# Narrow Band Nitride Phosphors

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# Need for Improved Down-Converters

## Emission band width reduction to drive efficiency improvements

- 2014 DOE SSL MYPP core technology research task down-converters

"Explore new high-efficacy wavelength conversion materials for the purposes of creating warm-white LEDs, with a particular emphasis on improving spectral efficiency with high color quality and improved thermal stability. Non-rare earth metal and nontoxic down-converters are encouraged."

- Focus on $Eu^{2+}$ doped nitride materials
  - Low doping levels, rare earth free host lattices
  - Strong absorption, high quantum efficacy, low thermal quenching
  - Stable, condensed lattice structures
  - Nontoxic, environmental friendly



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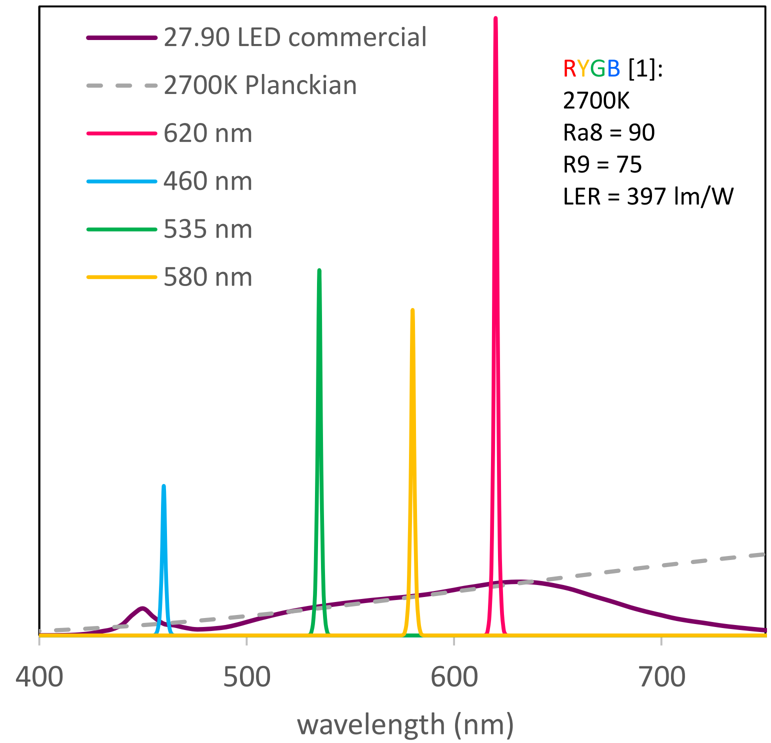
# Structural Limitations of State-of-the-Art Red $Eu^{2+}$ Phosphors

- Industry standard materials show broad *composed* emission bands originating from multiple $Eu^{2+}$ sites
  - ***(Sr,Ca)SiAlN$_3$:Eu*** ("SCASN") shows statistical distribution of Si and Al on same site, SiAlON formation tendency
  - ***(Ba,Sr)$_2$Si$_5$N$_8$:Eu*** ("BSSN") shows two chemically quite different M sites
- Emission FWHM in the ~2000 – 2400 $cm^{-1}$ (~70 – 100 nm) range
- ~ 40% LER penalty (2700 K, CRI90) compared to theoretical limit [1]




[1] see Phillips, J. M., M. E. Coltrin, et al. (2007) Laser & Photonics Review 1(4): 307-333



