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Progress in narrowband red-emitting phosphors for solid-state lighting

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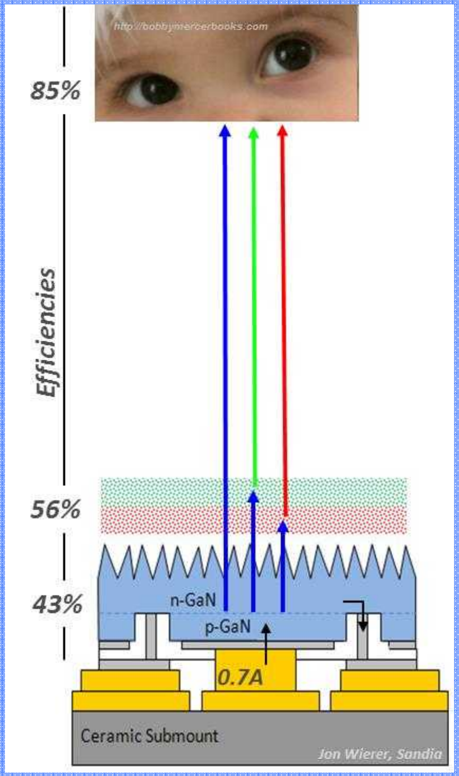
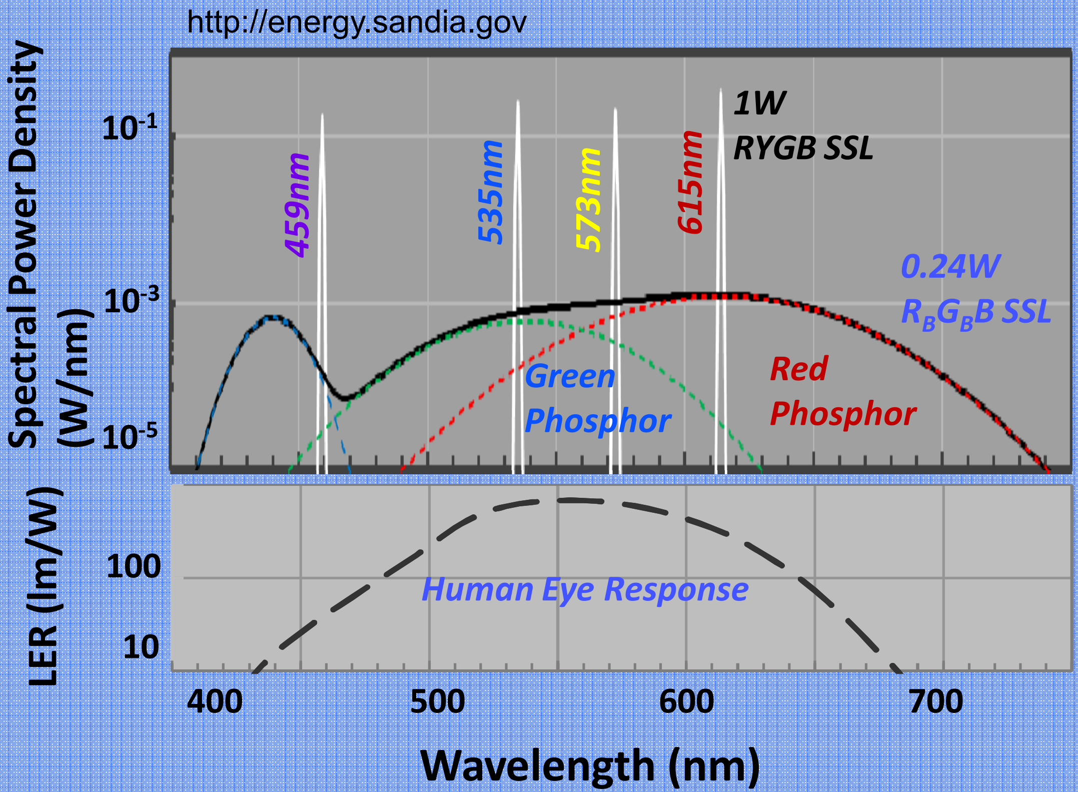
Wavelength downconversion approach to solid-state lighting (SSL)





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

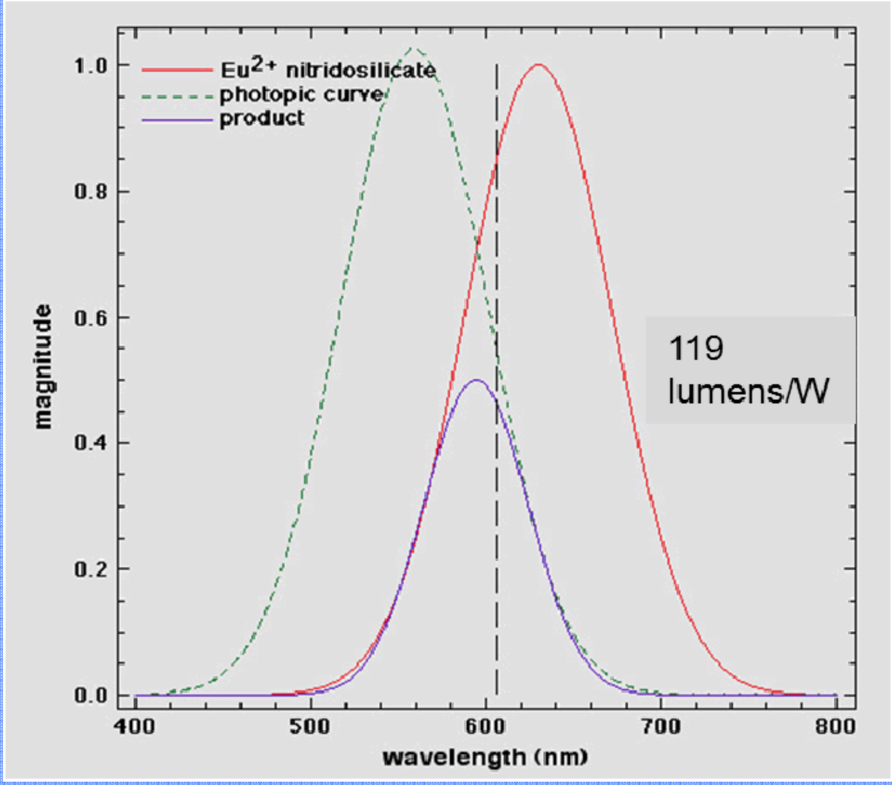
- Warm white target: CCT=3,000K; CRI=85*
- A narrowband red component is critical to reaching the target.

Tsao *et al*., Proc. IEEE, 98, 2010

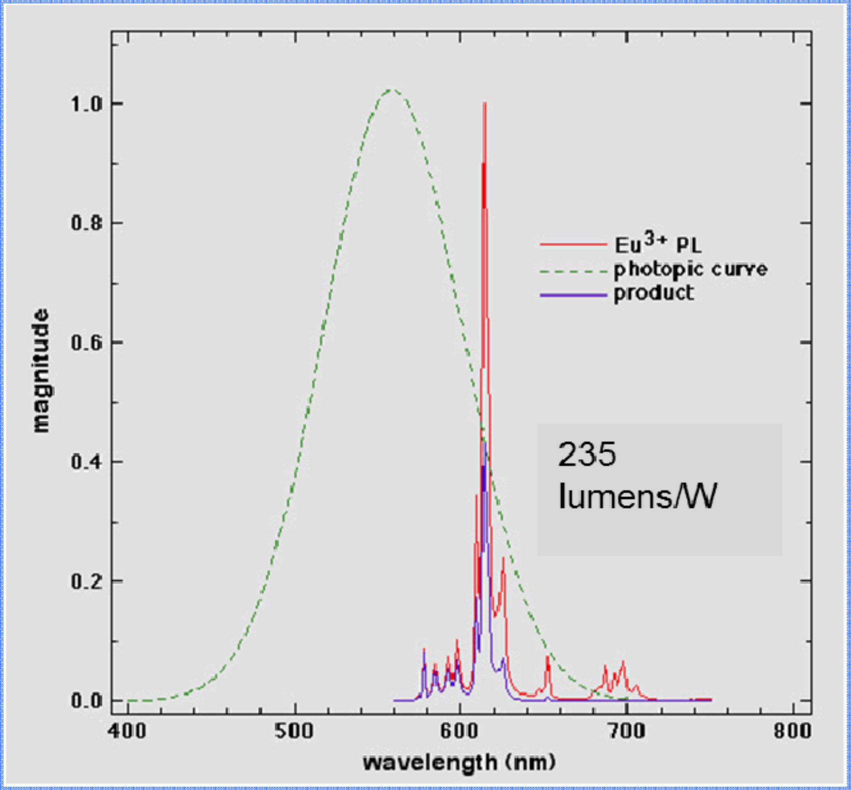
*DOE's SSL R&D 2012 Multi-Year Program Plan

Narrow red emission from Eu^{3+} is ideal for SSL

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



Eu^{3+} red emitters are narrow, FWHM ~5 nm.

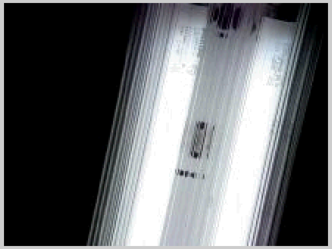


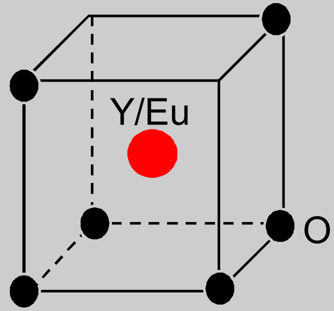
- The luminous efficacy of radiation (LER) for red emission (>606 nm) can be significantly increased with narrow bandwidth emitters.

Shea-Rohwer *et al.*, ECS JSS, 2, R3112 (2013).

