Synthesis of Lanthanide-Doped Nanoparticles with Luminescent Properties for the Production of LED White Solid State Lighting

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Project Funding: **MRL**

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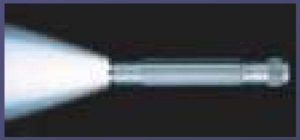
What is so good about Solid State LED (Light Emitting Diode) Lighting?



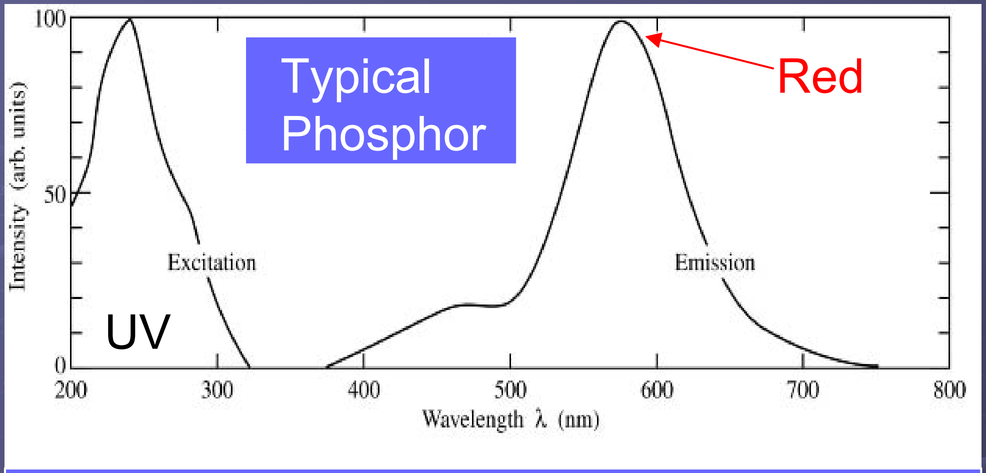
<u>Background</u>: Solid state lighting has the potential to be more energy efficient, more durable and longer lasting than current incandescent or fluorescent lighting technology.

<u>Comparison of Lighting Technologies</u> (Light Emitting Diodes (LEDs) for General Illumination, An OIDA Technology Roadmap Update 2002, November 2002.).

Light Source	Efficiency	Lifetime
Incandescent Bulb	16 lumens/watt	1000 hours
Fluorescent Lamp	85 lumens/watt	10,000 hours
Today's White LEDs	**25 lumens/watt**	**20,000 hours**
Future White LEDs	***Up to 200 lumens/watt***	***100,000 hours***

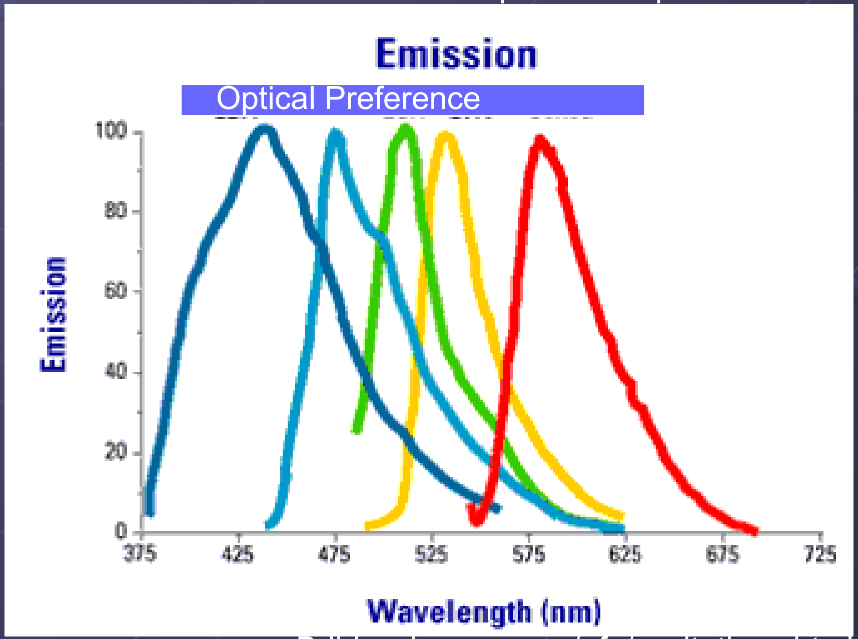
Emission

- Absorb UV light and reemit at visible wavelength (λ) or color.
- Doped compounds photoluminesce at different colors.
- Some success[1] with LaF_3 and Lanthanide (Ln) dopants. But synthesis of capping agent was difficult and the size/shape of particles was poor.