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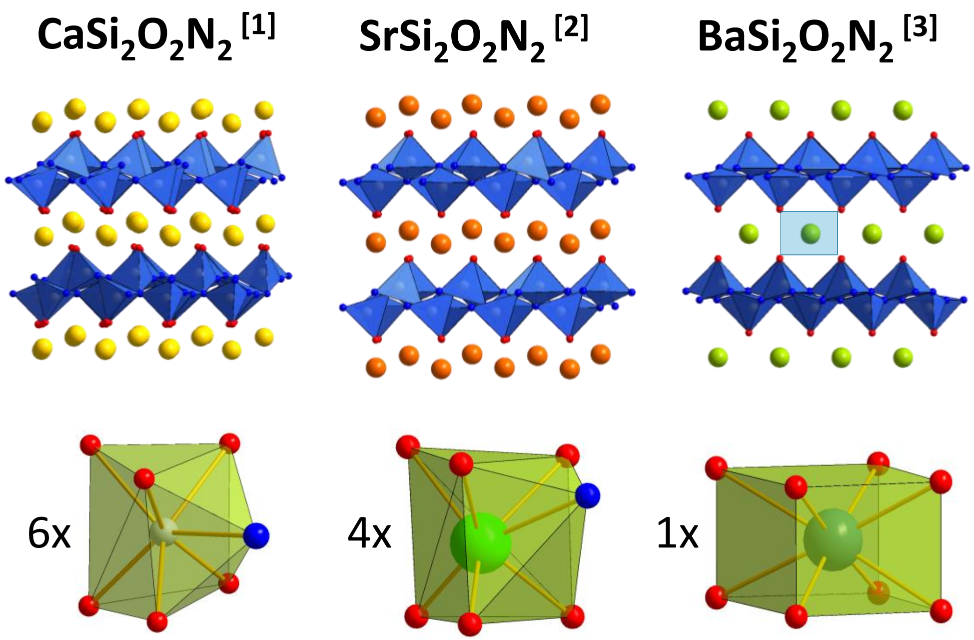
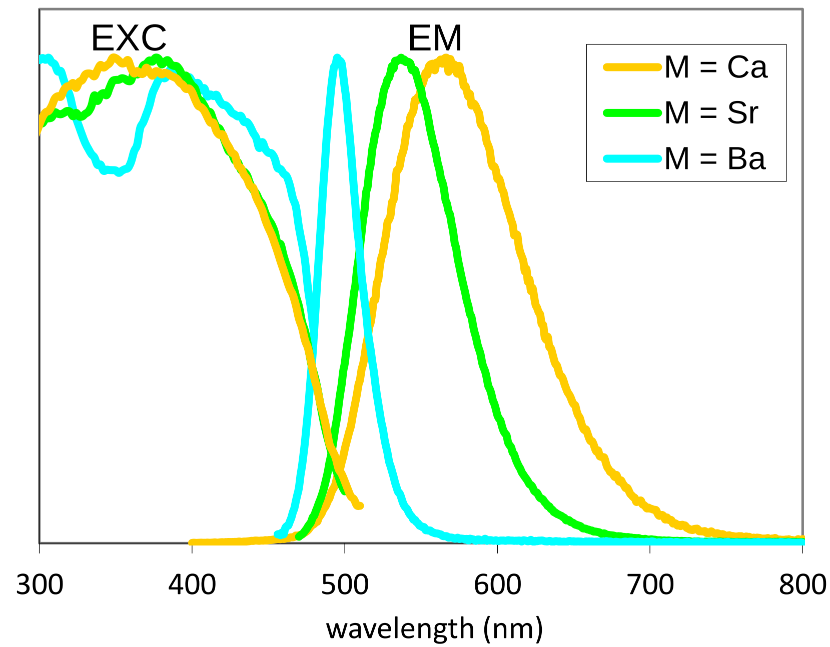
# $MSi_2O_2N_2$:Eu - Model Compounds for Structure – Emission Property Relations