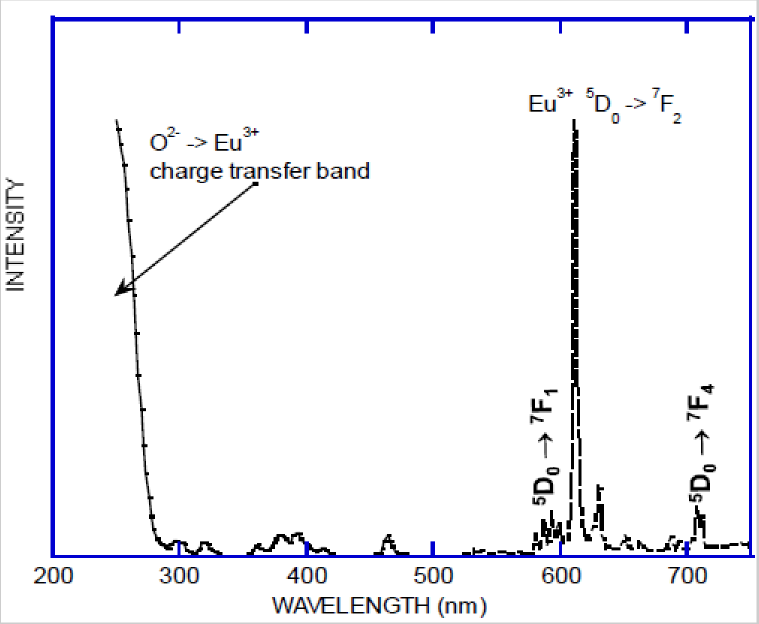
Eu^{3+} revolutionized fluorescent lamps and TVs

▪ $Y_2O_3:Eu^{3+}$ in fluorescent lamps

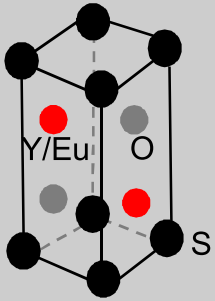




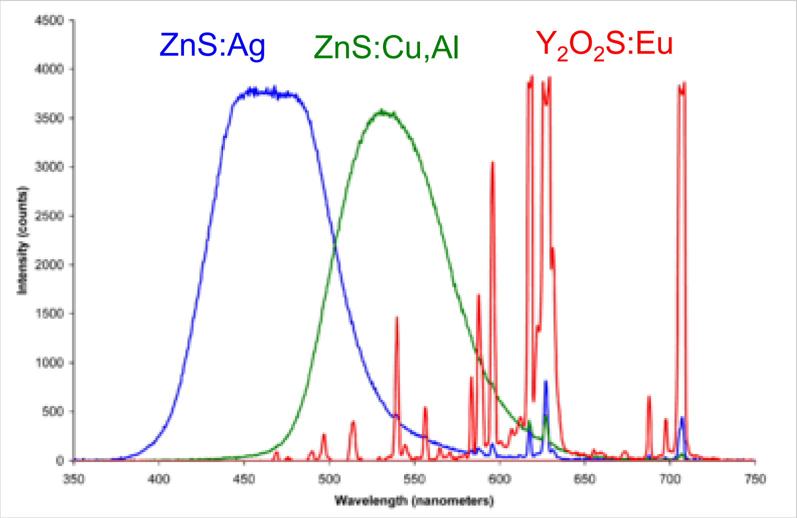
- 254 nm Hg line excites the $O^{2-} \rightarrow Eu^{3+}$ charge transfer band



▪ $Y_2O_2S:Eu^{3+}$ in TVs



- Electron bombardment → e-h pairs.
- e's migrate on Y^{3+}; h's migrate on O^{2-}/S^{2-} and recombine radiatively at Eu^{3+} sites.



- **Will white LEDs also benefit from Eu^{3+}?**

Phosphors must satisfy numerous criteria for SSL

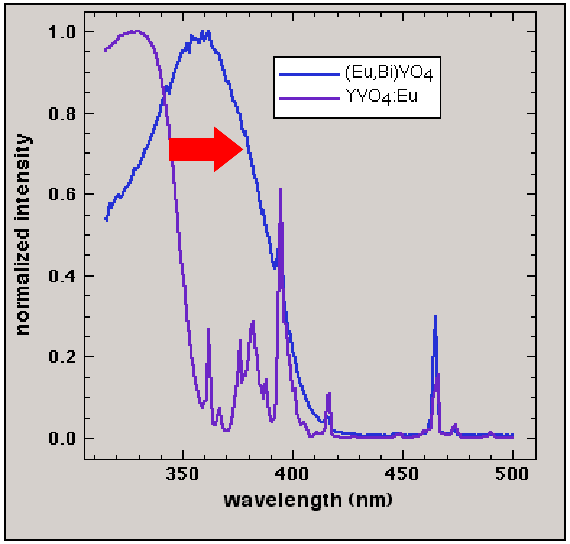
- High quantum yield
- Low reflectance at excitation wavelength
- Low thermal quenching
- Photo-stability
- Thermal stability
- Chemical stability
- Saturation resistant
- High luminous efficacy of radiation
- Excitable with blue light
- No unwanted green/yellow absorbance
- Enables high CRI & low CCT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

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

Development of Eu^{3+}-doped phosphors for SSL

- Shift the M-O CT band edge from UV to blue. (M=V, Mo, W).

- $(Y,Bi)VO_4$



➢ CT band red-shifts when V-O and Bi-O participate in the absorption.

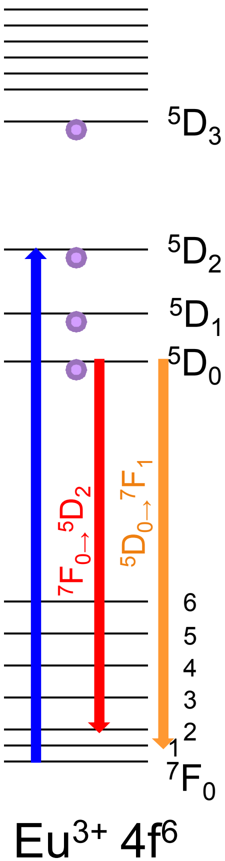
- AMO_4 & A_3MO_6 (A=Ca,Sr,Ba; M=Mo,W)
- Ln_2MoO_6 (Ln=Y,Gd)

➢ CT band edge ~380-430 nm for 6-coordinated Eu^{3+} in molybdates.
➢ QY is low.

- Identify host lattices in which blue excitation is more efficient than CT band excitation.

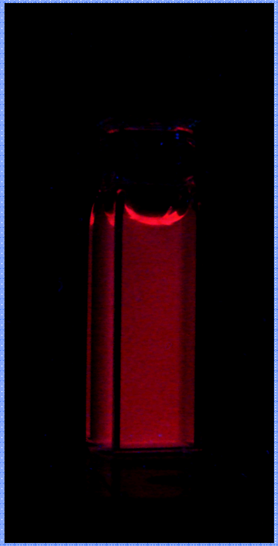
- $EuKNaTaO_5$
- La_3NbO_7
- $K,RETa_2O_7$
- $LaTaO_4$
- $CaLaSnNbO_7$
- $Y_2Ti_2O_7$

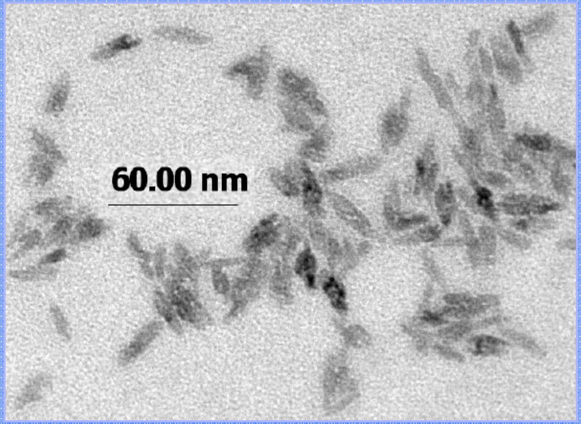
- 4f-4f transitions are forbidden, low oscillator strength ($\sim10^{-6}$).
- The spin-forbidden nature of the $^7F_0 \rightarrow {}^5D_2$ transition can be relaxed.



