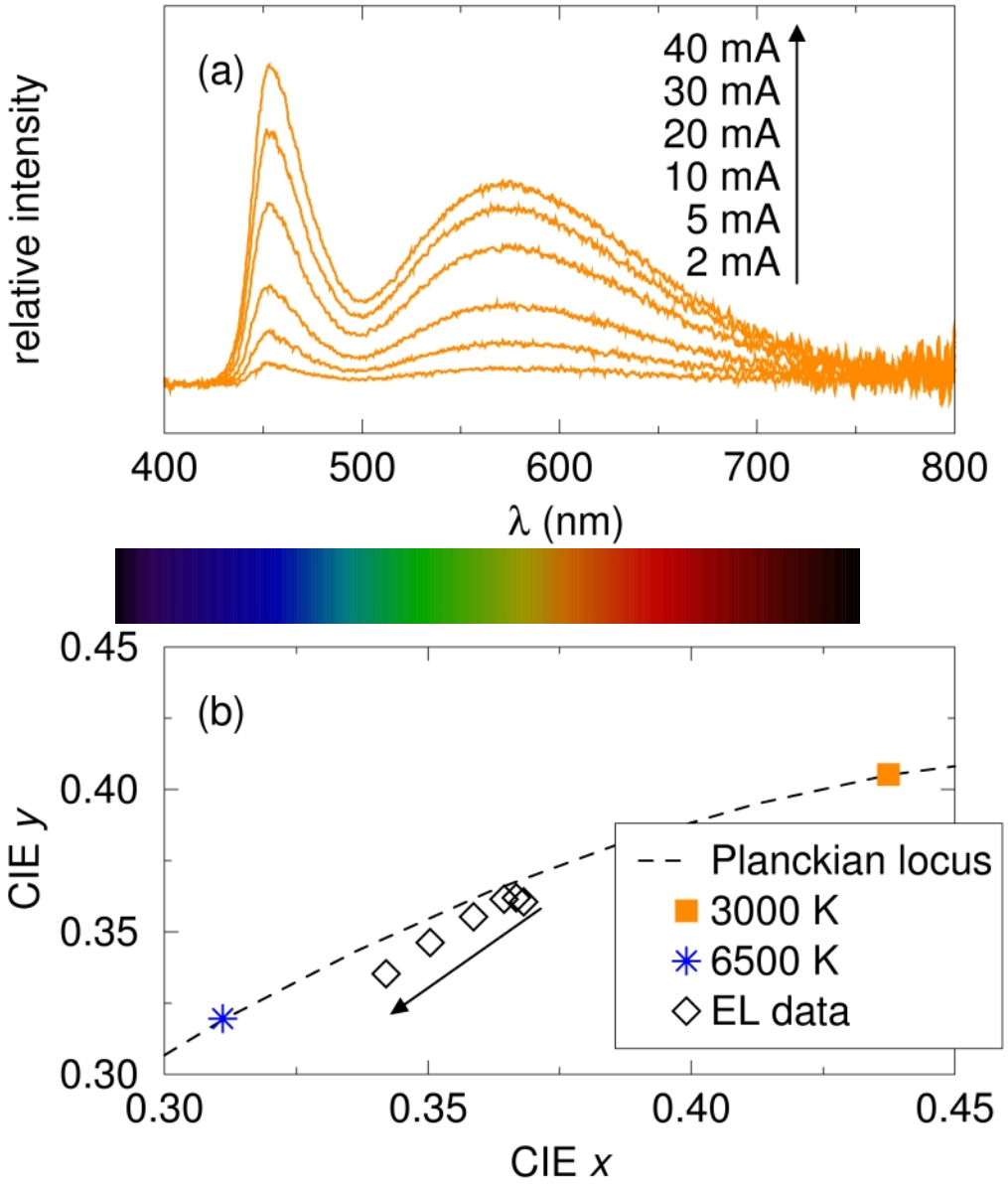
Prepared from La_2O_3,$SrCO_3$, Al_2O_3, CeO_2
1400°C to 1500°C, 5%H_2/N_2, 4 h

$LaSr_2AlO_5$



Appropriate absorption and emission positions for blue + yellow = white. Maximum emission intensity for 2.5 atom-% Ce^{3+} substitution.

$LaSr_2AlO_5$

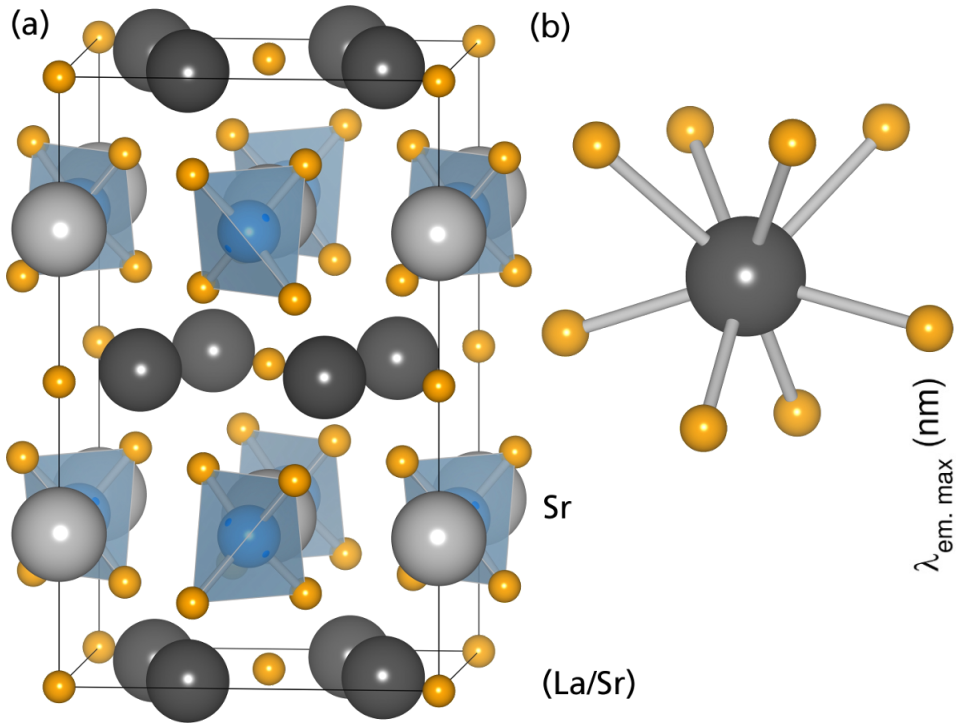


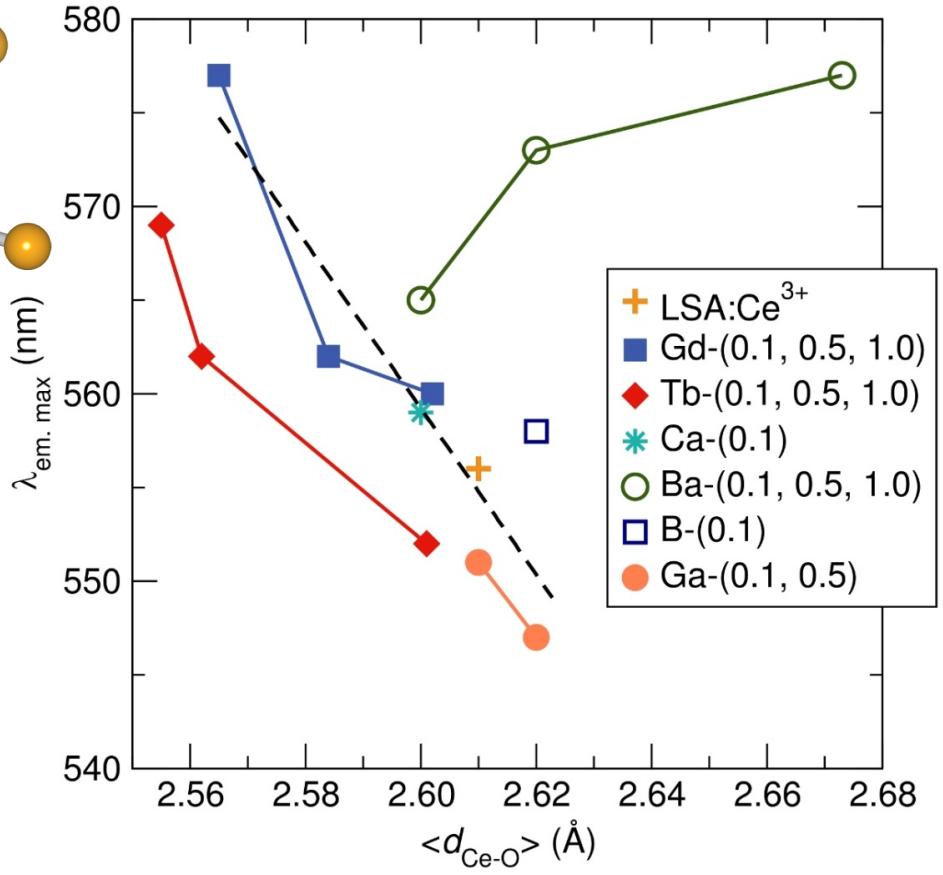
Phosphor mounted on an InGaN chip (Natalie Fellows).

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

Im, Kim, Fellows, Masui, Hirata, DenBaars, Seshadri, *Appl. Phys. Lett.* **93** (2008) 091905.

$LaSr_2AlO_5$: Tunability

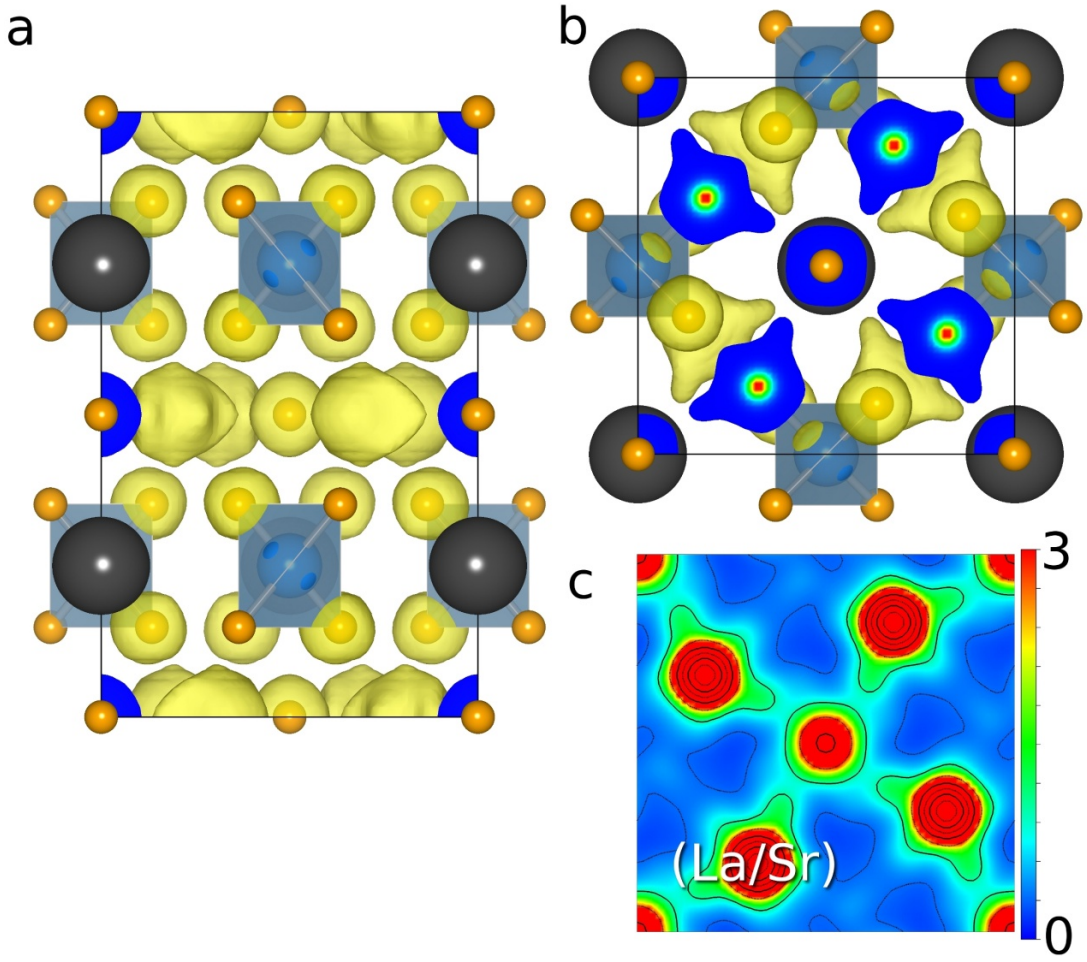




For most compositions, the emission peak scales with compression of the CeO_8 polyhedron.