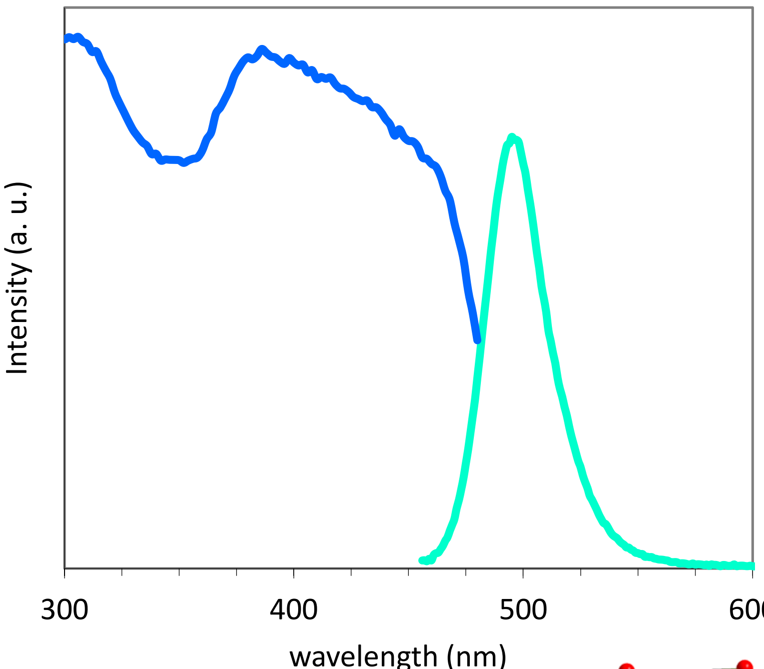


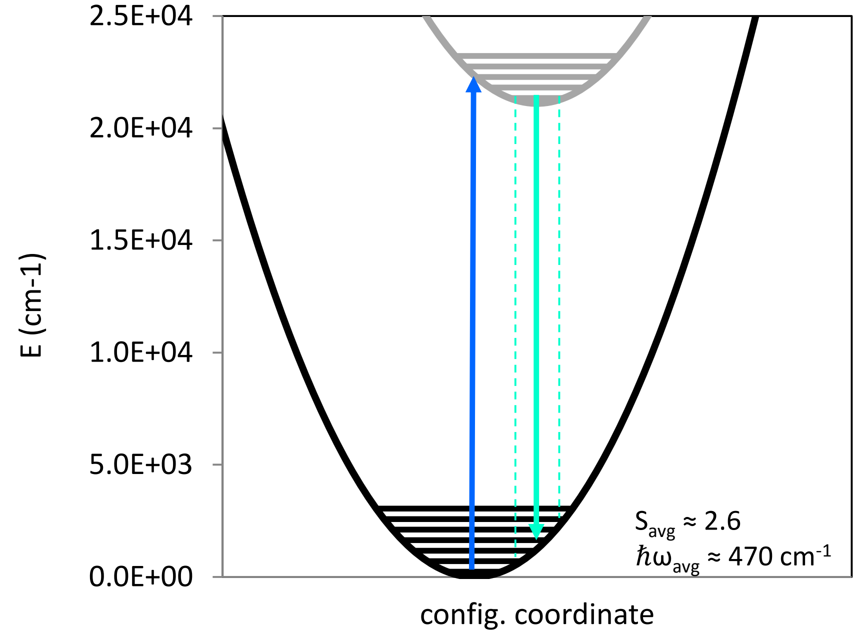




- $Si_2O_2N_2^{2-}$ layers as common structural motif
- Differences in local cation coordination → differences in luminescence properties; cyan (Ba), green (Sr) and yellow (Ca) emission
- Small Stokes shift, very narrow band emission for M = Ba

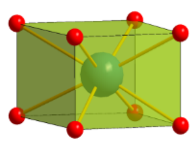
[1] H. A. Höppe, F. Stadler, O. Oeckler, W. Schnick, *Angew. Chem. Int. Ed.* **2004**, *43*, 5540
[2] O. Oeckler, F. Stadler, T. Rosenthal, W. Schnick, *Solid State Sci.* **2007**, *9*, 205
[3] J. Kechele, O. Oeckler, F. Stadler, W. Schnick, *Solid State Sci.* **2009**, *11*, 537-543

