Development of Red Downconverters for Solid-State Lighting

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I. Inverse micellar synthesis of “white-emitting” CdS QDs.

II. Inverse micellar synthesis of doped CdS QDs.

III. High temperature synthesis of CdTe core/shell heterostructures.

IV. Hydrothermal synthesis of doped oxides.

SSLS EFRC

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Statement of Problem and Goal

• Current white LEDs based on blue-pumped YAG:Ce have poor color rendering.

• Adding a red emitter significantly increases the CRI, but also significantly reduces the luminous efficacy of radiation (lumens/Watt of light emitted).

• Blue-pumped red emitters are scarce and none have been identified that have:

- narrow emission bandwidth,
- ideal emission wavelength,
- broad blue absorbance,
- high quantum yield,
- low thermal quenching,
- photostability, etc.

• Our goal is to develop a scientific approach to the rational design and synthesis of such a blue-pumped red emitter.

Red downconverters must meet numerous criteria to be satisfactory for solid state lighting

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

We are pursuing two classes of downconverters

CdTe quantum dot heterostructures

Pros

Tunable, narrow bandwidth emission
Broad blue absorption
High oscillator strength
- large absorption cross section
- fast PL decay dynamics

Low scattering
High quantum yield

Cons

High photostability undemonstrated

Doped oxide phosphors

Pros

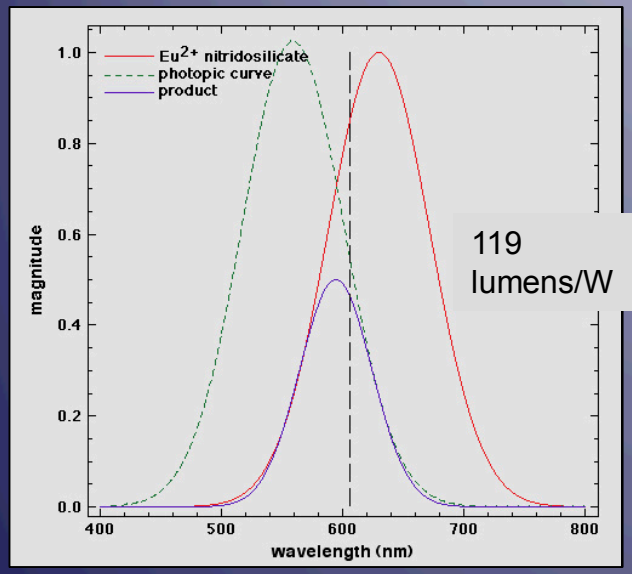
Narrow bandwidth emission
High quantum yield
Low thermal quenching
Chemical stability
Thermal stability

Cons

Narrow blue absorption
Low oscillator strength

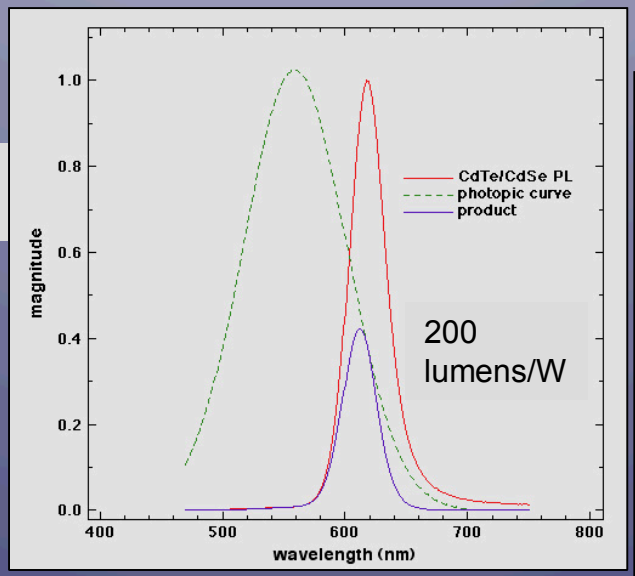
Significant increases in the luminous efficacy are possible with these downconverters

Good



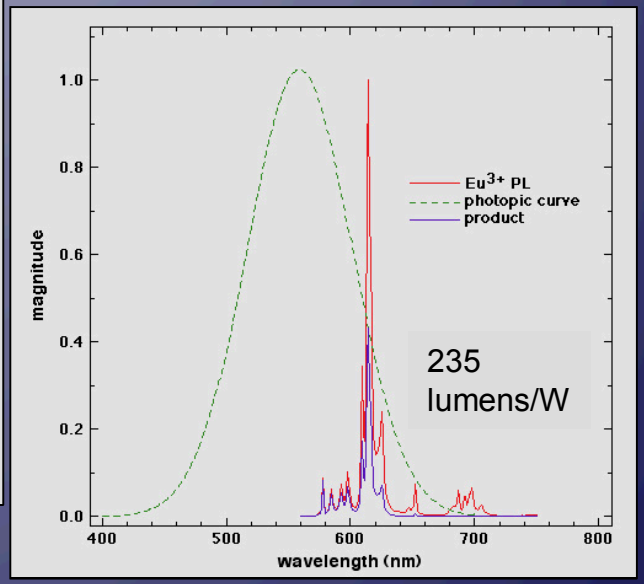
Commercial Eu^{2+}-doped phosphors have broad emission extending into the deep red spectral region.

Better



SNL CdTe QDs have narrow red emission FWHM ~30 nm

Best



SNL Eu^{3+}-doped phosphors have narrow red emission FWHM~5 nm

- The LER for red emission (>606 nm) can be significantly increased with narrow bandwidth emitters.

A brief review of our II-VI Quantum Dot research for SSL

I. Inverse micellar synthesis of “white-emitting” CdS QDs.

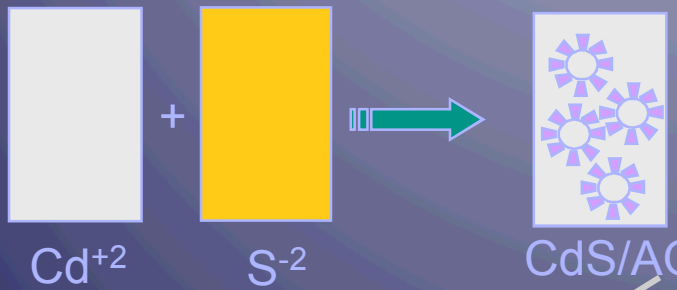
II. Inverse micellar synthesis of doped CdS Qds.

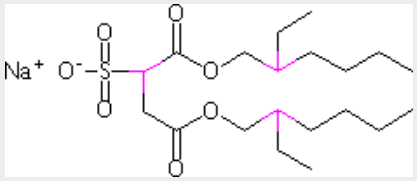
III. High temperature synthesis of CdTe core/shell heterostructures.

I. Inverse micellar synthesis of white-emitting CdS QDs

- Synthesis developed by Lianos and Thomas, 1986
- Photolysis found to improve QY (Harruff and Bunker, 2003)

AOT inverted microemulsions





AOT - Dioctyl sodium sulfosuccinate

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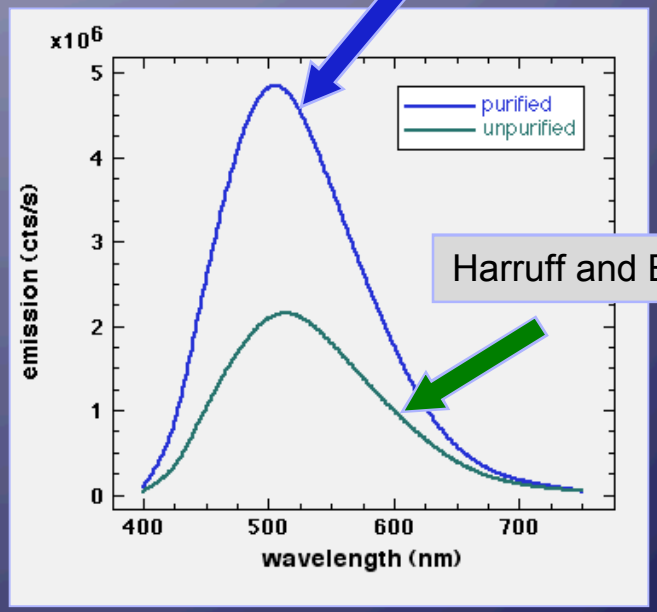
Harruff and Bunker



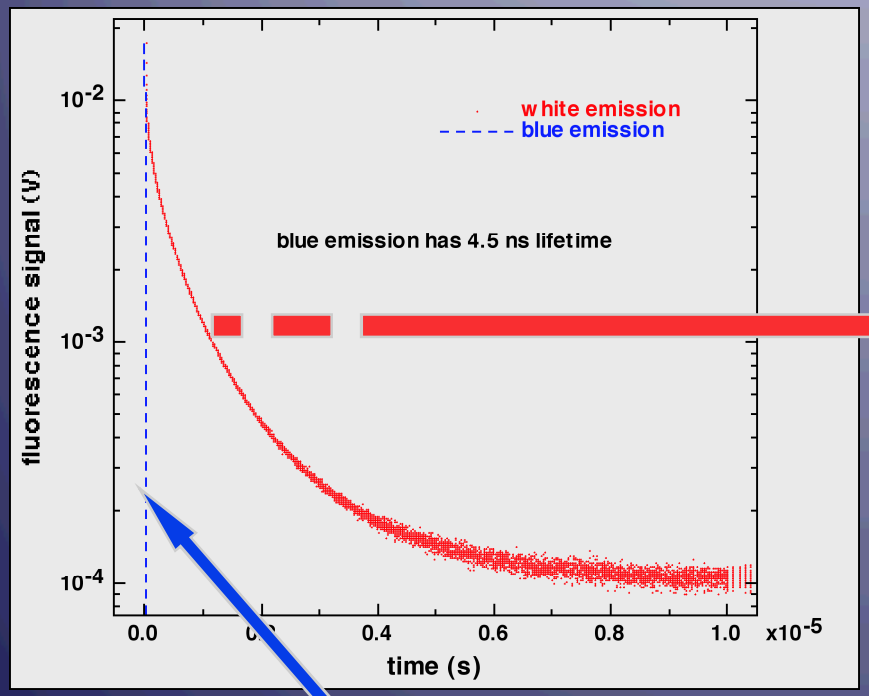
- This synthesis yields weakly luminescent solutions of QDs.
- The luminescence increases when the water is removed, as water evidently quenches the emission.

White-emitting CdS quantum dots

CdSe CdS:Mn CdS CdS CdSe

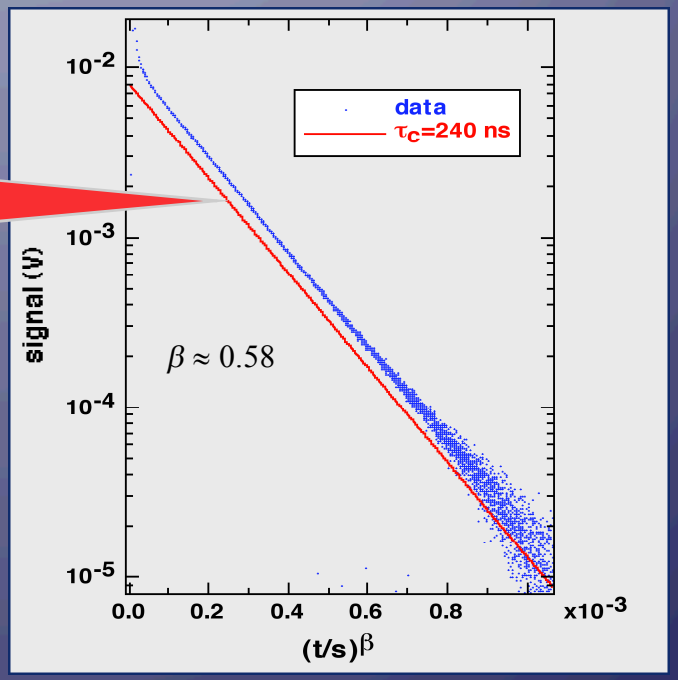
- The white emitting material seemed to have the potential for a single-phosphor white LED (UV pumped) but the QY is low.

The stretched exponential PL decay of white-emitting QDs indicates trap state mediated emission



blue emission: τ=4.5 ns

$$S(t) \sim e^{-(t/\tau_{ch})^{\beta}}$$



characteristic time is 240 ns

- The decay is two orders of magnitude slower than that of QDs having narrow emission.