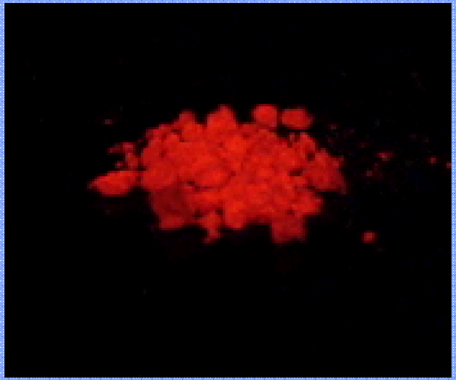
Eu^{3+}-doped nanophosphors made at SNL

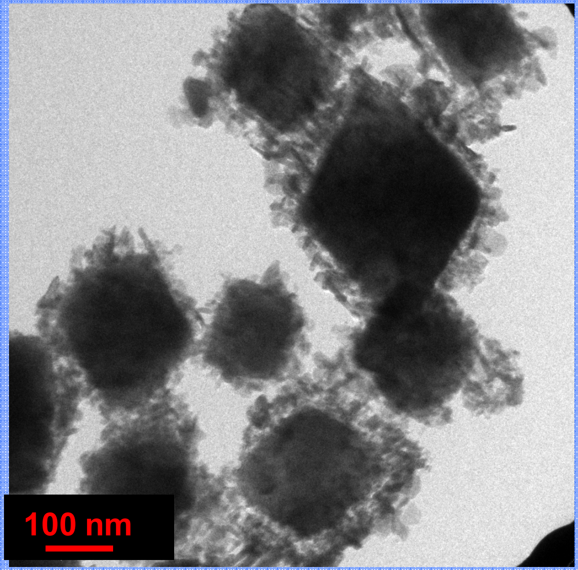
Zircon structure:
$YVO_4:Eu^{3+}$



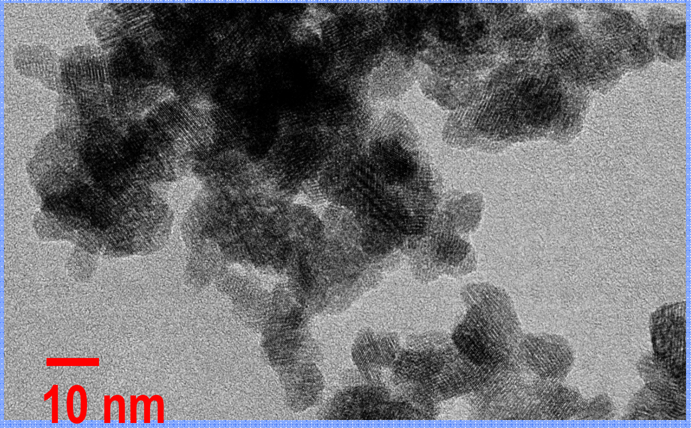


Pyrochlore:
$M_{1-2x},GdTa_2O_{7-x}:Eu^{3+}$
$M = K^+, Rb^+, Cs^+$

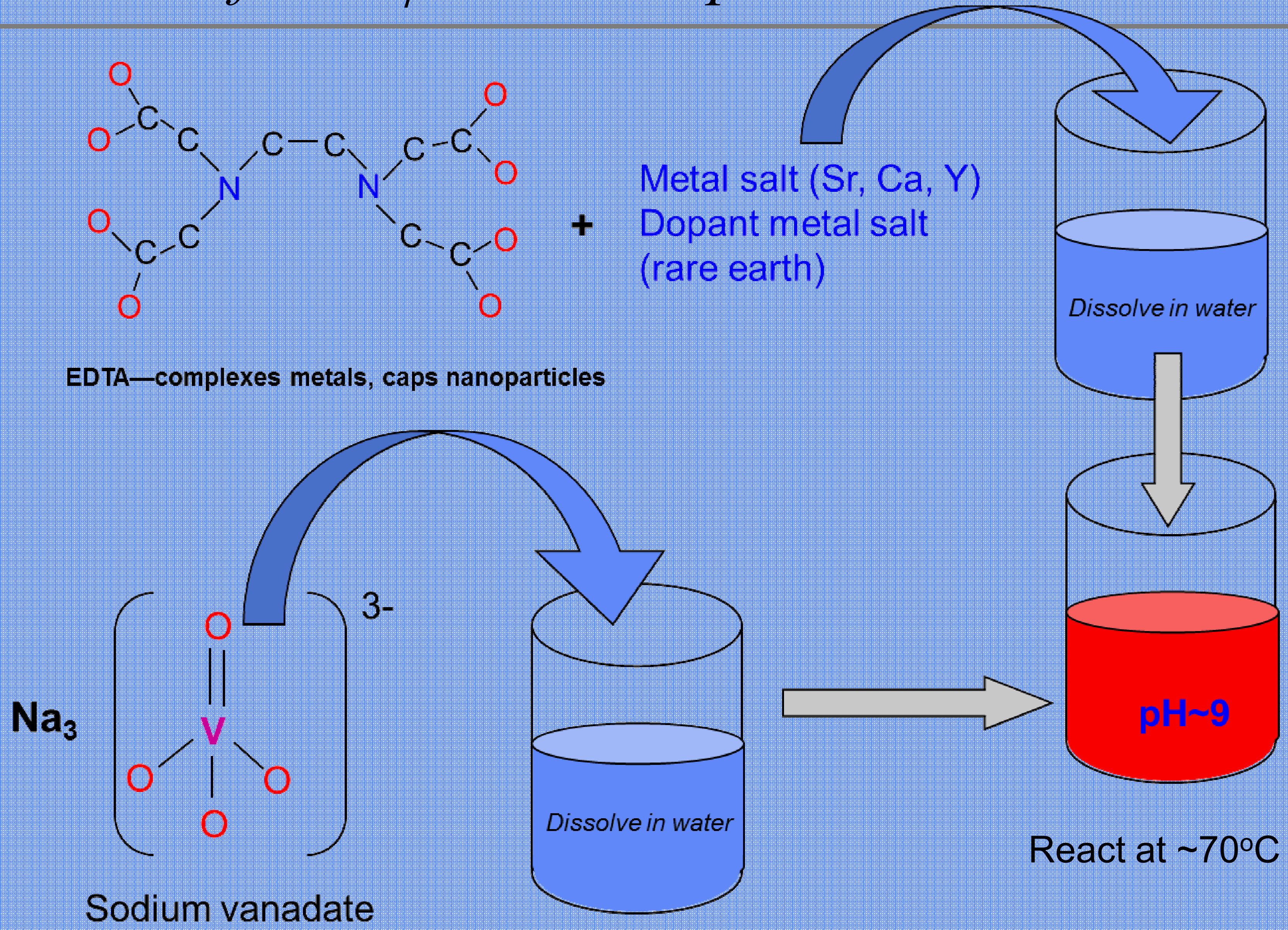




Pyrochlore:
$(M,RE)Ta_2O_7:Eu^{3+}$
$M = K^+, Cs^+; RE = Lu, Y$

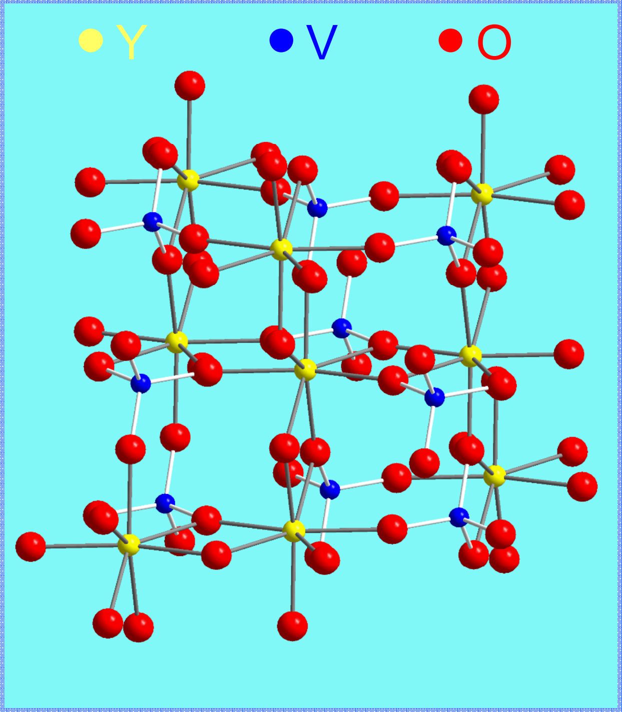


Synthesis of $YVO_4:Eu^{3+}$ nanoparticles



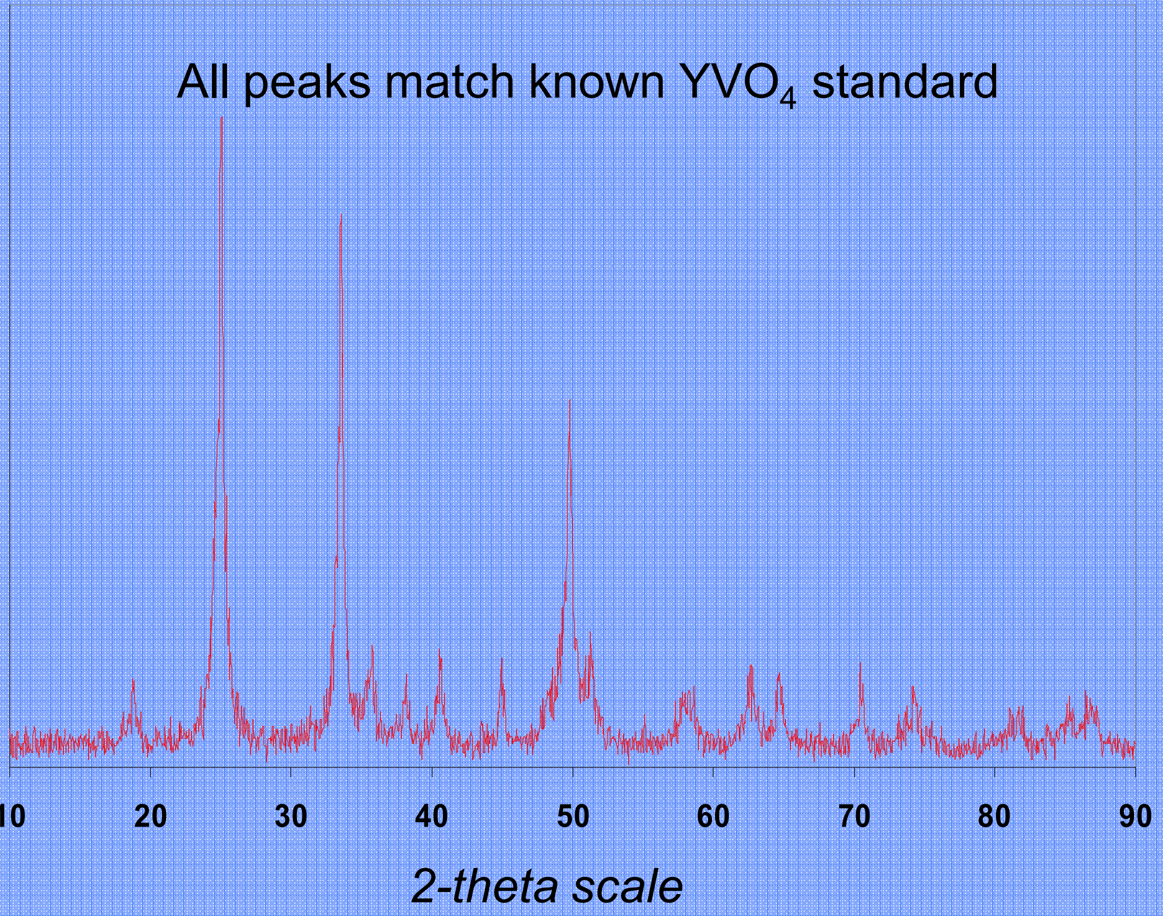
Nano-YVO_4 structure characterization

YVO_4

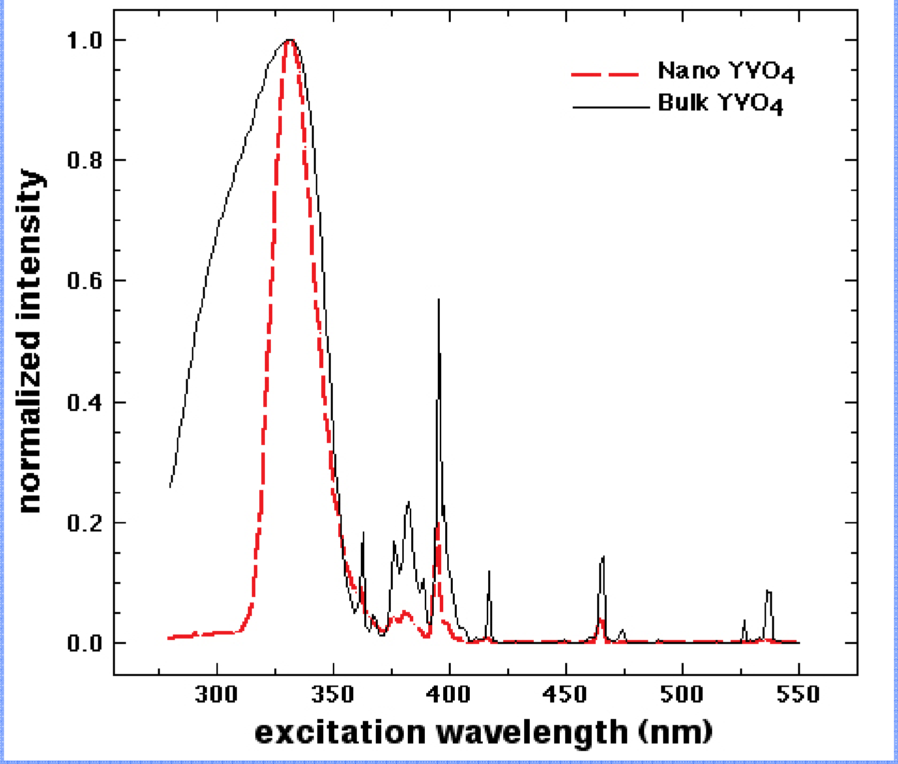


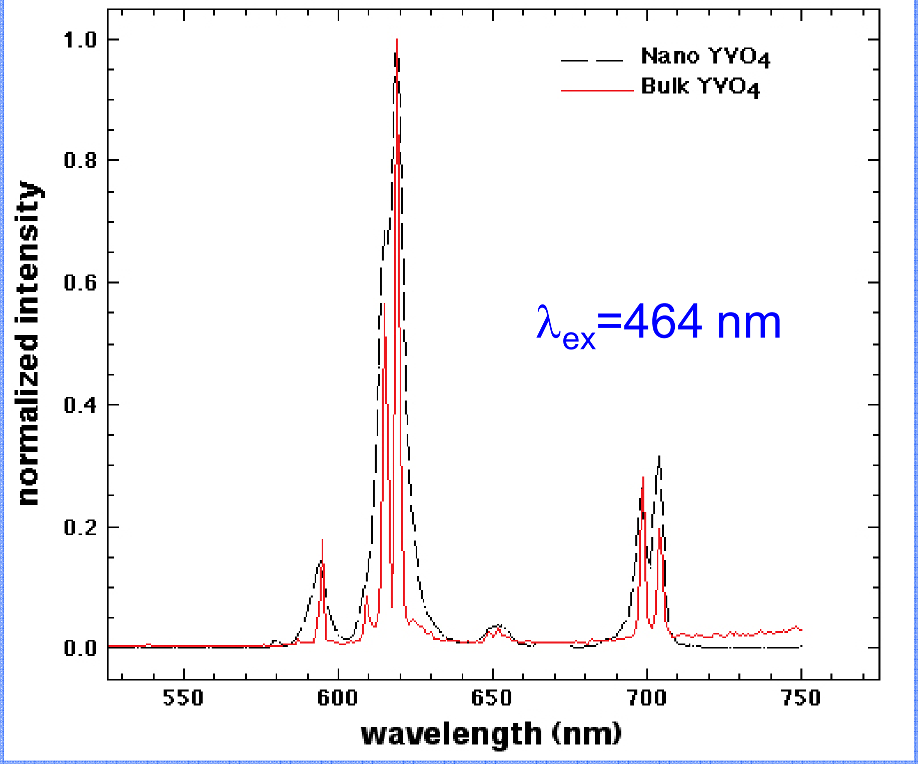
Zircon-type structure
Regular VO_4 sites
8-coordinate Y site