Excitation and Emission

rpi.edu//chap11/F11-12-R.jpg



Bdbiosciences.com/gfp/excitation.shtml

[1] Stouwdam et al.,Chem. Mater. 2003, 15

Goals

- Project Goal: Develop more easily synthesized nanoparticles with uniform size and shape that are soluble in organic solvents for tunable optical properties.

- RET Participant's Goal: Synthesize Lanthanum Fluoride nanoparticles doped with a lanthanide (Eu or Ce) and a capping agent (PVA) and characterize these particles by XRD, PL and TEM techniques.

Synthesis of Nanoparticles:

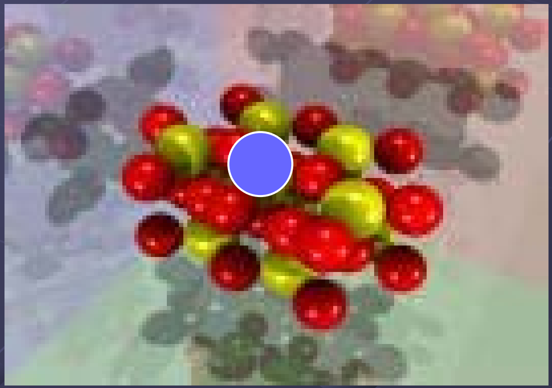
For Uncapped solutions:

$La(CH_3CO)_3 + NH_4F + Dopant^{1} \xrightarrow{60°C\ /\ 2\text{-}20\ hrs.} LaF_3{:}Ln^{2}$

For Capped solutions:

$La(CH_3CO)_3 + NH_4F + Dopant^{1} + PVA^{3} \xrightarrow{75°C\ /\ 2\ hrs.} LaF_3{:}Ln^{2}$

1) Dopants: $Eu(NO_3)_3$ and $Ce(NO_3)_3$
2) Ln = Lanthanide Series (Eu, Ce, etc.)
3) Capping Agent: PVA = Polyvinyl Alcohol



Abulafia.mt.ic.ac.uk/crystal/laf3_40

Analysis Methods

Analysis of powder samples was conducted by:

- UV Lamp –Visual (Qualitative) fluorescence
- XRD – X-Ray Diffractometer for compound fingerprint identification.
- PL – Quantitative emission wavelength determination of fluorescence.
- TEM – Size and shape distribution of nanoparticles and crystal structure.

