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Phosphors and Quantum Dots for Solid-State Lighting

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SSLS EFRC

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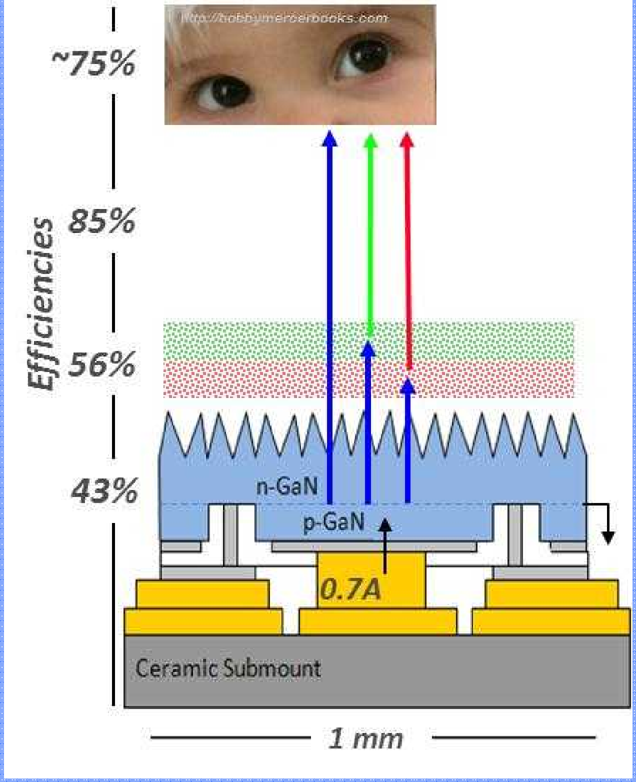
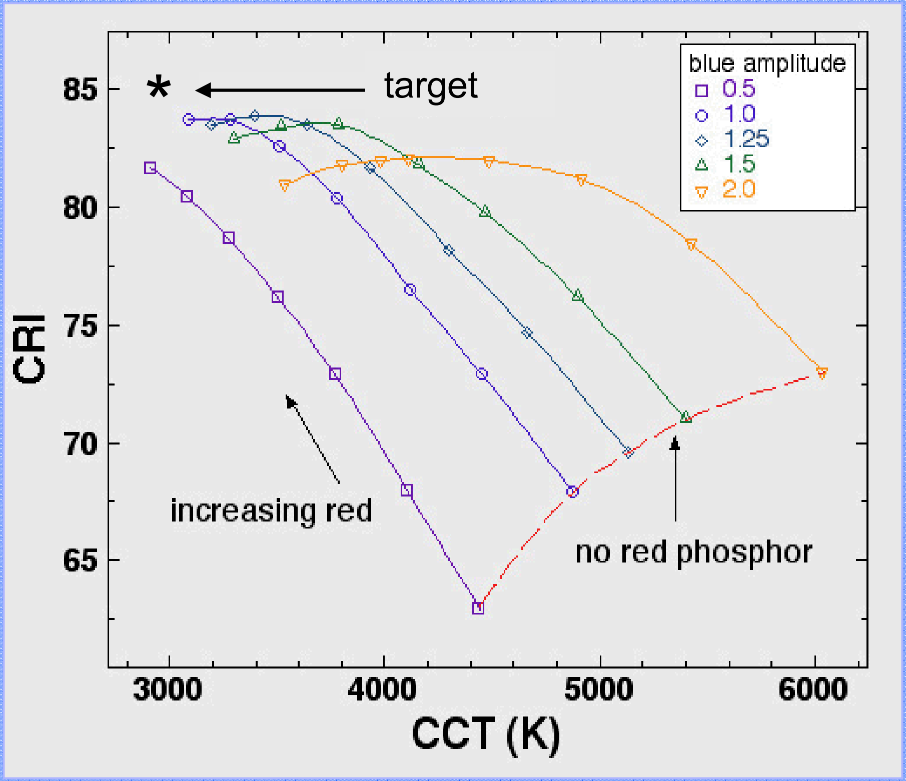
Wavelength downconversion approach to solid-state lighting (SSL)





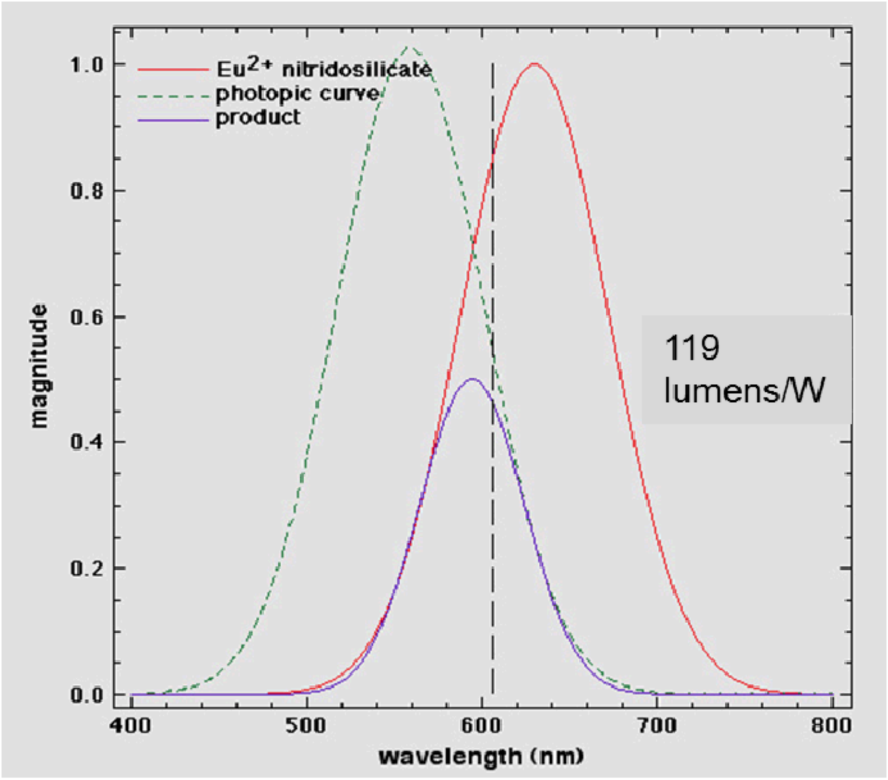
- Blue InGaN LEDs combined with green and red downconverters yields white light with improved CRI and CCT.

- Warm white target: CCT=3,000K; CRI=85*
- The red component is critical to reaching the target.

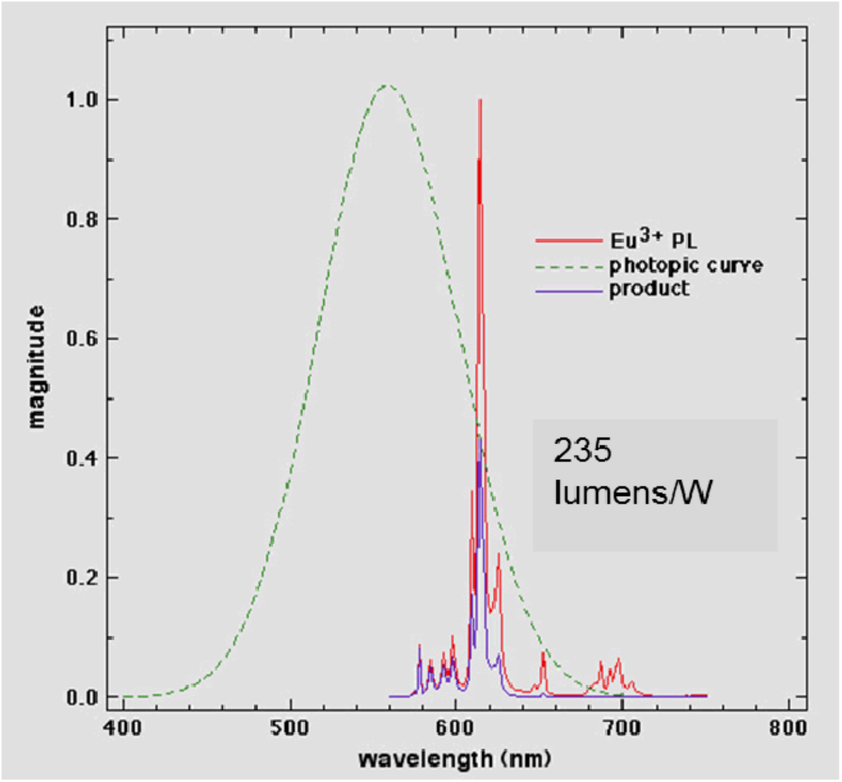
*DOE's SSL R&D 2012 Multi-Year Program Plan

Narrowband red emitters are needed for warm white LEDs

Current red emitters (Eu^{2+}) are too broad, FWHM ~100 nm.



Eu3+ red emitters are narrow, FWHM ~5 nm.



• The luminous efficacy of radiation (LER) for red emission (>606 nm) can be significantly increased with narrow bandwidth emitters.

*DOE's SSL R&D 2012 Multi-Year Program Plan

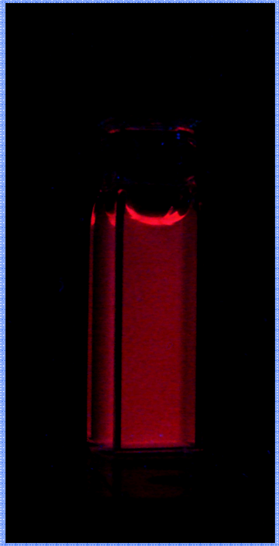
SSL downconverters must satisfy numerous criteria

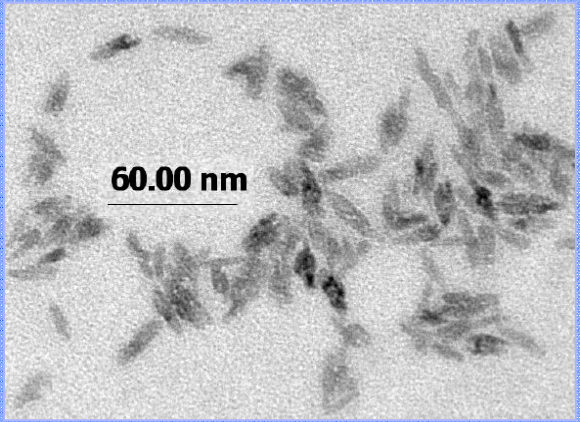
- High quantum efficiency
- Low reflectance at excitation wavelength
- Low thermal quenching
- Photo-stability
- Thermal stability
- Chemical stability
- Saturation resistant
- High luminous efficacy of radiation
- Excitable with blue light
- No unwanted green/yellow absorbance
- Enables high CRI & low CCT
- Non-toxic
- Chemically inert
- Low light scattering

- **Currently there are no red emitters that satisfy all of these requirements.**