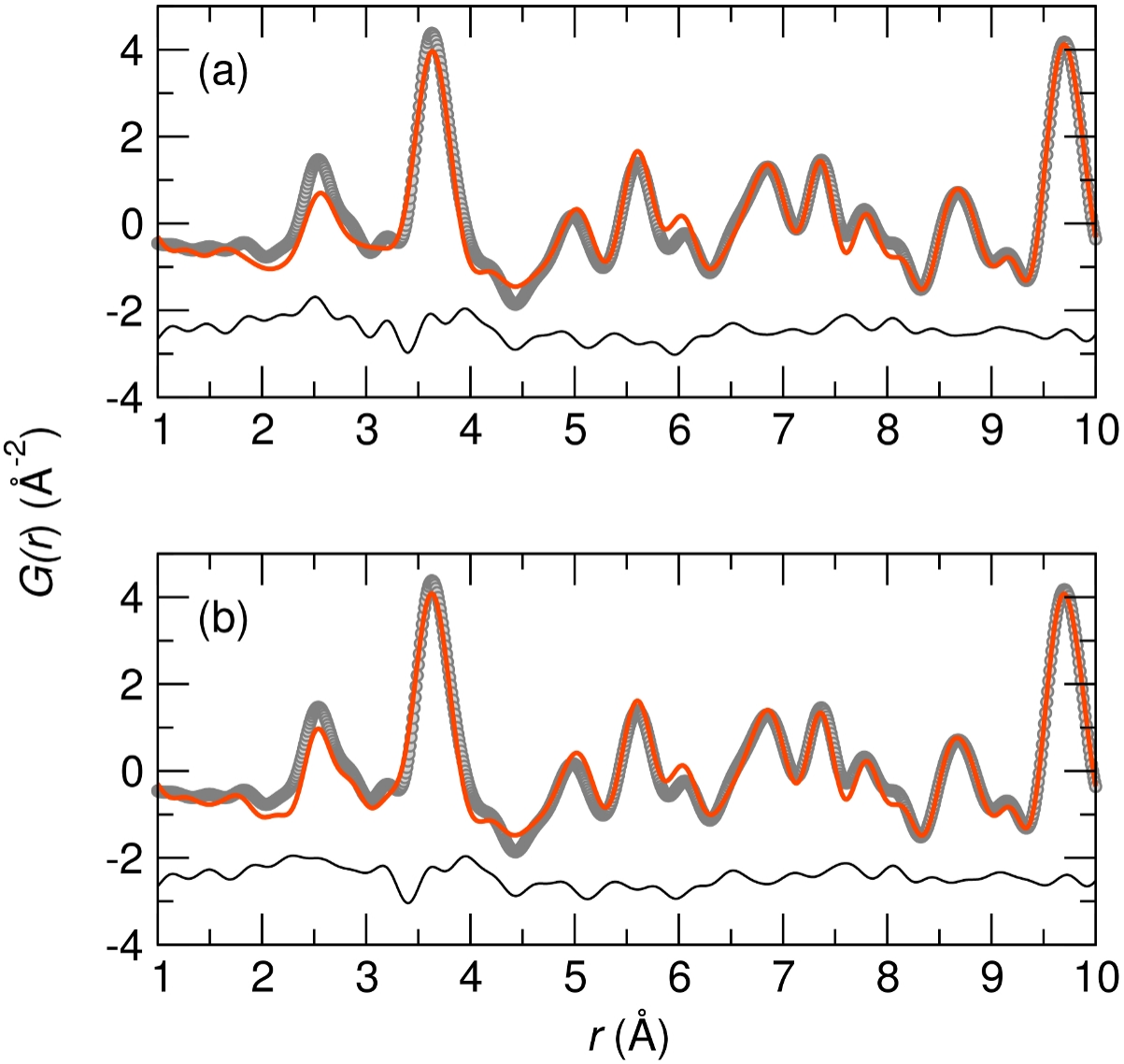
Im, Fellows, DenBaars, Seshadri, Kim, *Chem. Mater.* **21** (2009) 2157

$LaSr_2AlO_5$: 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.

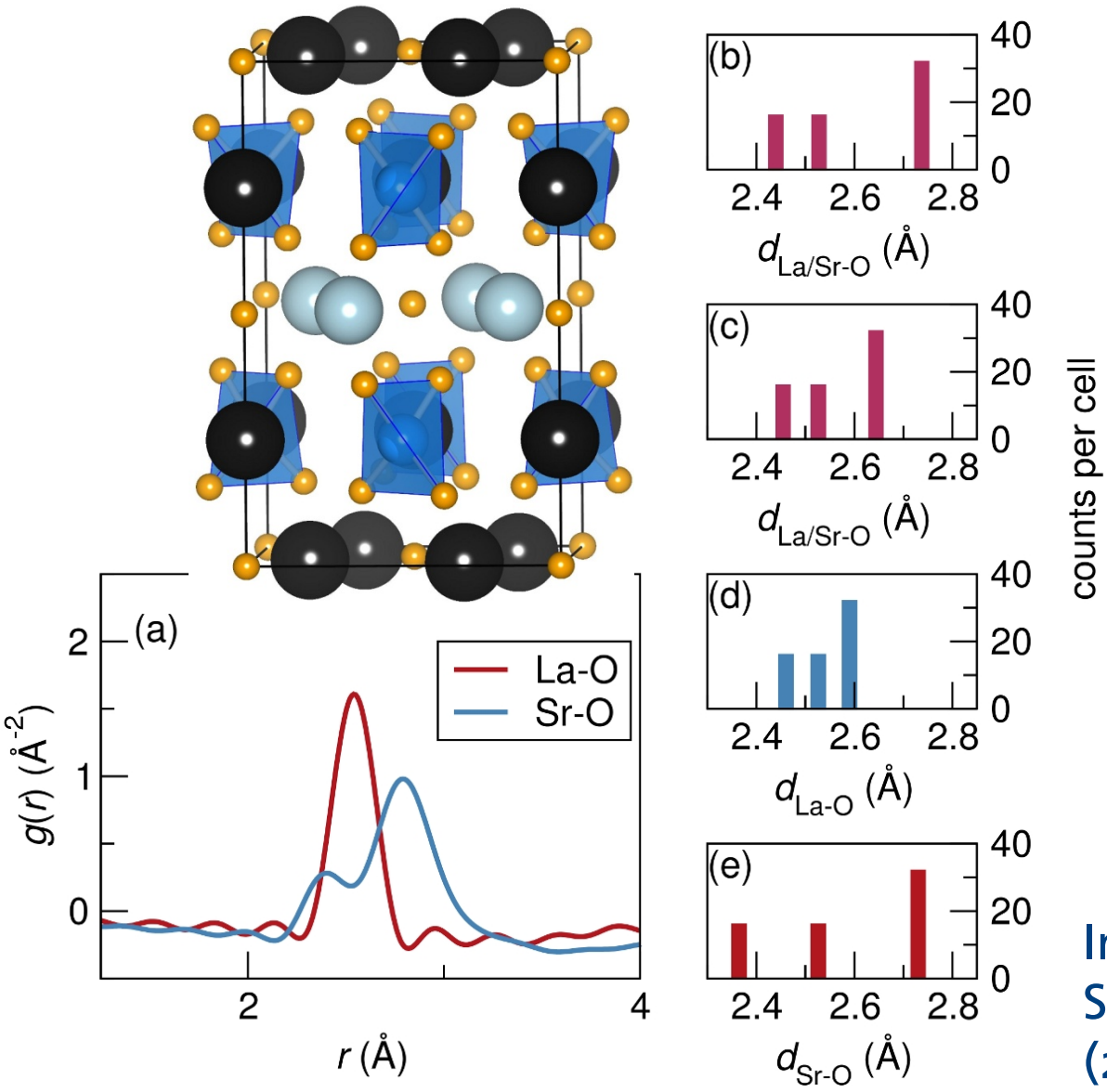
$LaSr_2AlO_5$: Local structure



(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.

$LaSr_2AlO_5$: Local structure

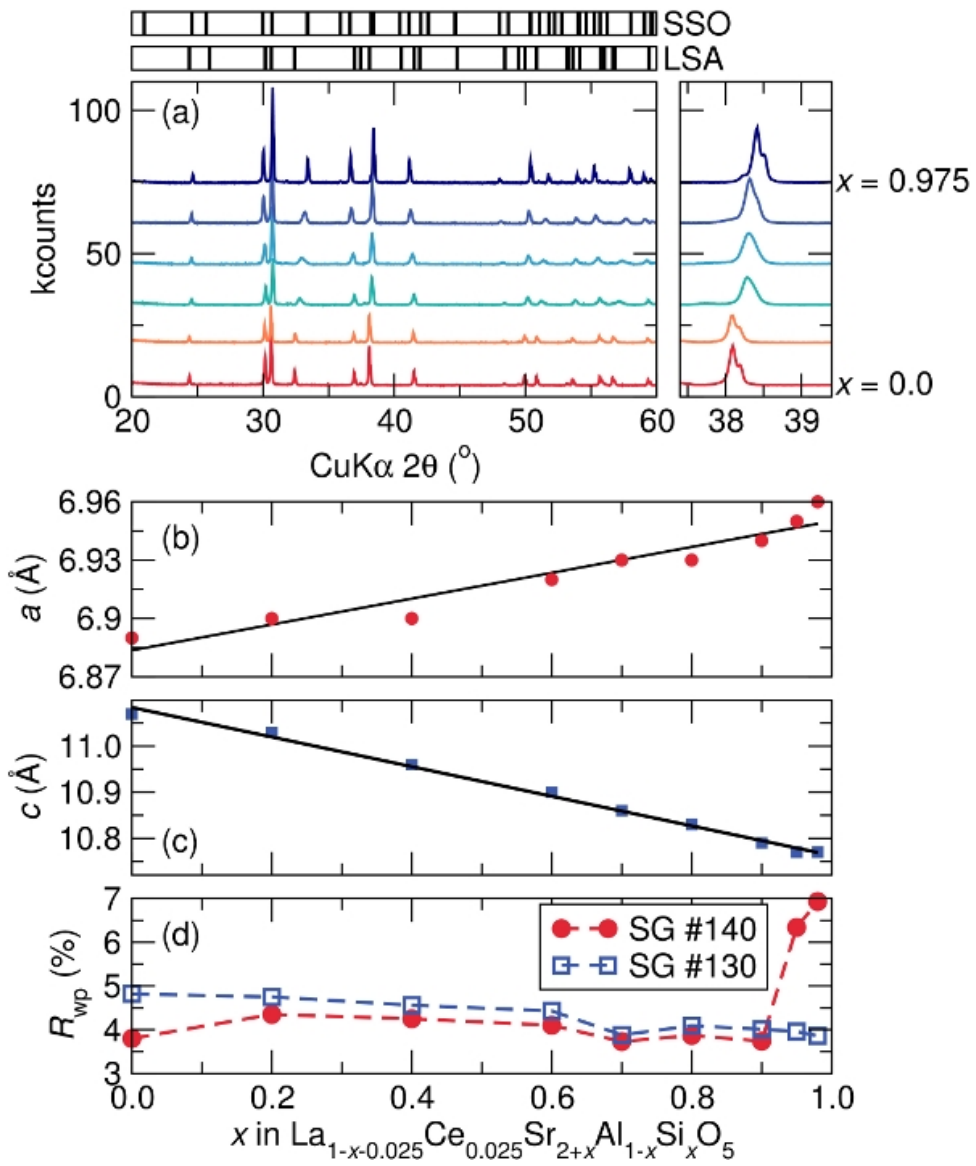


PDF local coordination of La and Sr are distinct; modeled using an ordered structure.

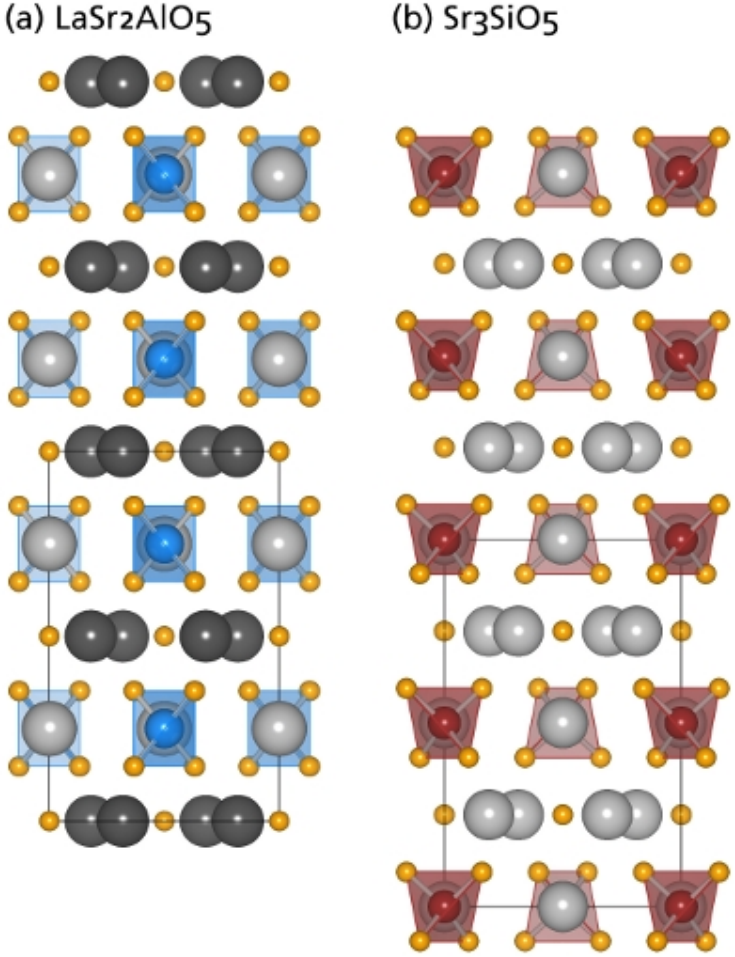
Coordination of La/Ce more regular than suggested by average structure.

Im, Page, Fellows, DenBaars, Seshadri, *J. Mater. Chem.* **19** (2009) 8761.