Nano-YVO_4



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



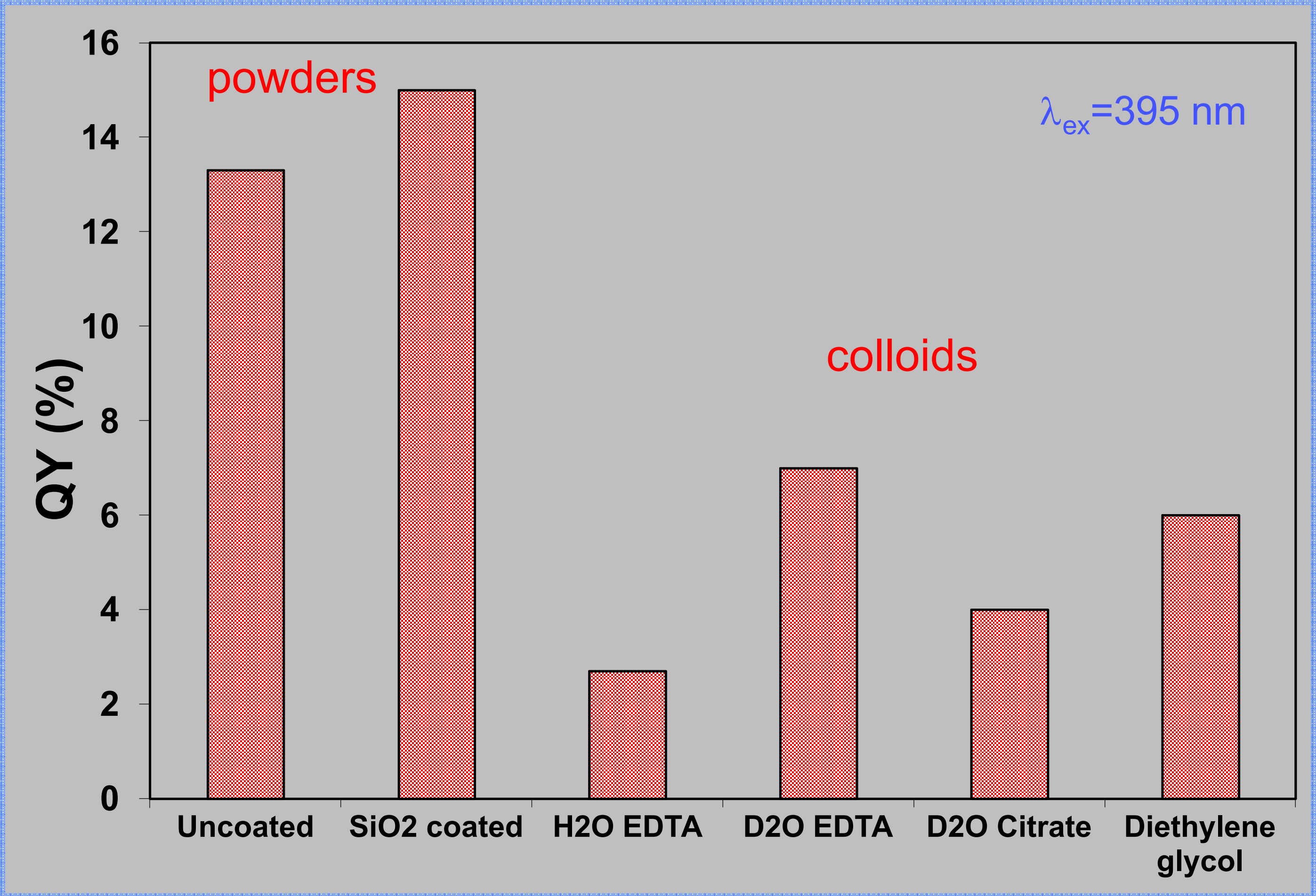


- Absorption peaks at 395 and 465 nm are more intense in bulk YVO_4.
- Strong UV absorption in bulk and nano-YVO_4.

- Eu^{3+} emits at ~619 nm, as in bulk YVO_4.
- Nano-YVO_4 has broader emission
- peaks than bulk YVO_4 due to the Eu^{3+} crystal field variations in the lattice.*

*- Blasse & Bril, *J. Inorg. Nucl. Chem.*, 29, 2231 (1967).
Huignard et al., *J. Phys. Chem. B*, 107, 6754 (2003).

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



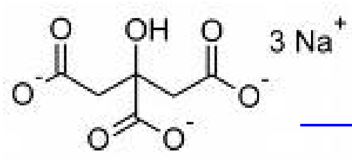
- We increased the QY to 15% (near-UV excitation) with SiO_2 coatings.
- QY's of 15-25% reported for nano-YVO_4:Eu under UV excitation.
- The QY is currently too low for SSL applications.

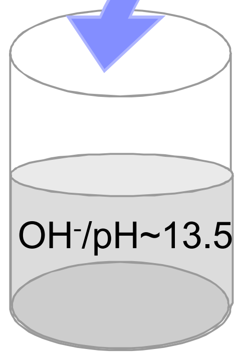
Hydrothermal synthesis of tantalate phosphors

$RECl_3 \cdot 6H_2O$ in DI H_2O

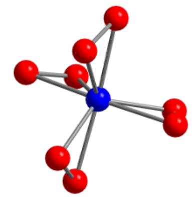
+

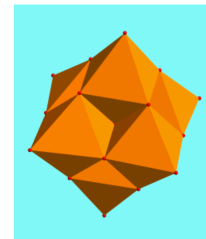
Citrate in DI H_2O





Anionic Ta precursor in DI H_2O





$M_3[Ta(O_2)_4]^{3-}$ or $M_8[Ta_6O_{19}]^{8-}$ M= Cs, K, Rb

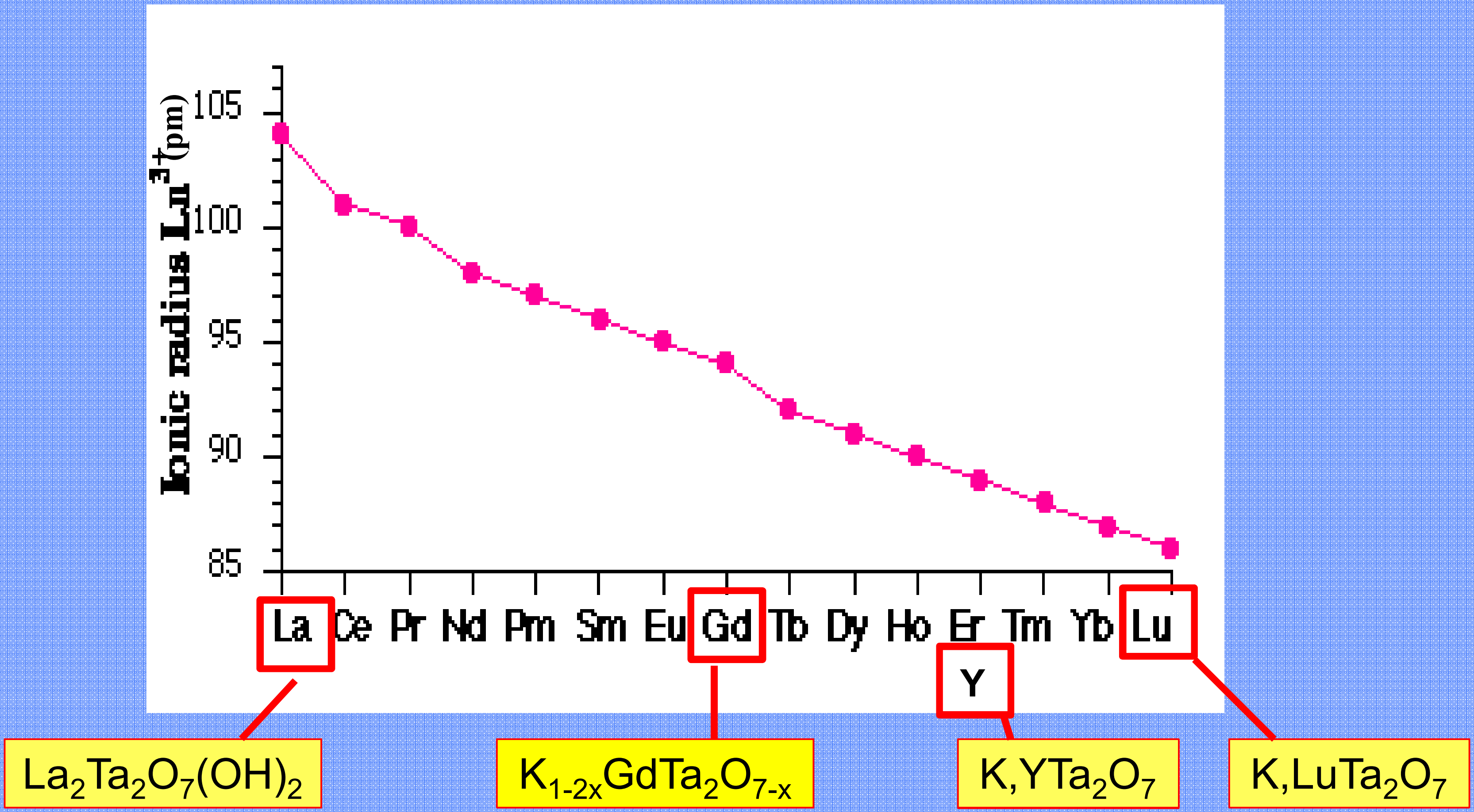
RE=Gd, Lu, Y, Eu, La

Hydrothermal treatment at 220^{o}C

Pyrochlores:
$(RE,M)Ta_2O_7$
$(RE,M)_{1-2x}Ta_2O_{7-x};$ x=1/3

Orhotantalates:
$La_2Ta_2O_7(OH)_2 \xrightarrow{anneal} LaTaO_4$

RE ionic radius affects the lattice structure



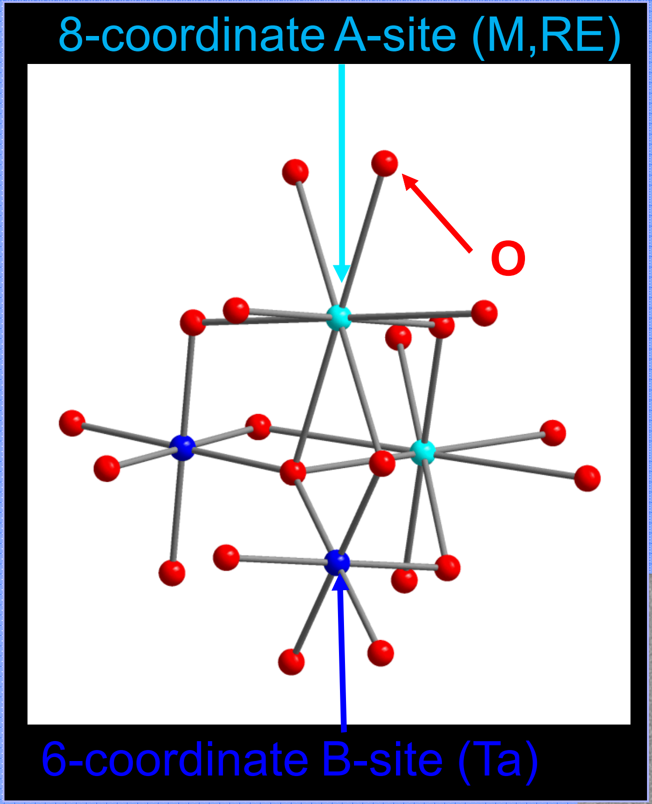
Not a pyrochlore.
No oxygen vacancies.
Weak emission.