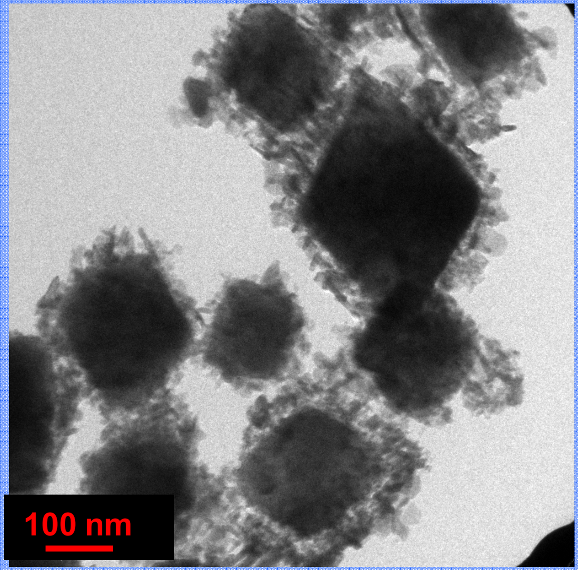
Narrowband red-emitting nanophosphors made at SNL

Zircon structure:
$YVO_4:Eu^{3+}$

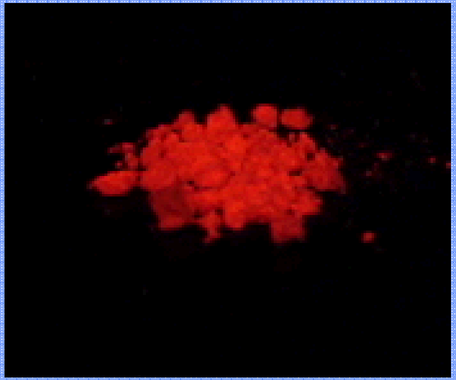


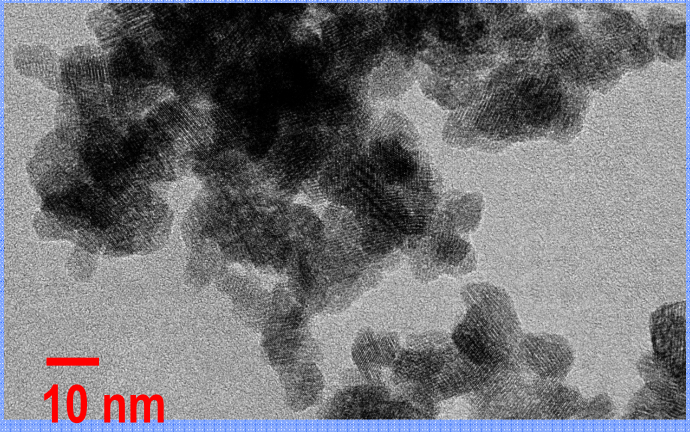


Pyrochlore:
$K_{1-2x},GdTa_2O_{7-x}:Eu^{3+}$

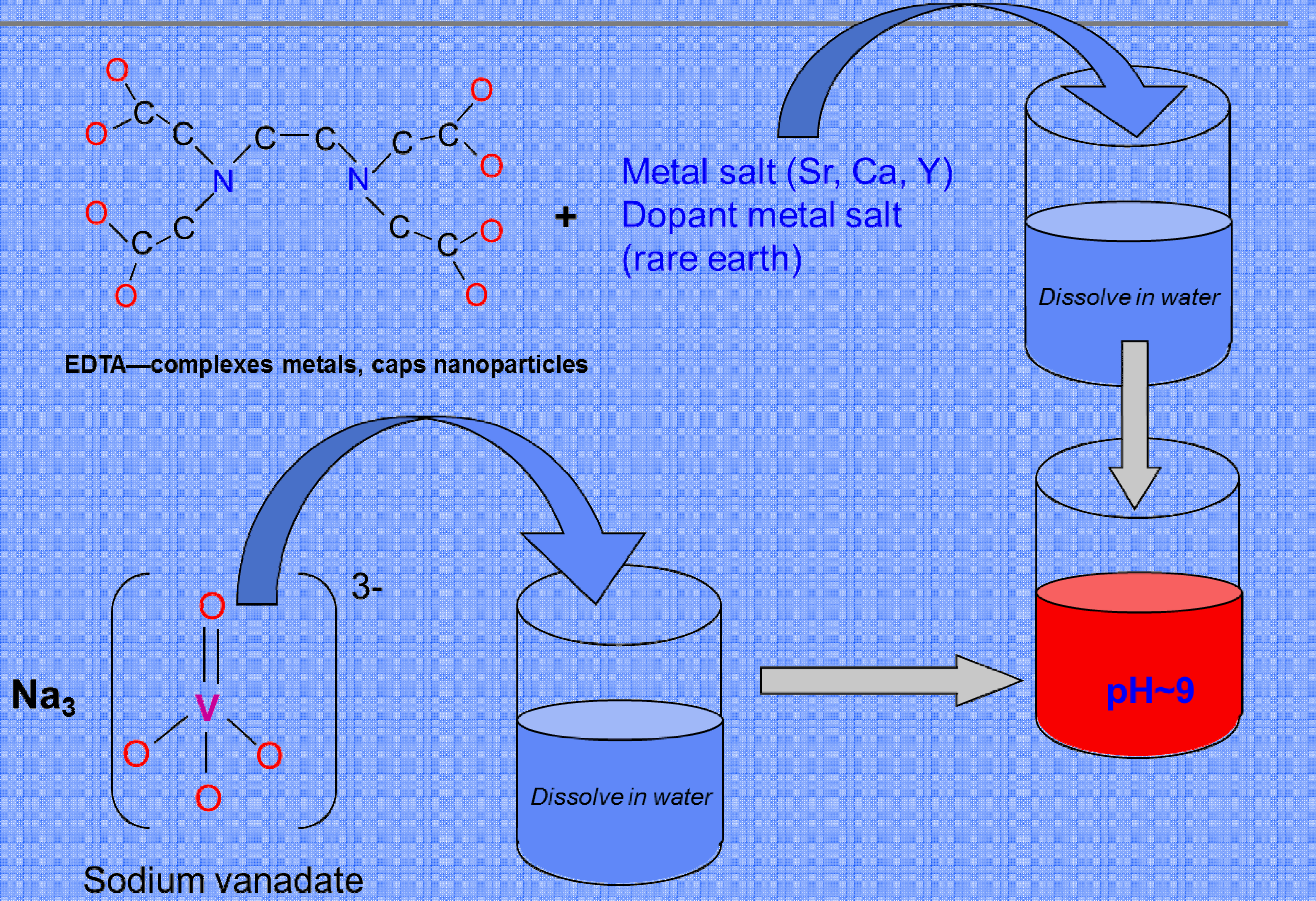


Pyrochlore:
$(A,RE)Ta_2O_7:Eu^{3+}$
$A = K^+, Rb^+$; RE = Lu, Y



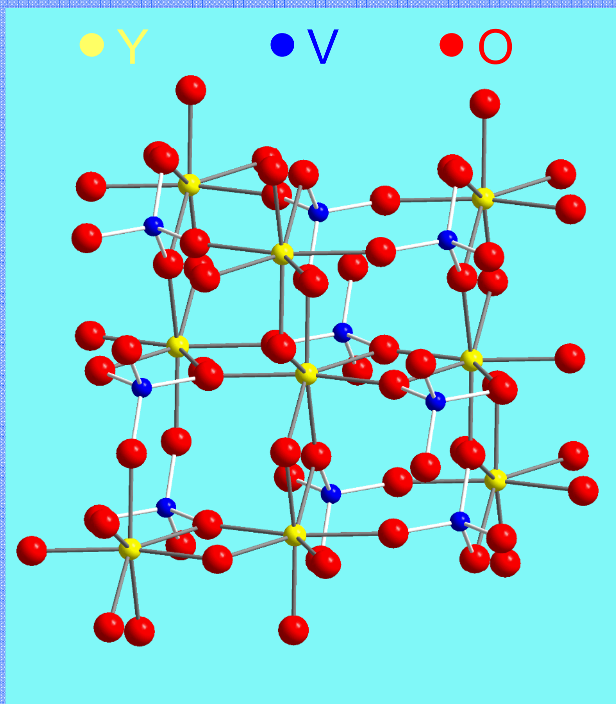


Synthesis of $YVO_4:Eu^{3+}$ nanoparticles



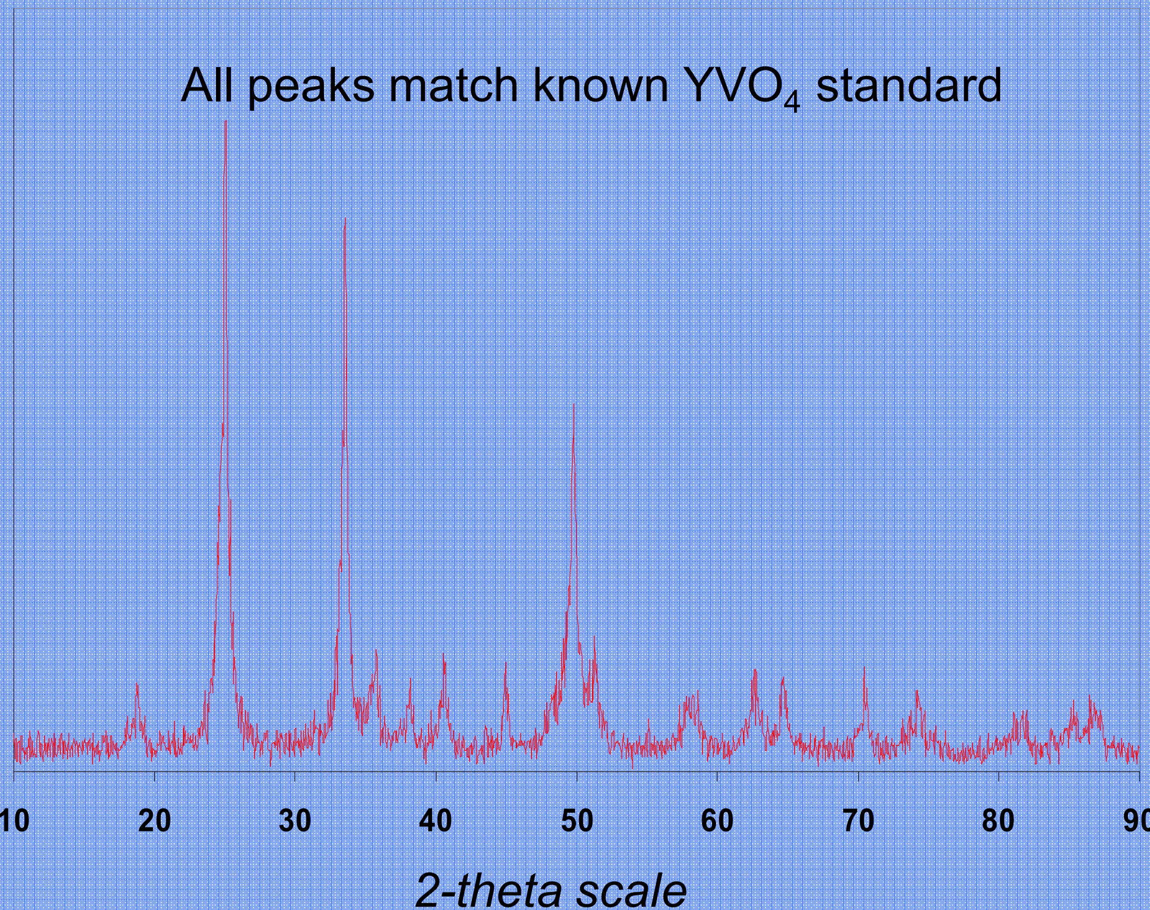