Results – Fluorescence

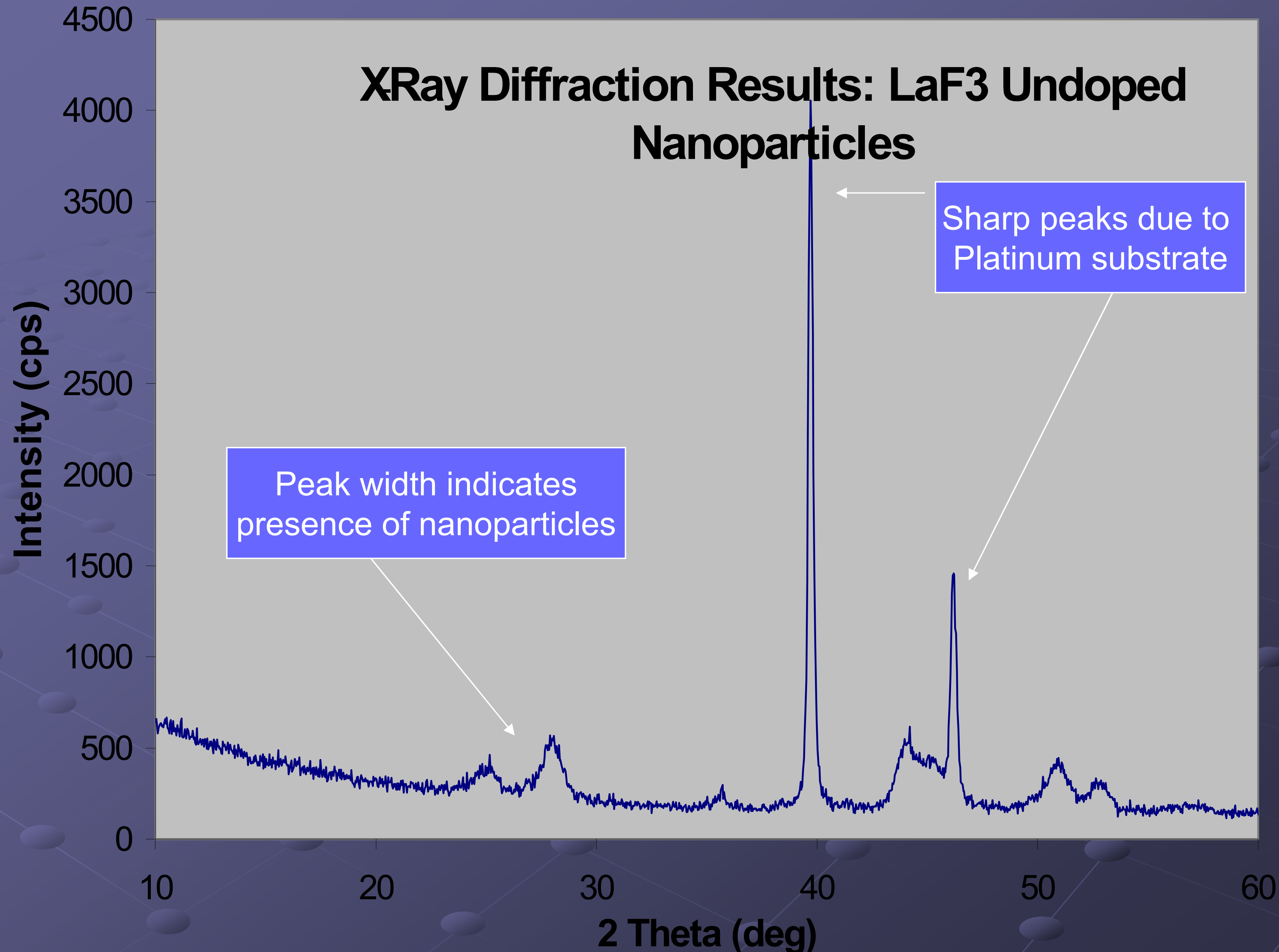
Compound	Visual Fluorescence (at 254 and 312 nm)	PL (Excitation Wavelengths at 260, 360 and 390 nm)
LaF_3 Undoped	None	NA
LaF_3:Ce (2%)	Weakly violet when powder was heated at 200°C overnight	No appreciable peaks observed
LaF_3:Ce (1%)	None	NA
LaF_3:Eu (2%)	Weakly red	No appreciable peaks observed
LaF_3:Eu (2%) with PVA Capping Agent	Weakly red	NA