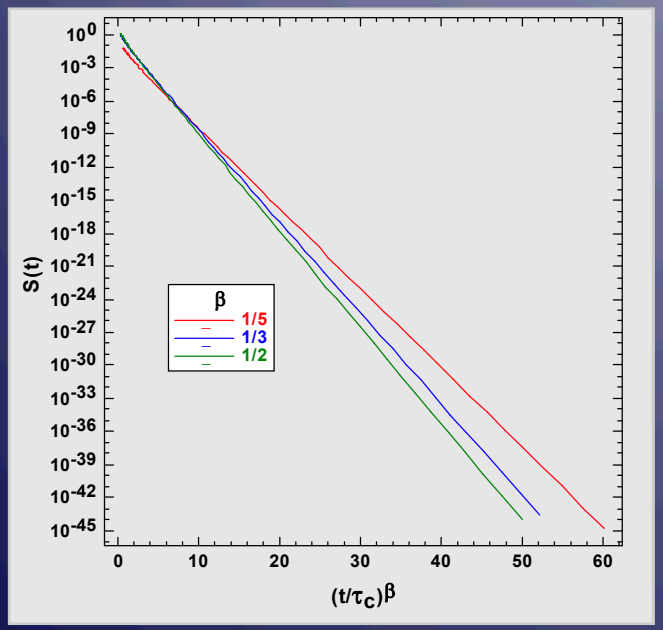
L.E. Shea-Rohwer and J.E. Martin, J. Lumin. 127, 499-507 (2007)

A stretched-exponential decay indicates a broad distribution of relaxation times h(τ)

What distribution gives a stretched exponential decay?

$$h(\tau) = ce^{-(\tau/\tau_{ch})^{\alpha}} \quad \beta = \alpha/(1+\alpha) \quad S(t) \sim e^{-(t/\tau_{ch})^{\beta}}$$

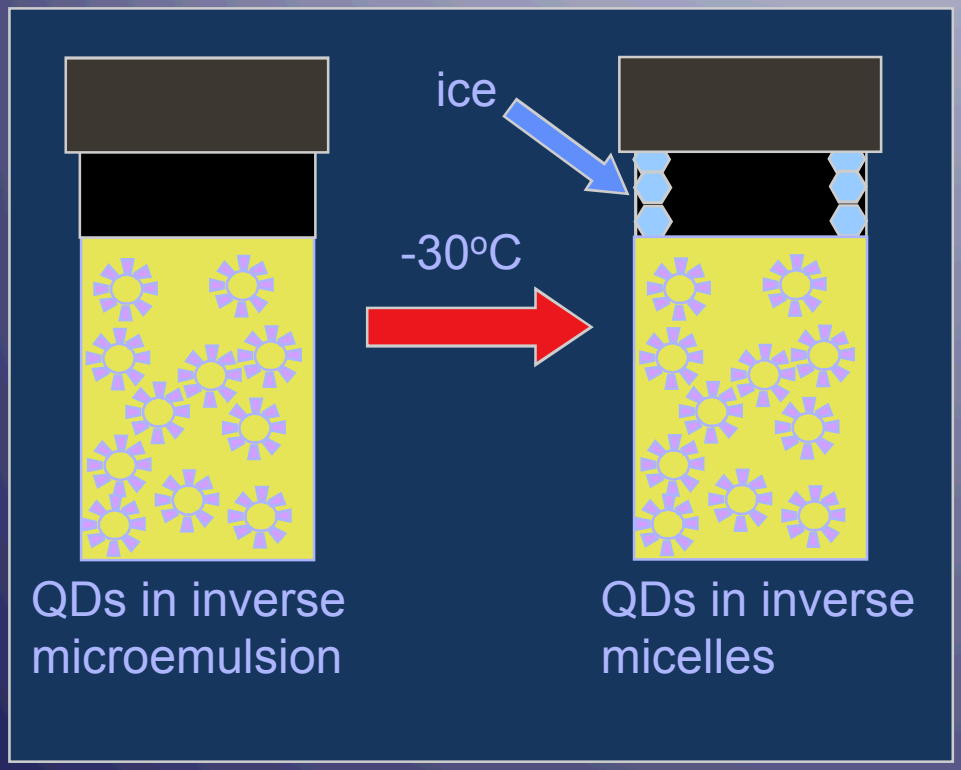
$$ex: \; h(\tau) \sim e^{-\tau/\tau_{ch}} \quad \text{gives} \quad \beta = 1/2$$



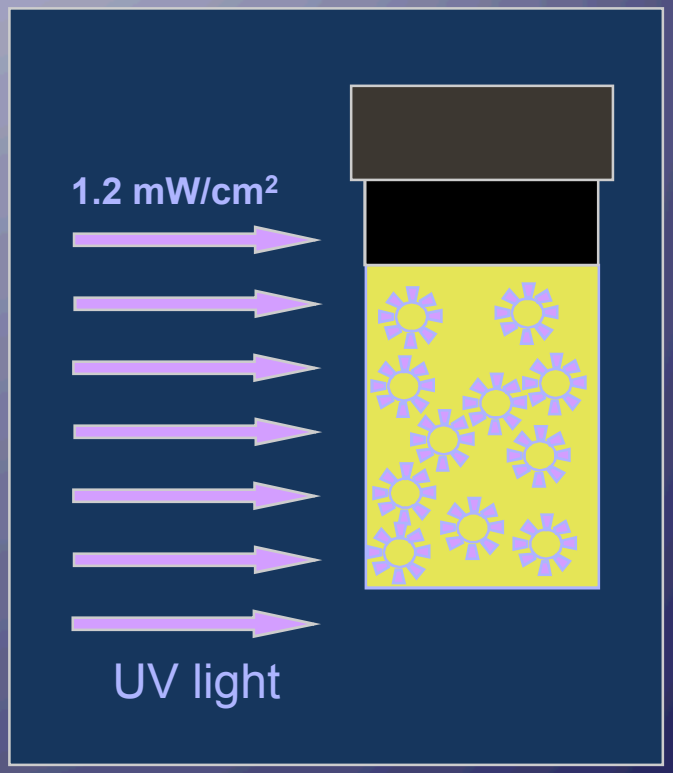
- White-emitting QDs have an exponential distribution of lifetimes.
- Can these trap states be blocked by ligation with Lewis bases?
- Will trap state blocking increase the QY?
- What is the combined effect of photolysis, purification and ligation on the PL emission and QY?

J.E. Martin and L.E. Shea-Rohwer, J. Lumin. 121, 573-587 (2006)

Increasing the QY through purification and photolysis



Purification



Photolysis

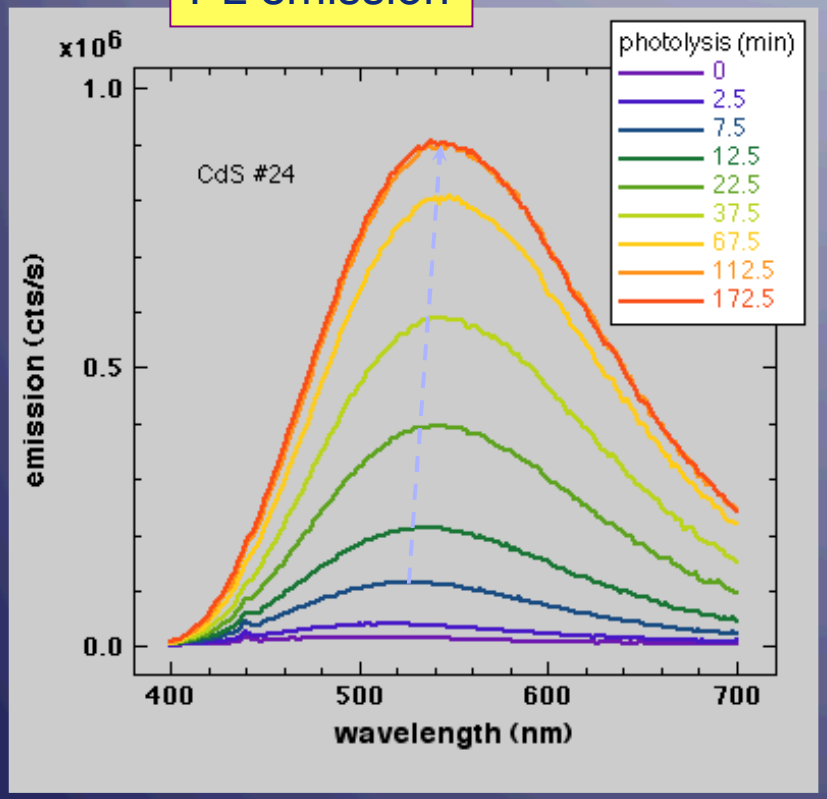
- The combination of these processes substantially increases the QY.

L.E. Shea-Rohwer, J.E. Martin and D.F Kelley, J. Electrochem. Soc. 157, J1-J7 (2010)

Photolysis dramatically increases light emission

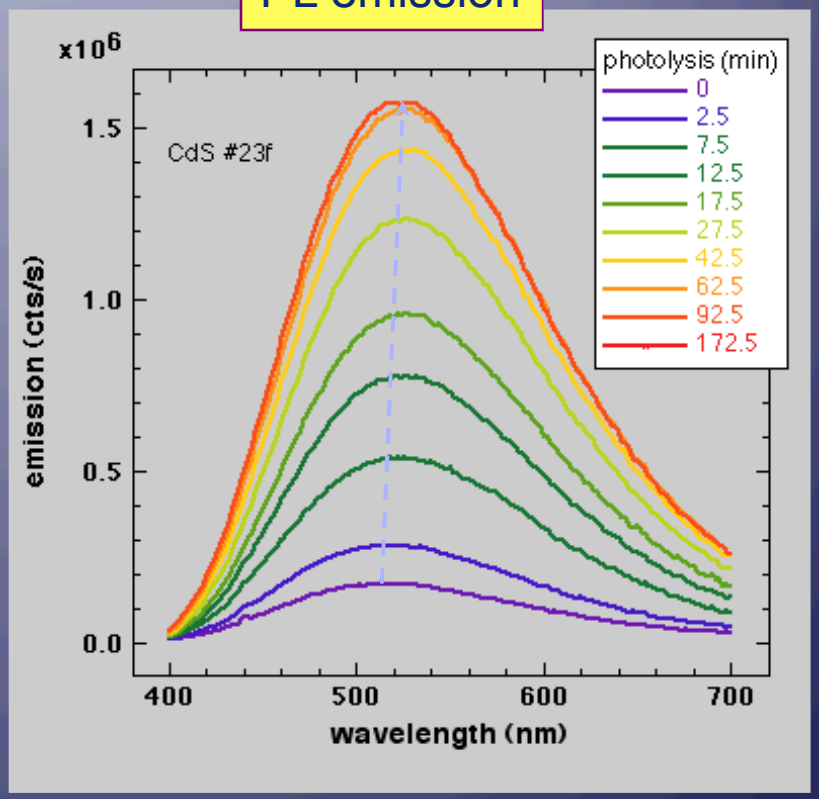
excitation @ 390nm

PL emission



unpurified

PL emission

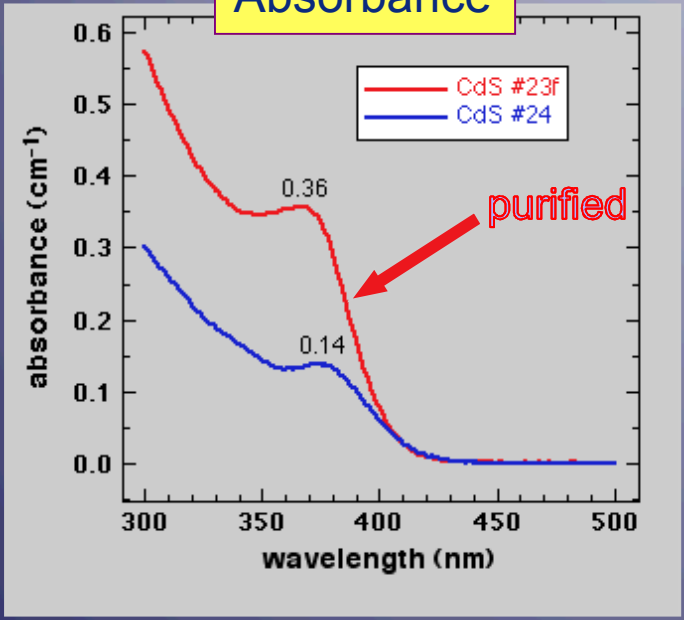


purified

- The purified sample exhibits significantly greater emission. Why?

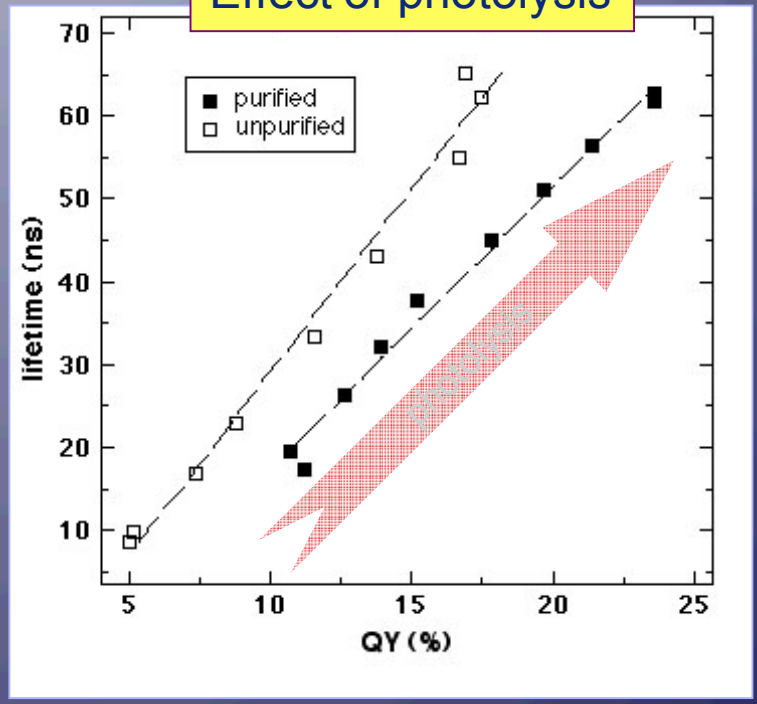
The increased emission is due to increased absorbance and QY

Absorbance



Purification increases the absorbance

Effect of photolysis



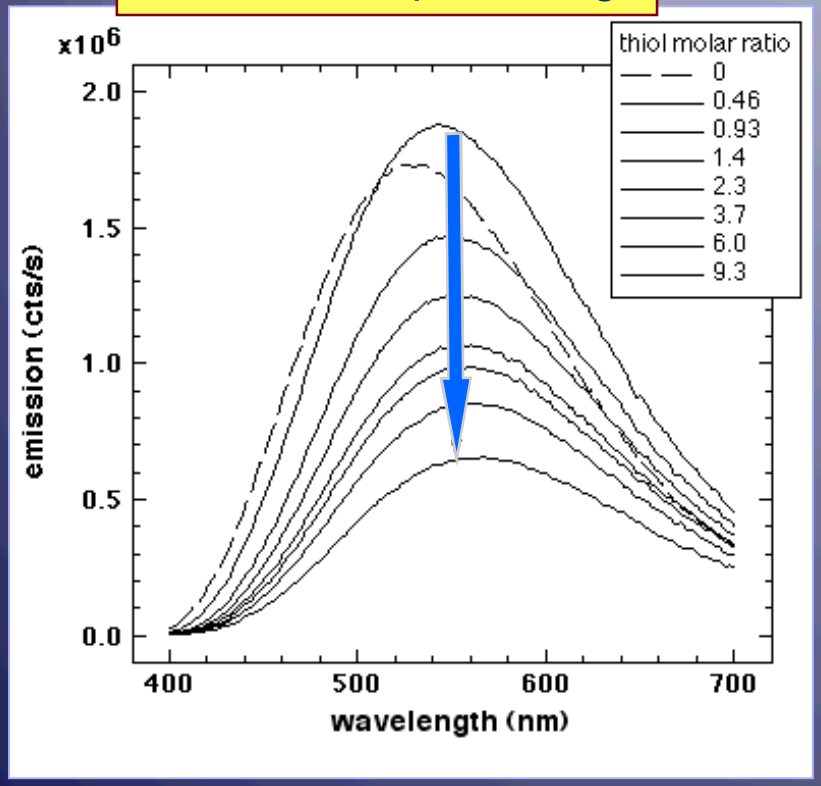
Photolysis and purification increase the QY

- The mechanism of these increases is unclear, but the proportionality between lifetime and QY indicates non-radiative parallel decay channels are being shut down.
- Purification and photolysis increase the QY to 24%.