# Narrow $Eu^{2+}$ Emission in $BaSi_2O_2N_2$



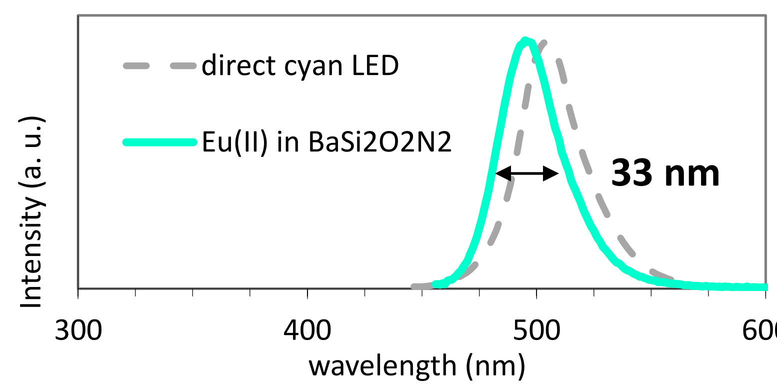




Cube-like coordination



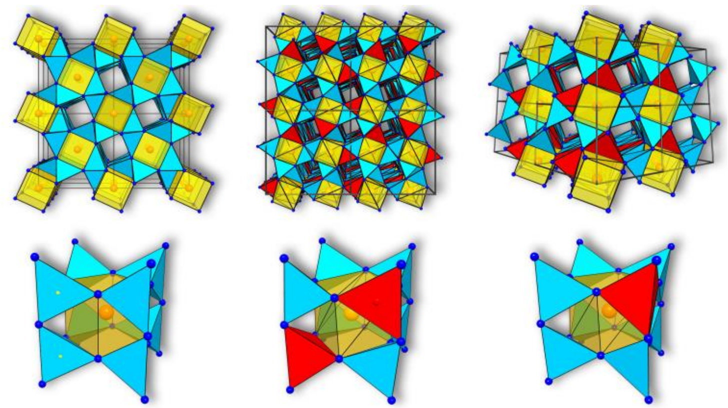
- strong ligand field
- hindered relaxation around Eu(II)* due to elongated Eu – L contacts (compared to octahedral coordination)

- same emission FWHM as cyan InGaN

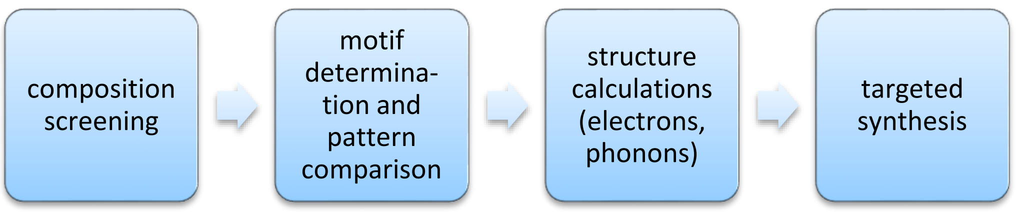


# Search for Narrow Red

- Narrow red: $EuN_8$ instead of $EuO_8$ cube?
- $SrMg_3GeN_4$ & $SrMg_2Ga_2N_4$: 1st nitride materials described by Park et al. in 2008 [1] showing cuboidal $SrN_8$ units
- Order variants known for a variety of oxide compounds (R. Hoppe et al. 1984 - 96), e.g. $NaLi_3SiO_4$ – what about nitrides?



- (General) research approach:





[1] Park, D. G., Y. Dong, et al. (2008). Solid State Sciences 10(12): 1846-1852.