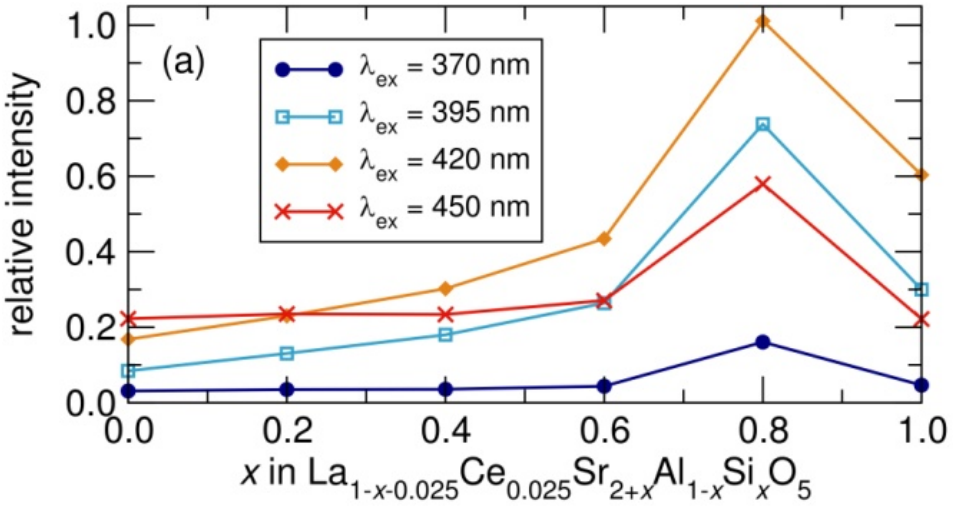
$LaSr_2AlO_5$-Sr_3SiO_5 solid solution

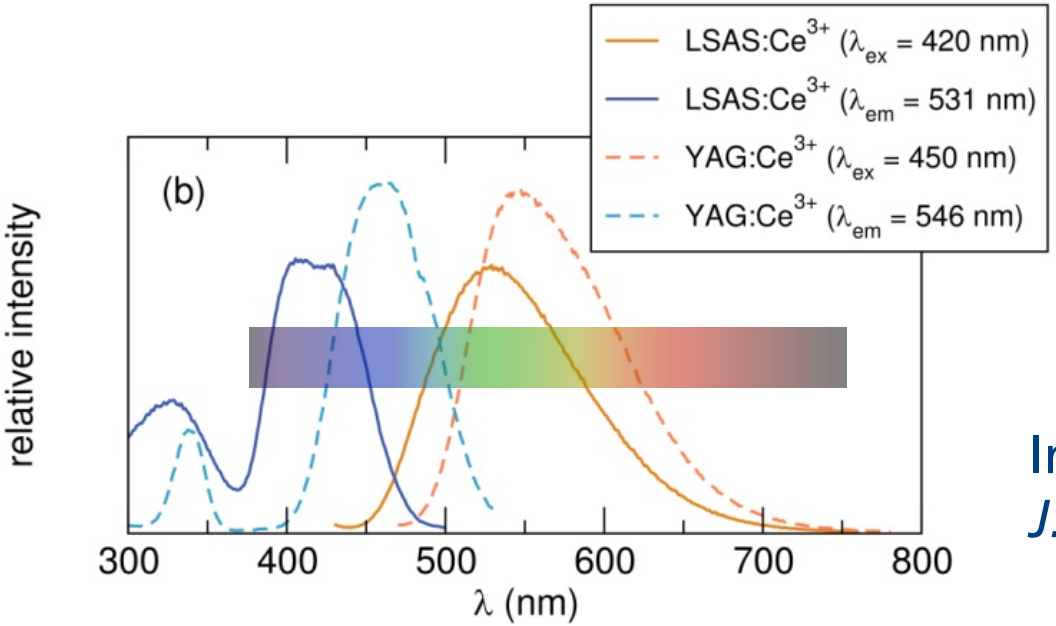


Solid solutions between two end-members with distinct crystal structures.



$LaSr_2AlO_5$-Sr_3SiO_5 solid solution





Emission intensity in the solid solution goes through a maximum.

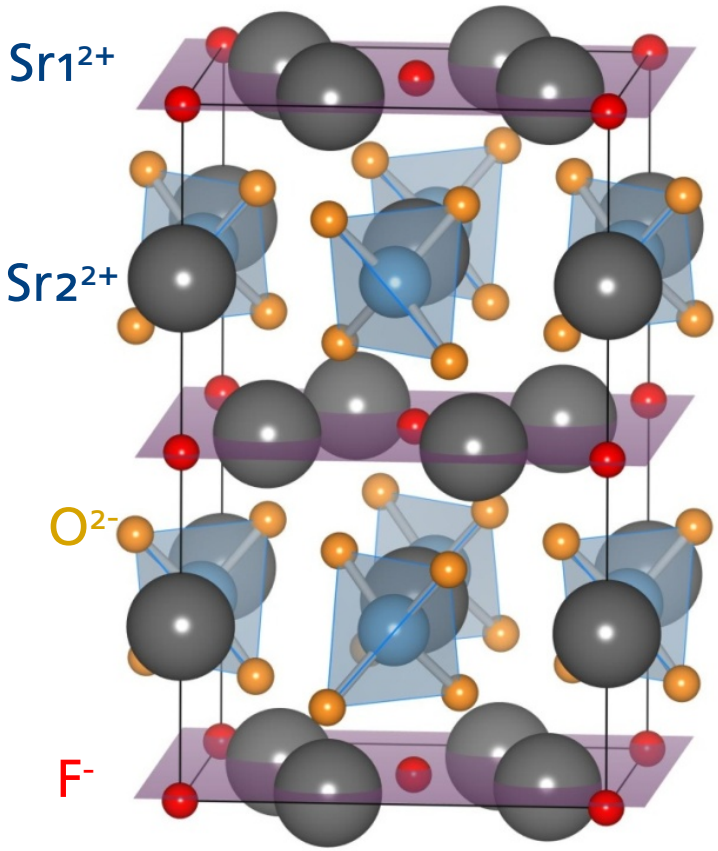
Absorption and emission features remain appropriate for white lighting.

Much more efficient phosphor than the LSA end-member.

Im, Fellows, DenBaars, Seshadri, *J. Mater. Chem.* **19** (2009) 1325.

Oxyfluorides: $Sr_{3-x}AlO_4F:Ce^{3+}_x$

Sr_3AlO_4F (*I4/mcm*, 140)

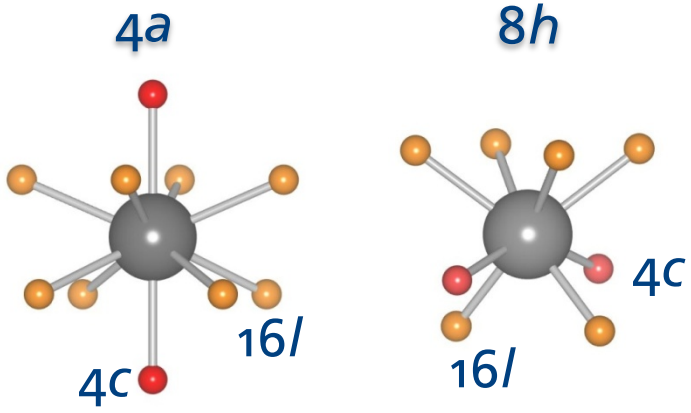


Compound, with (suggested) well ordered fluorine layers

Modification of the the LSA phosphor

$LaSr_2AlO_5 \longleftrightarrow Sr_3AlO_4F$

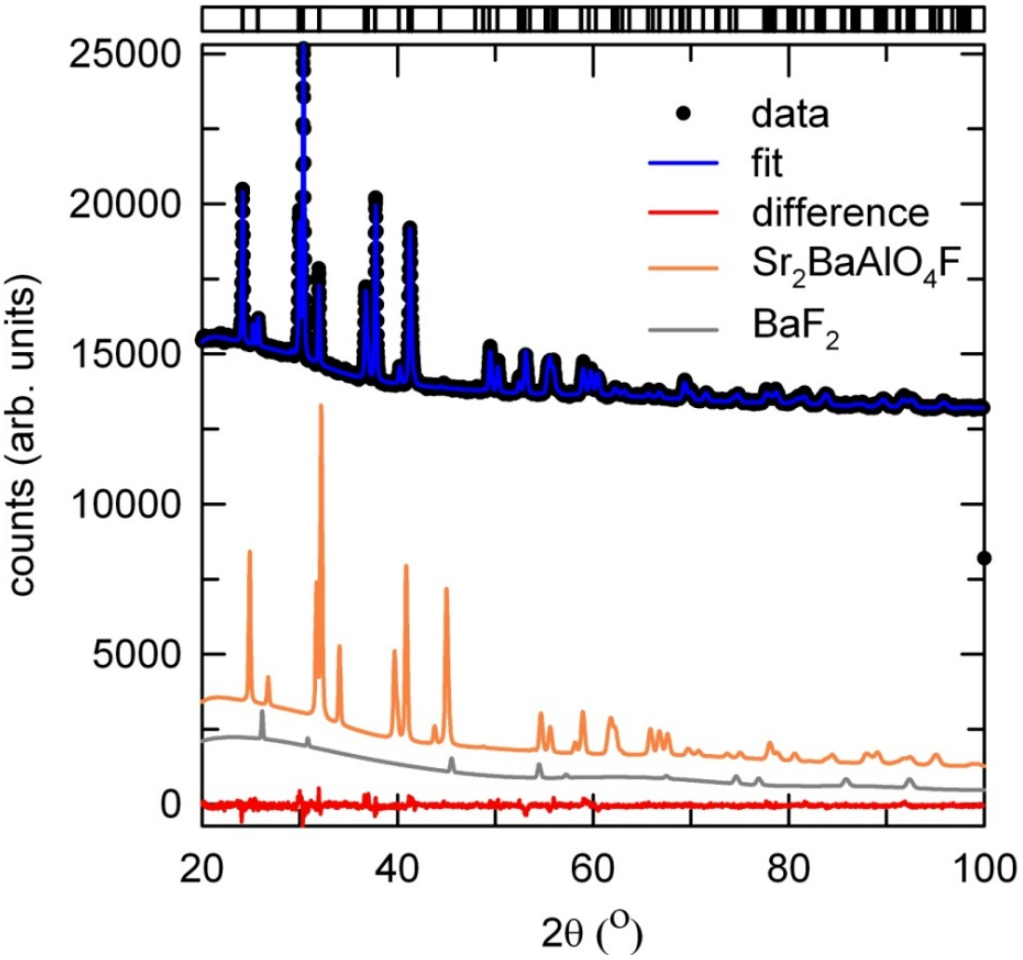
La^{3+} changed to Sr^{2+}
Fluoride for charge compensation



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

Vogt *et al. J. Solid State Chem.* **144** (1999) 228.

$Sr_{3-x}Ba_xAlO_4F:Ce^{3+}$, an efficient green phosphor:



atoms	site	BVS
Sr	8*h*	1.99
Ba	4*a*	1.93

Ba addition into SAF:Ce^{3+} stabilizes the host

a = *b* = 6.9189(6) Å, *c* = 11.2071(7) Å

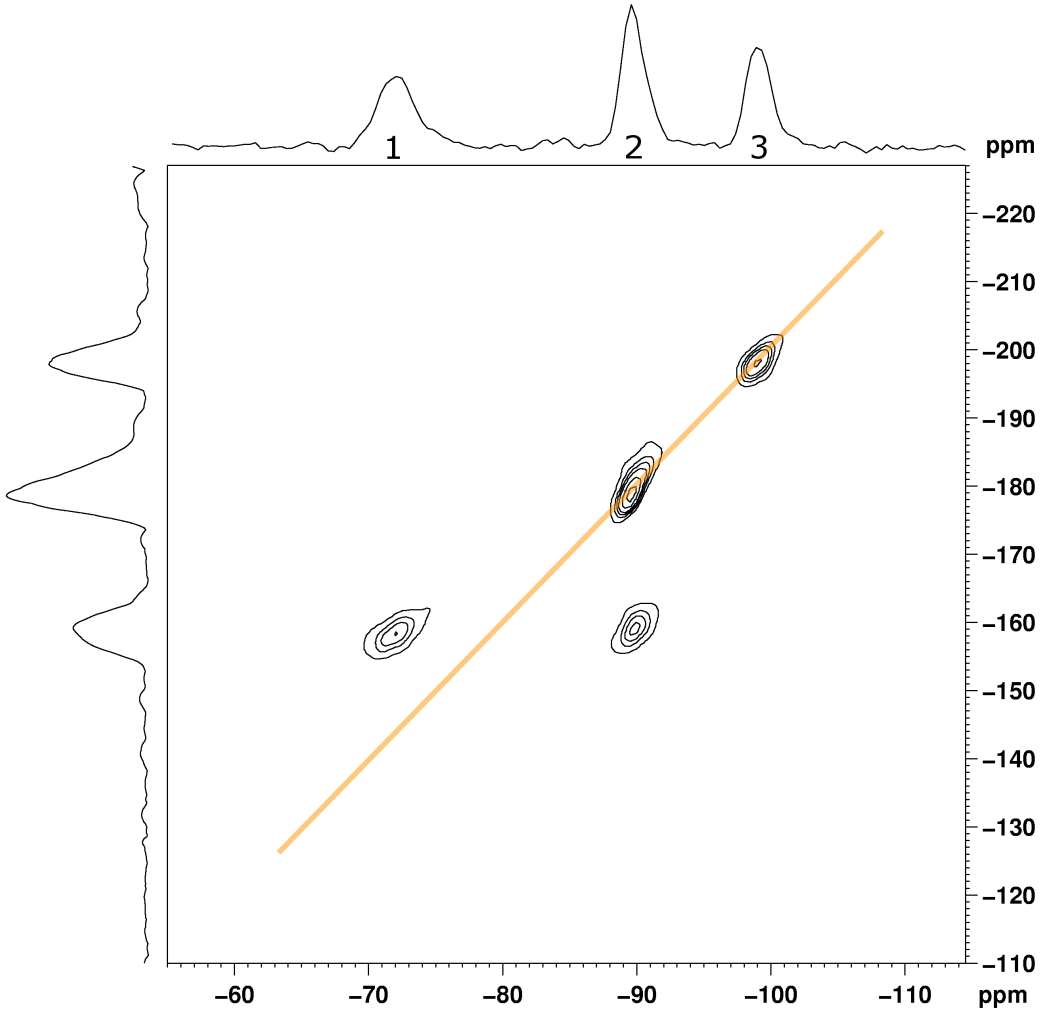
$Sr_{3-x}Ba_xAlO_4F:Ce^{3+}$, an efficient green phosphor:

Locating F in the structure is key since optical properties depend on the nature of the $Ce^{3+}O_xF_y$ 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.