L.E. Shea-Rohwer, J.E. Martin and D.F Kelley, J. Electrochem. Soc. 157, J1-J7 (2010)

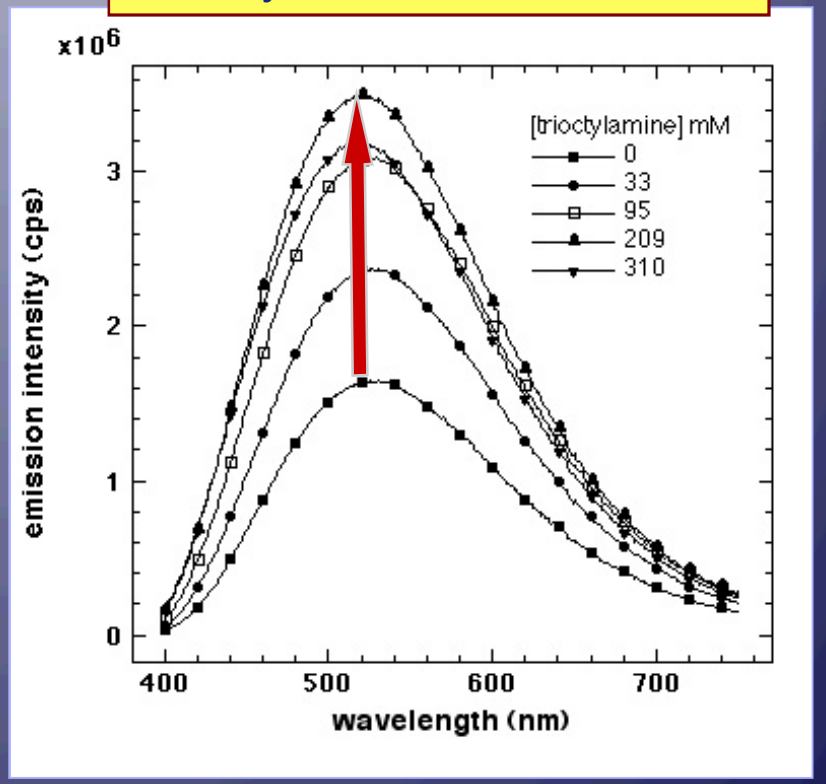
Surface ligands can quench or enhance the emission

Alkane thiol quenching



- Alkane thiols act as soft Lewis bases with high polarizabilities that can act as hole traps.

Tertiary amine enhancement



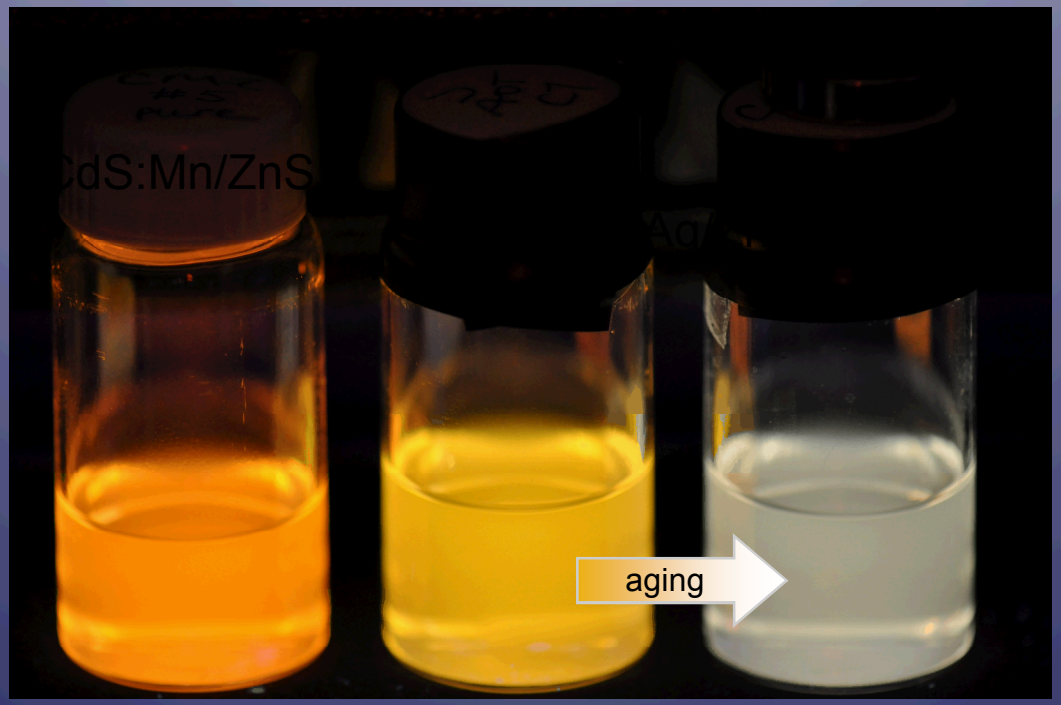
- Tertiary amines act as hard Lewis bases that remove surface trap states.

- Tertiary amines increase the QY to nearly 40%.
- However, we could not obtain futher QY increases and chose to take a new direction.

II. Doped QDs

Can doped QDs have impact on lighting?

Can we eventually synthesize acceptor-donor QDs?

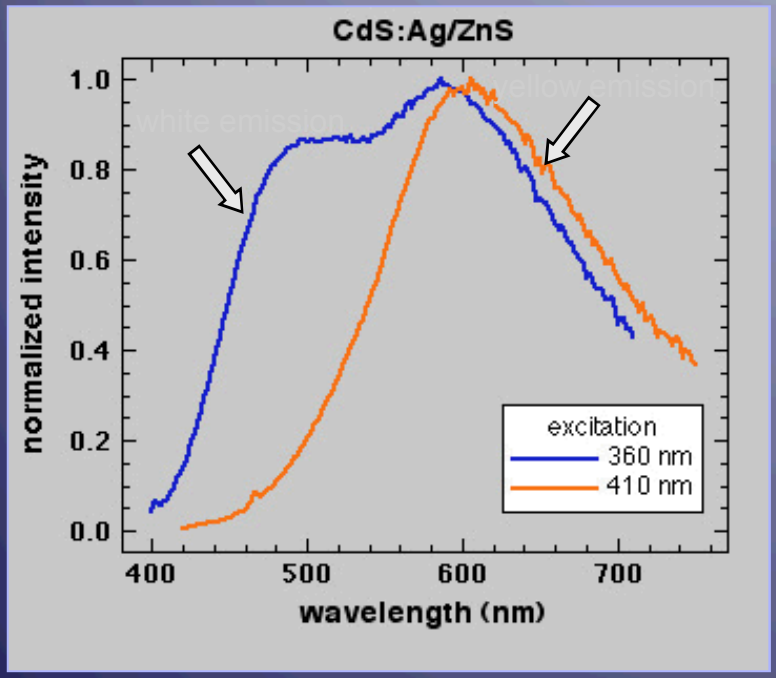


- After 5 days the emission from a Ag-doped core-shell QD turned white!

J.E. Martin and L.E. Shea-Rohwer, J. Lumin. 128, 1407-20 (2008)

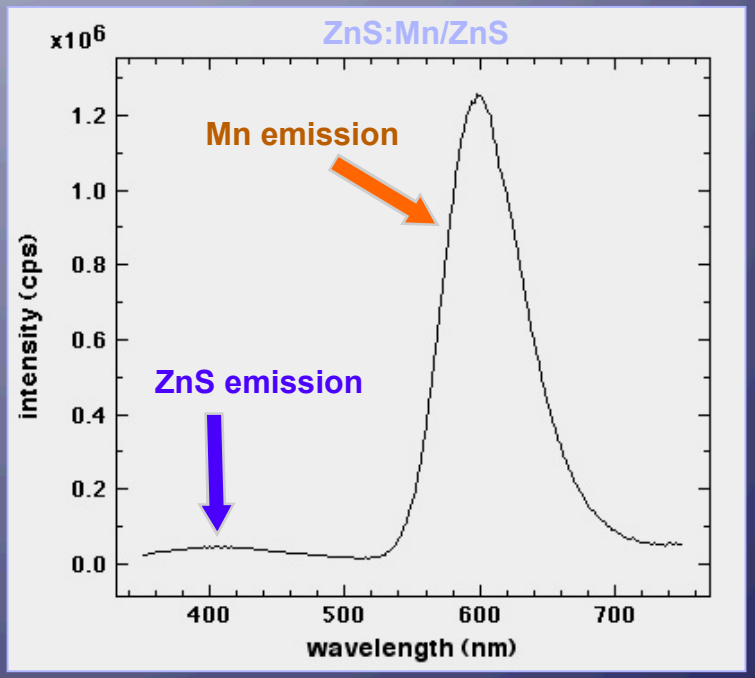
Emission from Ag- and Mn-doped QDs

For Ag-doped QDs the emission depends on excitation wavelength



- Better color quality (CRI=89; CCT=4055K) than undoped CdS (CRI~74; CCT~6000K).

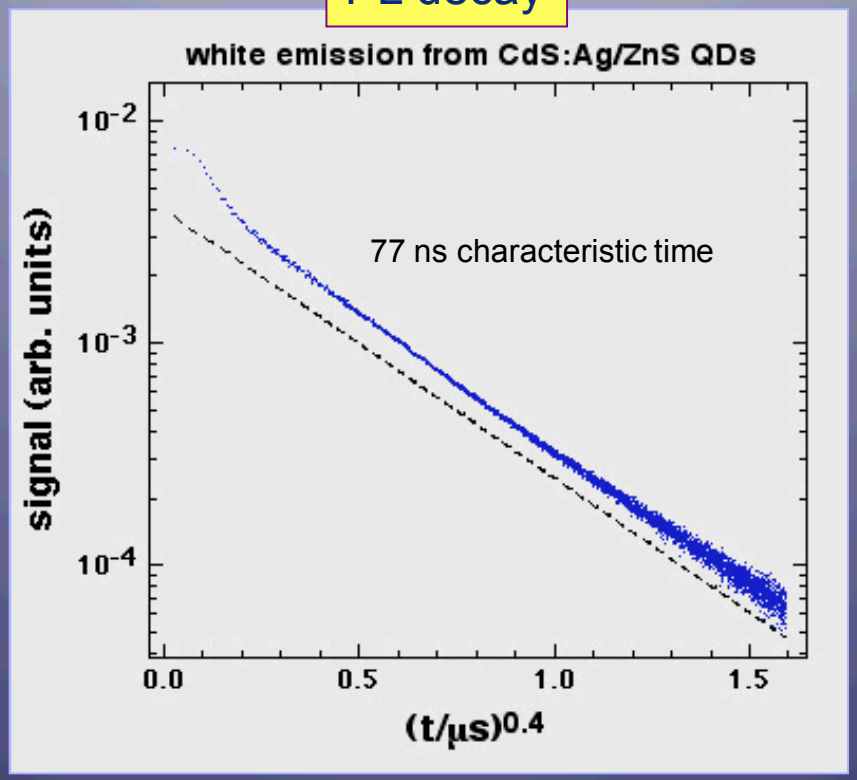
Orange emission from Mn-doped QDs



- QY of 13% vs the 8% reported in literature.