Pyrochlore.
Oxygen vacancies.

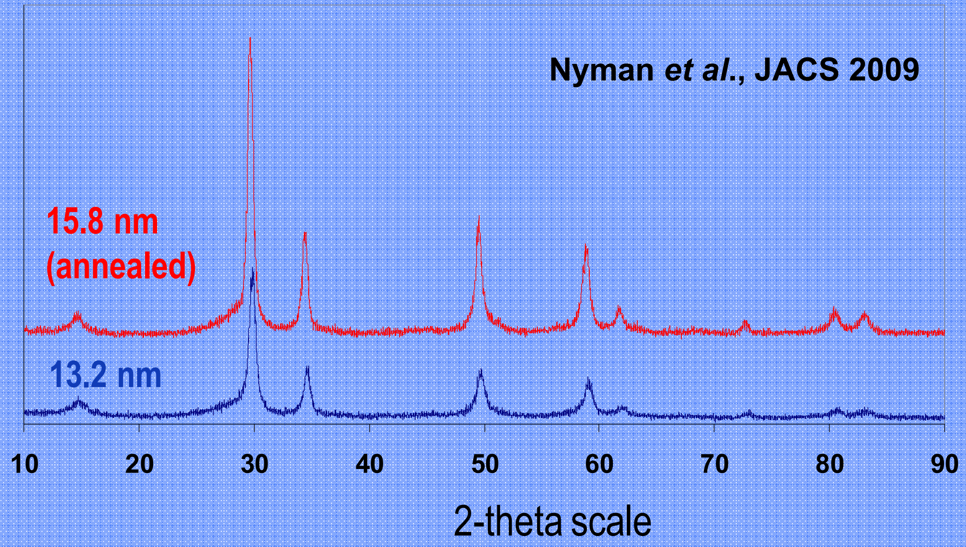
Pyrochlores.
No oxygen vacancies.

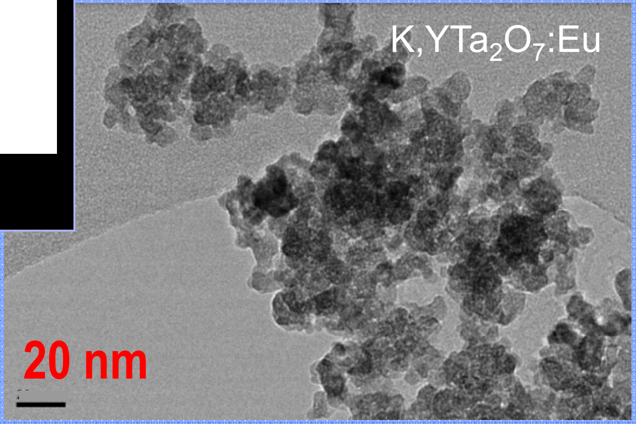
Yttrium and lutetium tantalate nanophosphors

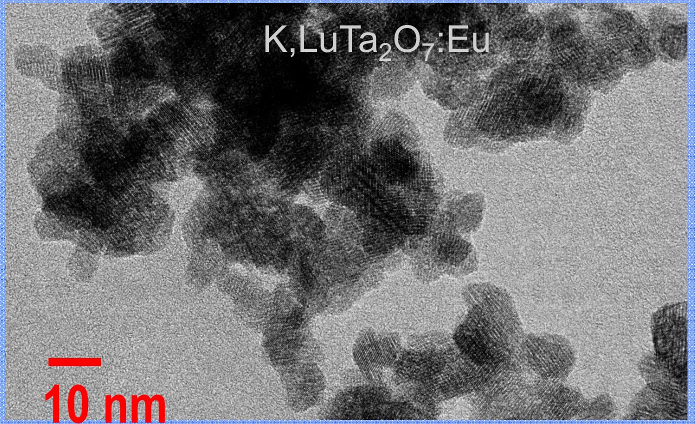
Pyrochlore structure: AB_2O_7



XRD of K,$LuTa_2O_7$



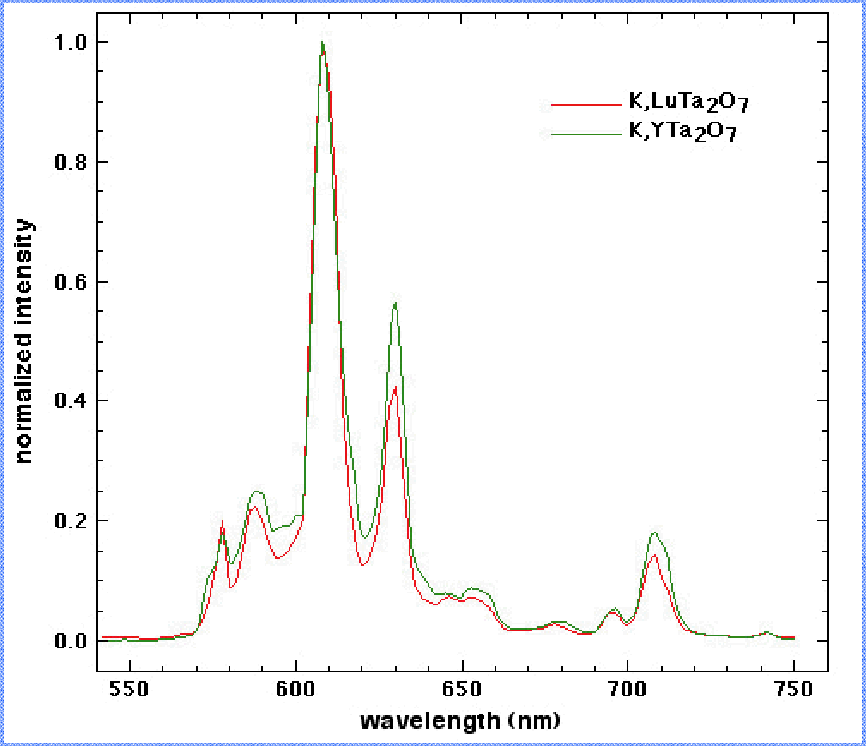




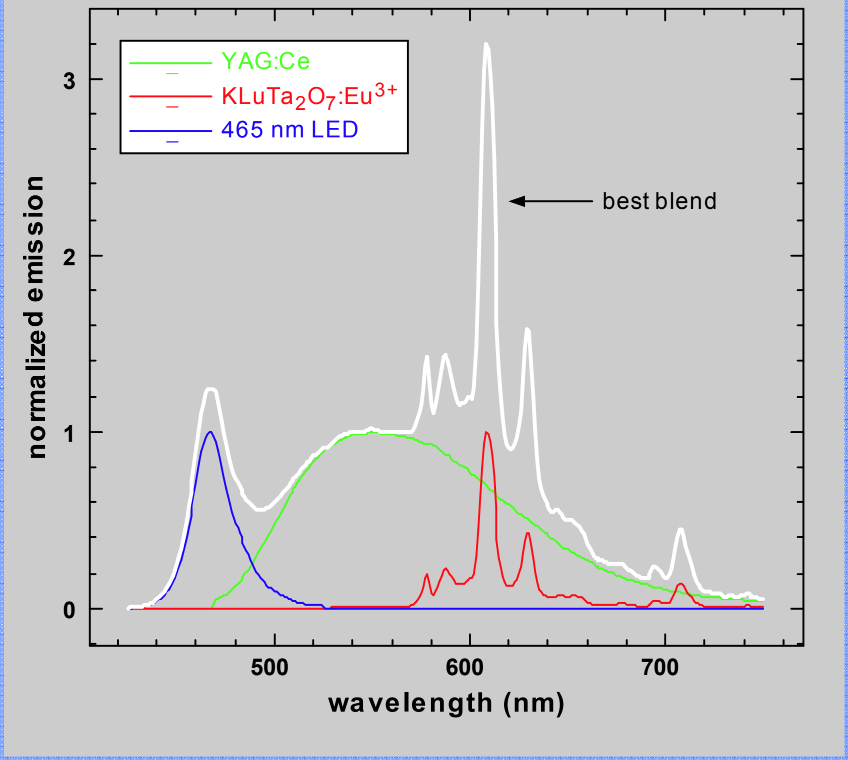
- These pyrochlores retain their small size even after annealing at 900^{o}C.

Photoluminescence of Y and Lu tantalates

Narrowband red emission from $K,Y/LuTa_2O_7:Eu^{3+}$



Improvements in white LED color quality are possible



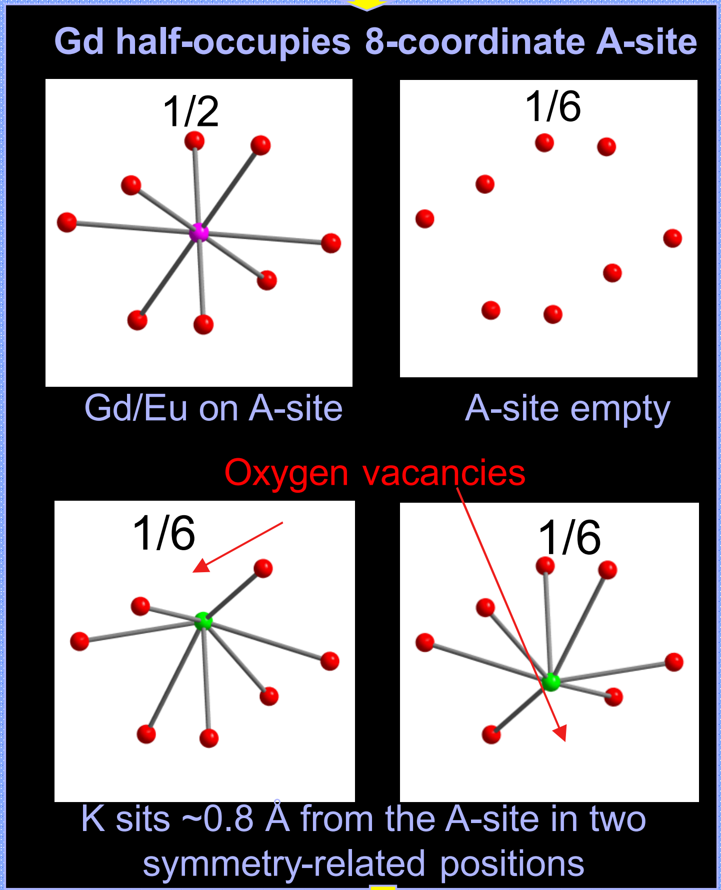
- Peak emission at ~610 nm, which is nearly ideal for lighting.
- QY as high as 67% under blue excitation.

- Theoretical blends of YAG:Ce and Lu tantalate have CRI=84 and CCT=3400K.
- CRI=71 and CCT=5400K without a red component.