Nano-YVO_4 structure characterization

YVO_4

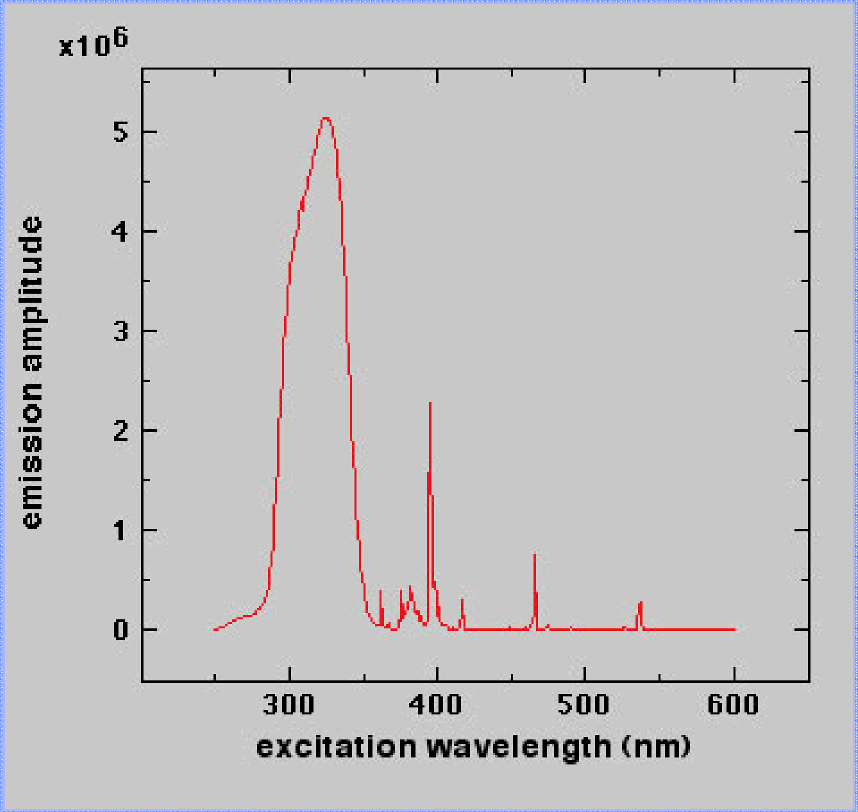


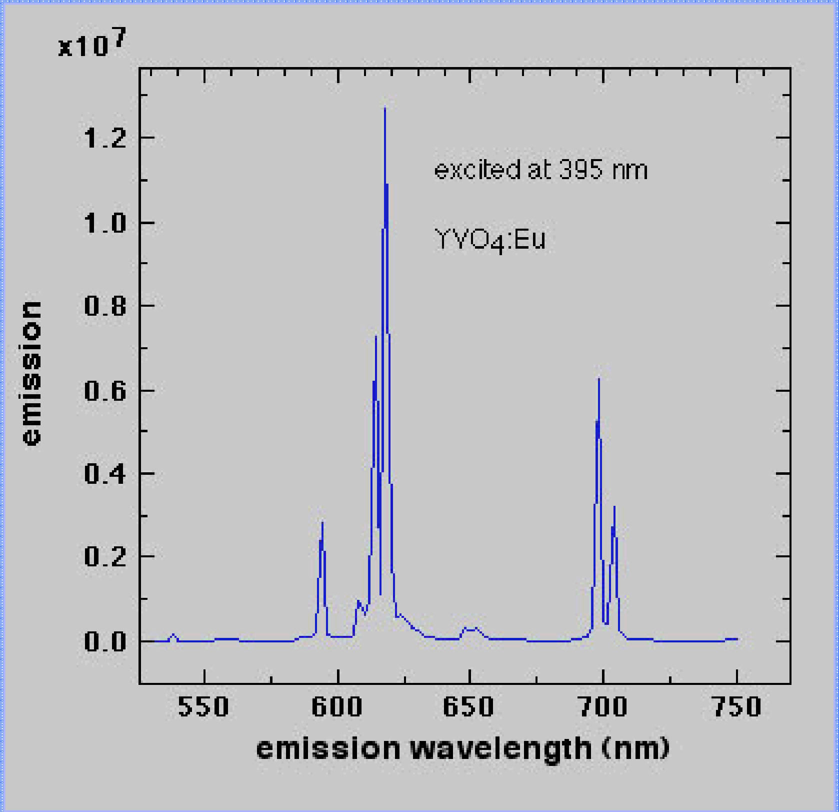
Zircon-type structure
Regular VO_4 sites
8-coordinate Y site

Nano-YVO_4



Nano-YVO_4:Eu^{3+} has bulk PL properties

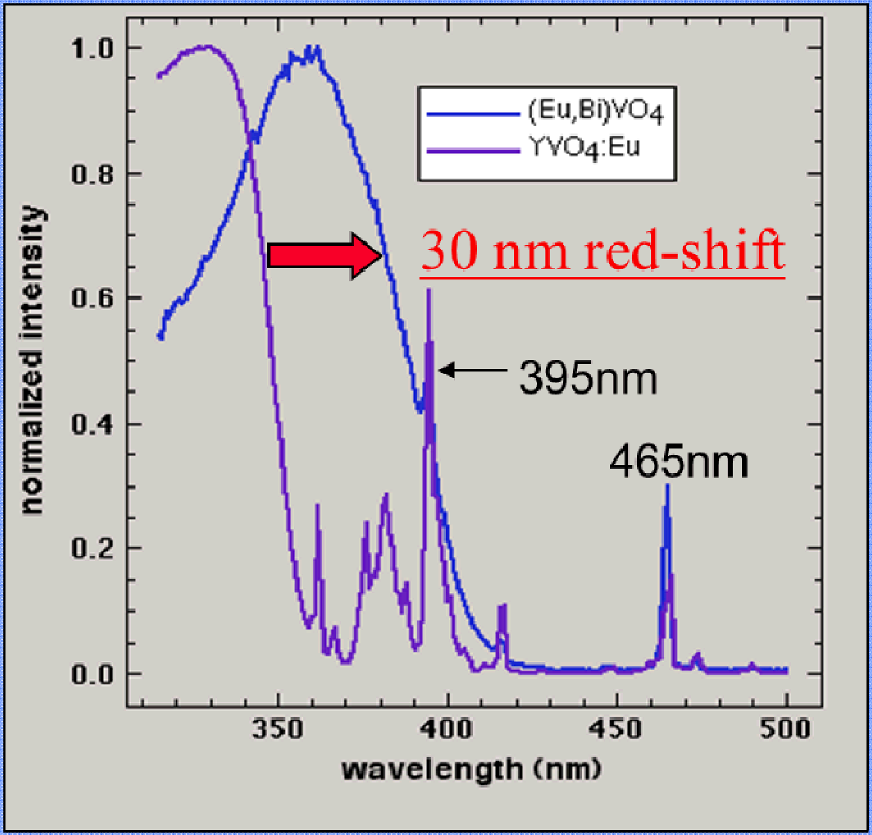


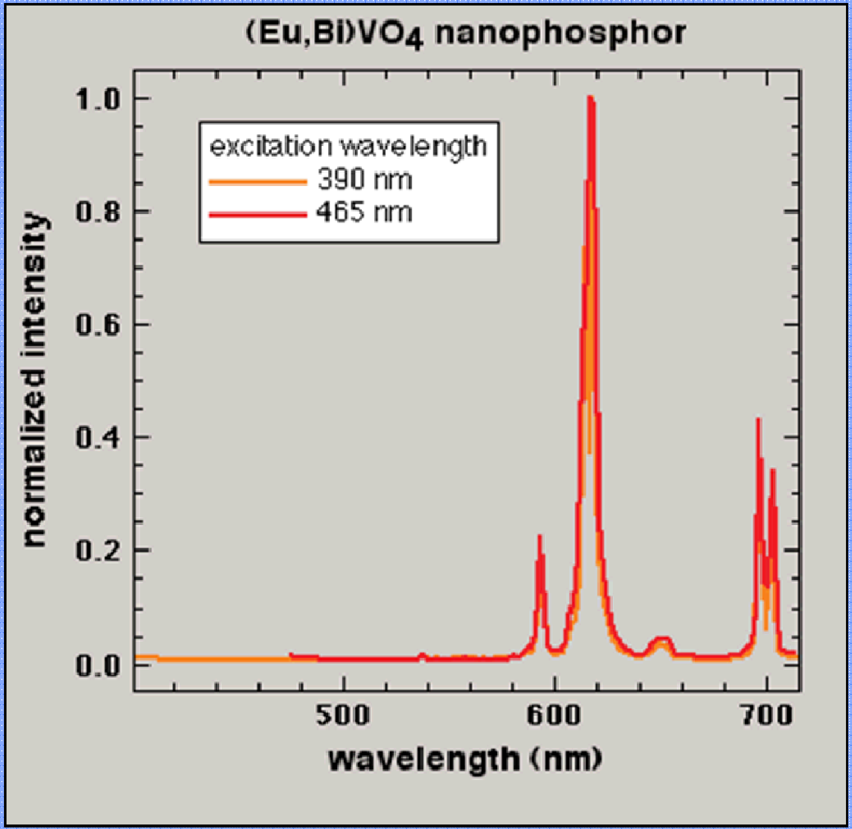


- Absorption at 395 and 465 nm is ideal for InGaN LED excitation.
- Strong UV absorption.

- Eu^{3+} emits at ~619 nm, as in bulk YVO_4.
- FWHM ~4 nm.