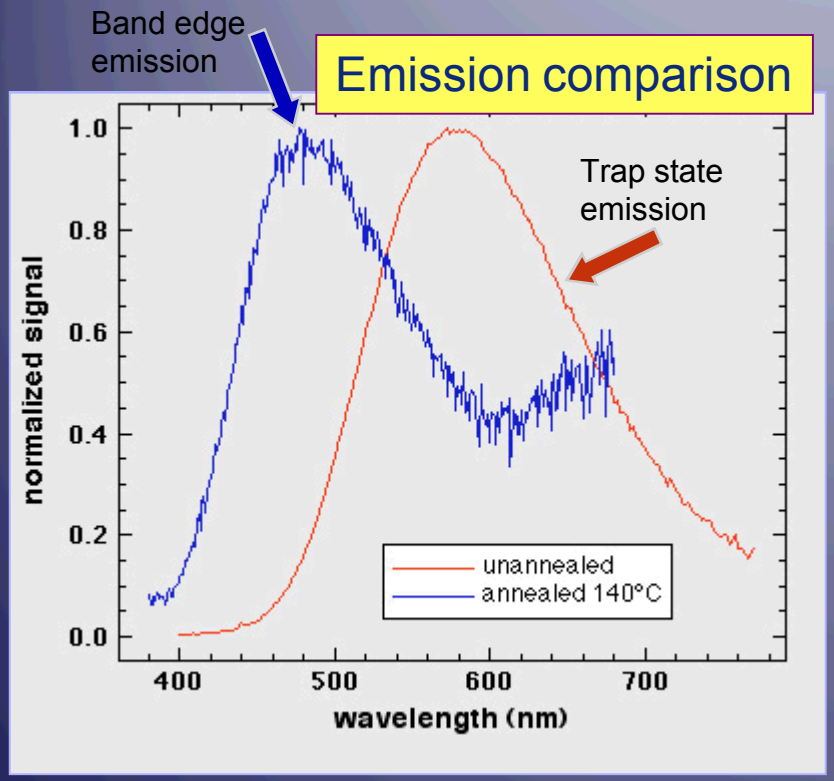
Ag-doped CdS/ZnS QDs have a stretched exponential PL decay

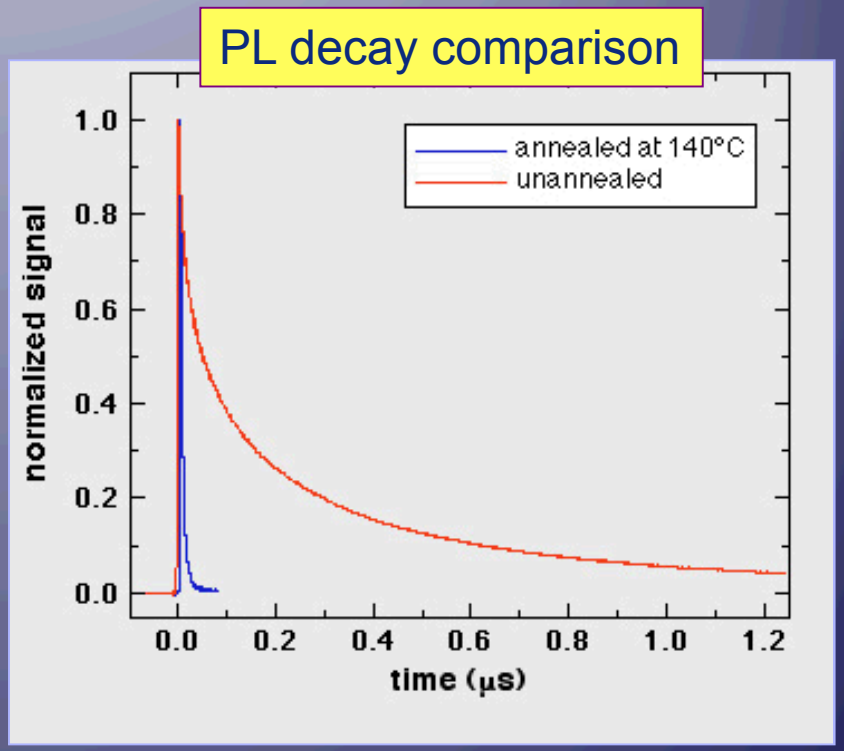
PL decay



- The SE decay is similar to that of undoped CdS QDs, indicating that trap states still play a role in recombination.

Annealing affects the emission and lifetime of the QDs





- Orange emission becomes blue upon annealing at 140°C.
- The emission blue-shift is accompanied by a significant decrease in the lifetime.

Does the Mn diffuse out during annealing?

Summary

- CdS QDs made in inverse micelles exhibit trap-state-mediated white emission.
- This white emission is attractive for lighting, but even after purification, photolysis, and ligation, the QY did not exceed 40%.
- Doped QDs made in inverse micelles did not exhibit the narrow bandwidth or high QYs needed for SSL.
- These results led us to conclude that a new direction is needed – the development of photostable CdTe-based heterostructures.

Why CdTe QDs?

- CdTe QDs have extremely high extinction coefficients, so toxicity and cost are low (<1 ng per LED).
- Negligible scattering will reduce losses due to back scattering of the excitation onto the LED chip.
- Wavelength tunability is a plus, enabling multiple SSL product lines.
- Broad excitation in the blue makes emission insensitive to variations in LED pump wavelength.

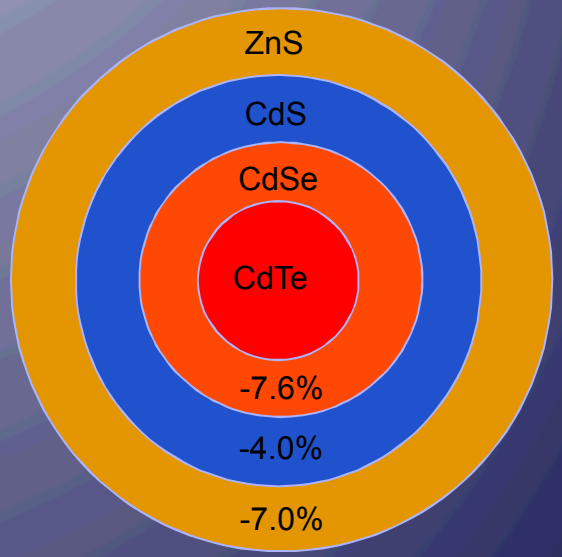
Can a photostable core/shell heterostructure be created?

material	mismatch	E_{cb} (eV)	E_{vb} (eV)	E_{gap} (eV)
CdTe (cu)	+7.6%	4.0	5.5	1.5
CdSe (h)	0.0%	4.3	6.0	1.74
CdS (h)	-4.0%	4.1	6.6	2.5
ZnTe (cu)	+2.6%	3.6	5.8	2.24
ZnSe (cu)	-6.3%	3.5	6.2	2.58
ZnS (cu)	-11.0%	3.2	6.9	3.7

- ZnS is photostable, but the lattice mismatch is large, so a strain-graded approach is needed.

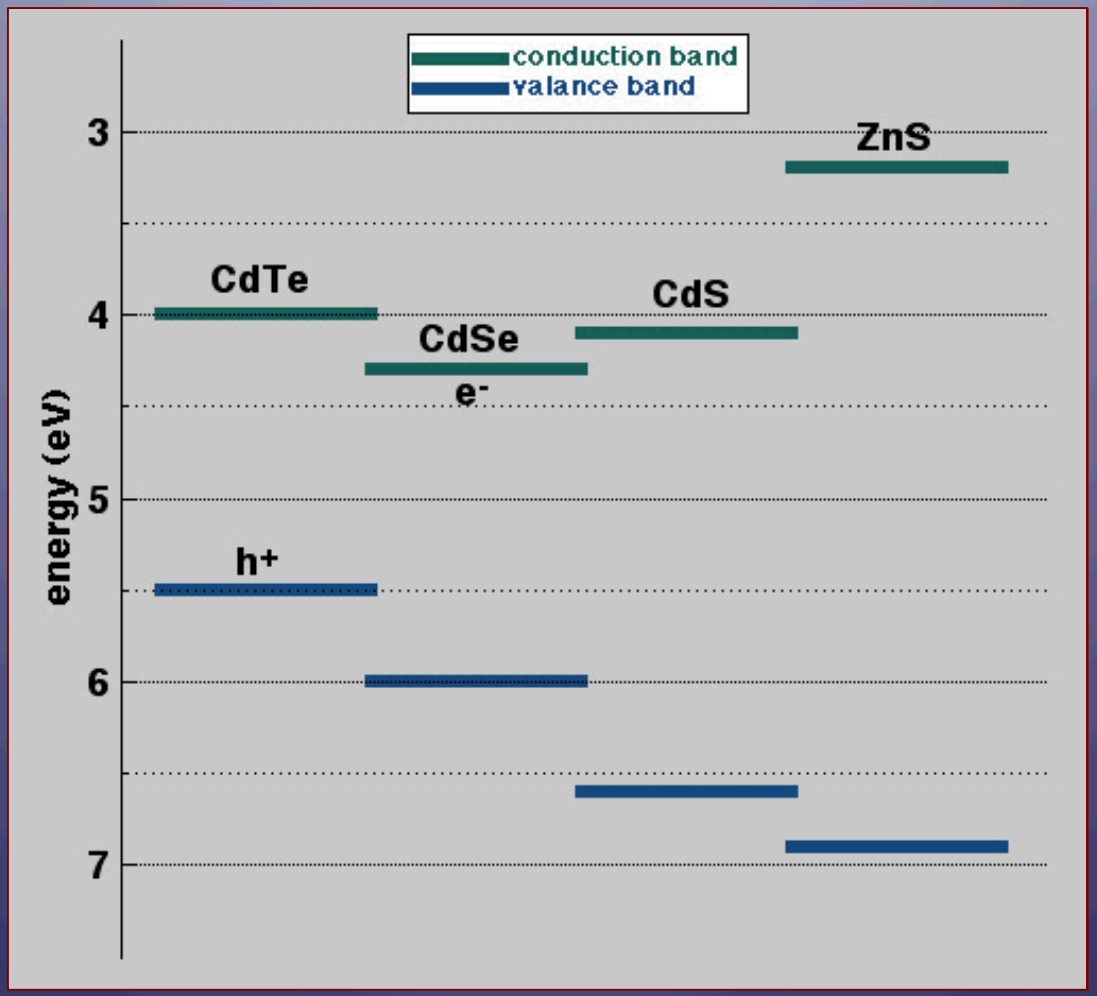
Strain-graded heterostructure

Type I (mismatch)	Type II (mismatch)
CdSe/CdS (-4%)	CdTe/CdSe (-7.6%)
CdSe/ZnS (-11%)	ZnTe/ZnSe (-8.9%)
CdSe/ZnSe (-6.3%)	ZnTe/CdSe (-2.6%)
CdTe/ZnSe (-13.9%)	ZnTe/CdTe (+5.0%)
CdSZnS (-7.0%)	



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

Valence and conduction band energies



- The energies for the unstrained lattice indicate a Type II heterostructure where the hole remains in the CdTe and the electron is in the CdSe shell.

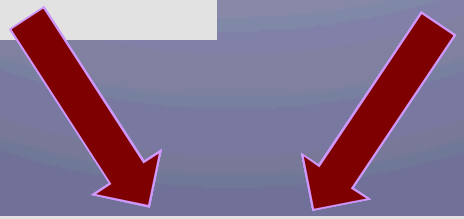
Synthesis of CdTe cores

Formation of TOPTe precursor

1. Mix Te powder, trioctylphosphine, octadecylphosphonic acid & octadecene.
2. React at 160^{o}C until Te dissolves to form a yellow liquid.

Formation of cadmium oleate

1. Mix cadmium oxide, oleic acid & octadecene.
2. React at 240^{o}C until Cd reacts to form a clear liquid.



1. TOPTe is injected into cadmium oleate at 280^{o}C until Cd reacts to form a clear liquid.
2. Solution is heated at 260^{o}C for up to 10 minutes.

Formation of CdSe shell

SILAR

Selective **I**on **L**ayer **A**bsorption and **R**eaction

Peng et al. JACS 125, 12567-75 (2003)

Formation of TOPSe precursor

1. Mix Se powder, trioctylphosphine & octadecene.
2. Se dissolves at 25°C to form a transparent liquid.

Formation of cadmium oleate

1. Mix cadmium oxide, oleic acid & octadecene.
2. React at 240°C until Cd reacts to form a clear liquid.

1. TOPSe is injected dropwise into CdTe core solution over a period of 5 minutes.
2. Solution is reacted for 10 minutes.
3. Cadmium oleate is injected dropwise in CdTe core solution over a period of 5 minutes.
4. Solution is heated for 10 minutes.
5. Process is repeated until the desired number of layers are formed.

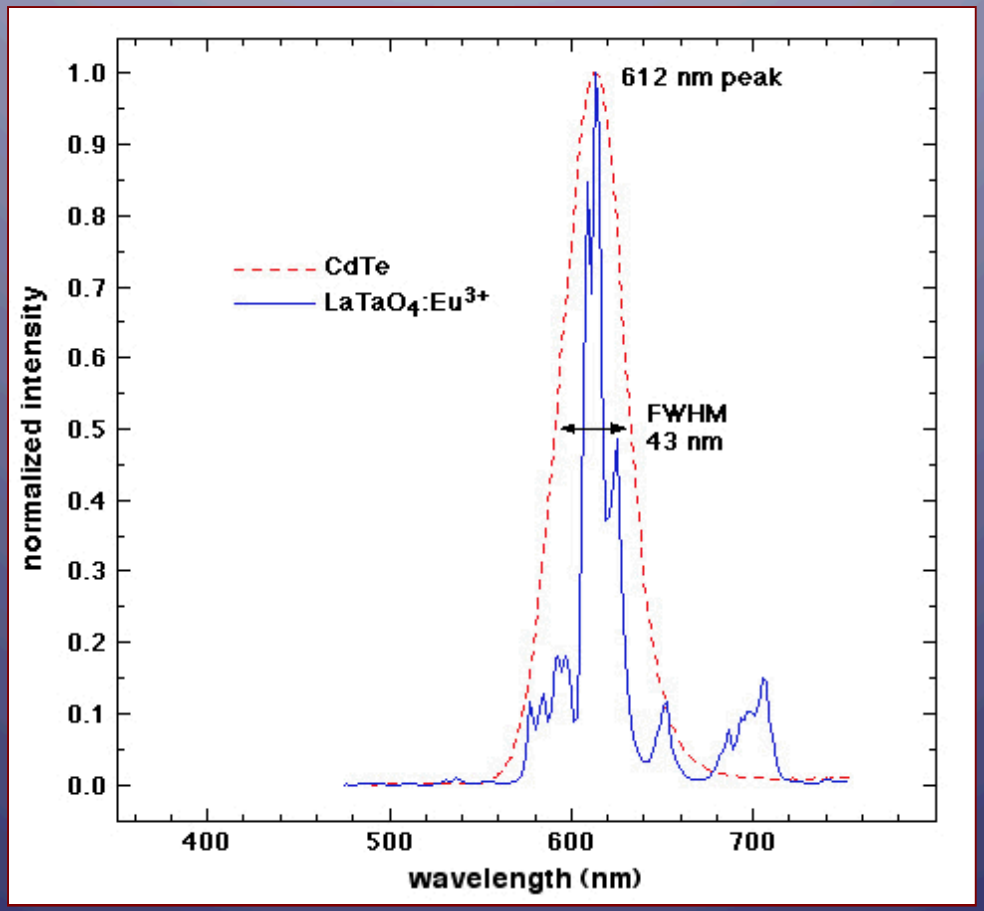
- The formation of other shell materials is similar.