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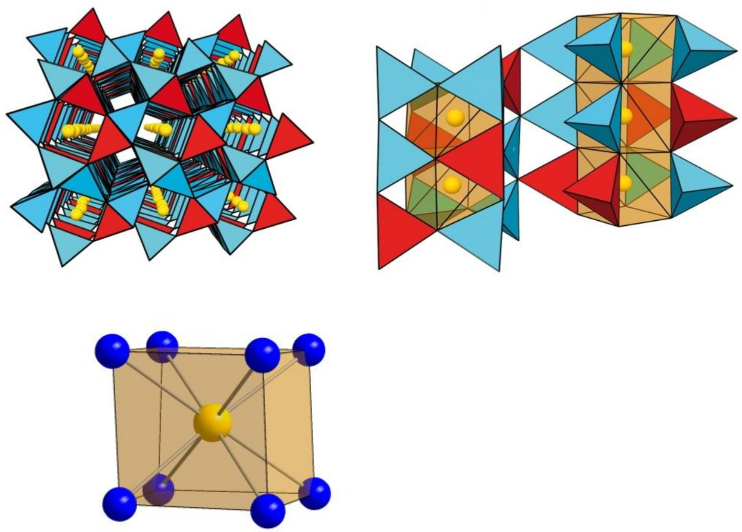
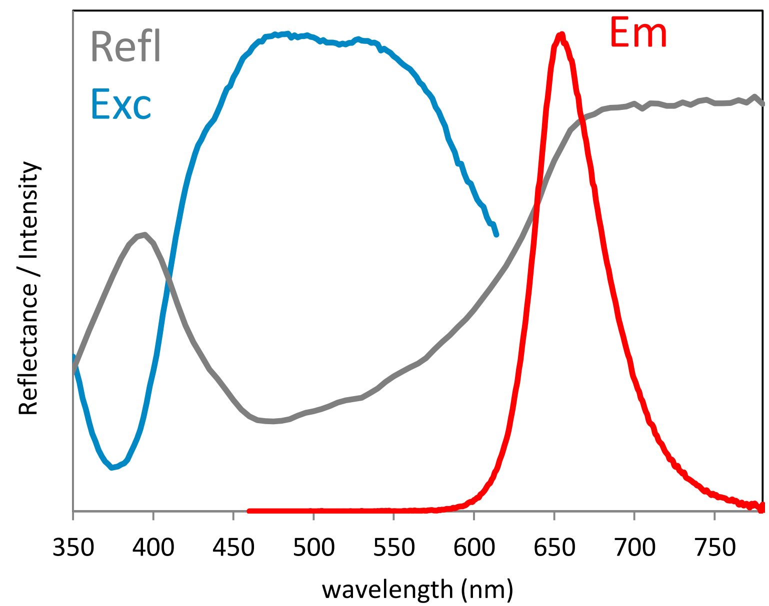
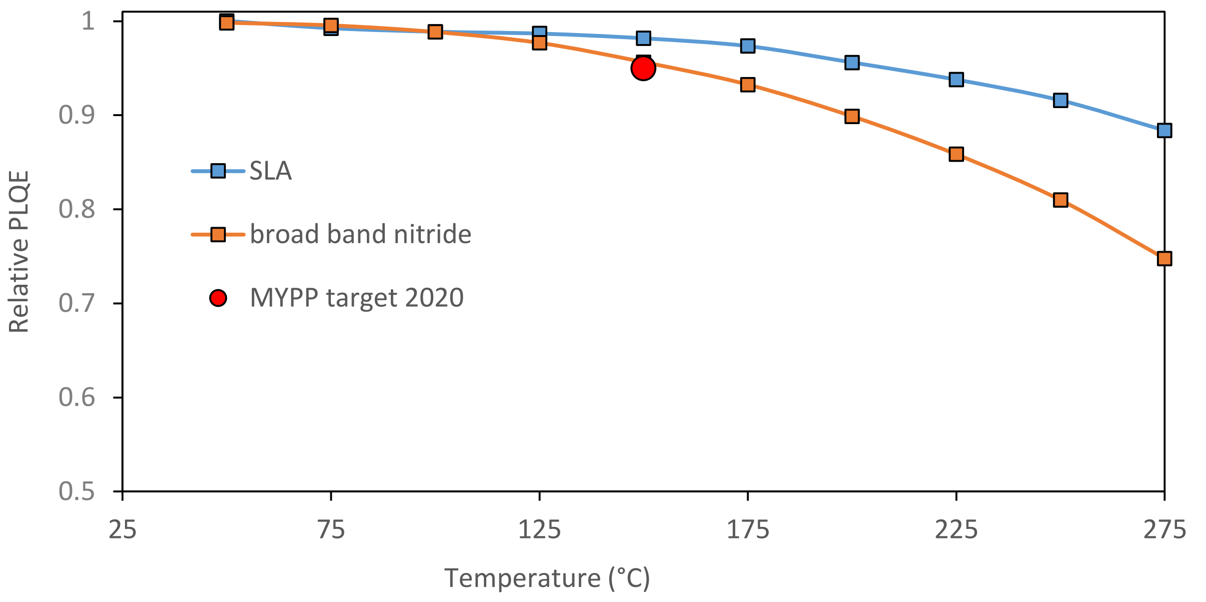
# SLA: 1st Narrow Band Red $Eu^{2+}$ Emitter