When Gd replaces Y/Lu in these tantalates, favorable lattice distortions result: $K_{1-2x}(Gd,Eu)Ta_2O_{7-x}$; x = 1/3

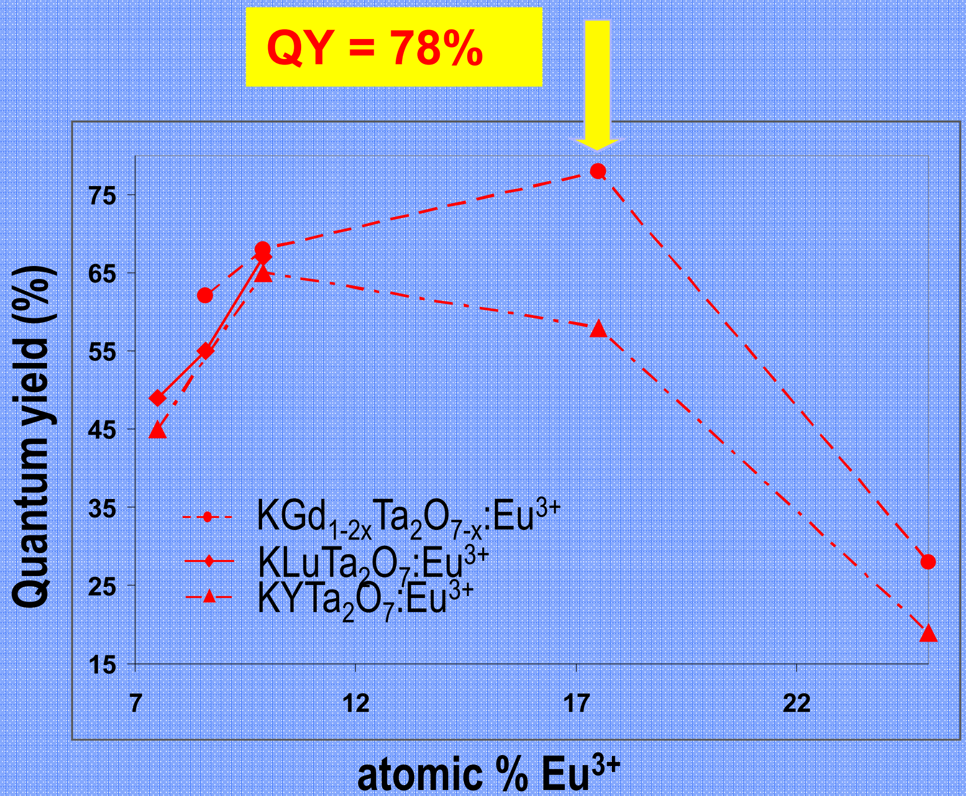
1. Gd creates oxygen vacancies in pyrochlores.

2. These vacancies create lattice distortions.



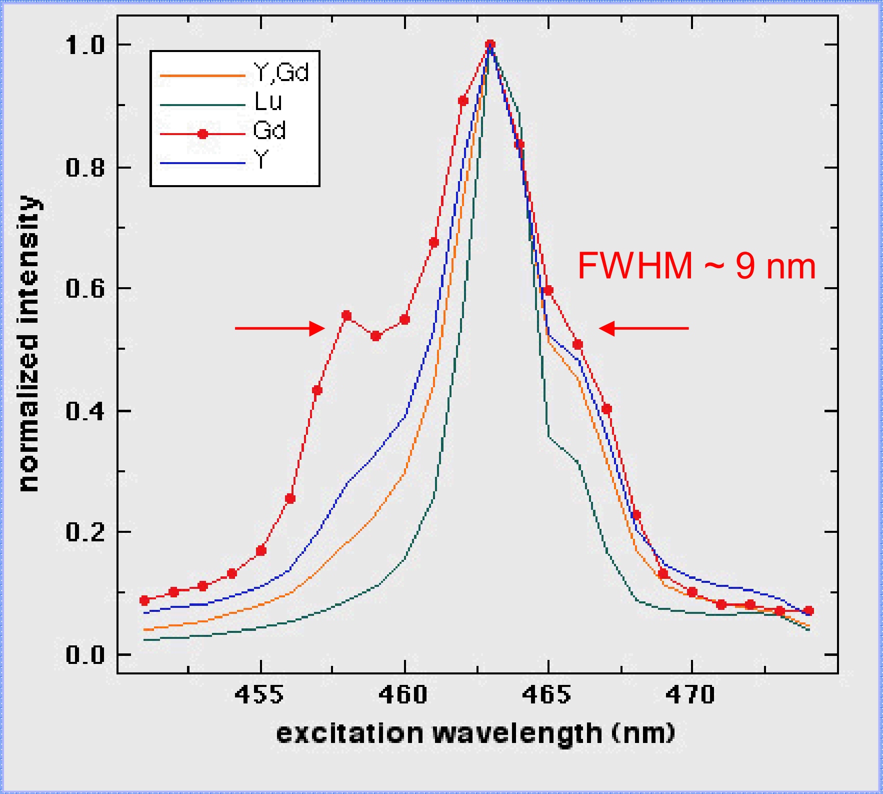
3. These lattice distortions affect the Eu emission.

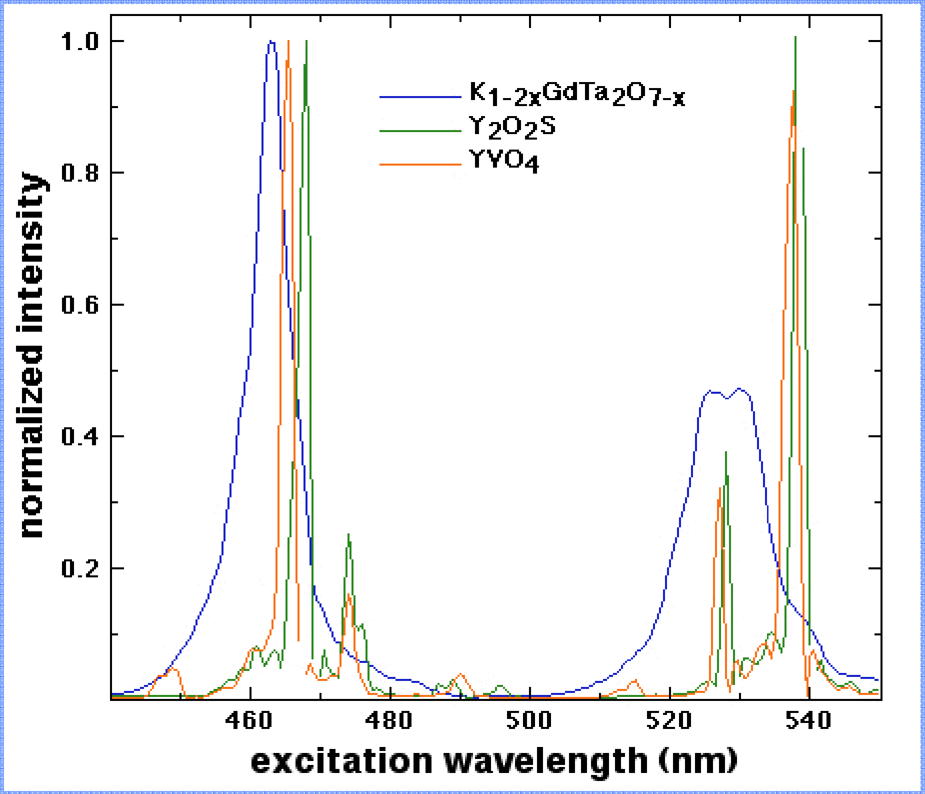
4. The QY of the Gd pyrochlore is higher than that of the Lu & Y pyrochlores.



Nyman *et al.*, JACS, 131, 11652 (2009).

Lattice distortions broaden the blue absorption linewidth

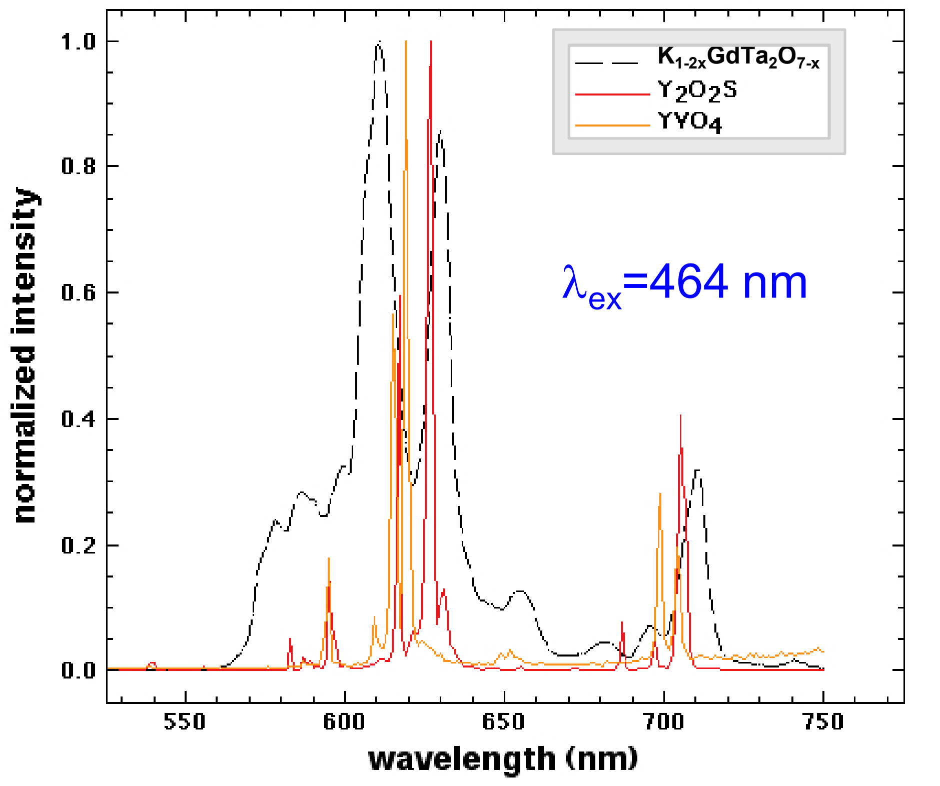




- The blue absorption linewidth is broadest in the Gd tantalate.
- Gd tantalate nanophosphor has a broader blue absorption linewidth than bulk Eu^{3+}-doped phosphors.

- Broad blue absorption enables excitation with a range of LED wavelengths.

Eu^{3+} emission in Gd tantalate nanophosphors and bulk phosphors

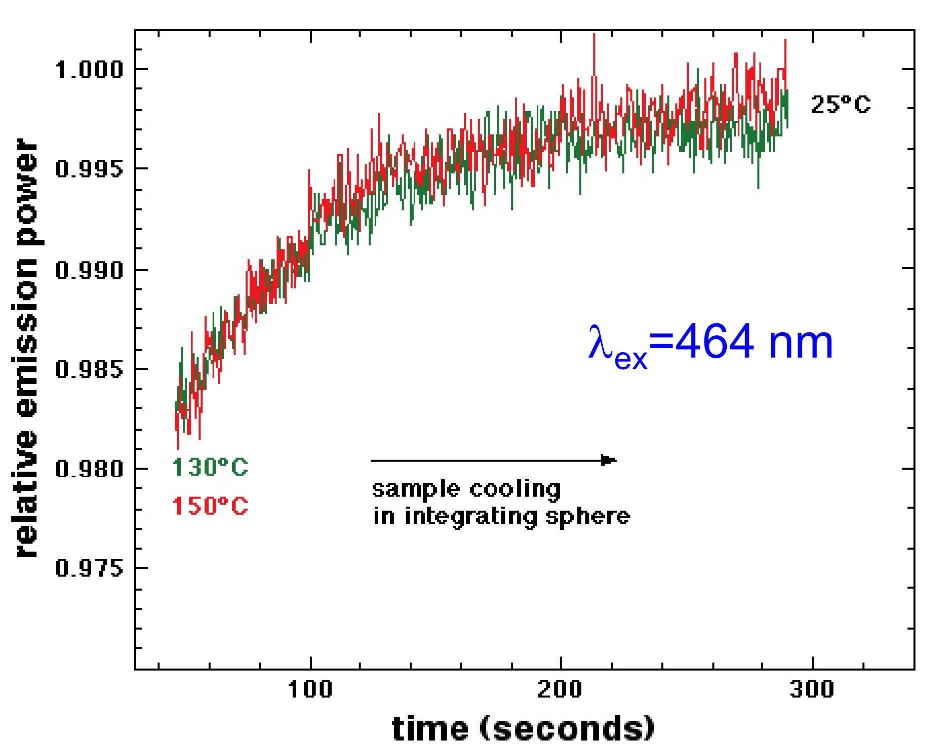


- Broader Eu^{3+} emission peaks in the nanophosphor than in the bulk phosphors.
- Under blue excitation, QY=78% (Gd tantalate); 20% (Y_2O_2S); 35% (YVO_4).