A few QD samples from our lab

- Both as-synthesized and diluted samples are shown.

CdTe QDs can have narrow red emission

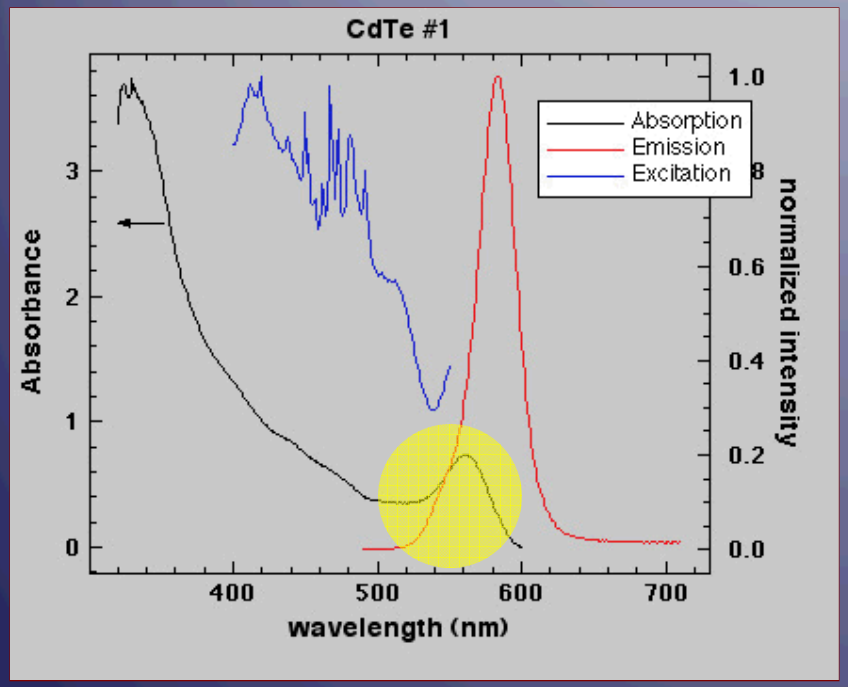
CdTe QD emission is compared to that of Eu^{3+}



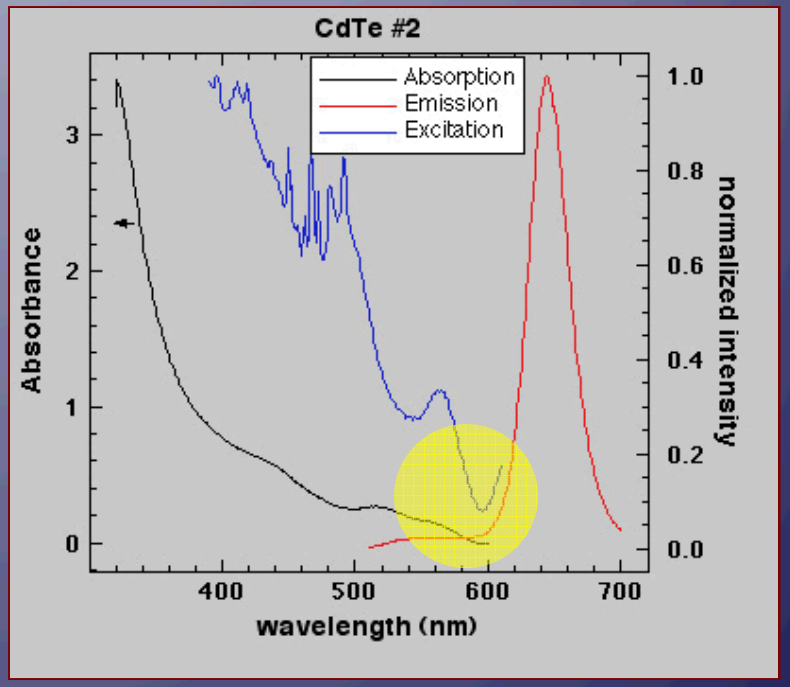
- The red emission of these materials is 2.5x narrower than that of the nitridosilicates used in warm white LEDs.

A CdSe shell eliminates self absorption

Yellow-emitting CdTe QDs



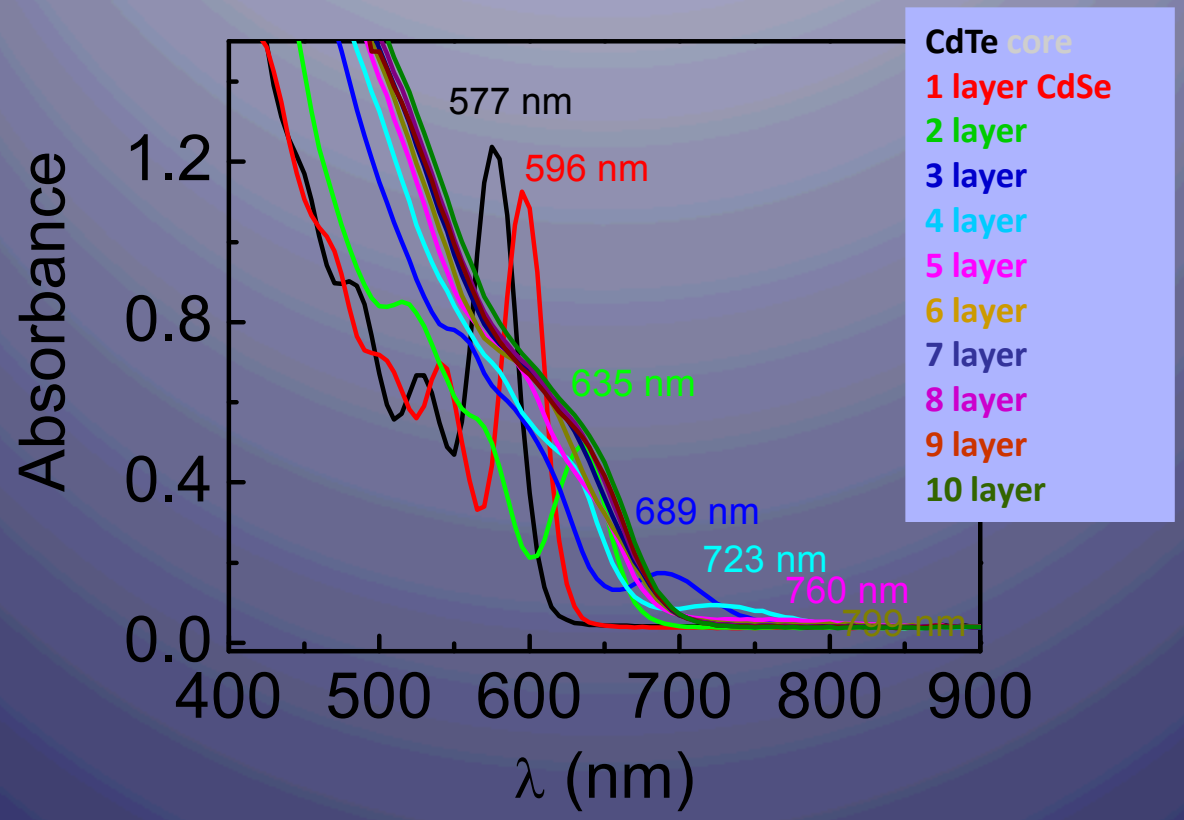
Red-emitting CdTe/CdSe core shell QDs



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

The absorbance red-shifts with increasing shell thickness

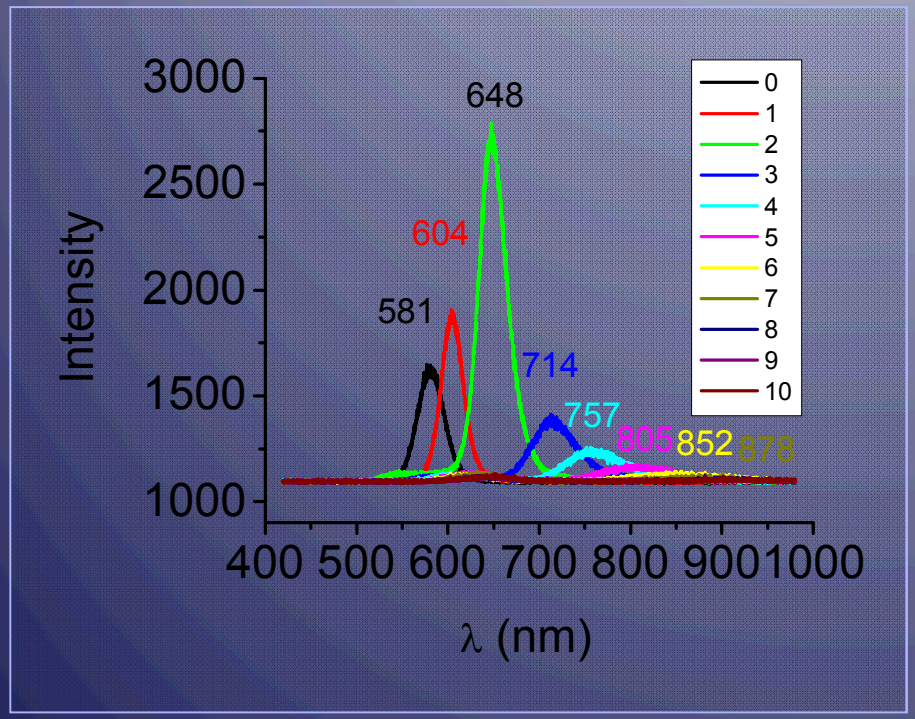
CdTe $D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - (194.84) = 3.38$ nm

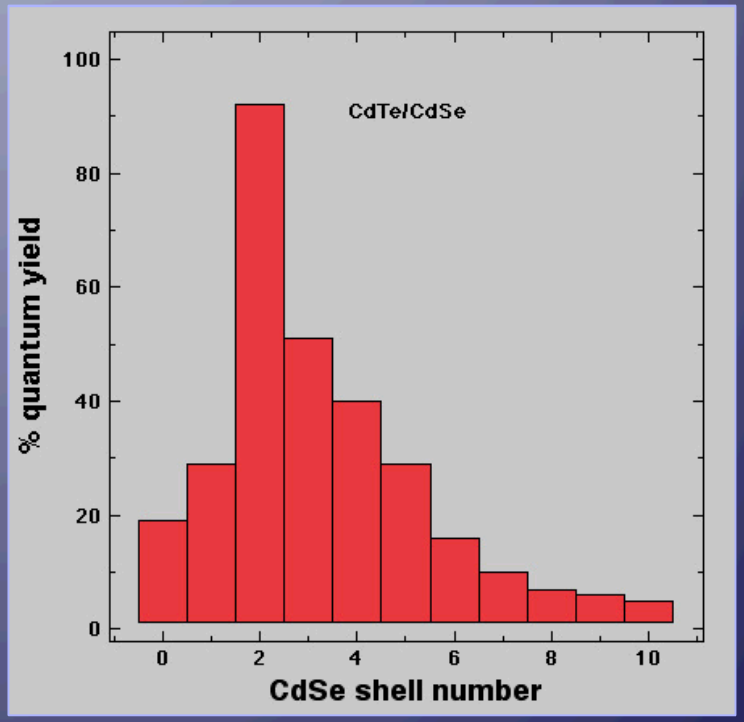


- The emission also red-shifts and the PL lifetime increases.