Co-doping with bismuth yields efficient excitation

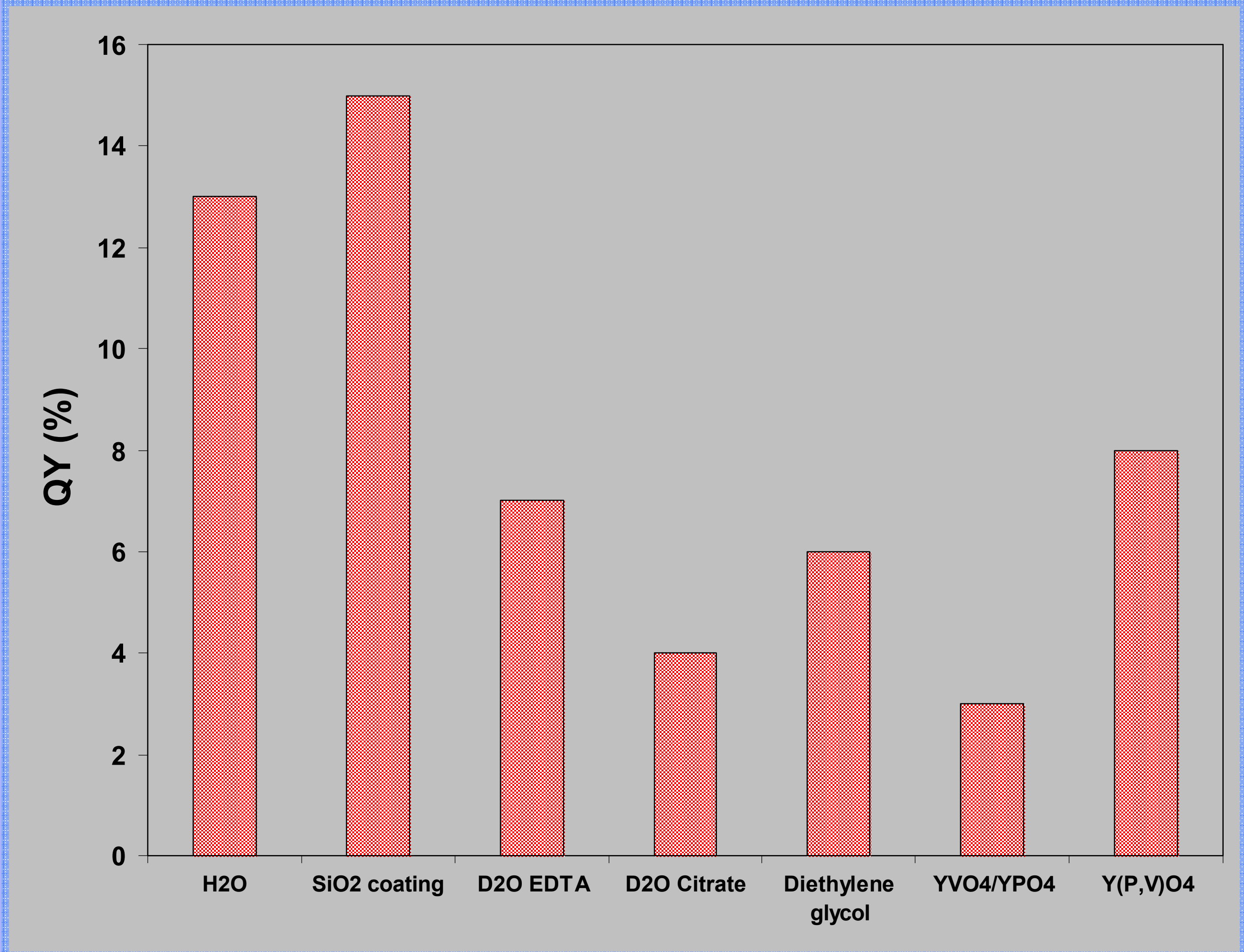




- Bi^{3+} transfers energy to Eu^{3+}.
- Enhanced 395 & 465nm absorptions.
- Red-shifted UV absorption.

- Narrowband red emission is preserved.

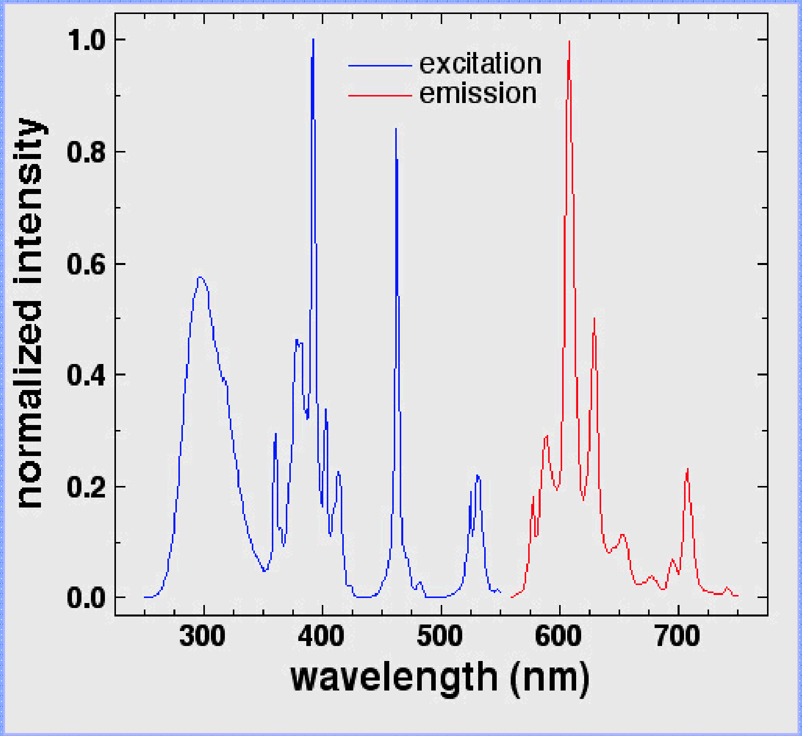
The QY of nano-$YVO_4:Eu^{3+}$ is affected by synthesis variations



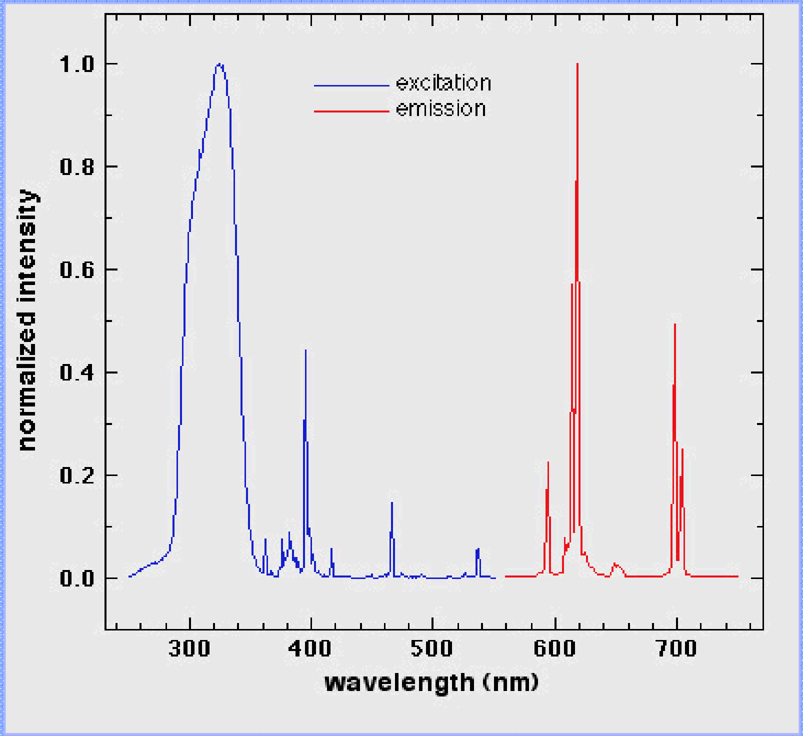
- We increased the QY to 15% (near-UV excitation) with SiO_2 coatings.
- QY's of 15-25% reported for these materials under <u>UV</u> excitation.
- The QY is currently too low for SSL applications.

Pyrochlore tantalates have advantages over YVO_4

Pyrochlore: $K,YTa_2O_7:Eu^{3+}$



Zircon structure: $YVO_4:Eu^{3+}$

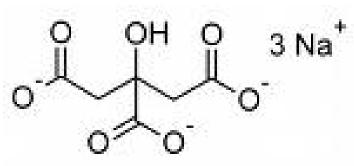


- Weak UV absorption.
- Stronger blue absorption and less deep red emission than YVO_4.

- Strong UV absorption.
- Deep red emission >700 nm.

Hydrothermal synthesis of pyrochlore tantalate nanophosphors

Synthesis: RE(citrate)

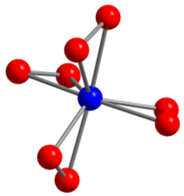


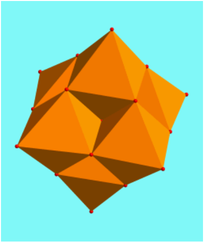
precip

OH^-/pH-13.5

dissolve

Anionic Ta precursors





RE=La, Gd, Lu, Y, Eu

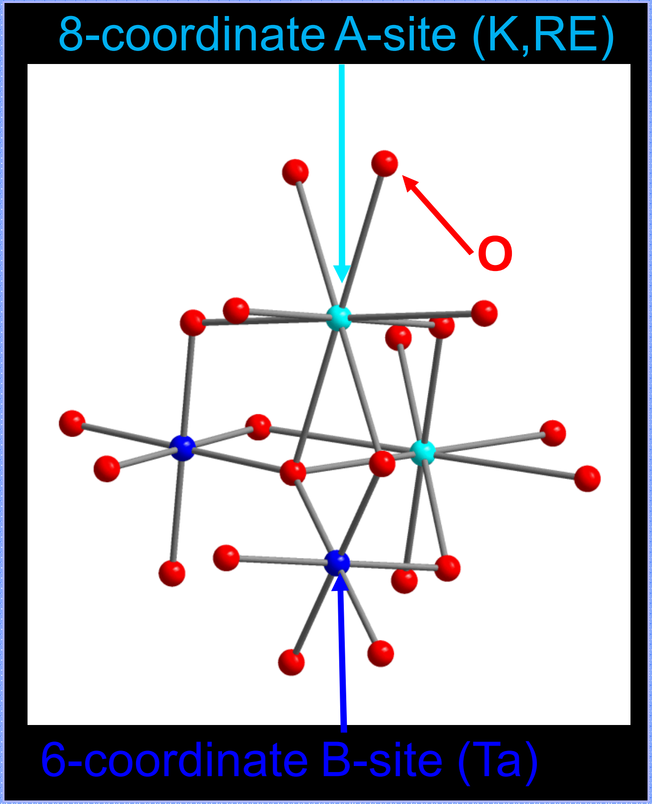
$[Ta(O_2)_4]^{3-}$, $[Ta_6O_{19}]^{8-}$

Hydrothermal treatment at 220°C

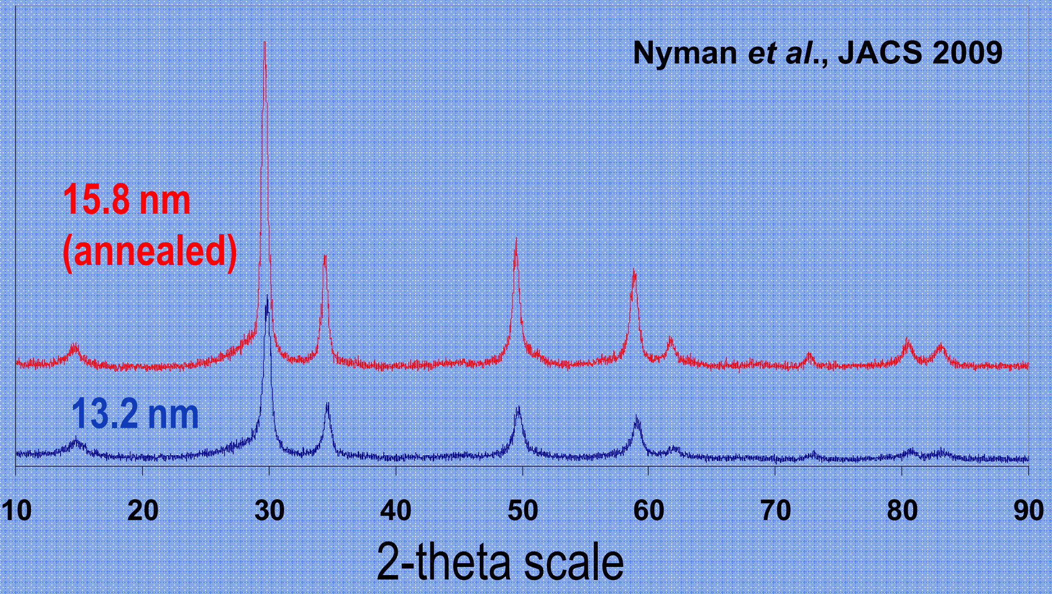
Pyrochlores: $(RE,A)Ta_2O_7$; A=alkali
$(RE,A)_{1-2x}Ta_2O_{7-x}$