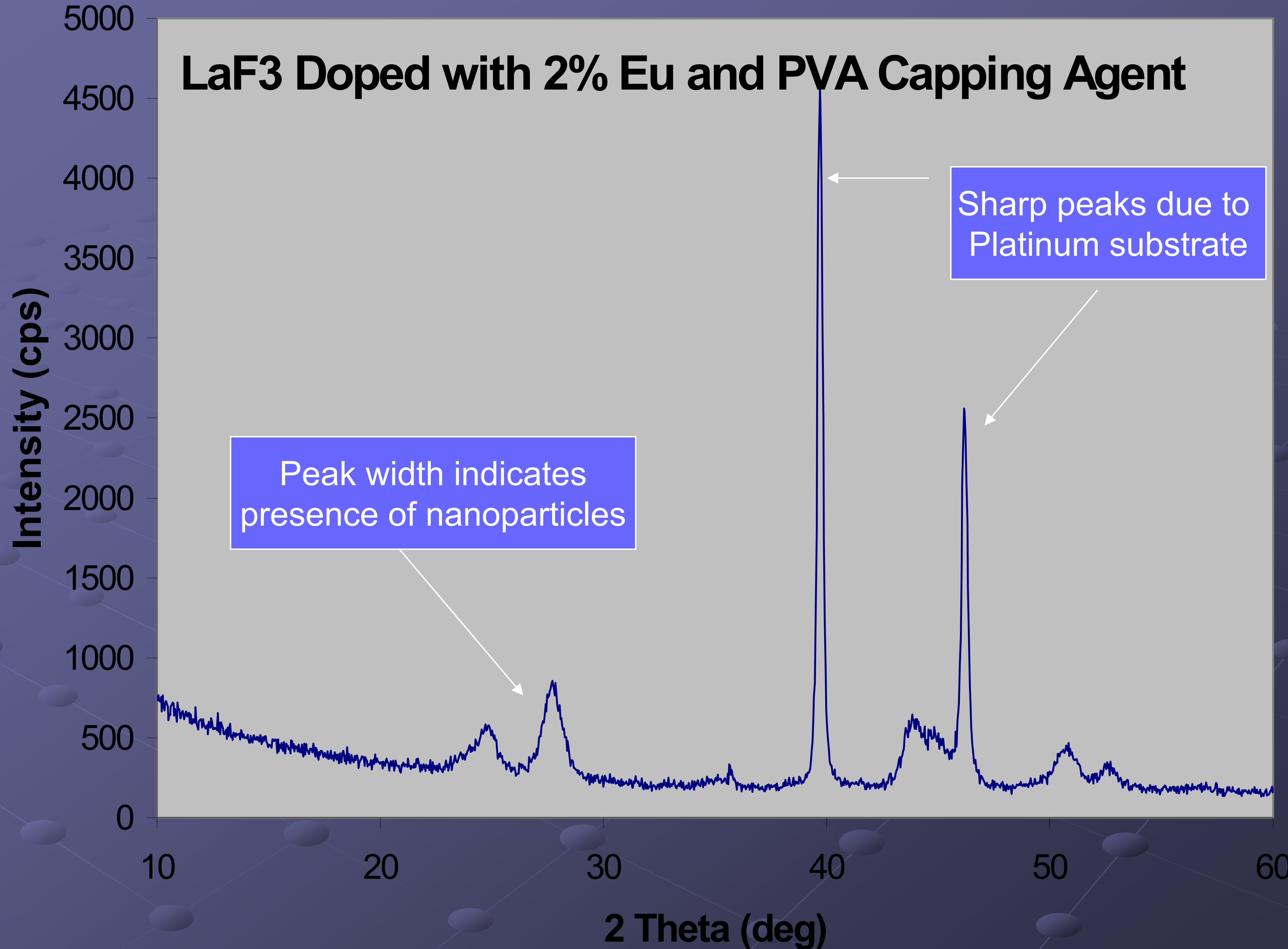
Results – X-Ray Diffraction

Compound	X-Ray Diffraction Pattern[1] & Comments
LaF_3 Undoped	Match Confirmed, ***The width of the peaks indicates the presence of nanoparticles***
LaF_3:Ce (2%)	Match with LaF_3 pattern; nanoparticles present
LaF_3:Ce (1%)	Match with LaF_3 pattern; nanoparticles present
LaF_3:Eu (2%)	Match with LaF_3 pattern; nanoparticles present
LaF_3:Eu (2%) with PVA Capping Agent	Match with LaF_3 pattern; nanoparticles present