Emission of CdTe/CdSe core/shell QDs

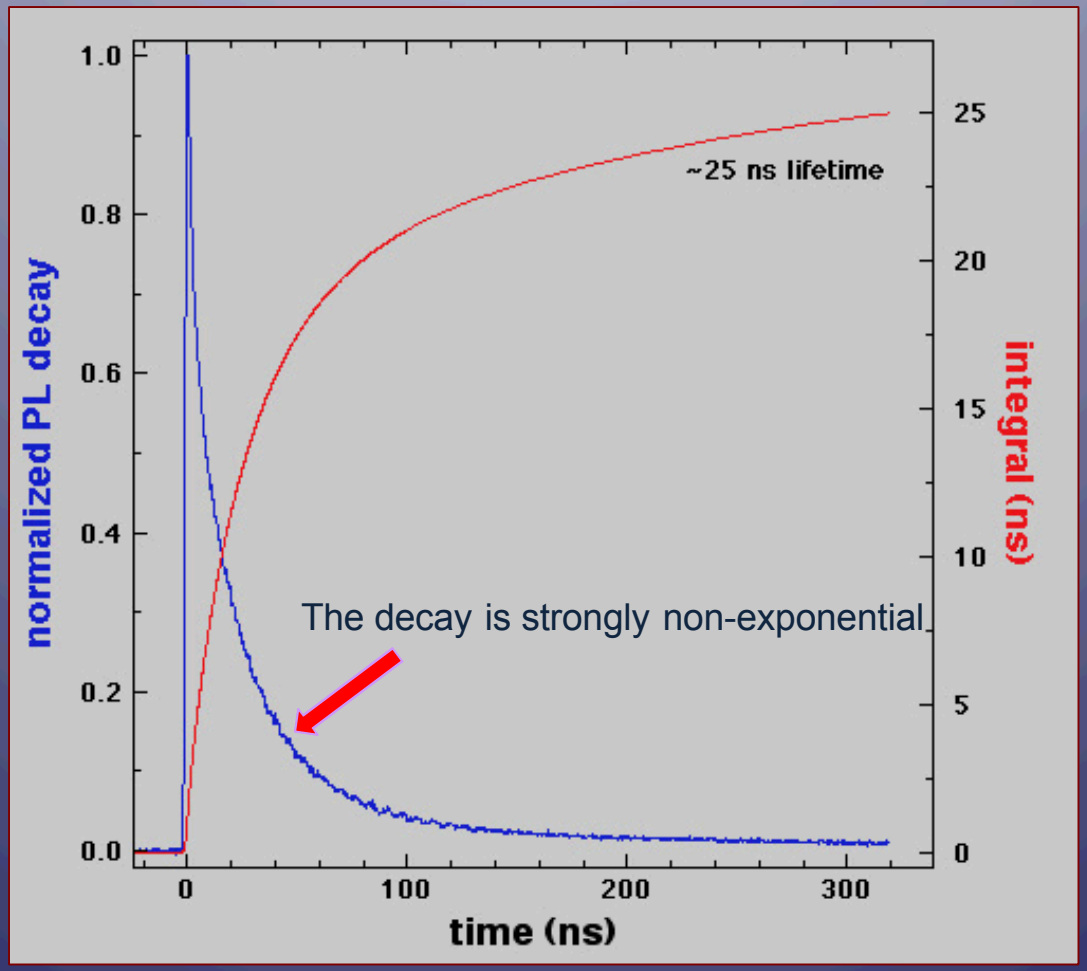
405 nm excitation





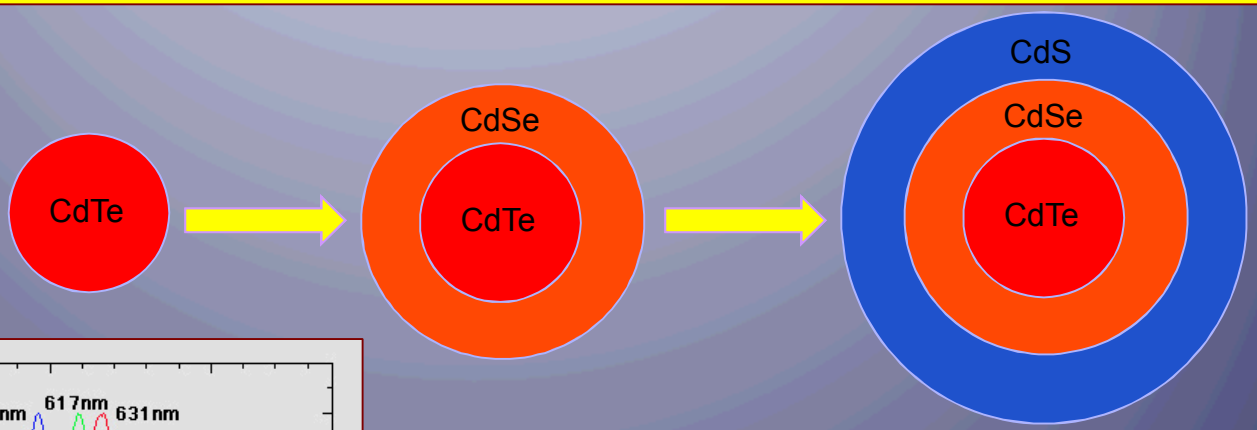
- **The emission red shifts and the QY is a strong function of the shell thickness, becoming optimal at 2 layers.**

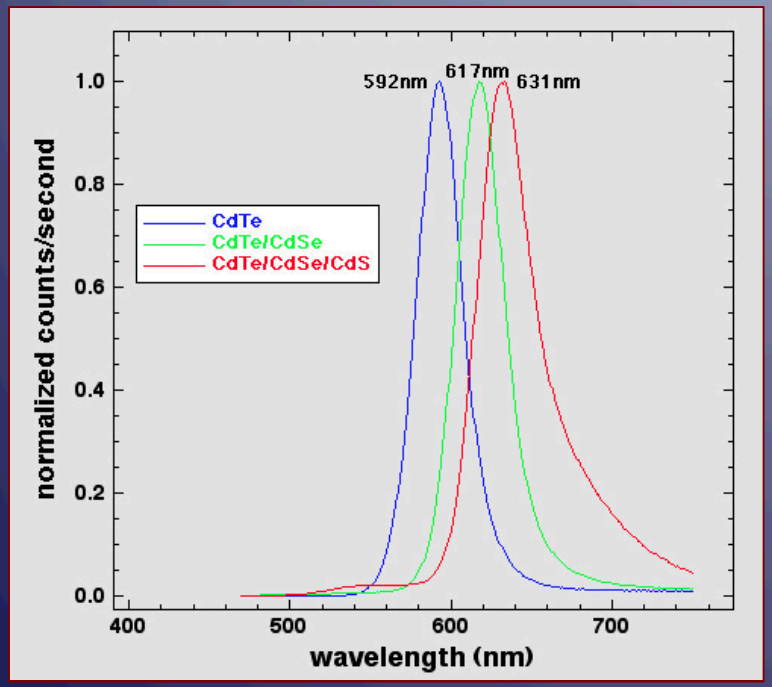
The fast PL decay of CdTe QDs indicates high oscillator strength

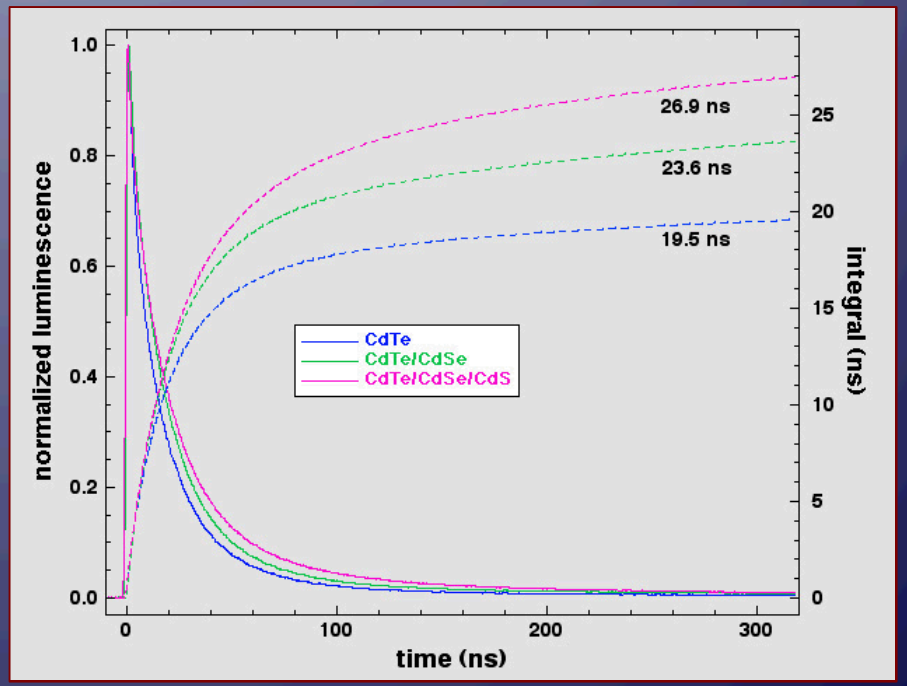


- The absorption cross section is consequently very large.

Effect of shell formation on PL emission and lifetime







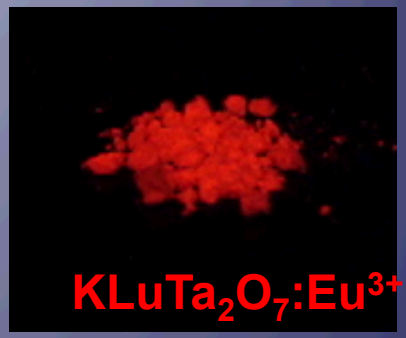
- The increased lifetime is due to a reduction in the electron/hole overlap.

Future directions

- Our challenge is to find the shell thicknesses that:
  - maintain high QY,
  - result in a 615 – 635 nm emission peak,
  - result in photostability when encapsulated.
- Once these synthetic goals are met we will investigate issues critical to solid-state lighting, such as thermal quenching, CCT, CRI.

Doped Oxide Phosphors

- Our challenge is to find a host lattice in which red emitters:
  - can be excited with blue light
  - have narrow emission at ~615 nm with high QY
  - can absorb enough blue light for practical use.



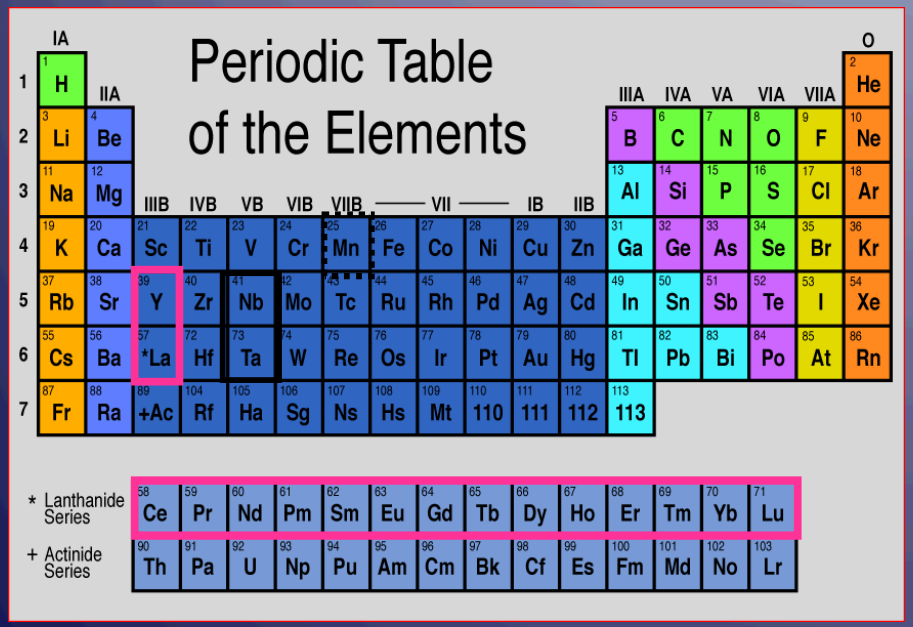
- Eu^{3+} is an ideal narrow red emitter for fluorescent lighting, but what about for solid-state lighting?

Strategies for choosing host lattices for red emitters

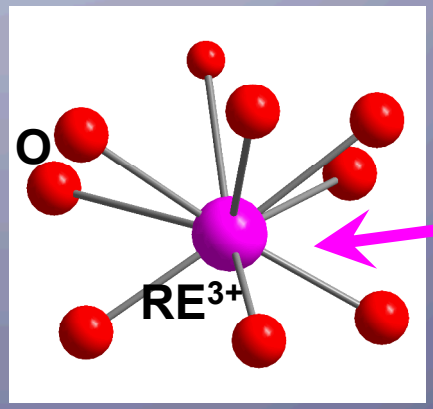
Oxide lattices:

Rare-earth tantalates and niobates

- Electrochemically and chemically inert
- Two sites for substitution of emitters
- RE host radius= La > Gd > Y

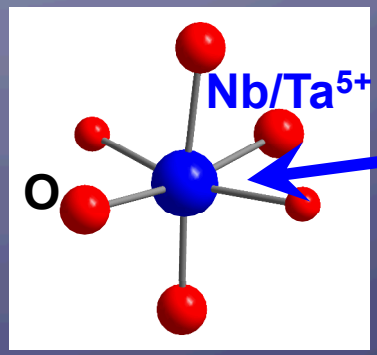


Lattice **Red Emitter**



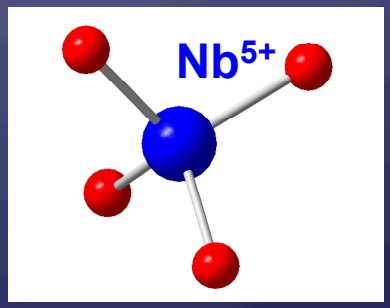
Sm^{3+}, Eu^{3+}

8-9 La-O bonds 2.3-2.9 Å



Mn^{4+}

6 Nb/Ta-O bonds 2.0 Å

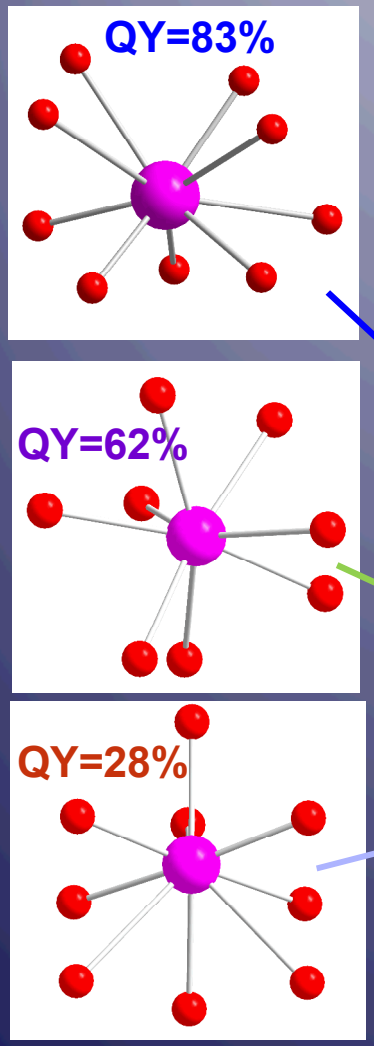


4 Nb-O bonds ~2.0 Å

The QY of (La,Eu)TaO_4 can be optimized through synthesis

Nyman et al., Chem. Mater., 21, 4731-4737 (2009).
Nyman et al., J. Solid-state Chemistry, submitted June 2011