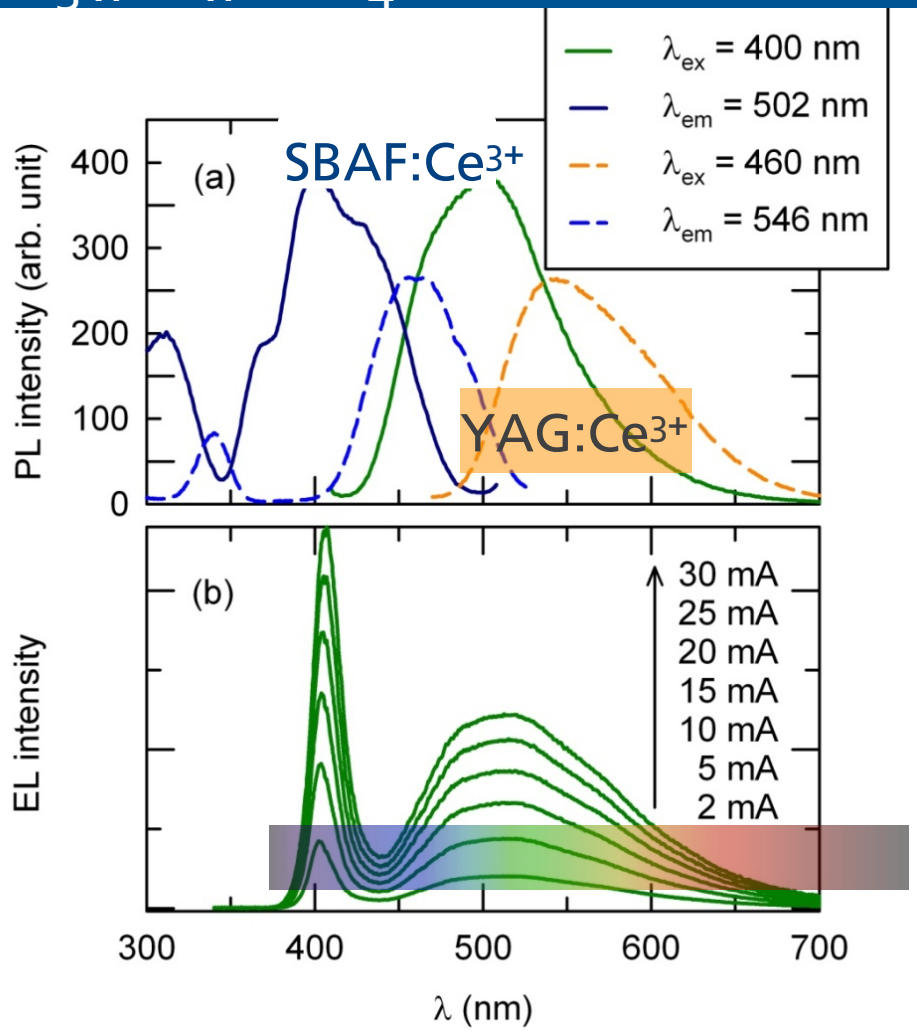
3 is impurity.

2—2 correlations are importan
1—2 correlations are importan
1—1 are not.



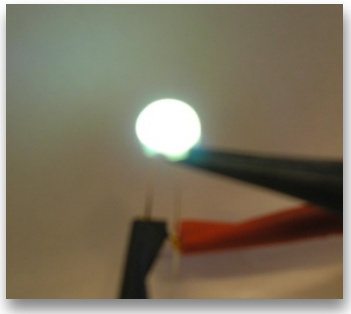
Dr. Jerry Hu, UCSB MRL

$Sr_{3-x}Ba_xAlO_4F:Ce^{3+}$, an efficient green phosphor:



Quantum efficiency (QE) data

Sample	QE (%)
$SAF:Ce^{3+}$	83
$SBAF:Ce^{3+}$	95
$YAG:Ce^{3+}$	81



30 lm/W at 20 mA (λ_{max}=405 nm chip)

Prototype LED image

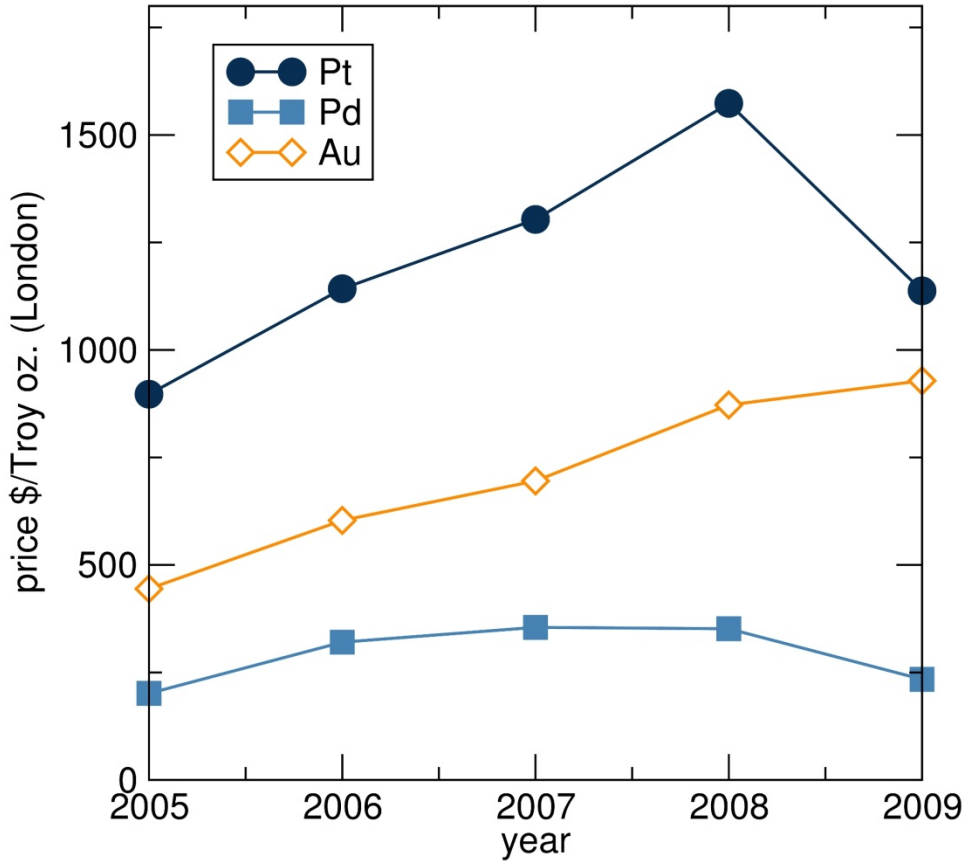
Im, Fourré, Brinkley, Sonoda, Nakamura, DenBaars, Seshadri, *Optics Express* **17** (2009) 22673; Im, Brinkley, Mikhailovsky, Hu, DenBaars, Seshadri, *Chem. Mater.* (ASAP).