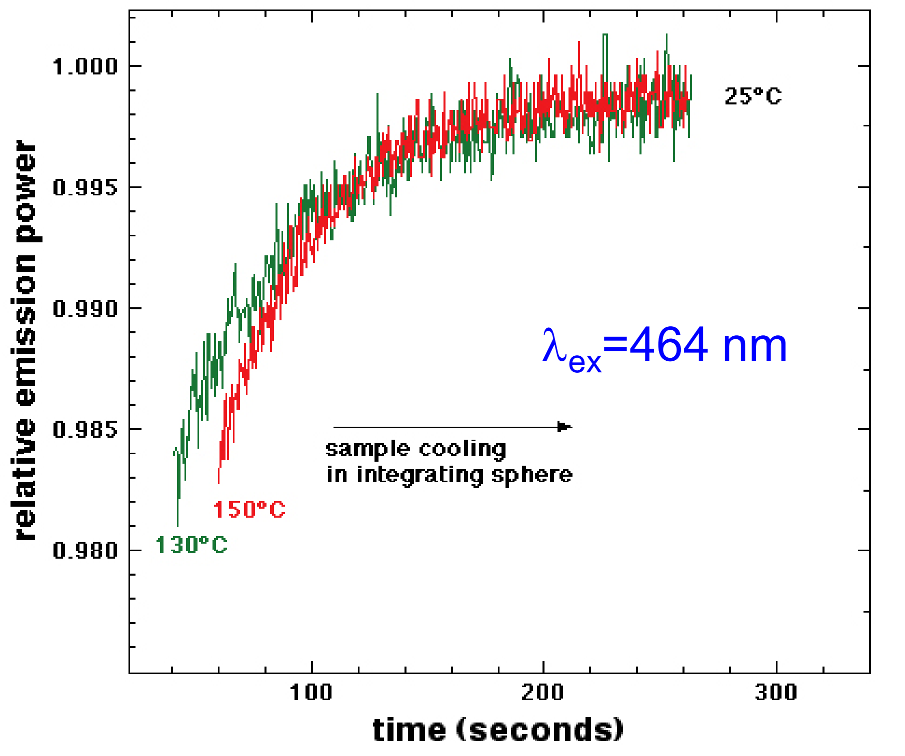
Thermal quenching (TQ) of pyrochlore tantalates

$$TQ_{130^oC} = 1 - \frac{QY_{130^oC}}{QY_{25^oC}}$$

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



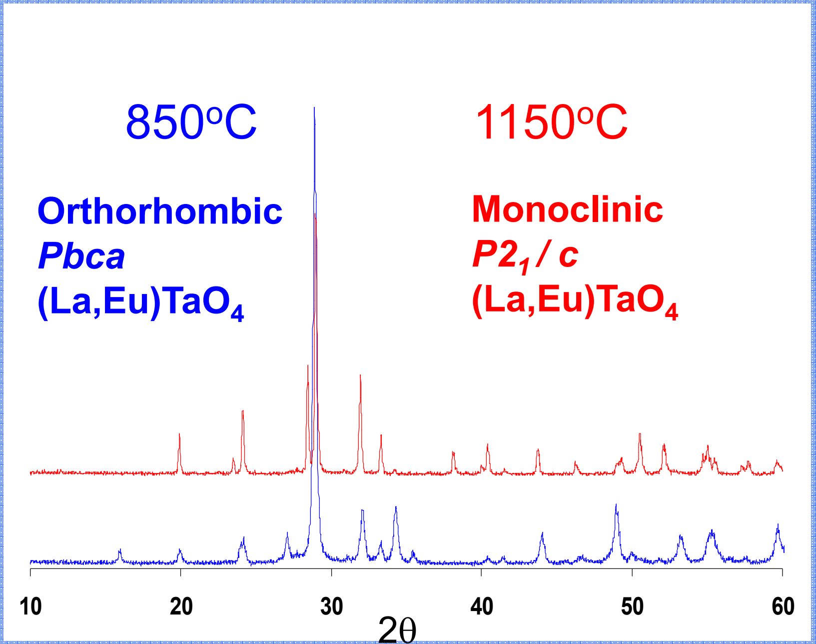
$K_{1-2x}GdTa_2O_{7-x}:Eu^{3+}$

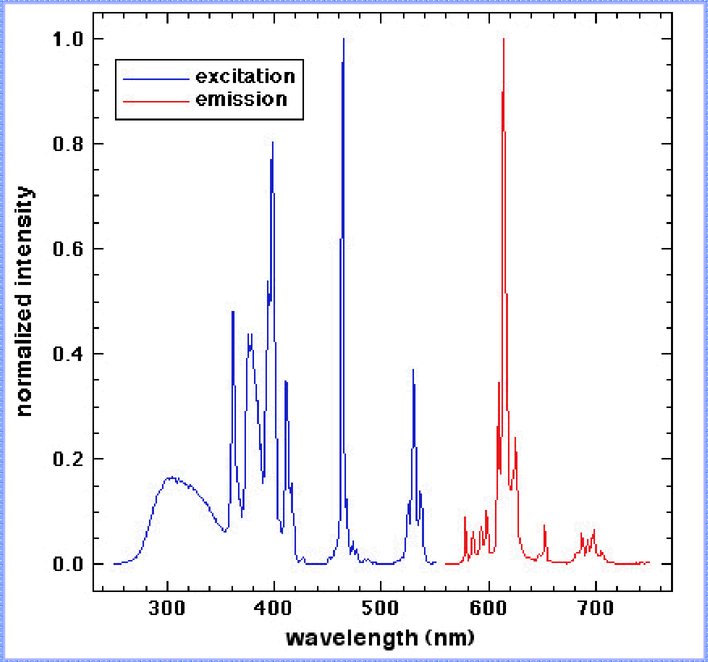


- TQ = 11% and 12% at 130°C and 150°C.
- TQ = 9% at 130 and 150°C.
- Gd tantalates have slightly less thermal quenching than Y/Lu tantalates.

Orthotantalate ($LaTaO_4:Eu^{3+}$) bulk phosphors

- Hydrothermal synthesis at 200°C produces **$(La,Eu)_2Ta_2O_7(OH)_2$** which is then annealed.

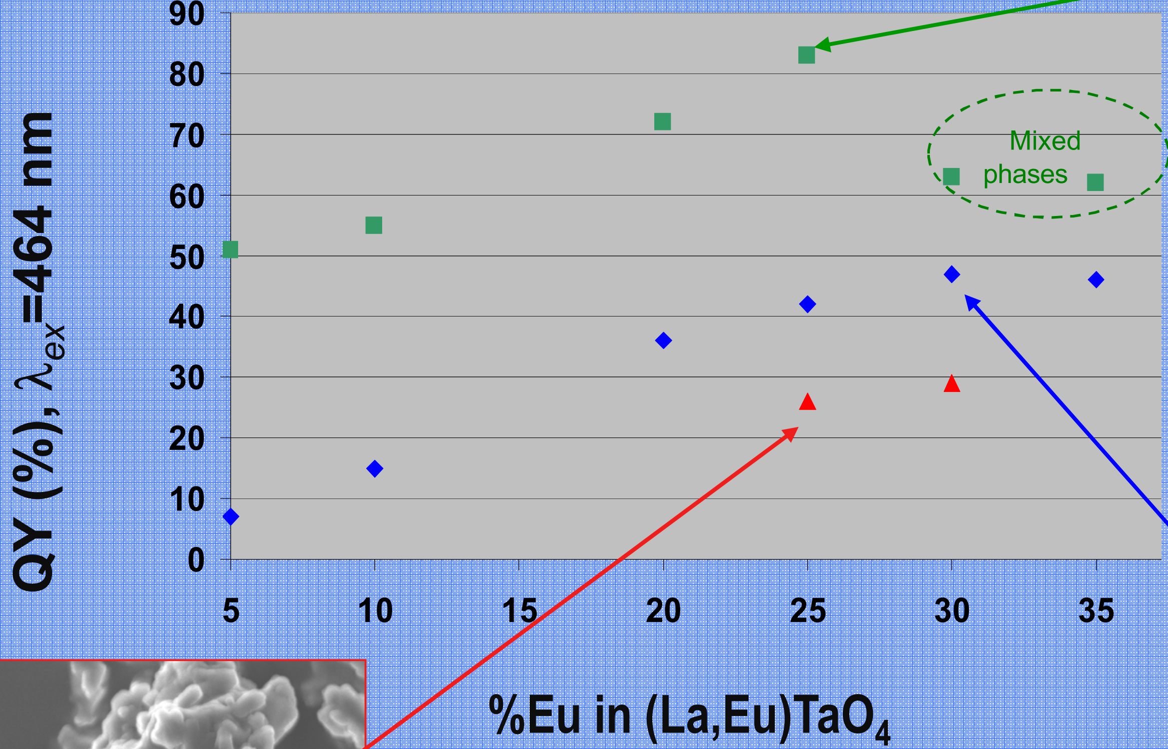




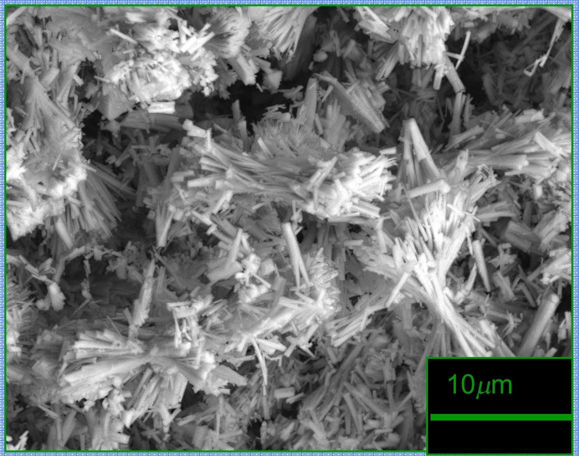
- Two different polymorphs are formed.
- Narrow red emission as in the pyrochlores.

Nyman *et al.*, Chem. Mater., 21, 4731 (2009).