Pyrochlore nanophosphor characterization

Pyrochlore structure: AB_2O_7



$(K,RE)Ta_2O_7$:Eu; RE = Lu or Y



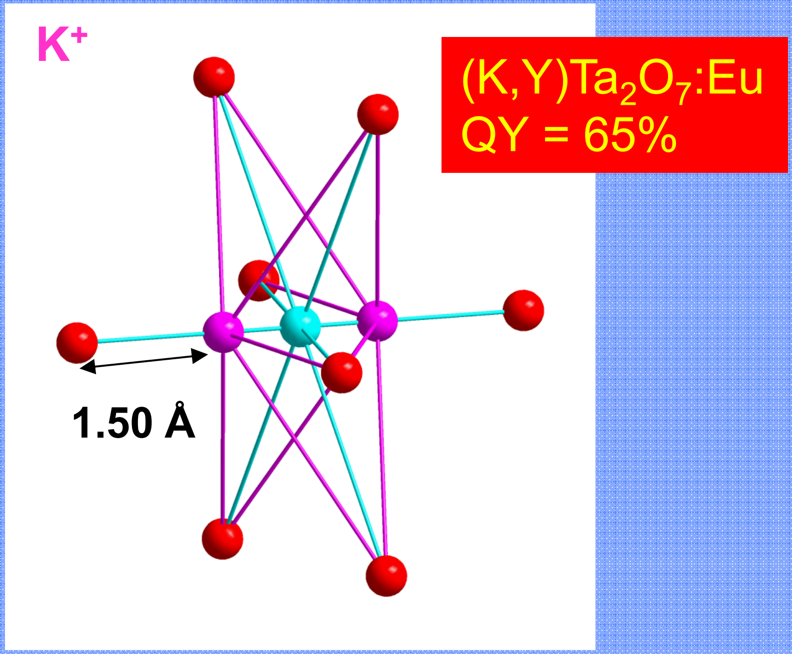
RE	r (Å)	QY(%)	τ (ms)
Lu	0.85	67	1.6
Y	0.893	65	1.5

- The Lu and Y pyrochlores have comparable QYs and lifetimes under blue excitation.

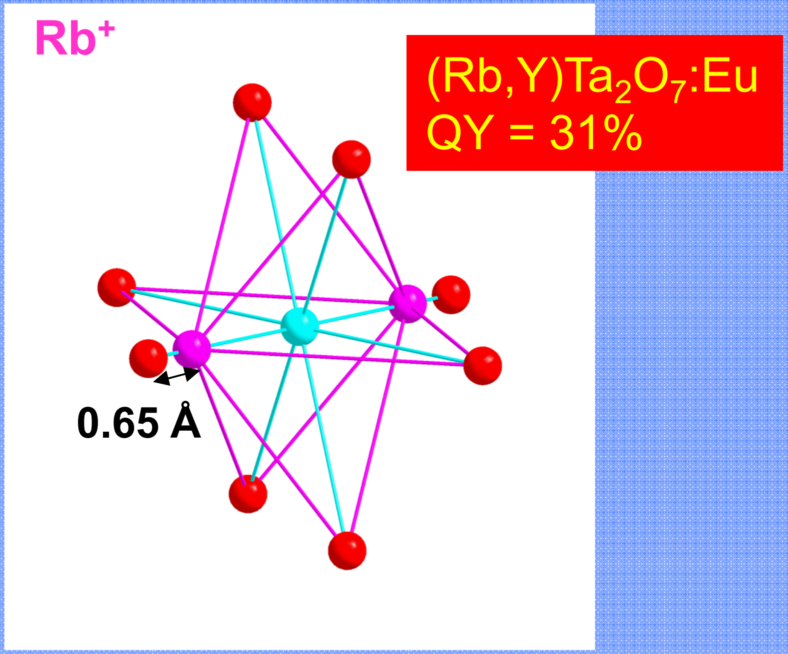
Pyrochlore tantalates offer flexibility in lattice structure.

Alkali substitutions can alter the symmetry of the A site and the alkali-O bond lengths.

● = O ● = Alkali ● = Ta



- 7-coordinated A site

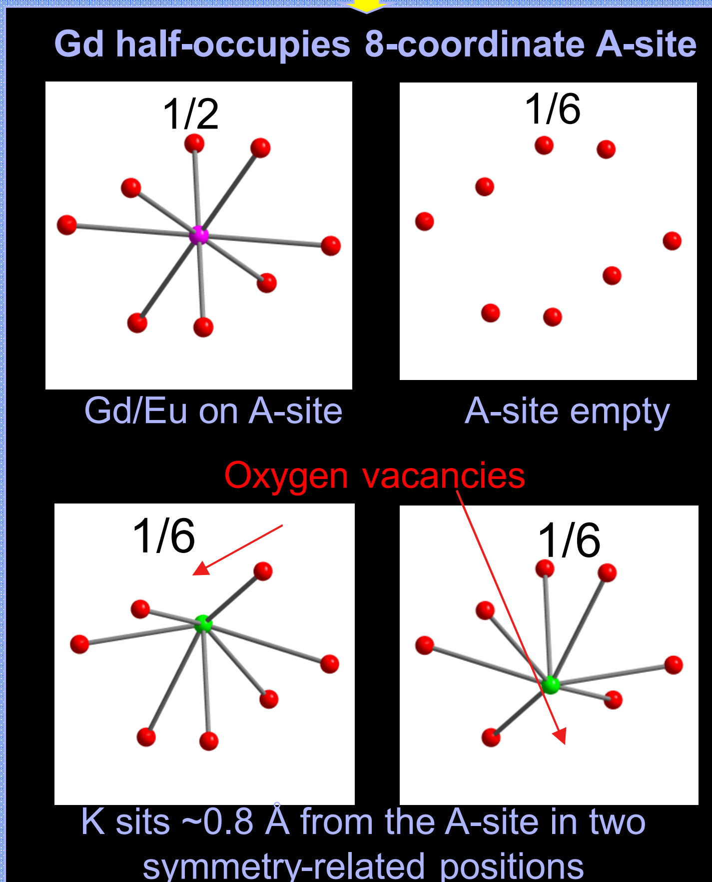


- 8-coordinated A site

- The QY increases with increasing A-site distortion.

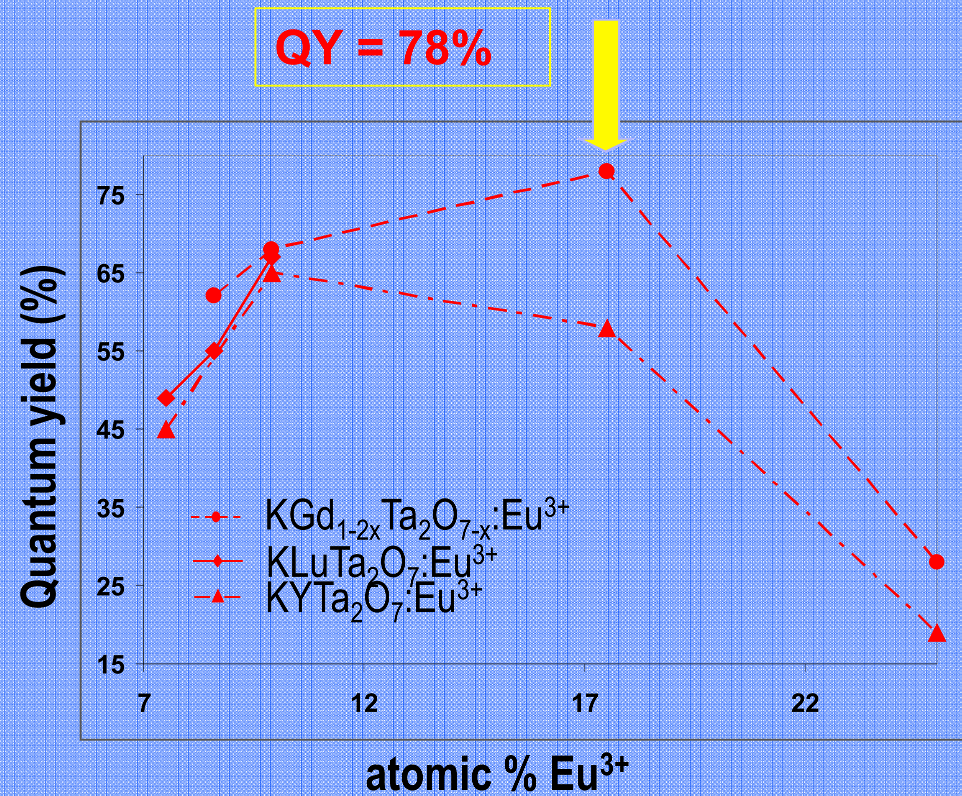
The addition of Gd increases the desired lattice distortions
$K_{1-2x}(Gd,Eu)Ta_2O_{7-x}$; x = 1/3

1. Gd creates oxygen vacancies in pyrochlores.
2. These vacancies create lattice distortions.



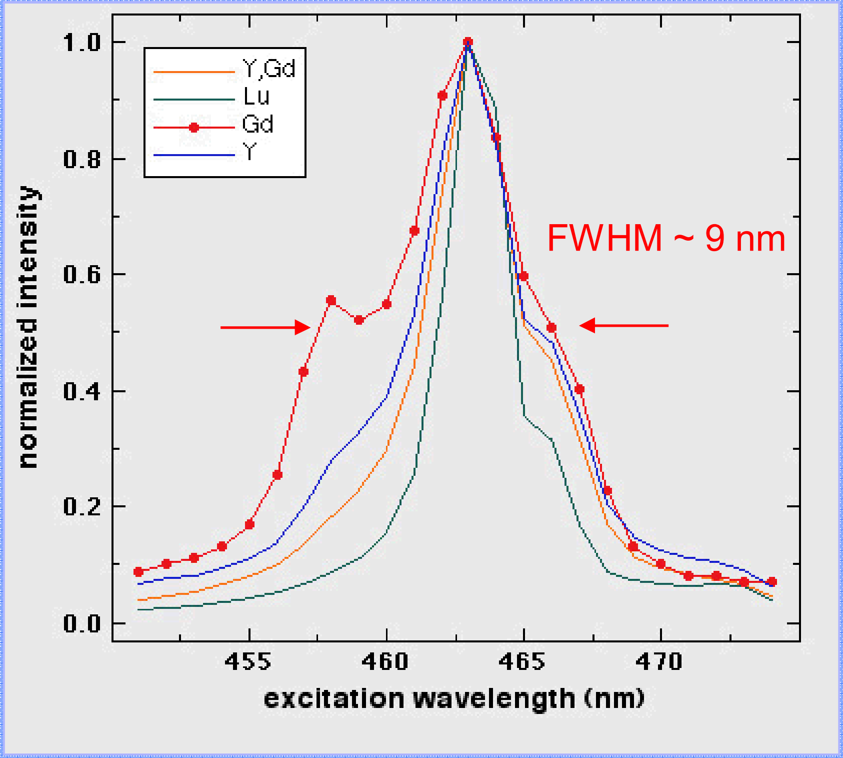
3. These lattice distortions affect the Eu emission.