Increasing QY, lower symmetry



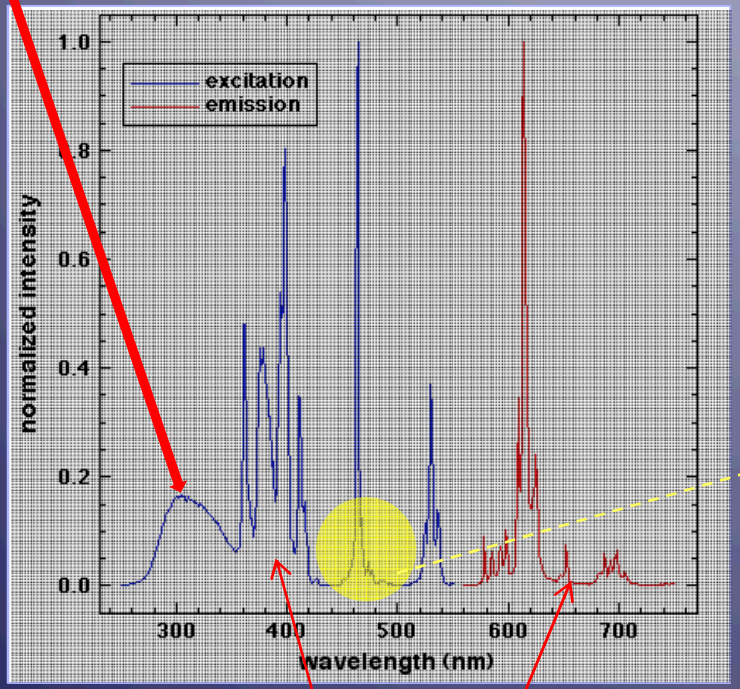
(La,Eu)TaO_4 polymorph	Obtained how?	Site symmetry	RE-O distances (Å)	RE-RE distances (Å)	Average RE-RE distance (Å)
Pbca (#61) (low-temperature)	Hydrothermal, 900 °C	1	2.320-2.975	3.916(×2) 4.186(×2) 4.229(×1) 4.402(×1)	4.139
$P2_1/c$ (#14)	Hydrothermal, 1150° C	1	2.368-2.822	3.914(×2) 3.998(×1) 4.132(×2) 4.325(×1)	4.069
$C\,mc2_1$ (#36)	Solid-state, 1150 °C	*m*	2.304-2.939	3.931(×2) 4.168(×4)	4.089

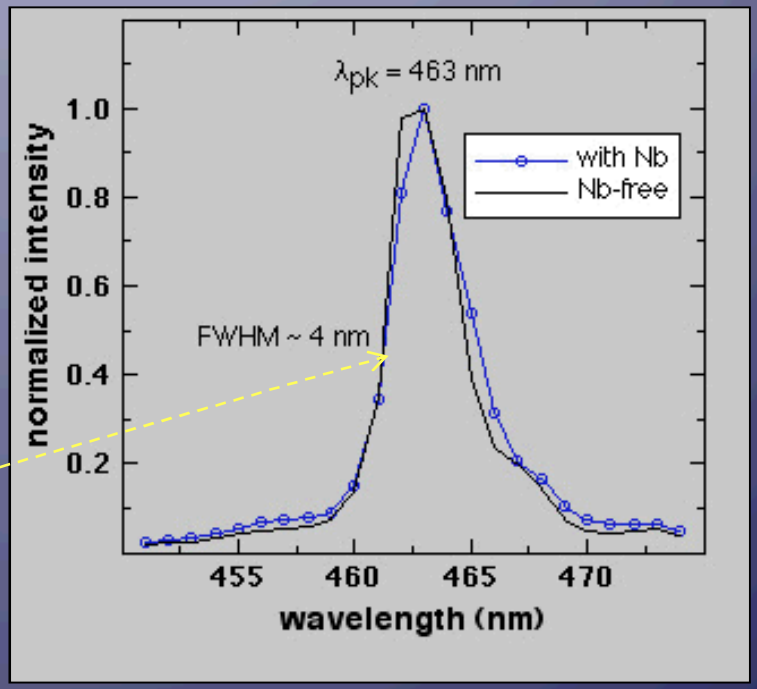
- The low temperature polymorph has the most distorted RE site and highest QY.
- The Eu^{3+} site lacks inversion symmetry, so the emission color is red.

The narrow red emission is accompanied by narrow blue absorption

$LaTaO_4$:25% Eu

Broad Eu^{3+}-O^{2-} charge transfer band.



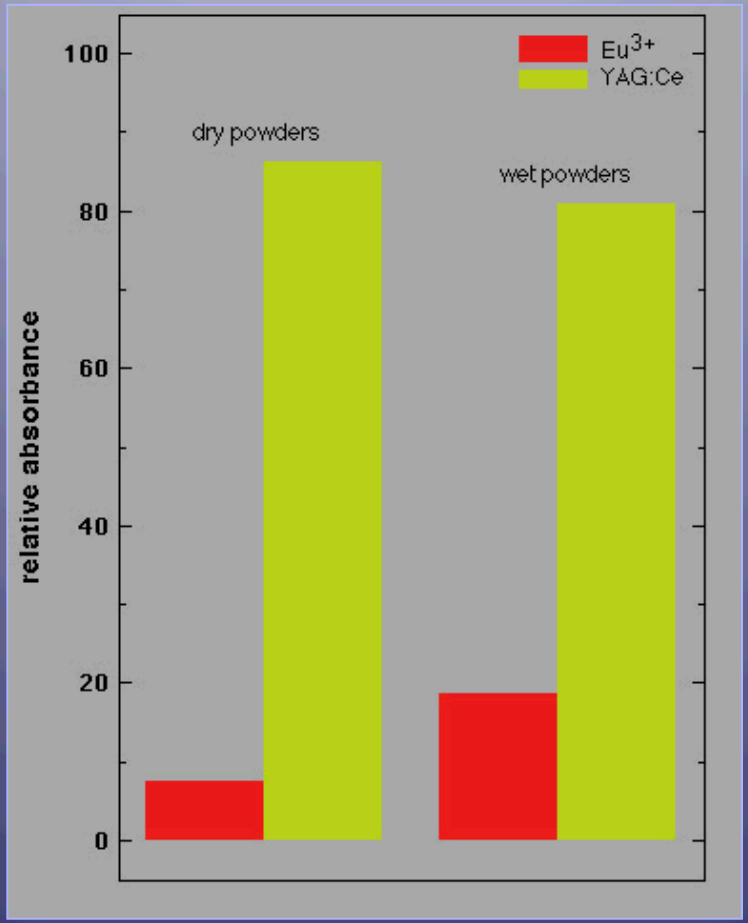


Narrow absorption and emission bands due to forbidden 4f-4f transitions.

The blue absorption linewidth is ~4 nm.

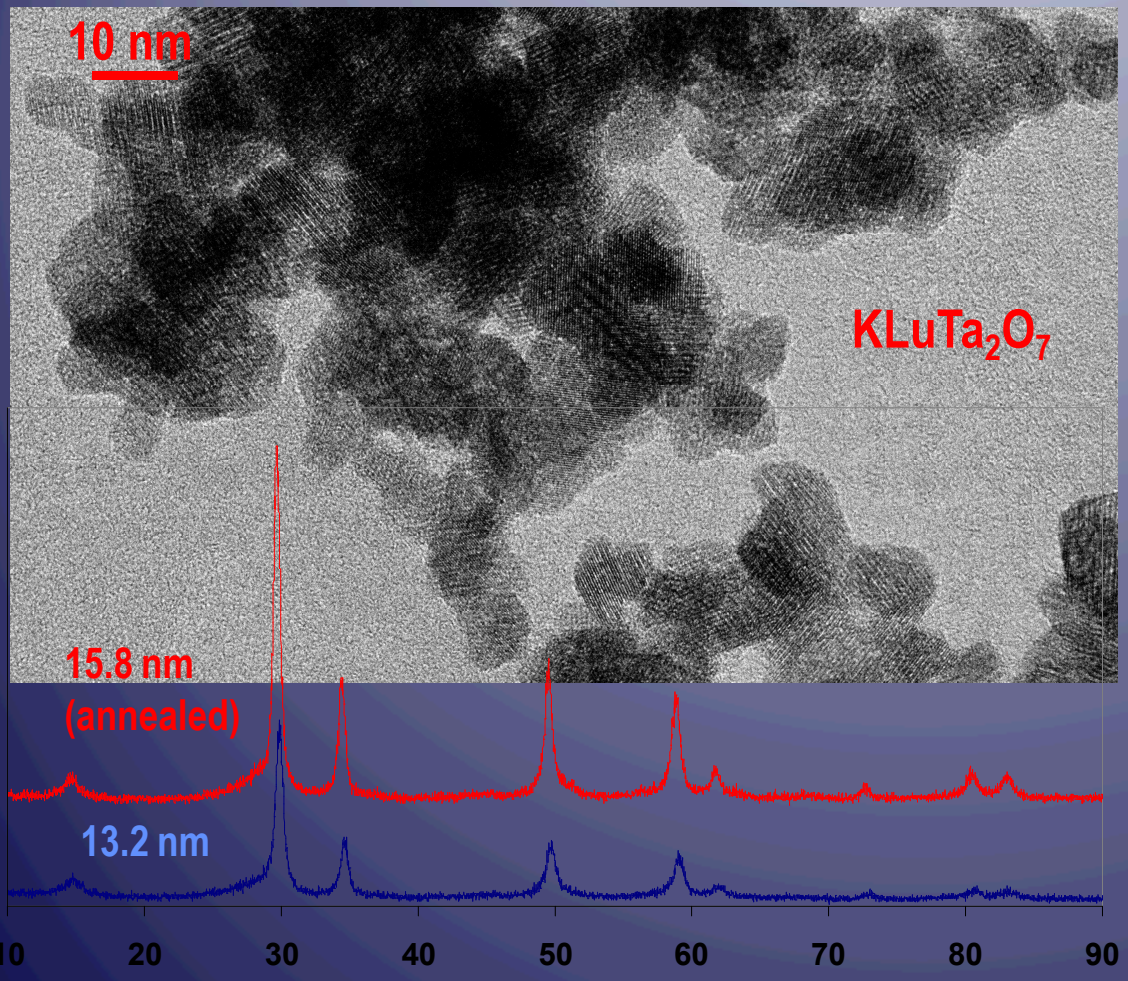
- The intensity of the CT band increases with decreasing Eu^{3+} concentration.
- Will the narrow blue absorption be a problem for SSL?

Blue absorption of $La(Ta,Nb)O_4:Eu^{3+}$ and $YAG:Ce^{3+}$ relative to carbon black



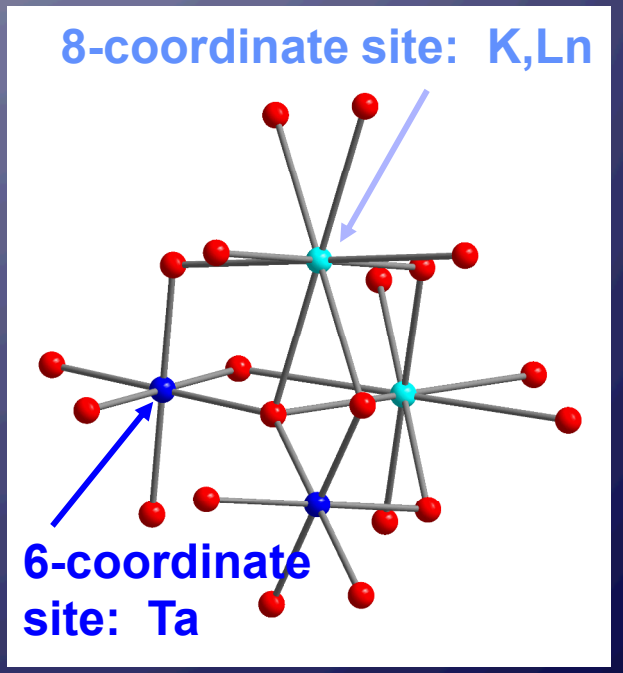
- One challenge is to increase the absorbance of the red phosphor.

Investigating the blue absorption of Eu^{3+} in RE tantalate pyrochlores



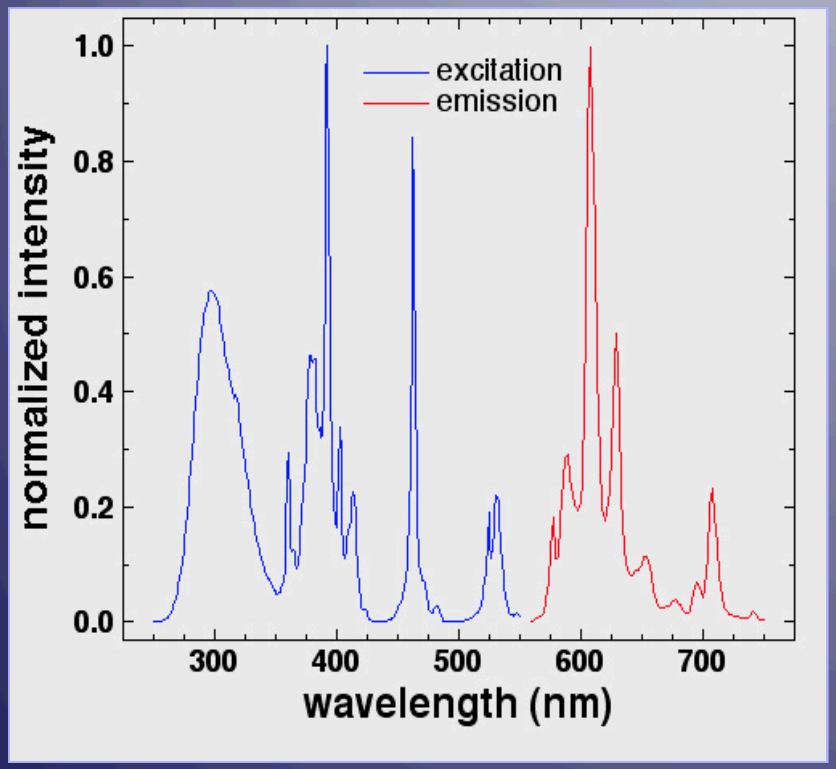
$KLnTa_2O_7$:Eu
F d -3 m

Ln	a (Å)
Lu	10.385
Y	10.447
*Gd	10.538

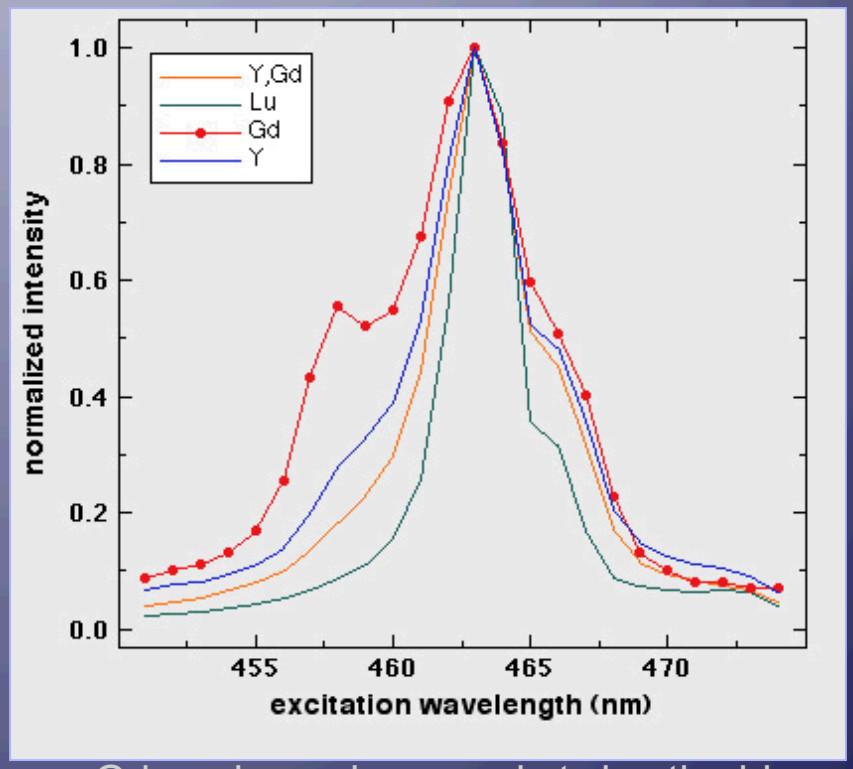


Nyman et al., JACS, 131, 11652-11653 (2009).