- Strontium aluminate with cuboidal $SrN_8$ coordination, chain-like arrangement of Sr atoms
- 2 Sr sites, structurally nearly identical
- Highly condensed network of ordered $LiN_4$ and $AlN_4$ tetrahedra
- Emission band located at ~650 nm, low energy Stokes shift and FWHM (970 and 1180 $cm^{-1}$)

# Thermal Stability of SLA Red Emission




- SLA meets MYPP target of 95% rel. QY (150°C/25°C)
- High QE up to T > 200°C
- Stability over time comparable with commercial red nitride emitters



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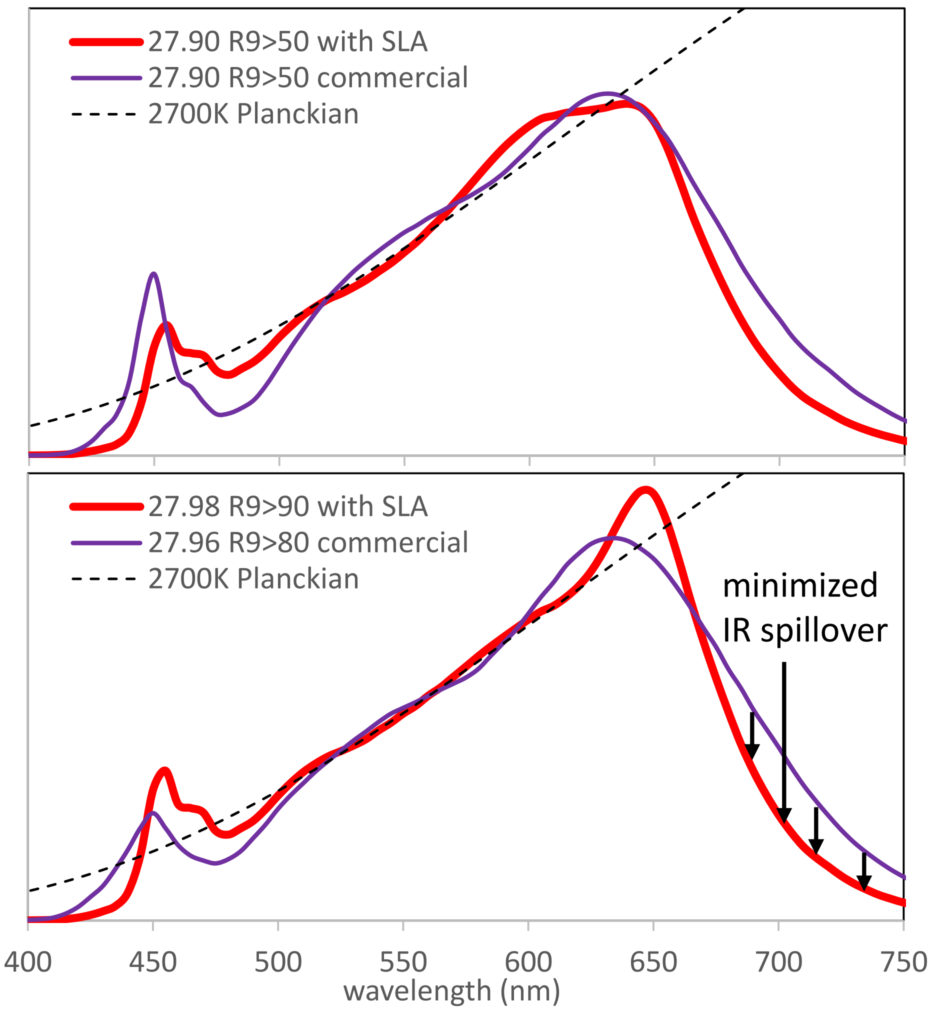
# Warm White LED Application