4. The QY of the Gd pyrochlore is higher than that of the Lu & Y pyrochlores.



Nyman *et al.*, JACS 2009

The blue absorption linewidth is broadest in the Gd pyrochlores

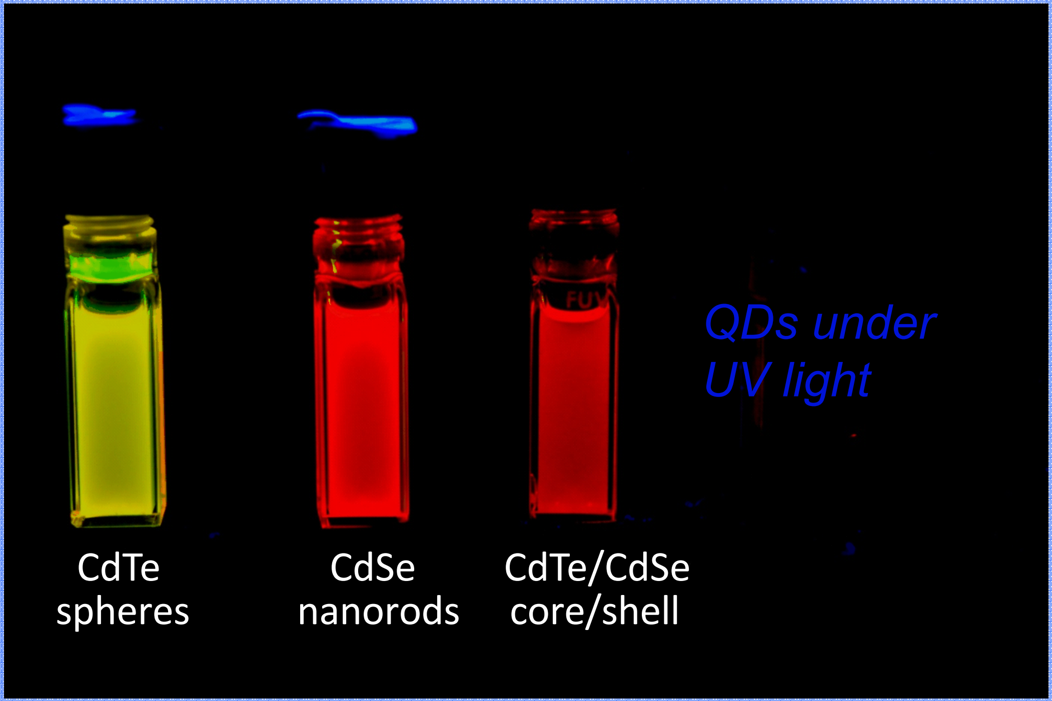


- Broad blue absorption enables excitation with a range of LED wavelengths.
- A transparent, ~1 mm thick material would enable enough blue absorption.

Summary of Eu^{3+}- doped nanophosphors

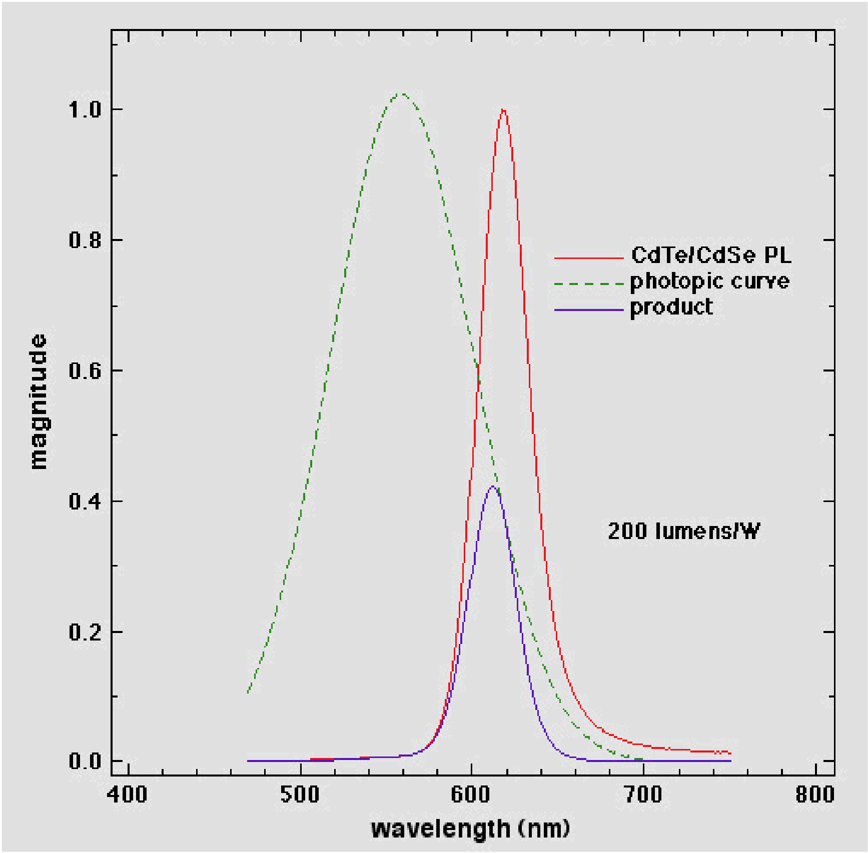
- Narrow band red emission at ~610 nm is ideal for warm white lighting.
- QY as high as 78%.
- Only 3% thermal quenching at 130^{o}C.
- Narrow blue excitation linewidth (~4-9 nm) with a small cross section due to the low oscillator strength of Eu^{3+}.
- Developing these materials into transparent wafers for SSL.

CdTe-based quantum dots



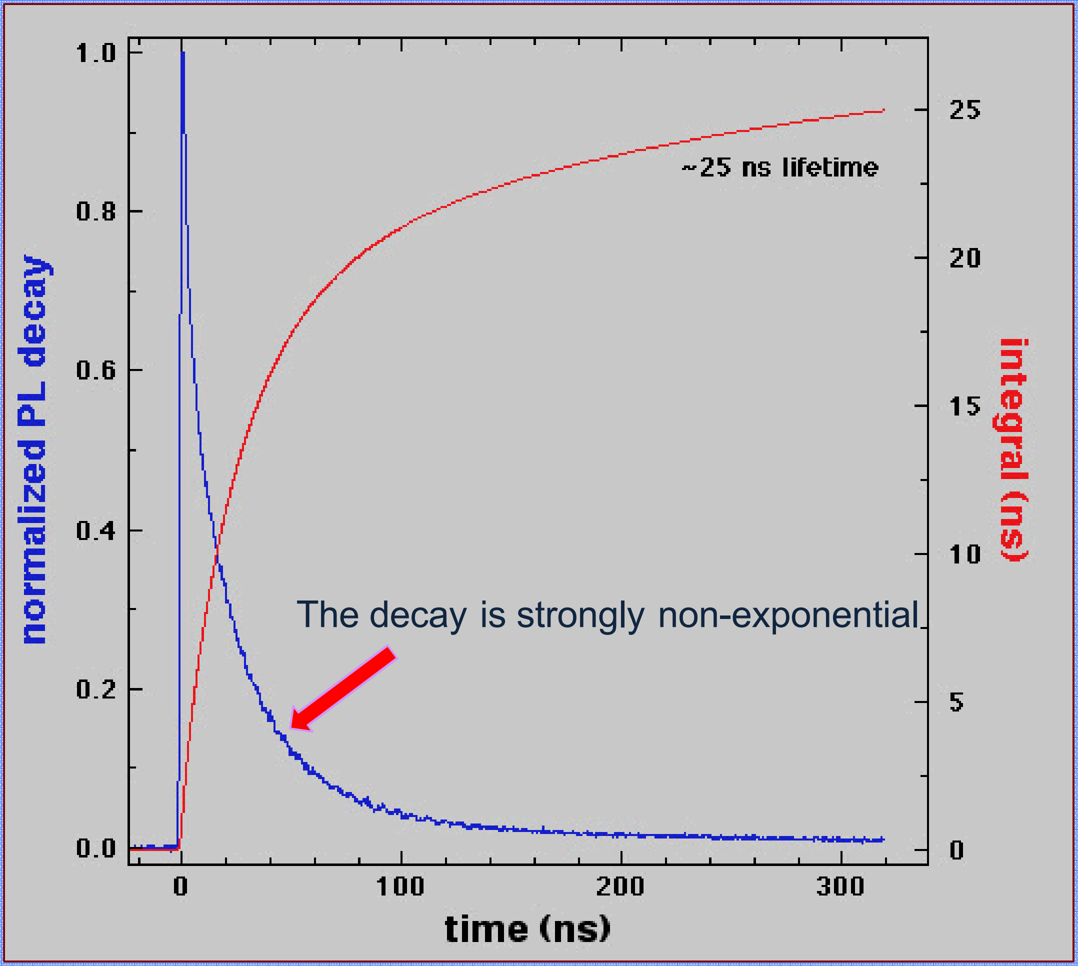
CdTe-based quantum dots can have narrow red emission

- CdTe/CdSe core/shell QD emission (FWHM~33 nm) gives a high LER (200 $lm/W_{emitted}$).



- The red emission of these materials is 2.5X narrower than that of the nitridosilicates used in warm white LEDs.