The blue absorption linewidth can be broadened in these lattices.



- The PL is similar to that of $LaTaO_4$.



- Gd analogue has nearly twice the blue excitation linewidth as the Lu analogue.

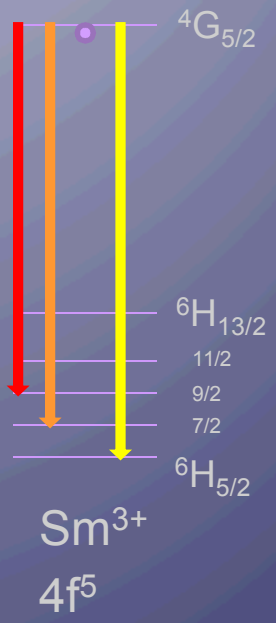
- **Only 3% thermal quenching at 130°C.**
- **The Gd analogue emits red light with a QY of 78%; blue linewidth is ~9 nm.**

Nyman et al., JACS, 131, 11652-11653 (2009).

Can we create a phosphor with broad blue absorption and narrow red emission?

- Sm^{3+} can emit narrowband red light due to 4f-4f transitions.

- The blue absorption of Sm^{3+} is broader than that of Eu^{3+}.

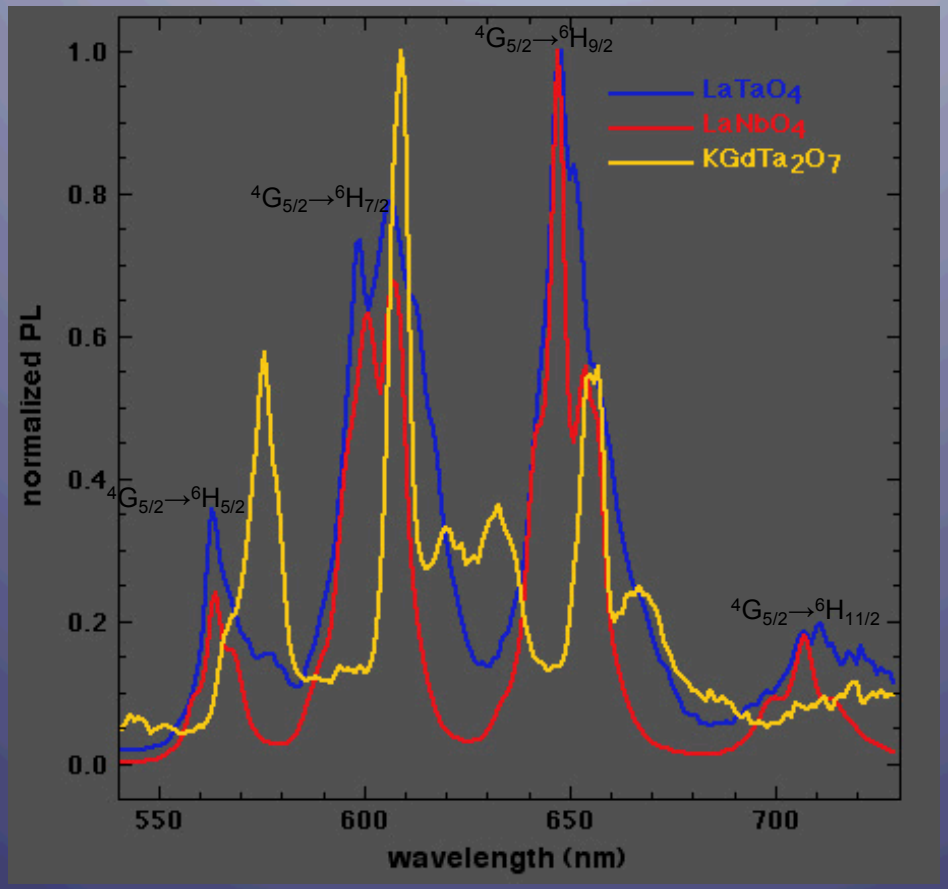


- Mn^{4+} is used for red emission in fluorescent lighting applications.

- The absorption bands of Mn^{4+} can be broad due to the strong influence of the crystal field.

- The emission color depends on the lattice.

Sm^{3+} transitions couple strongly to the lattice

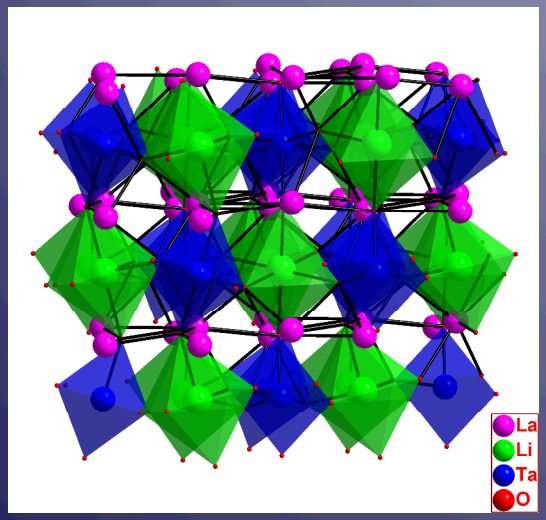


- The lattice affects which 4f-4f transitions appear, and their splitting.
- Narrowband red emission under blue excitation.

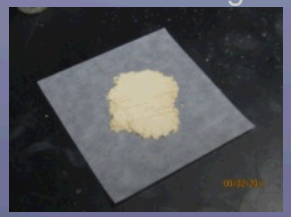
Mn^{4+} -doped tantalates/niobates

- Mn^{4+} is $3d^3$, and is therefore luminescent in an octahedral crystal field.
- Like Eu^{3+}, PL is due to parity-forbidden transitions having long lifetimes (ms).

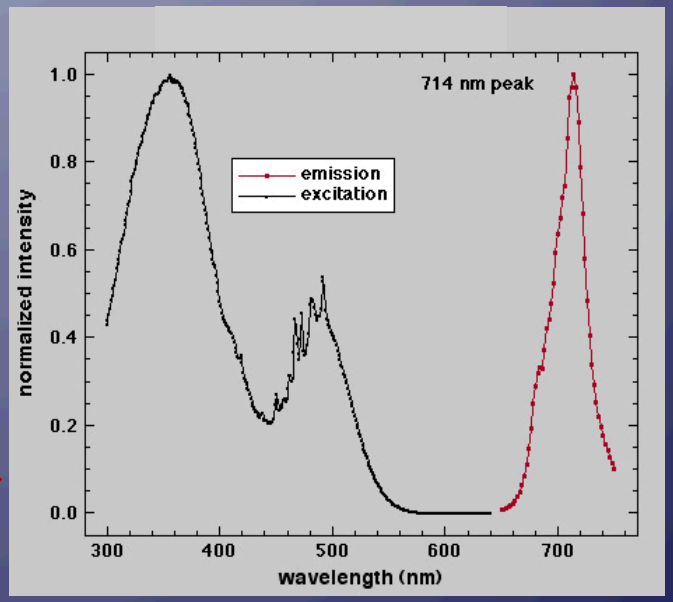
$La_2Li(Ta,Nb)O_6:Mn^{4+}$
perovskite



Under room light



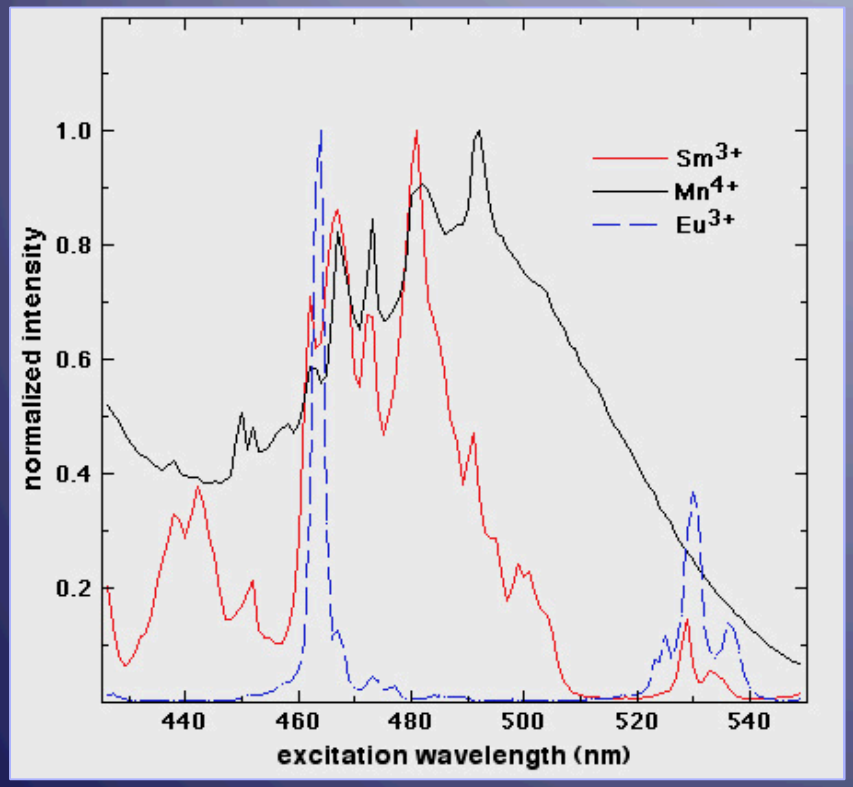
Under UV light



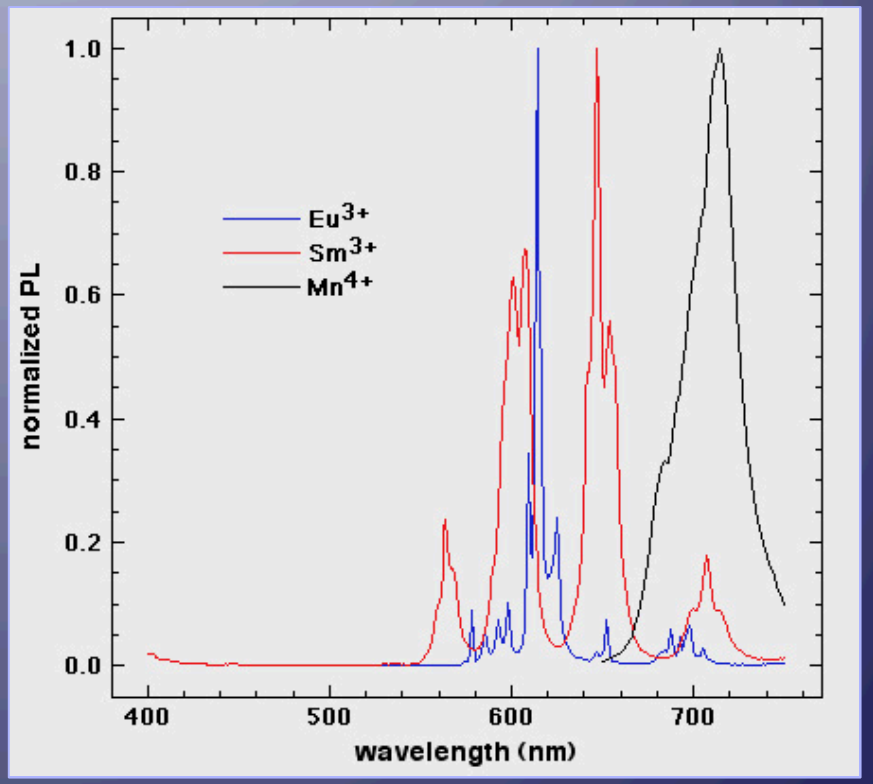
- **The broad absorption is due to coupling to lattice vibrations.**
- **The crystal field strength varies with vibration.**
- **The broad absorption is desirable for SSL, but deep red emission is not ideal.**

Summary of Sandia red-emitting phosphors

absorption



emission



- Sm^{3+} has much broader blue absorption bands than Eu^{3+}.
- Absorption of Mn^{4+} extends into the green spectral region.

- Sm^{3+} and Eu^{3+} give narrow red emission due to 4f-4f transitions.
- Mn^{4+} emits deep red at ~714nm.

Future Directions

- Increase the blue absorbance by fabricating transparent Eu^{3+}-doped tantalate/niobate monoliths.

- If successful, we will investigate methods of integrating this material with YAG:Ce to achieve warm white emission.

Acknowledgments

- Professor David Kelley, UC Merced

- ECS Luminescence & Display Materials Division