Pd^{2+} -substituted oxides for catalysis

PGM use

Motivation: Reducing PGM use in catalysts

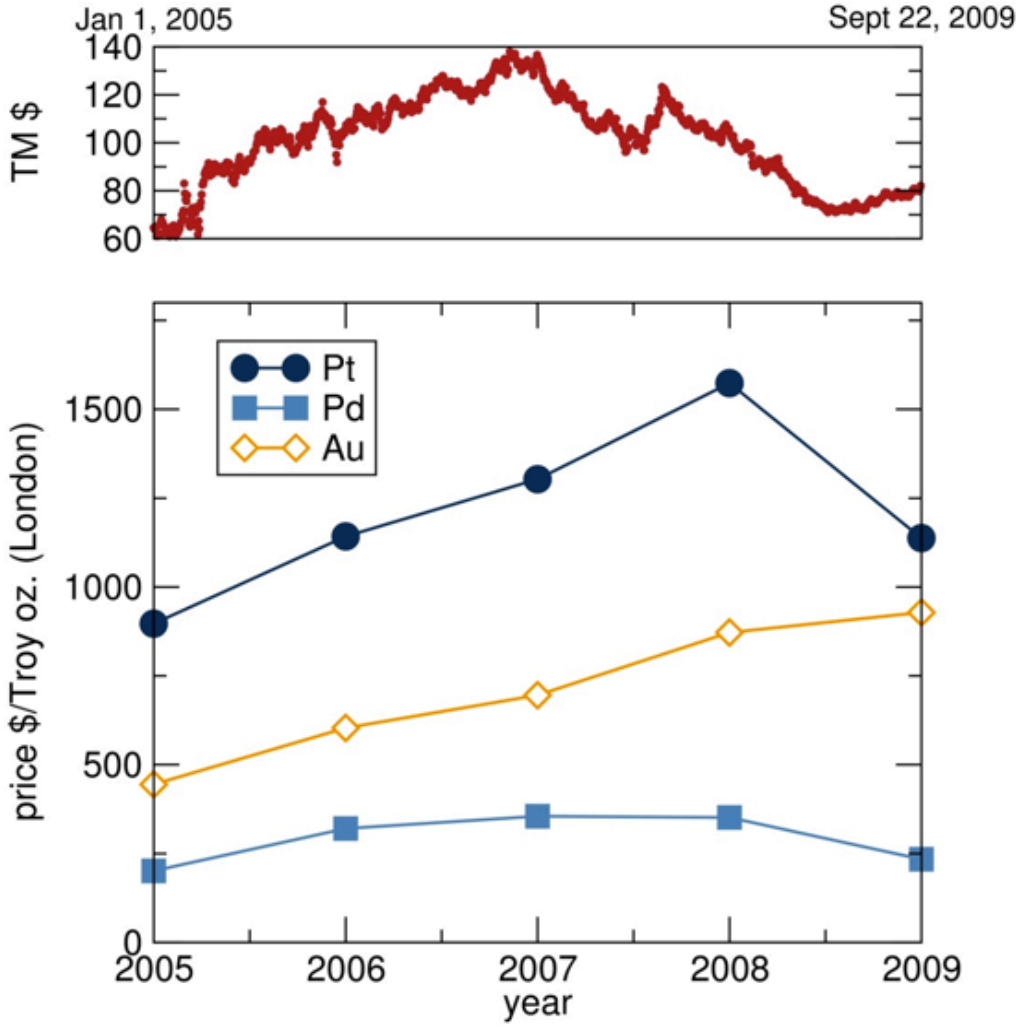
PGM = Platinum Group Metal



Fe	Co	Ni	Cu
Ru	Rh	Pd	Ag
Os	Ir	Pt	Au

Data from kitco.com

PGM use



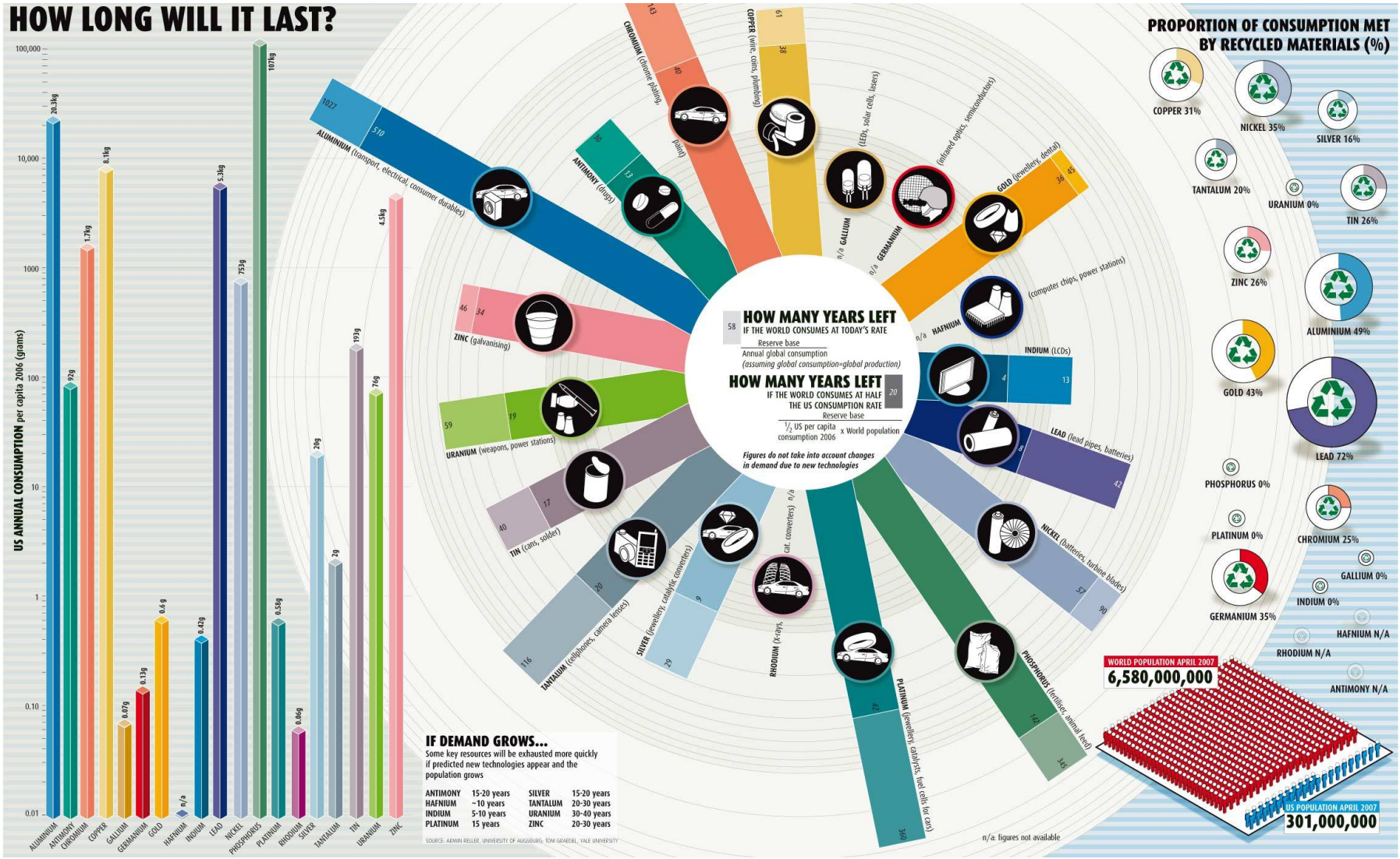
More that 50% of Pt use is in automotive catalysis: 3-way converters.

Price today (kitco):

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

Data from kitco.com and google finance

PGMs: A dwindling resource

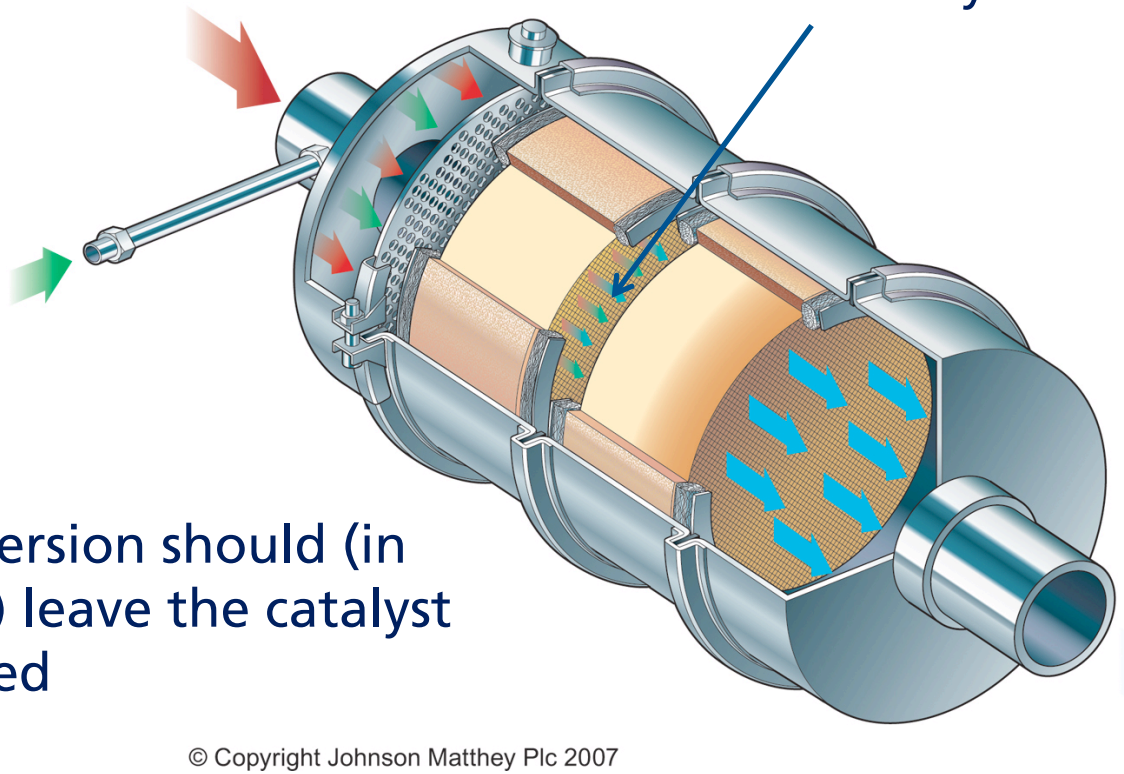


Earth's Natural Wealth: An Audit, New Scientist, 23 May 2007.

Three-way catalytic convertors

Catalyst: Oxide-supported PGM nanoparticles dispersed on ceramic honeycombs

hydrocarbons + CO + NO_x

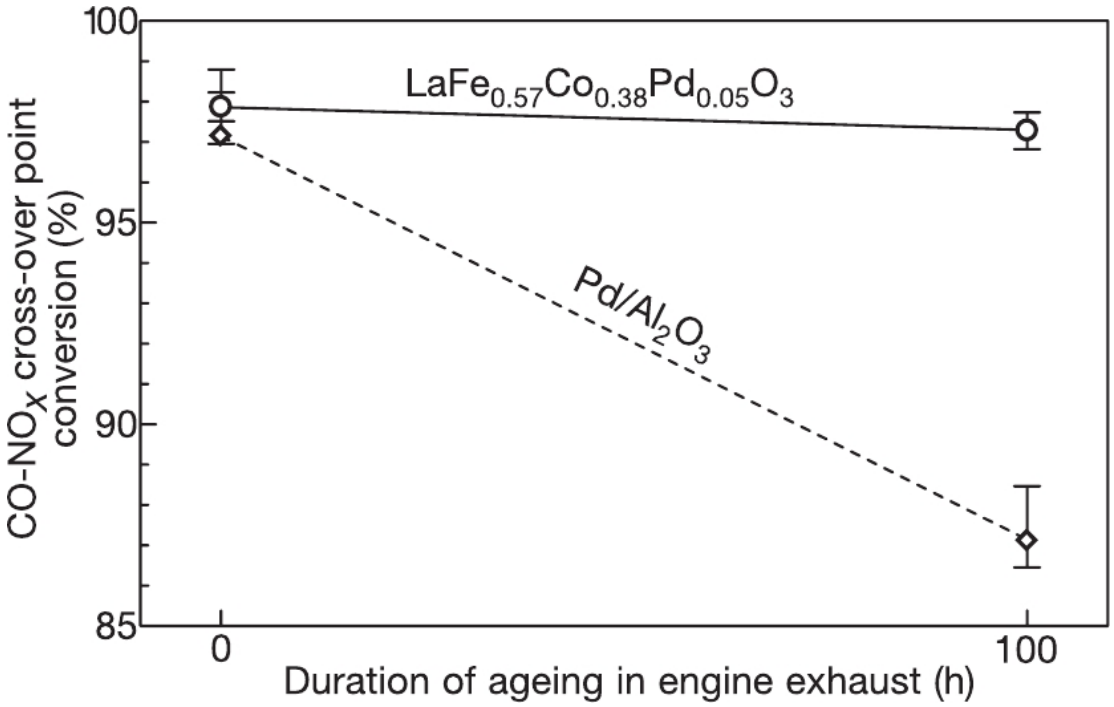


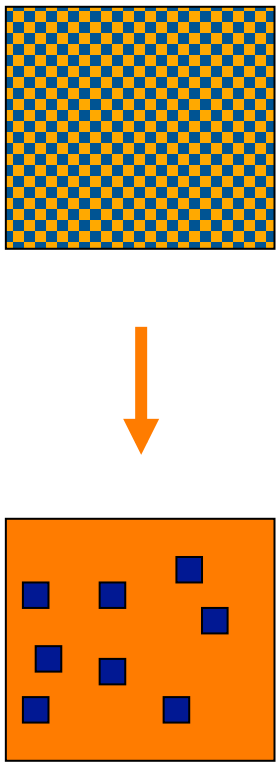
The conversion should (in principle) leave the catalyst unchanged

$N_2 + CO_2 + H_2O$

New catalyst paradigms

"Intelligent catalysts"





Oxidized state (Pd^{2+} in lattice)

Reduced state (supported Pd^{0} nanoparticles)

Nishihata, Mizuki, Akao, Tanaka, Uenishi, Kimura, Okamoto, Hamada, Self-regeneration of a Pd-perovskite catalyst for automotive emissions control, *Nature* **418** (2002) 164.

Pd^{2+} -substituted oxides for catalysis

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 ?

$BaCeO_3$:Pd

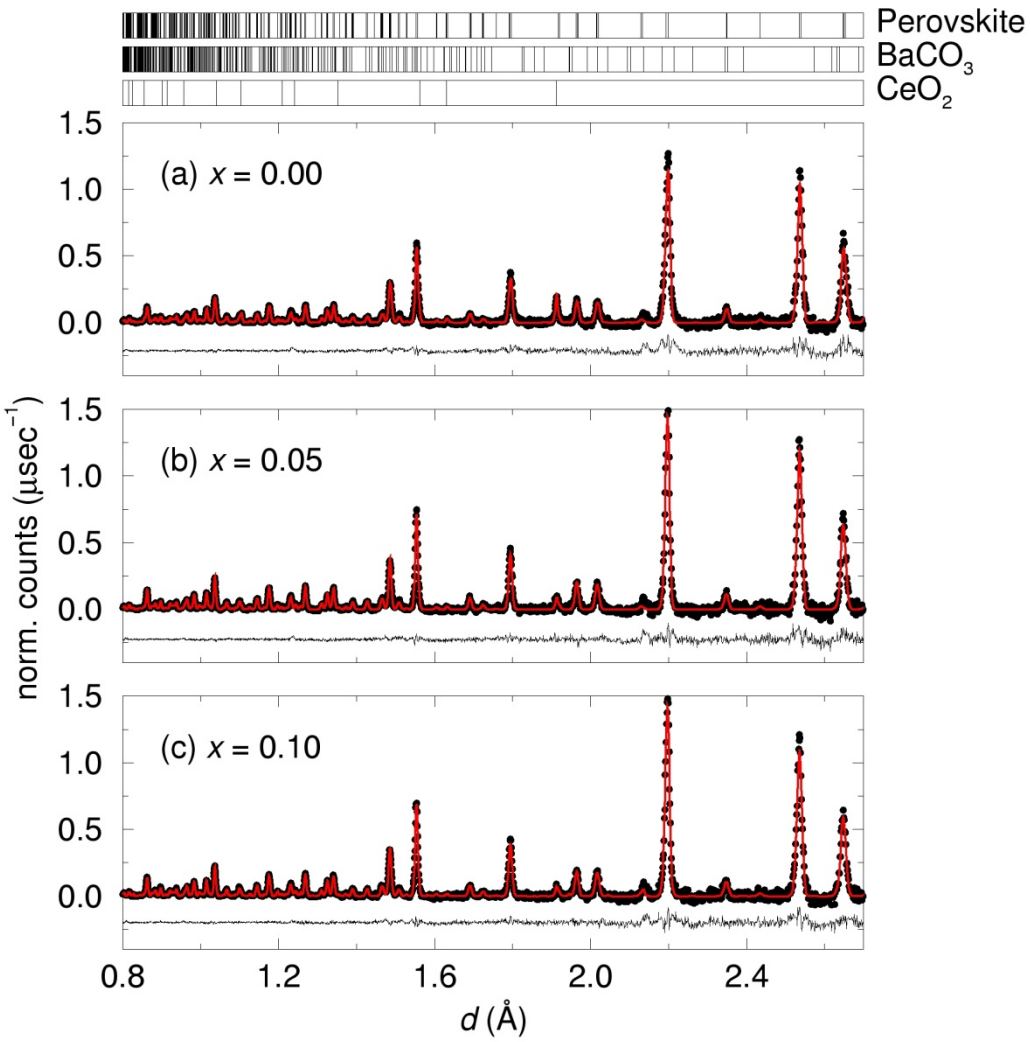
Perovskite $BaCeO_3$ as a host:

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

$BaCe_{1-x}Pd_xO_{3-\delta}$
with x = 0, 0.05, and 0.10

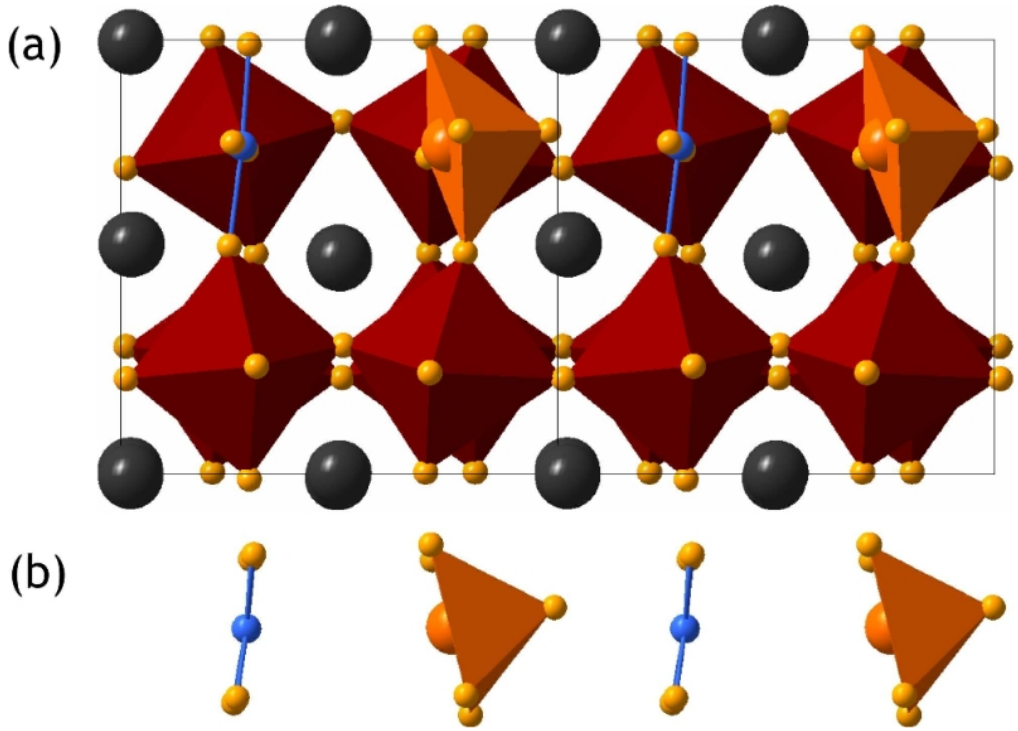
Samples prepared by solid state routes in O_2, between 800°C and 1000°C.