Cu Source at 1.54 Å

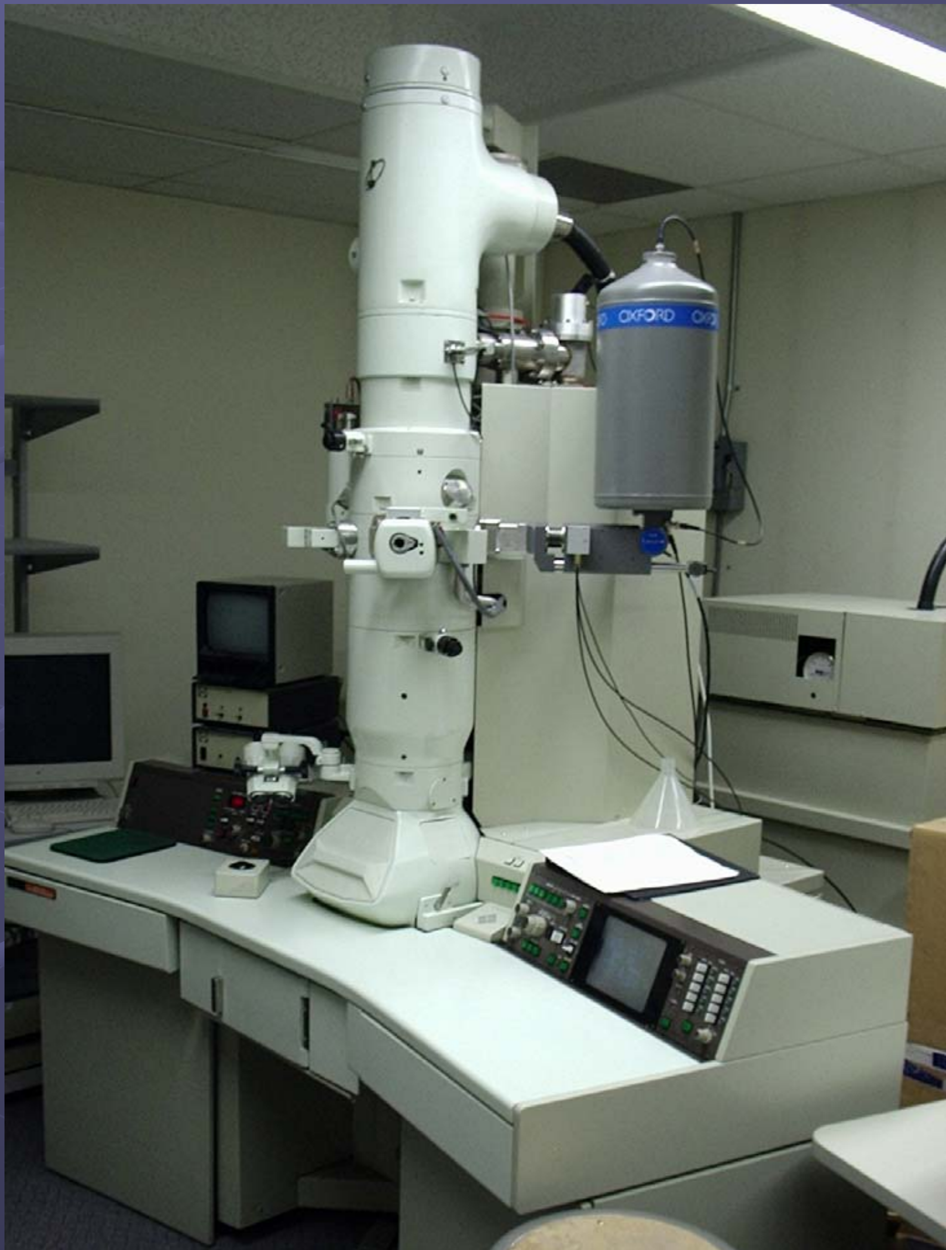
[1] by JCPDS powder diffraction card file


XRay Diffraction Results: LaF3 Undoped Nanoparticles
Sharp peaks due to Platinum substrate
Peak width indicates presence of nanoparticles
Intensity (cps)
2 Theta (deg)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
10
20
30
40
50
60