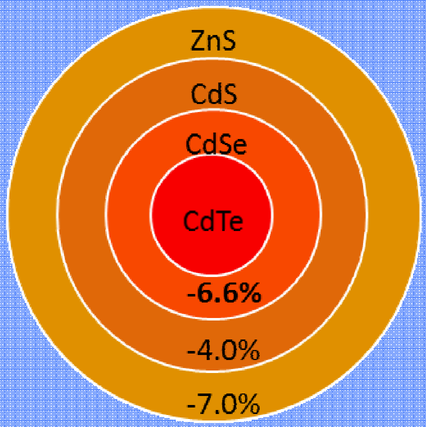
The fast PL decay of CdTe QDs indicates high oscillator strength

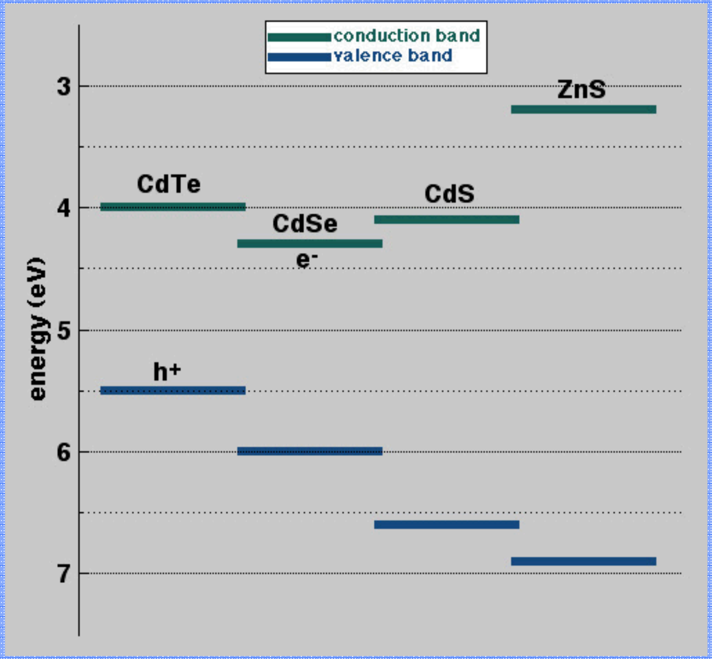


- The absorption cross section is consequently very large.

Our goal is a photostable strain-graded heterostructure

Type II core/shell QD





- h^+ is confined to the core
- e^- is in the CdSe shell.

Type I (mismatch)	Type II (mismatch)
CdSe/CdS (-4%)	CdTe/CdSe (-6.6%)
CdSe/ZnS (-11%)	ZnTe/ZnSe (-8.9%)
CdSe/ZnSe (-6.3%)	ZnTe/CdSe (-0.3%)
CdTe/ZnSe (-13.9%)	ZnTe/CdTe (+5.0%)
CdS/ZnS (-7.0%)	

- Each shell adds a compressive strain to the underlying heterostructure.

Synthesis of CdTe cores

CdO + Oleic Acid +ODE

Heat to 280 °C

Clear Cd Precursor

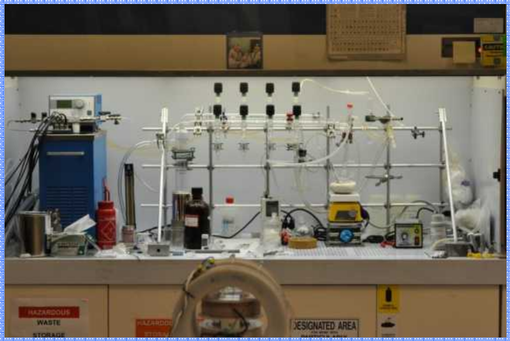
TOP/Te + ODPA + ODE

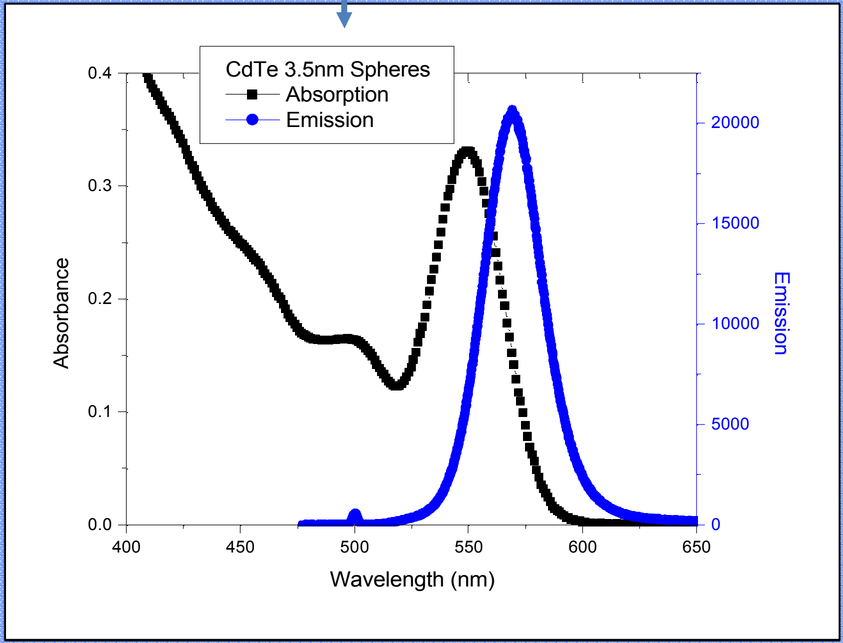
React at 260 °C

- *Yields ~3.5 nm spherical zinc-blende cores.*
- *Emission FWHM of 25-30 nm*

Precursor synthesis

Precursor and QD synthesis





Strong self-absorption

Cai *et al.*, J. Phys. Chem. C, 116, 2012

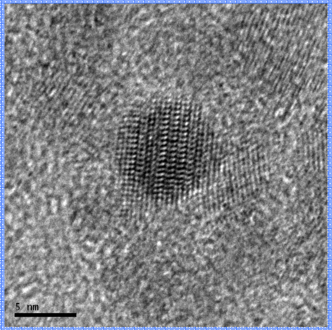
Selective Ion Layer Absorption and Reaction for CdSe shells

Se precursor: TOP/Se + ODE

Cadmium Oleate: CdO + Oleic Acid +ODE

Multiple injections
at 240-260 C

CdTe spherical cores



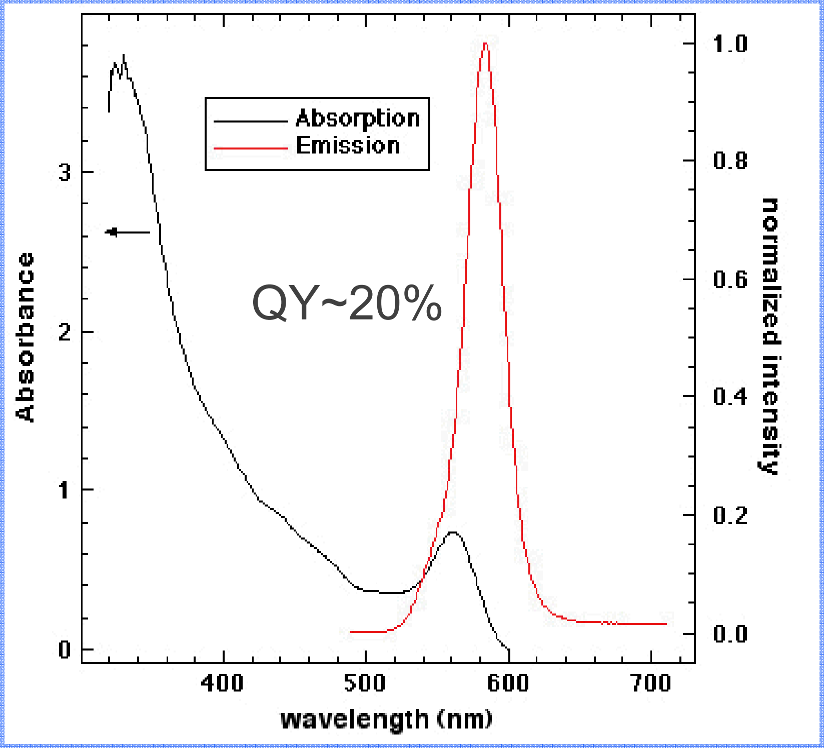
CdTe cores coated with 10 layers of CdSe

- Oleic Acid is a weakly binding ligand, so growth occurs on all facets to yield spherical zinc-blende shells.

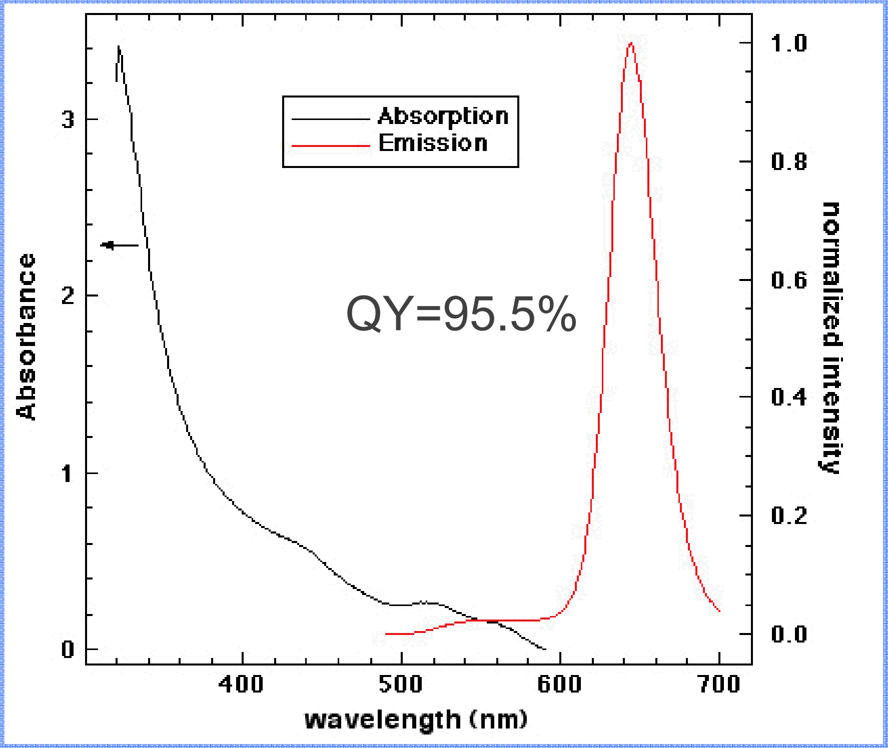
Cai *et al*., J. Phys. Chem. C, 116, 2012
Li *et al*., JACS, 125, 2003