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



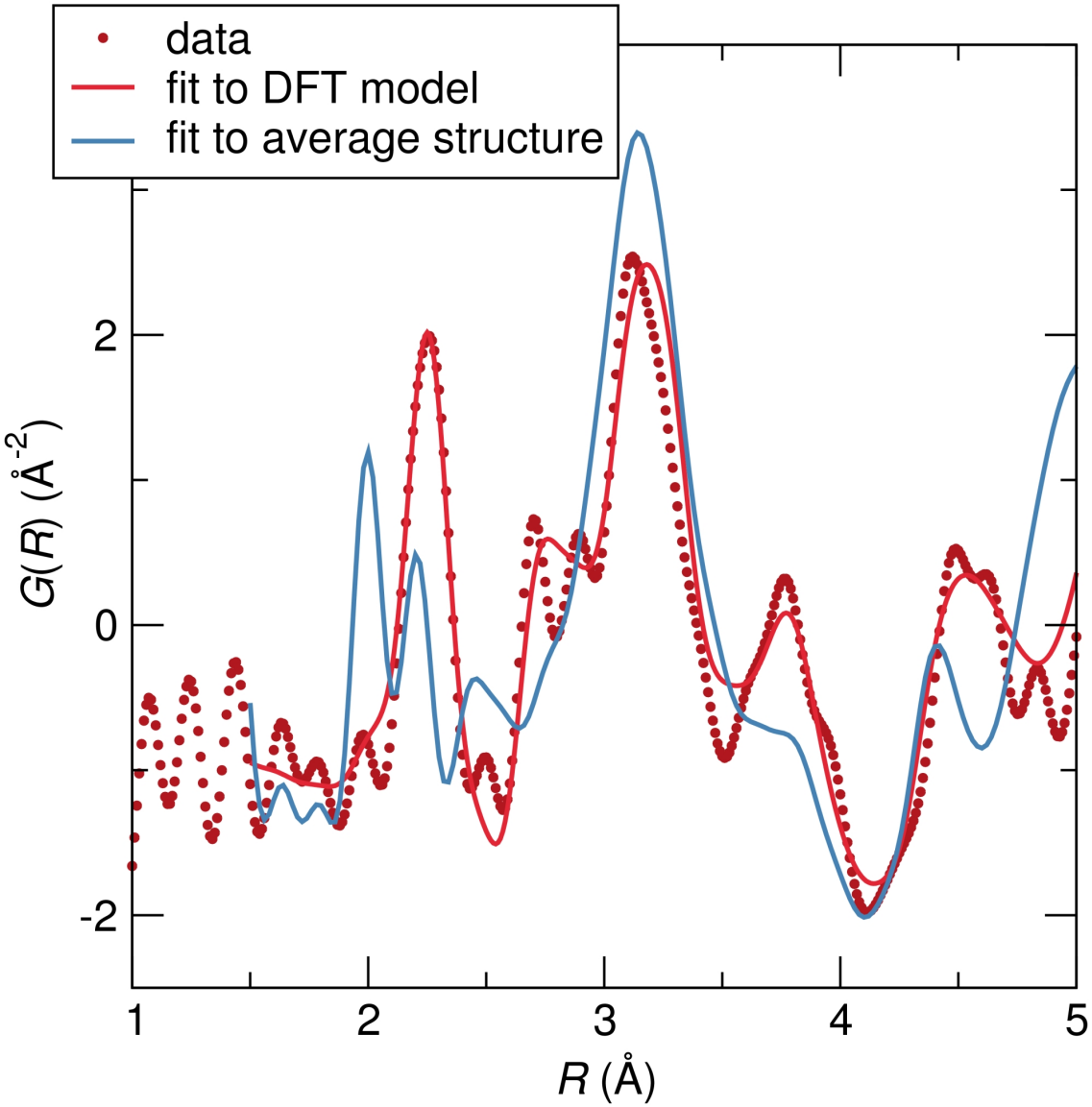
$BaCeO_3$:Pd: Modeling the substitution

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.

$BaCeO_3$:Pd: Modeling the substitution

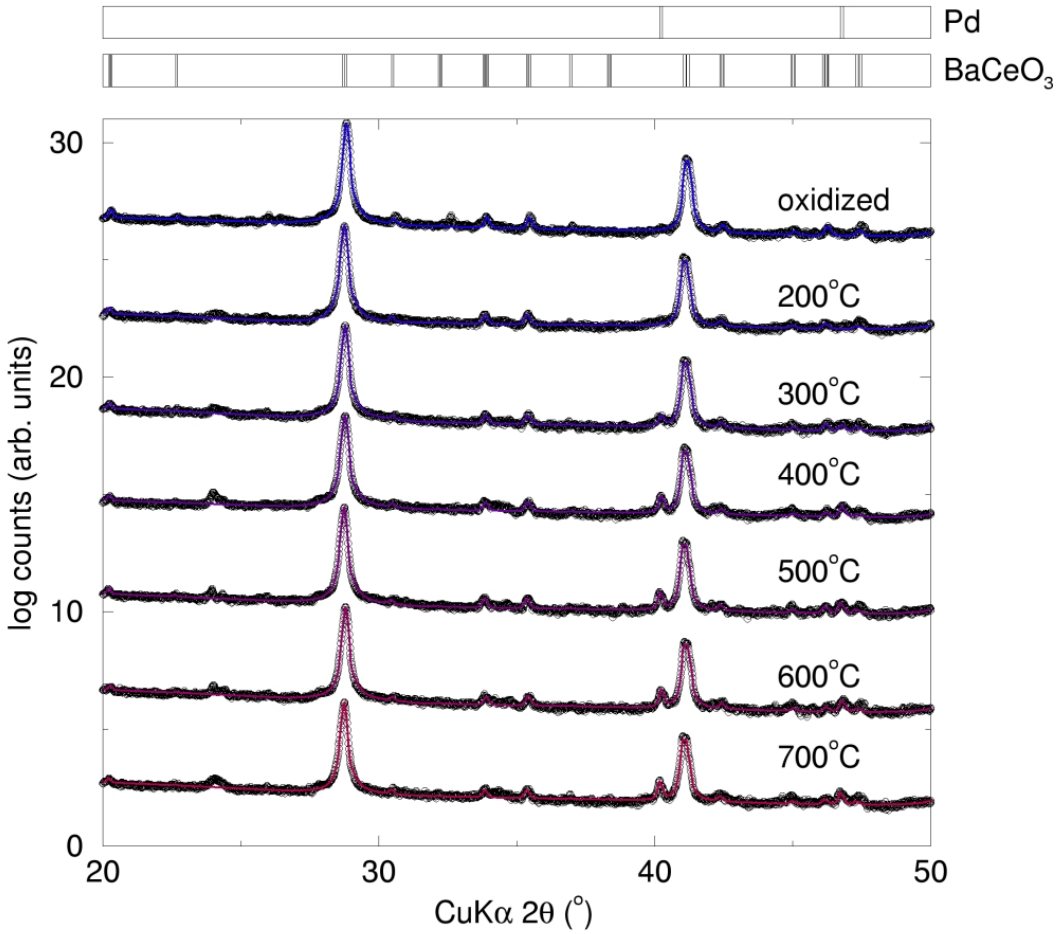


The (PDF) for the x = 0.10 sample is well-modeled by the DFT structure, but not by the average structure

Magnetic measurements suggest a diamagnetic system.

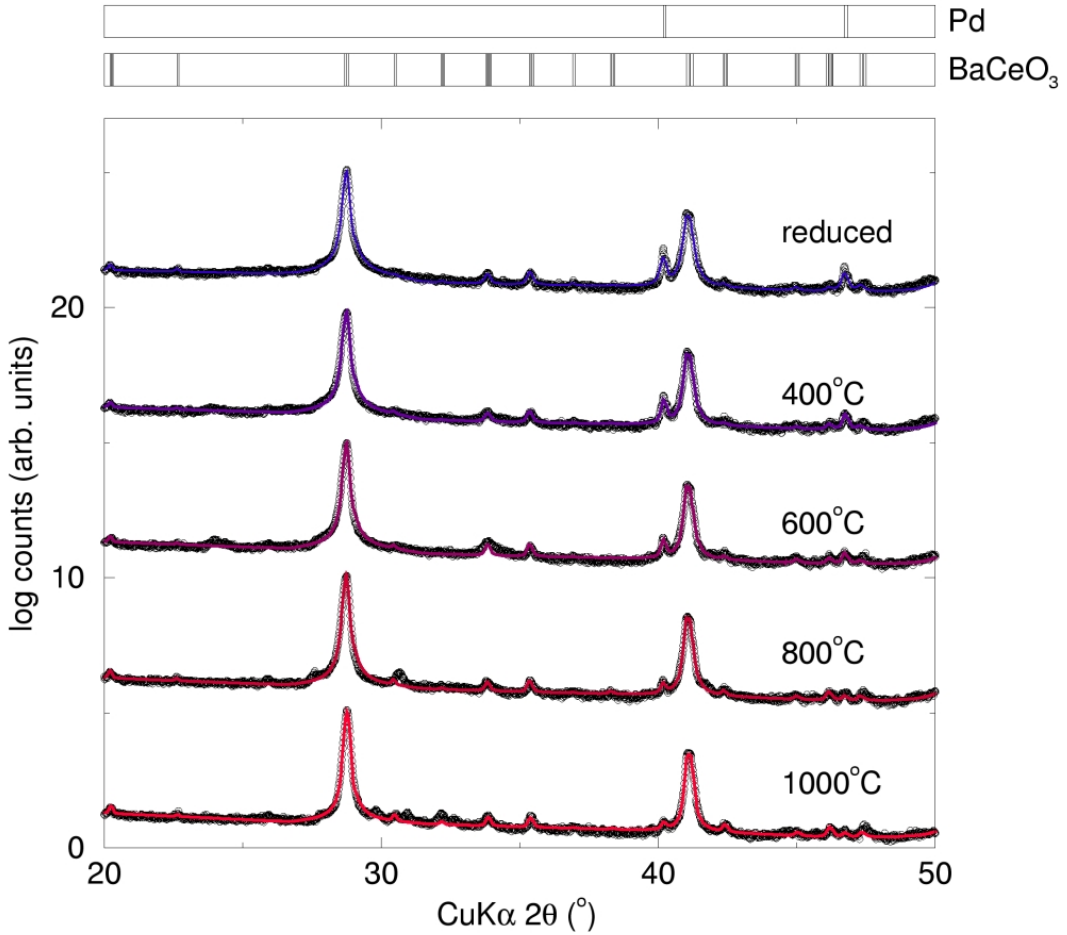
$BaCeO_3$:Pd: Intelligent ?

Egress of Pd as *fcc*-Pd upon H_2 reduction of x = 0.10 at different temperatures [5%-H_2/95%-N_2]



$BaCeO_3$:Pd: Intelligent ?