LaF3 Doped with 2% Eu and PVA Capping Agent
Intensity (cps)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
10
20
30
40
50
60
2 Theta (deg)
Sharp peaks due to Platinum substrate
Peak width indicates presence of nanoparticles

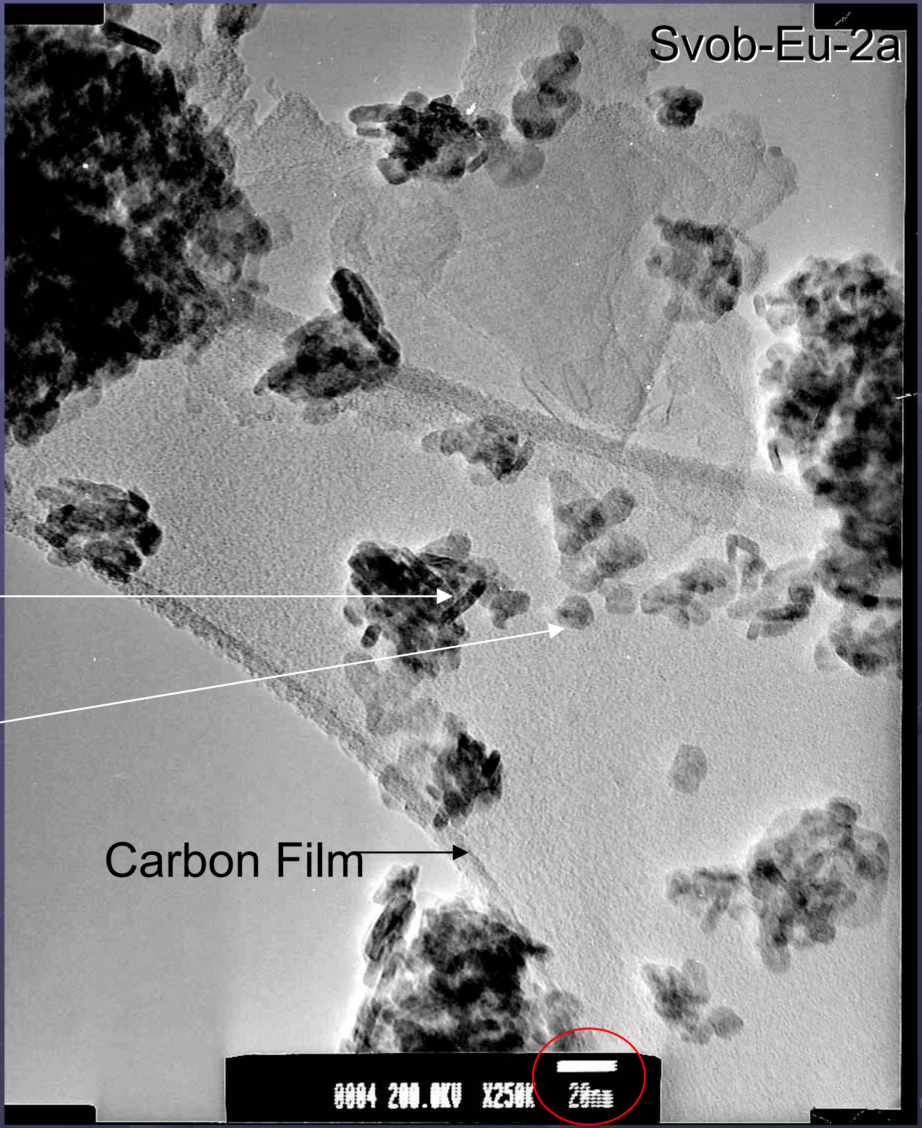
Results - TEM

Sample	Results
Svob-Eu-2a (XEDS Results: ***Eu: Average: 1.01%*** (Range: 0.93-1.24%)	Polydisperse nanoparticles. Crystalline and amorphous structures present.
Svob-Ce-2b (XEDS Results: ***Ce: 0.91%***	Polydisperse nanoparticles. Crystalline and amorphous structures present.
Svob-Eu-2b (XEDS Results: ***Eu: Average: 2.72%*** (Range: 2.39-3.35%)	No change observed in crystallinity or size/shape distribution. Higher dopant percentage by XEDS –heated longer
Svob-Eu-2c (Capped) (XEDS Results: ***Eu: 0.13%***	



Results – TEM

- No lattice fringes observed.
- Some amorphous particles observed.
- Elongated
- Spherical/Ellipsoidal
- Size distribution – 10-20 nm.