- highest LER gain for low CCT, high CRI
- multi phosphor mix
- CRI: 90-98, R9: 50-96
- ~4-12% LER increase (depending on CRI/R9)



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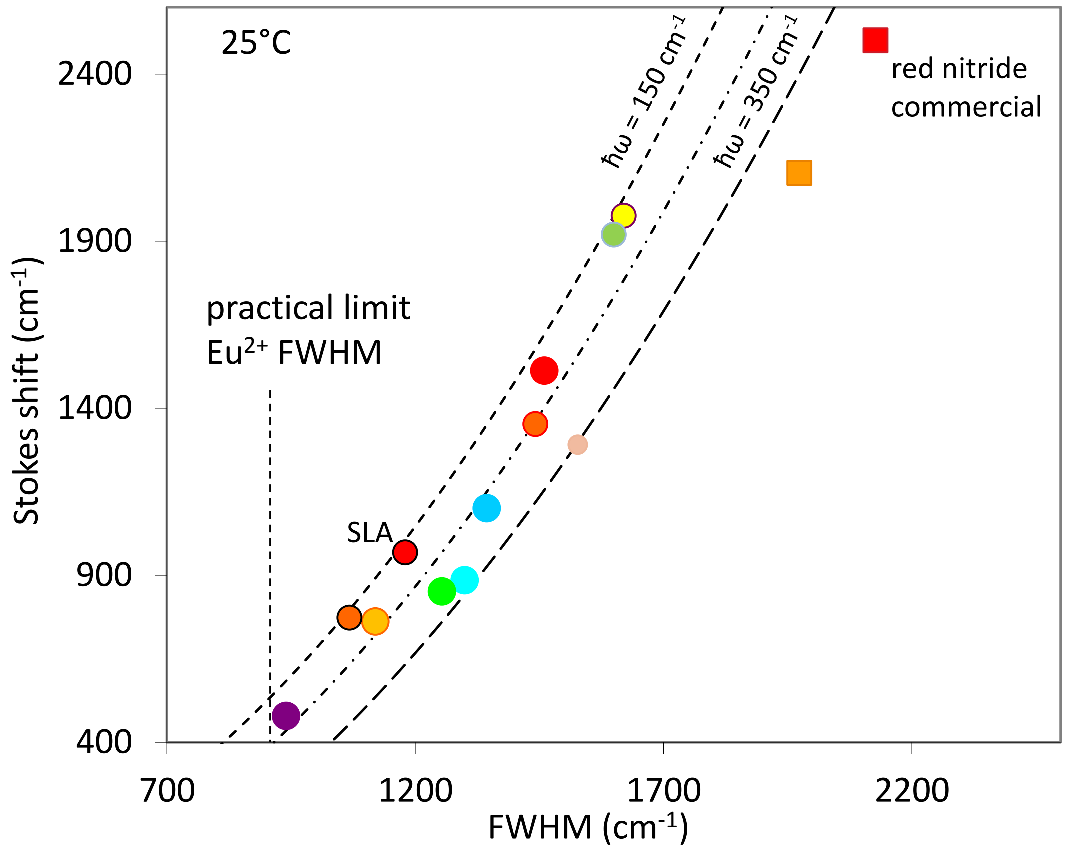
# Minimum $Eu^{2+}$ FWHM and Projected Efficiency Gains

- FWHM ~ 900 $cm^{-1}$ is seen as practical limit
- Expected efficiency gain over commercial 27.90 (R9 > 50) solution: ~**30%**
  - ***~618 nm peak wavelength, ~33 nm FWHM***
- DOE MYPP target 2020: <30 nm FWHM all colors
  - *challenging to be met with $Eu^{2+}$ in red spectral range*