CdSe shells reduce the self absorption

Yellow-emitting CdTe QDs

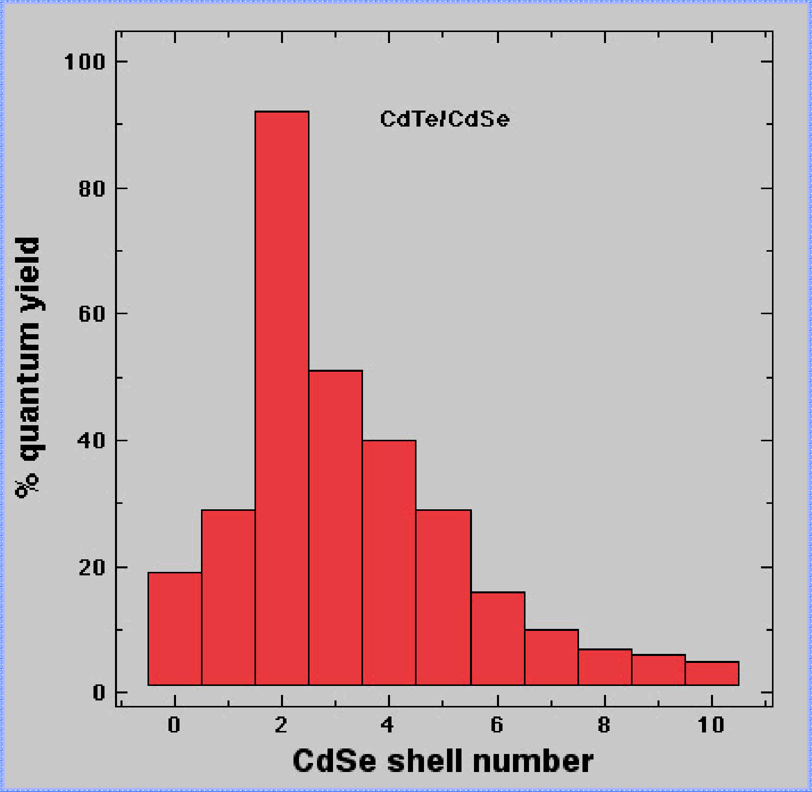


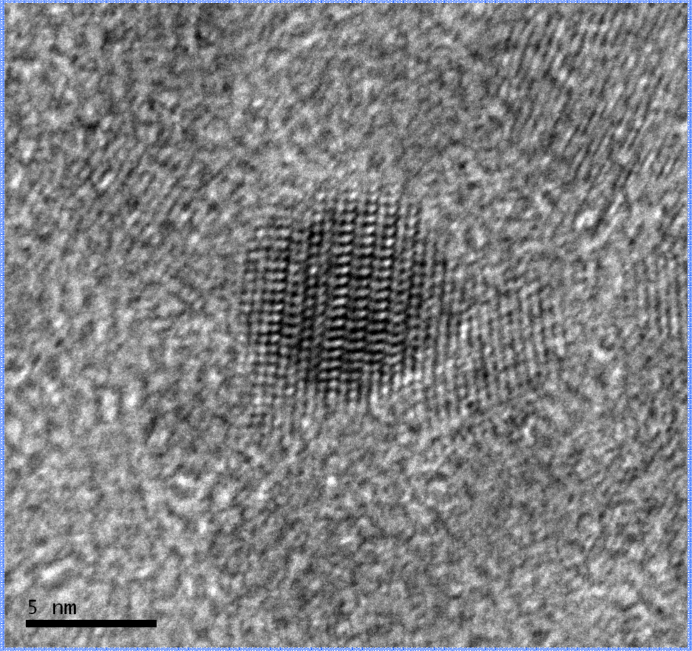
Red-emitting CdTe/CdSe core shell QDs



- The emission/absorption overlap can be reduced by coating with CdSe shells to create a Type II heterostructure.

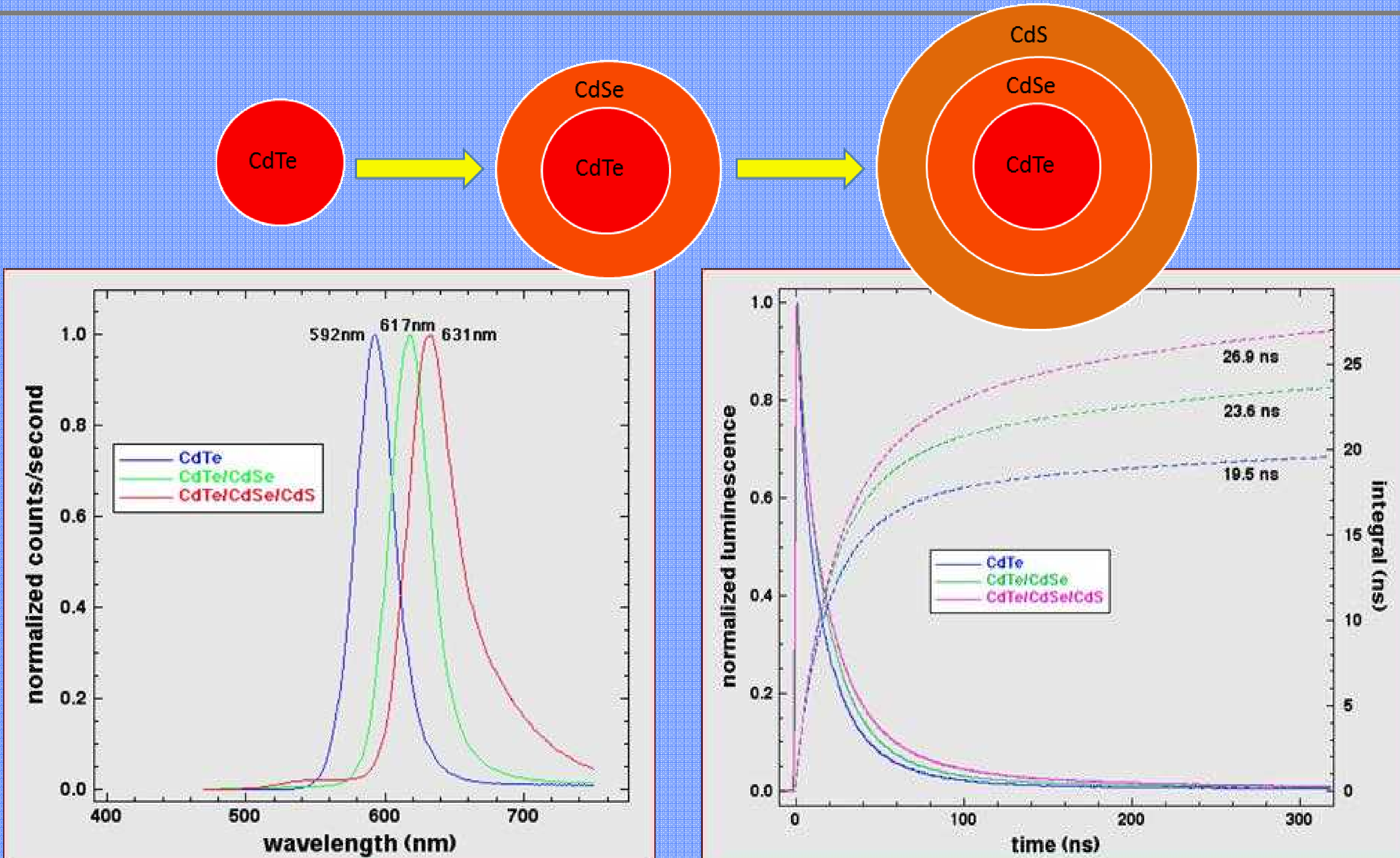
The QY is a strong function of the CdSe shell thickness





- The QY is optimal at 2 layers of CdSe.
- We can now routinely get QYs of 70% through the 5th shell.

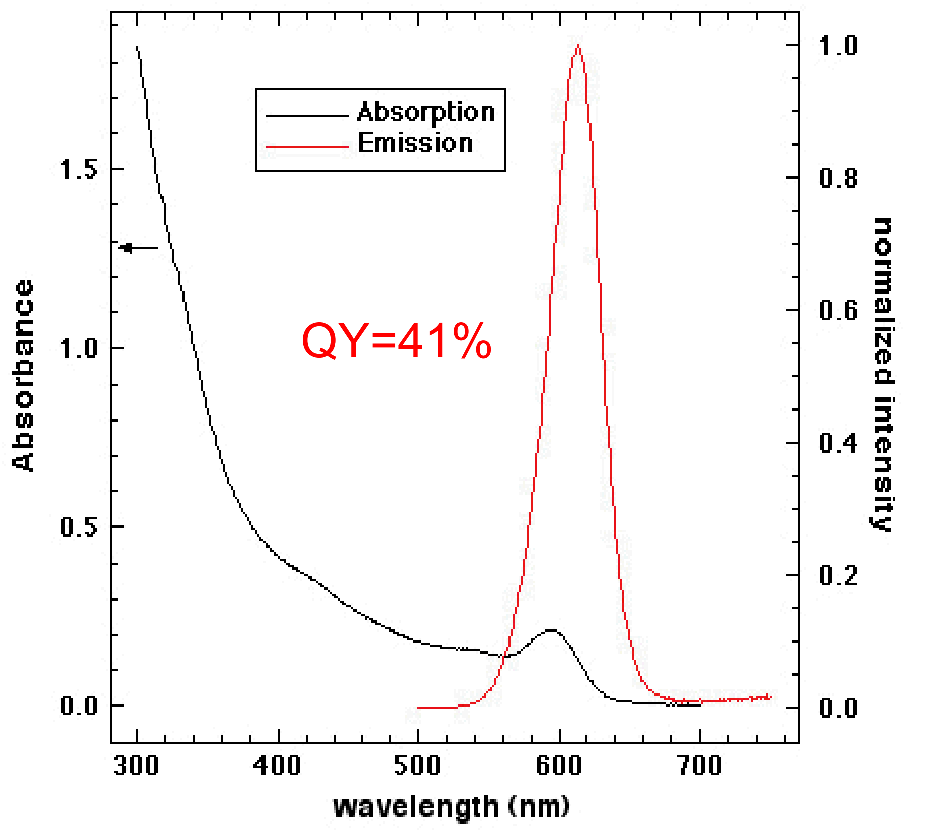
Effect of shell on PL emission and lifetime



- The increased lifetime is due to a reduction in the electron/hole wavefunction overlap.

We have synthesized CdTe/2CdSe/CdS/5ZnS QDs

- Even with all of these shells, the emission is ideally located for SSL.



LER=227 $lm/W_{emitted}$

- The QY is expected to increase if an intermediate alloy layer is formed between the core and shell interfaces to create a graded composition that would reduce the compressive strain.

The ZnS shells improve the thermal stability

$$TQ = [1-(QY_{100^oC}/QY_{25^oC})] \times 100$$

Sample	TQ @ 100°C	Recovery
CdTe	73%	90%
CdTe/2CdSe	39%	92%
CdTe/2CdSe/CdS	38%	92%
CdTe/2CdSe/CdS/5ZnS	**39%**	**100%**
CdSe/ZnSe	87%	67%

- Future work will focus on the mechanisms of thermal quenching.

Summary of CdTe – based quantum dots

- SILAR has been used to create a variety of spherical QD heterostructures:
  - CdTe/CdSe
  - CdTe/CdSe/CdS
  - CdTe/CdSe/CdS/ZnS
  - Shell thickness dependent optical properties and recombination dynamics were observed in all cases.
- QYs as high as 95% were observed and narrow emission peaks can be positioned to be of use for SSL if the CdTe cores are ~3.5 nm.
- Luminous efficacy of radiation as high as 227 $lm/W_{emitted}$.
- ZnS shell enables reversible thermal quenching at $100^{o}C$.
- Future work will focus on the reduction of lattice mismatch strain through

alloying.

Acknowledgments

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- Collaborators:
  - Dr. James Martin, Sandia National Laboratories
  - Professor May Nyman, Oregon State University
  - Professor David Kelley, UC Merced
  - Dr. Xichen Cai, UC Merced