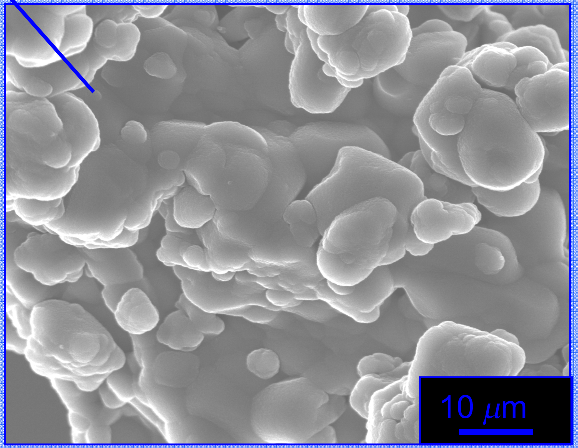
$LaTaO_4:Eu^{3+}$ QY under blue excitation

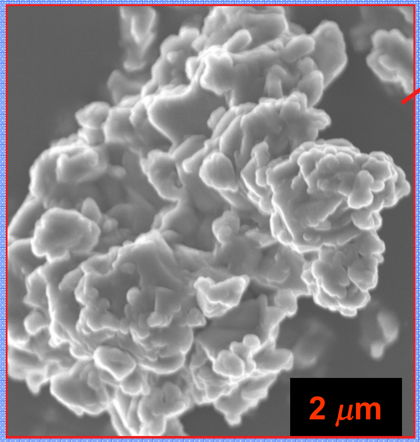


Hydrothermal synthesis, 900°C anneal



Hydrothermal synthesis, 1150°C anneal



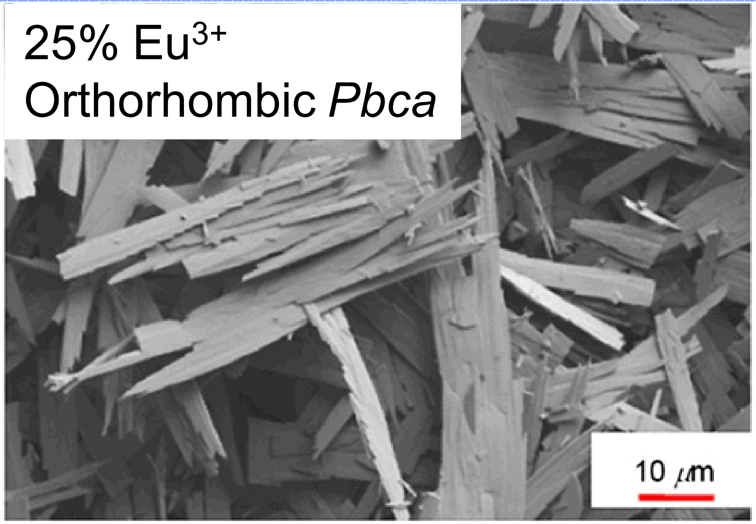


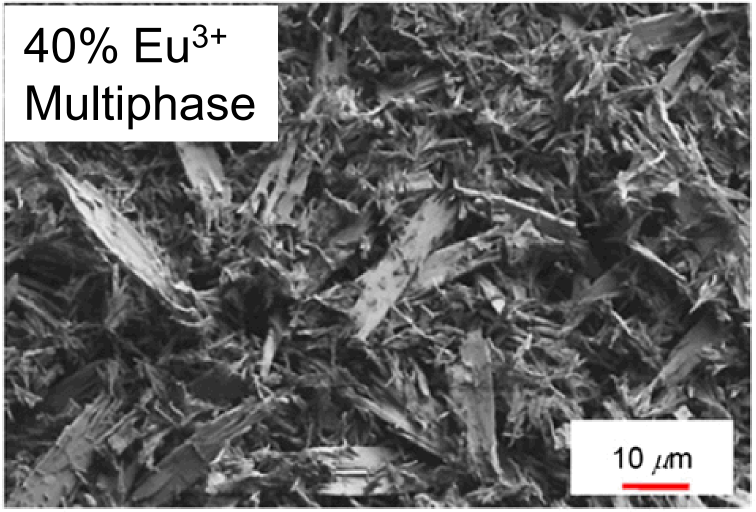
Solid-state synthesis, 1150°C anneal

- **QY=83% for the orthorhomic phase formed at 900°C.**
- **At Eu^{3+}>25%, the 900°C polymorph is no longer single phase.**

Eu^{3+} can compromise the phase purity of $LaTaO_4$

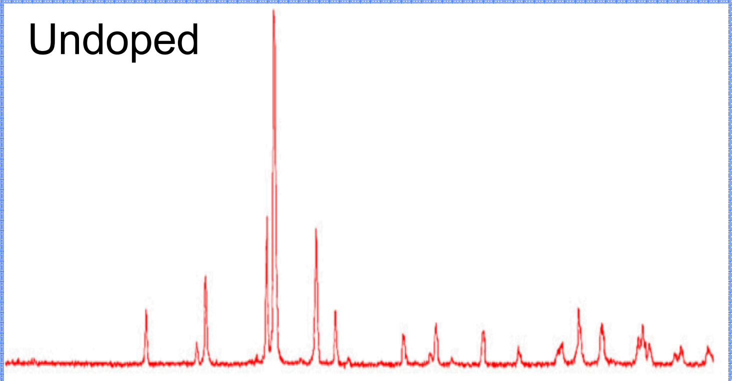
- **$LaTaO_4$ 900°C**

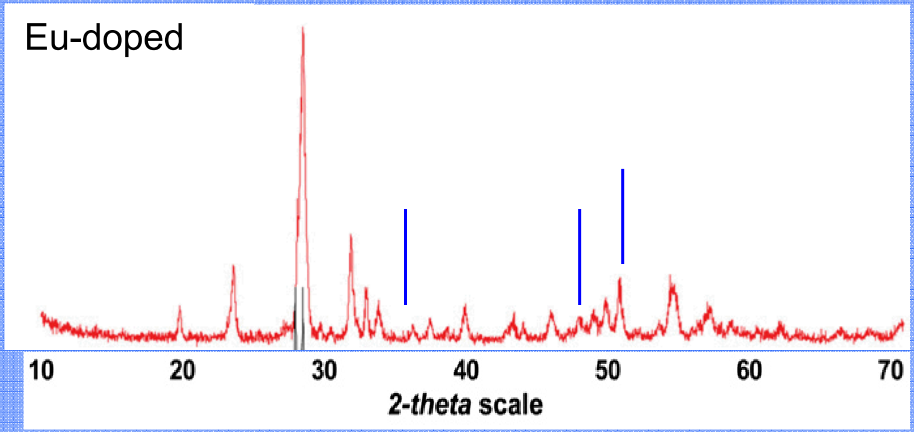




- **$LaTaO_4$:40%Eu^{3+} has ~50% of *Pbca* polymorph, plus other RE tantalate phases which have needlelike crystallites.**

- **$LaTaO_4$ 1150°C**



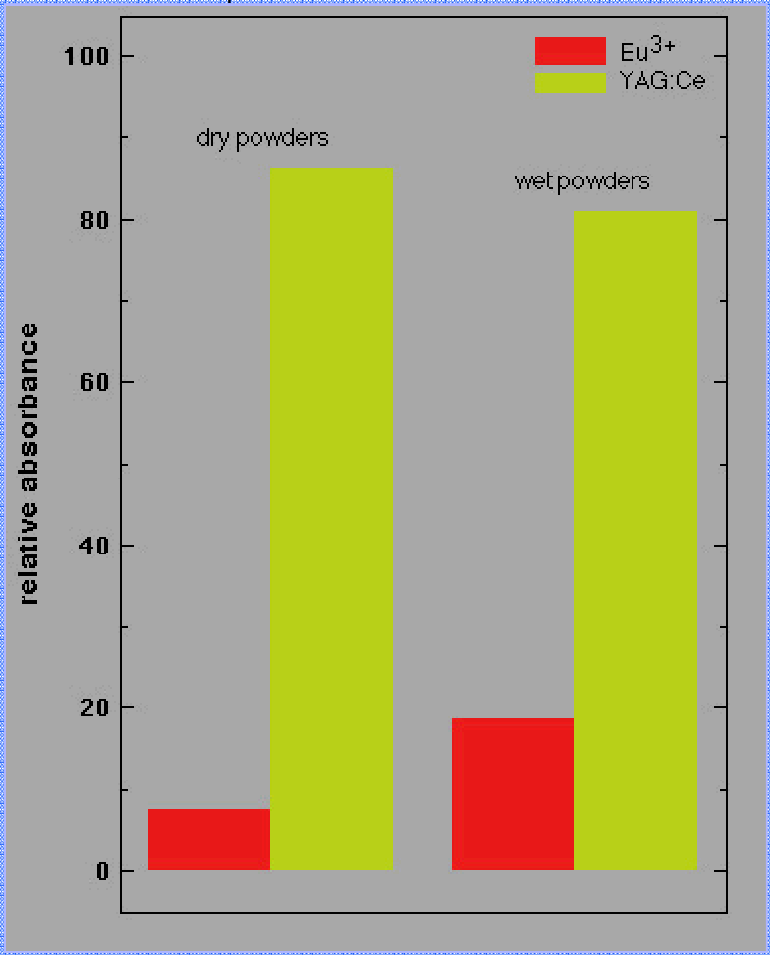


- **Undoped $LaTaO_4$ is monoclinic (*$P2_1/c$*).**
- **Eu^{3+}-doped samples contain monoclinic and orthorhombic (*$Cmc2_1$*) phases.**
- **QYs only reach 48%.**

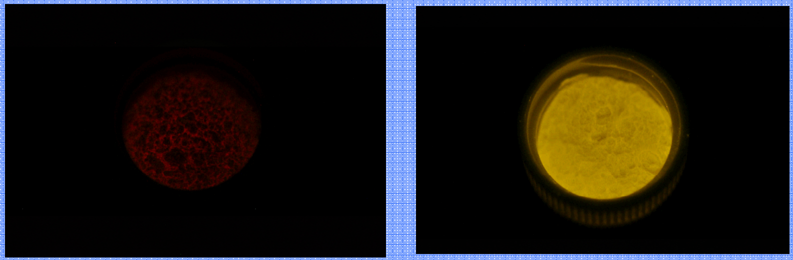
Bleier *et al*., JSSC, 184, 3221 (2011).

Although the QY is high, Eu^{3+} has low blue absorbance

Blue absorption of YAG:Ce^{3+} and $LaTaO_4$:Eu^{3+} relative to carbon black.



Blue illumination of $LaTaO_4$:Eu^{3+} (left) and YAG:Ce^{3+} (right) powders.



- The weak blue absorbance of Eu^{3+} is due to its low oscillator strength.

- The remaining challenge is to increase the absorbance of this phosphor, perhaps by forming it into a transparent, ~1mm thick plate.

Summary

- Eu^{3+}-doped YVO_4 and tantalate pyrochlore nanophosphors were produced.
- Their narrow red emission is ideal for warm white LEDs.
- Gd tantalate has higher QY (78%), lower thermal quenching (9% at 150^oC), broader blue absorption linewidth (9 nm) than the Y/Lu tantalates.
- Lattice distortions due to oxygen vacancies in Gd tantalate.
- Bulk $LaTaO_4$:25%Eu with orthorhombic structure has QY of 83%.
- At Eu^{3+}>25%, orthorhombic $LaTaO_4$ is no longer phase pure, so QY drops.
- Monoclinic $LaTaO_4$ is multi-phase, regardless of Eu^{3+} concentration, and its QY is lower than that of the orthorhombic phase.
- Narrow blue absorption of the Eu^{3+} phosphors necessitates the development of transparent plates for SSL.

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