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# Narrow Band $Eu^{2+}$ Red Status & Outlook

DOE MYPP 2014

**A.1.3 Down-Converters**

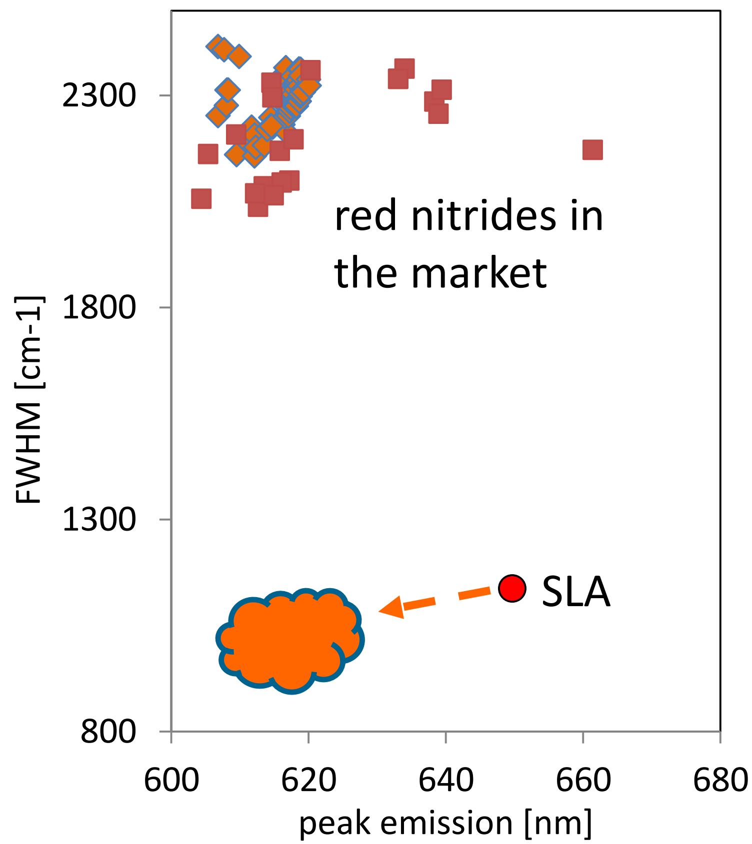
**Description:** Explore new, high-efficiency wavelength conversion materials for the purposes of creating warm-white LEDs, with a particular emphasis on improving spectral efficiency with high color quality and improved thermal stability and longevity. Non-rare earth metal and nontoxic down-converters are encouraged.

| Metrics | 2013 Status | 2020 Targets | 2014/15 | future |
|---|---|---|---|---|
| Quantum yield (25°C) across the visible spectrum | 95% (Green)<br>90% (Red) | 99% (Green)<br>95% (Red) | ✓ | |
| Thermal stability – Relative quantum yield at 150°C vs. 25°C | 90% | 95% | ✓ | |
| Average conversion efficiency[19] (pc-LED) | 70% | 74% | ✓ | |
| Spectral FWHM | 100 nm (Red) | <30 nm for all colors | **50 nm (Red)** | <30 nm green, < 35 nm red |
| Color shift over time (pc-LED) | Δu'v' <0.007 @ 6,000 hours | Δu'v' <0.002 over life | ✓ | tbd |
| Spectral efficiency relative to a maximum LER ~395 lm/W | 81% | 100% | **76% ($R_a8 > 90$, R9 > 50)*** | >95% |

* Emission peak shift to shorter wavelengths (615 – 630 nm) required to maximize LER gains

# Summary

- SLA is the first member of the new class of high efficiency narrowband red emitting nitride phosphors nearly showing a bisection of band widths of red nitride phosphors in the market
- Practical limit of $Eu^{2+}$ FWHM is seen at ~900 $cm^{-1}$ (25 – 35 nm, green → red) allowing an efficacy gain of ~30% by replacing commercial red nitride phosphors by future NBR phosphors
- Research to focus on identifying red emitters with shorter wavelength emission to maximize LER gains



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# Thank you