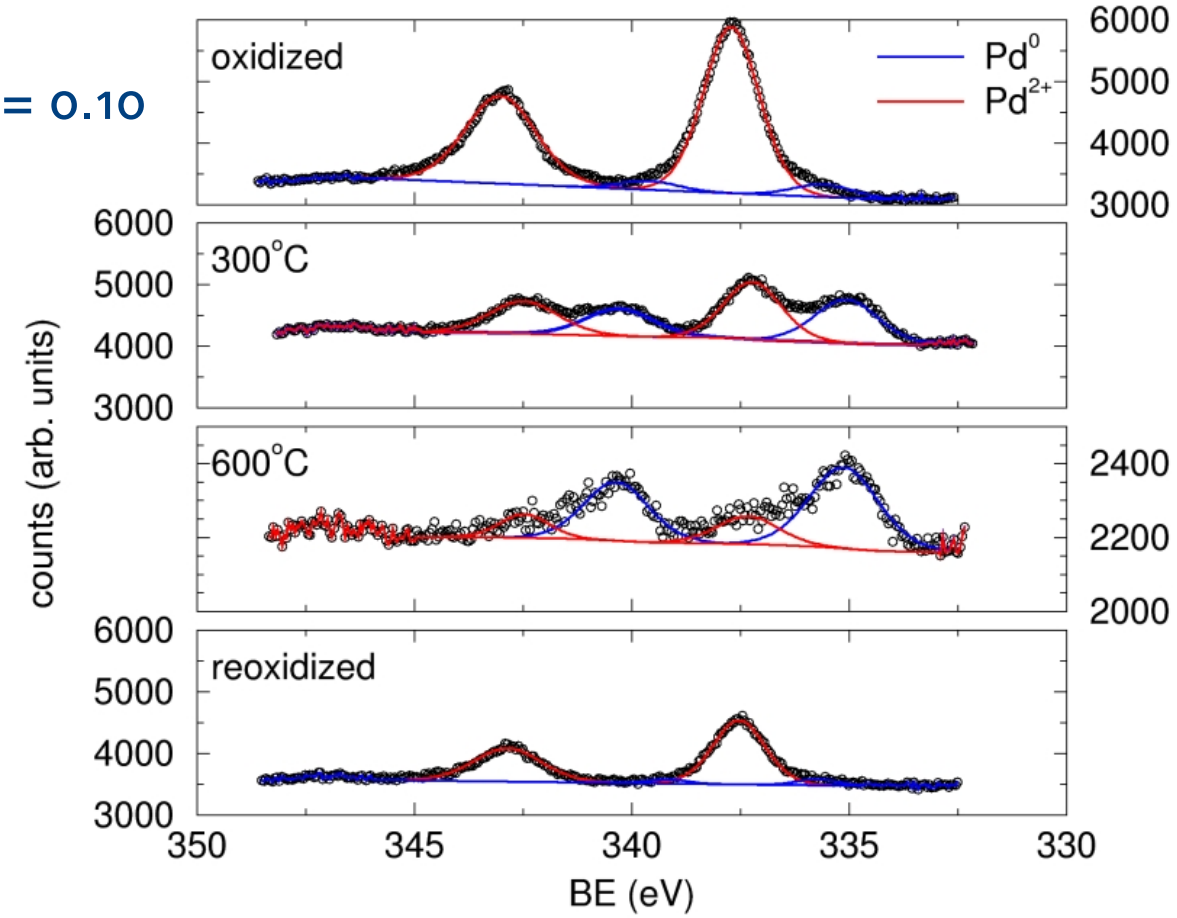
Ingress of Pd into the perovskite on heating the reduced two-phase sample in O_2 at different temperatures.



$BaCeO_3$:Pd: Intelligent ?

Pd core levels of the oxidized and reduced samples.

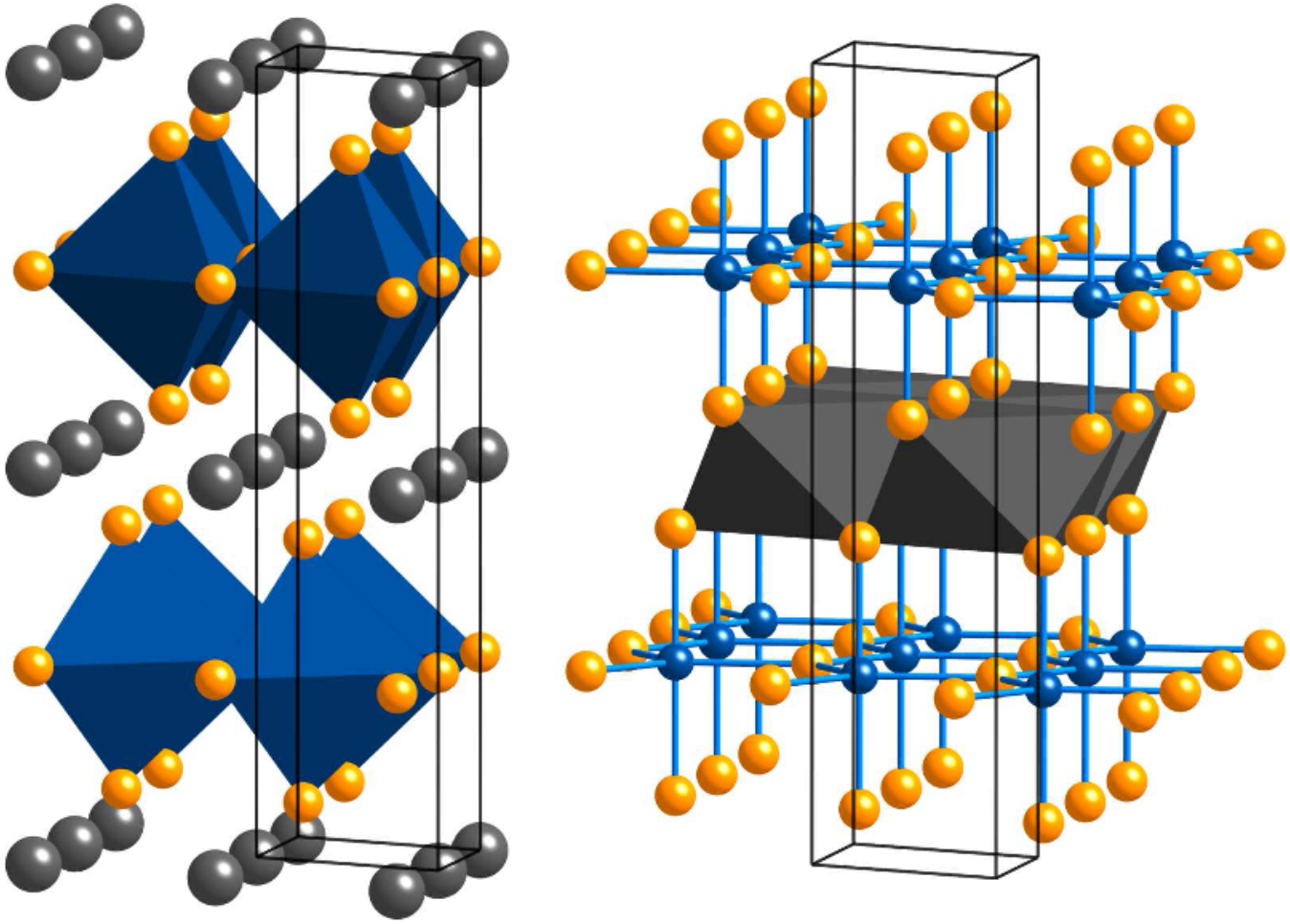
$x = 0.10$



Ce is always Ce^{4+}

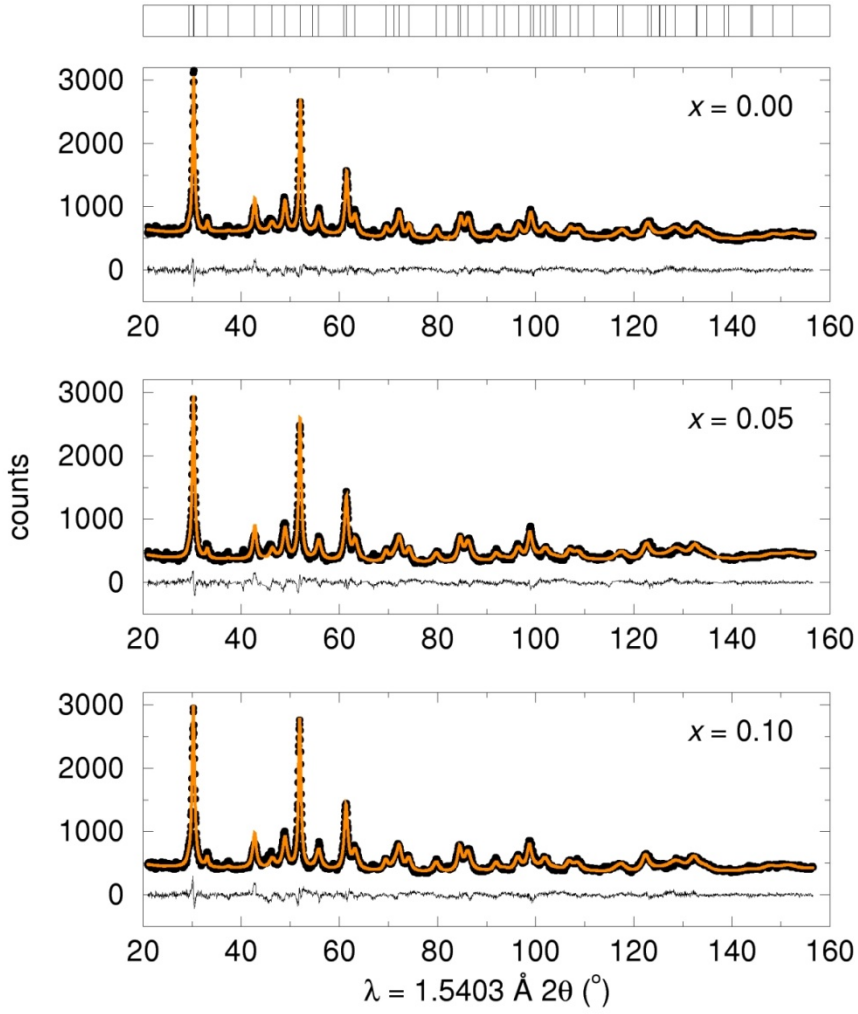
Li, Singh, Bennett, Page, Weaver, Zhang, Proffen, Rappe, Scott, Seshadri, *Chem. Mater.* 19 (2007) 1418.

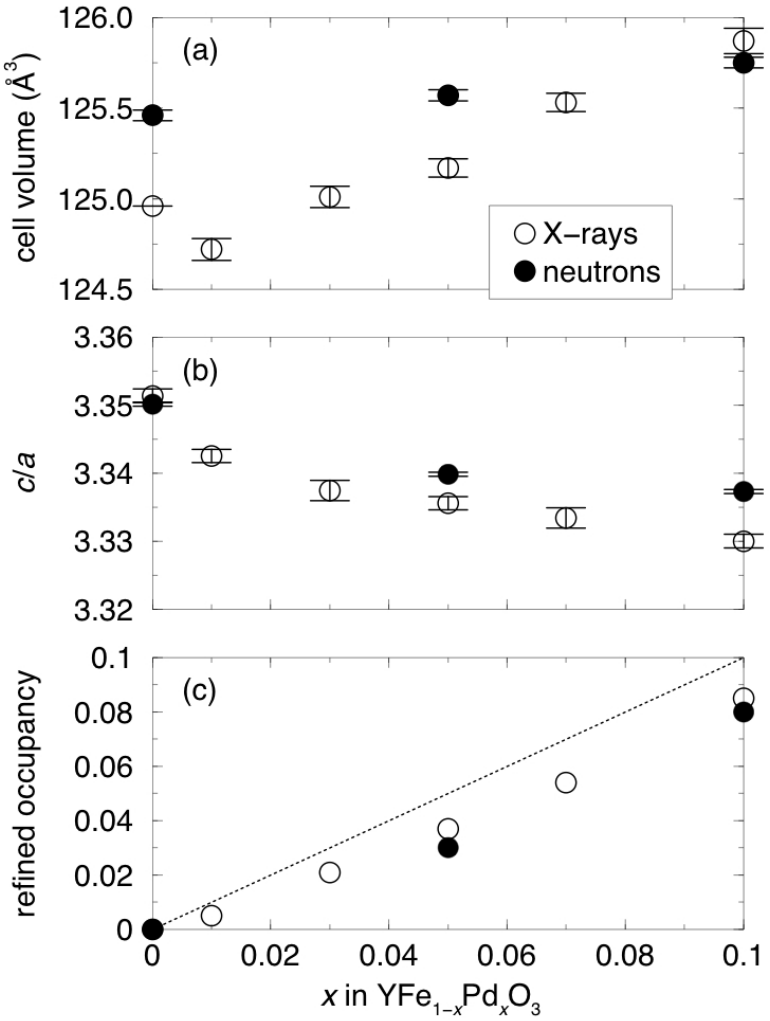
$YFeO_3$:Pd



$YFeO_3$ exists as a stable perovskite or a metastable (sol-gel prep.) hexagonal compound with the $YAlO_3$ structure. 5-coordinate Fe^{3+} in the hexagonal structure.