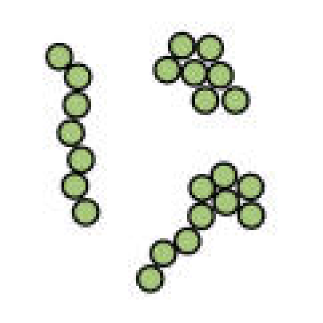


Results - Summary

Compound (LaF_3:dopant)	Fluorescence	XRD	TEM
Cerium doped (1-2%) nanoparticles	By Lamp: weakly violet when powder was heated. By PL: Weak peaks.	LaF_3 Match. Nanoparticles present.	Irregular shape. Size distribution 10-20 nm. Some agglomeration.
Europium doped (2%) nanoparticles	By Lamp: weakly red when solution heated longer. By PL: Weak peaks.	LaF_3 Match. Nanoparticles present.	Irregular shape. Size distribution 10-20 nm. Some agglomeration.
Europium doped (2%) nanoparticles *with PVA Capping Agent*	By Lamp: weakly red. By PL: NA	LaF_3 Match. Nanoparticles present.	Irregular shape. Size distribution 10-20 nm. Agglomeration.

Discussion and Analysis

- Once a material with a predictable percentage of nanoparticle sizes is generated, it will be possible to predict emission wavelengths to fine tune color.
- Mixing of these new materials may be an efficient way to produce higher quality white LED lighting.



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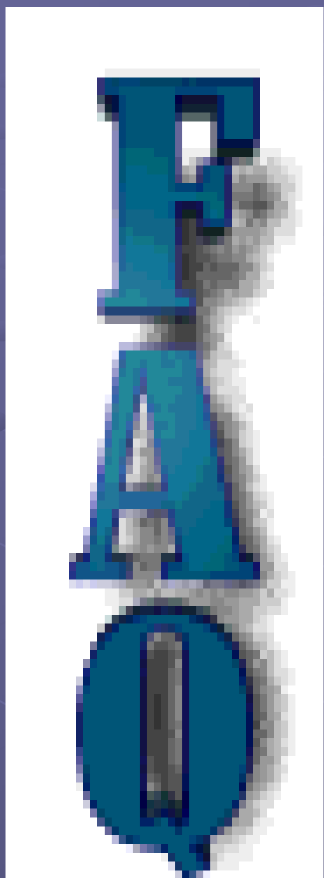
Project Conclusions



1. Nanoparticles were synthesized – and confirmed by XRD.
2. Doping confirmed by XEDS (TEM).
3. Amorphous structures may be responsible for weak fluorescence.
4. Capping with PVA did not show improvements in nanostructure uniformity in size and shape.

Passing On The Torch

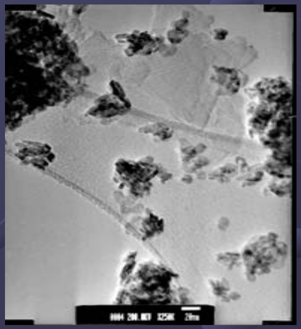
- Heat LaF_3:Ln solutions longer (for better doping) and at higher temperatures (for better luminescence).
- Try alternative capping agents (longer chain alcohols, diols or short chain alcohols)

RET Wrap-Up

- ***What did I learn this summer?***

Wow

1. I learned how to use a lot of new evaluation techniques for atomic structure, including an X-Ray Diffractometer, a Transmission Electron Microscope, and a Photoluminescence Spectrometer. Very cool!
2. I saw materials at close to atomic scale (nanometer scale)!



3. I improved my sense of materials research in the field of solid state lighting and I learned how these new materials may completely change lighting in the future.