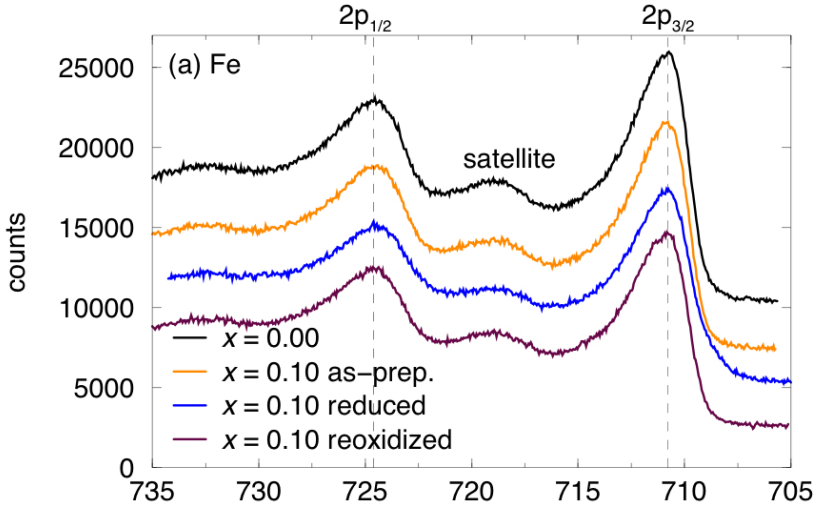
$YFeO_3$:Pd



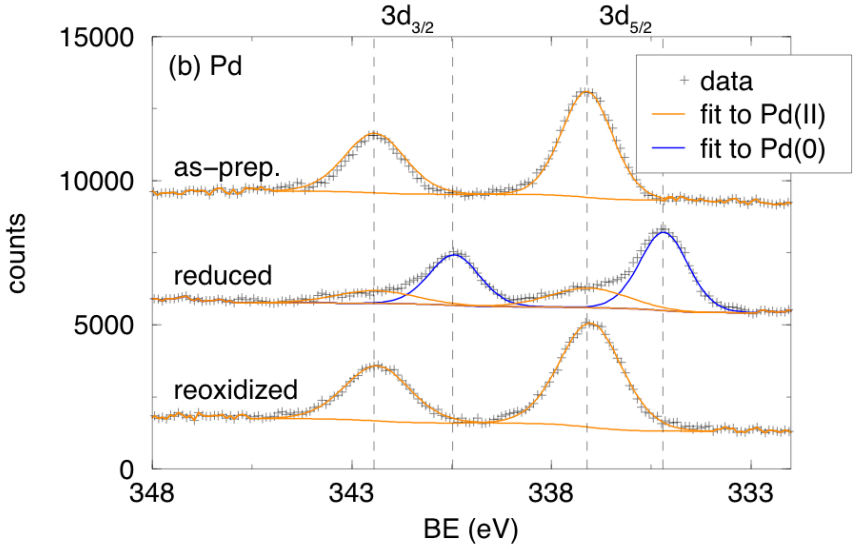


Neutron diffraction [NIST, BT-1] confirms substitution up to 8%.

$YFeO_3$:Pd – Ingress and egress of Pd



Fe core levels unchanged with oxidation/reduction.



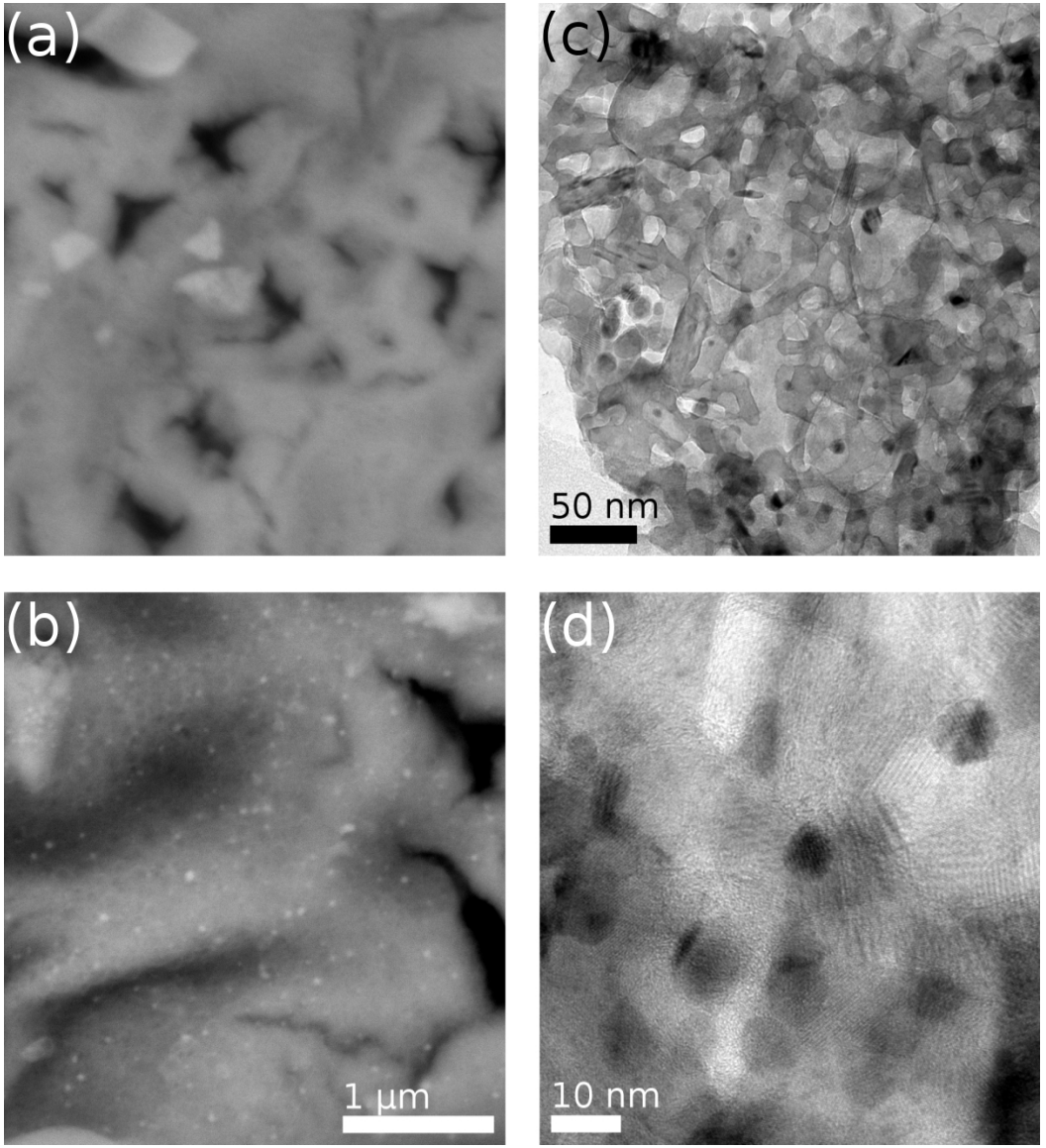
Pd core levels suggest ingress and egress under redox. Not all Pd^{2+} reduced.

$YFeO_3$:Pd – Ingress and egress of Pd

Pd nanoparticles seen after reduction in backscattering SEM and in TEM

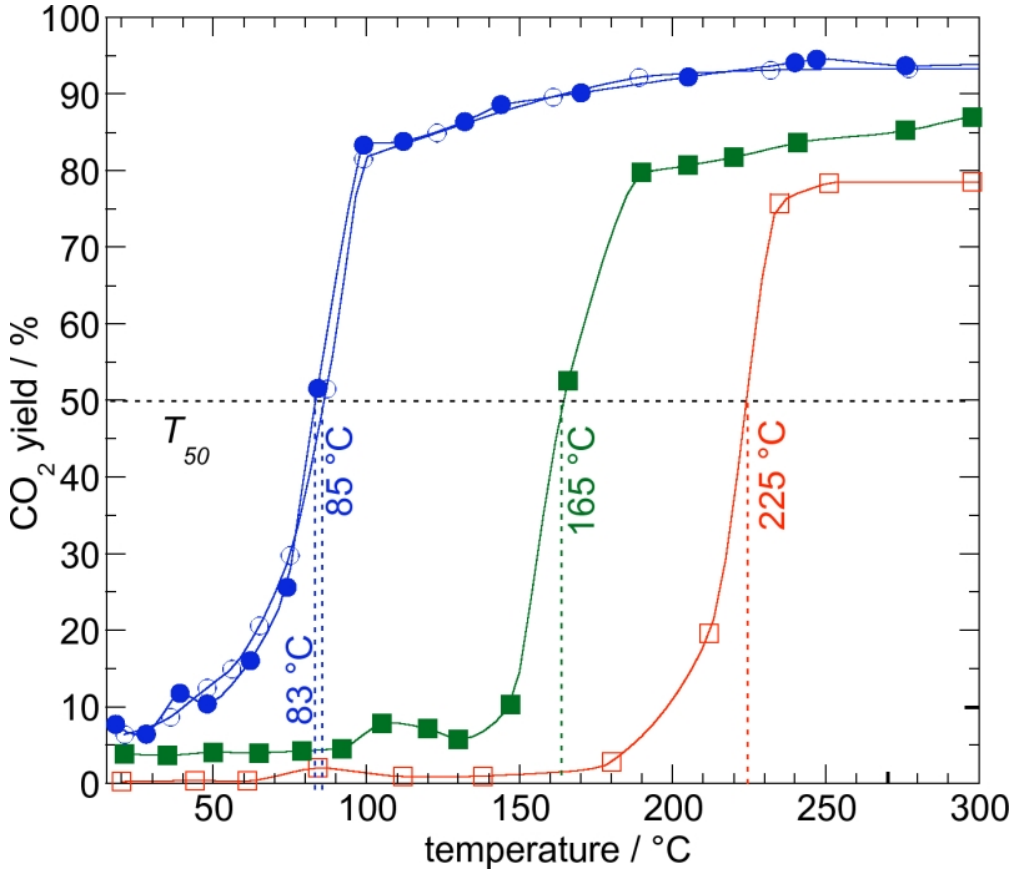
$YFeO_3$ [10%Pd] as-prepared

after 1st reduction [also (c) and (d)]



$BaCeO_3$:Pd: The catalytically active species

Good CO oxidation catalyst despite low surface area. The best catalyst is actually the as-prepared or re-oxidized sample with Pd^{2+}



Oxidized

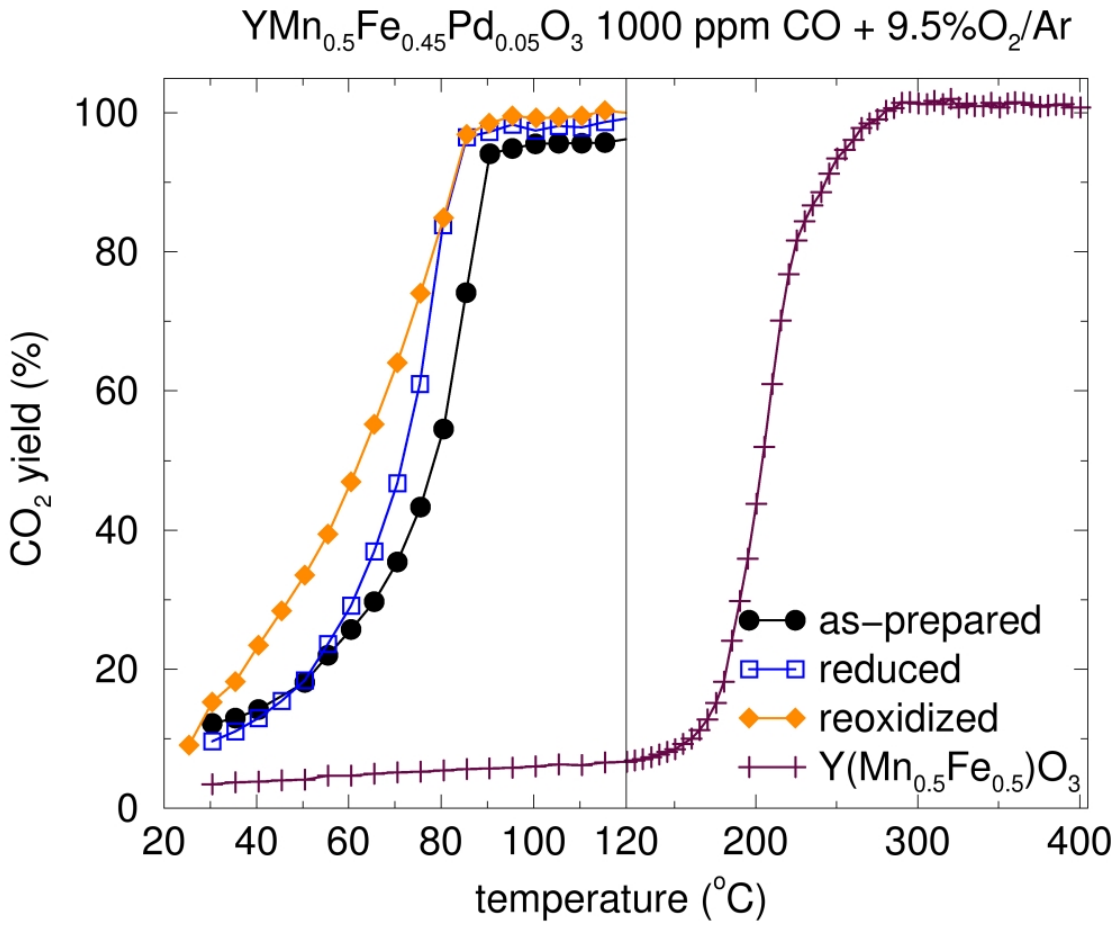
Reduced

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

Singh, Li, Bennett, Rappe, Seshadri, Scott, *J. Catal.* **249** (2007) 349.

$Y(Fe/Mn)O_3$:Pd: The catalytically active species

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



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

Li, Singh, Schladt, Stalick, Scott, Seshadri, *Chem. Mater*. **20** (2008) 6567.

Summary:

Ce^{3+} phosphors:

New phosphor materials, better understanding ...

Pd^{2+} catalysts:

A new catalyst paradigm, better catalysts ...