



Engineering Ceramic Nanophosphors for Optical Applications

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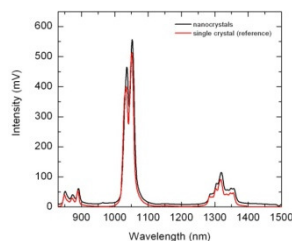
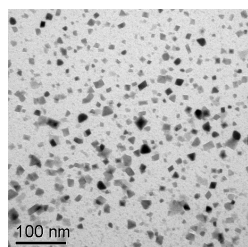
Core Efforts of Research Team

- Low-cost, scalable synthesis of phosphors using solution chemistry
- Systematic study and characterization of physical, chemical and optical properties
- Engineer surfaces and bulk properties of materials for devices
- Theoretical simulation and computation for design of novel dopant and codopant schemes to improve optical efficiency and enable unique emission properties

Current Research

Forms of Materials

Nanoparticles

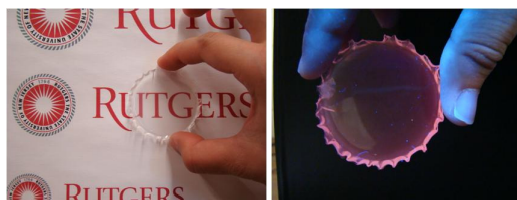


Optical Fibers

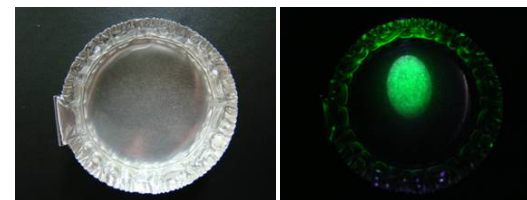


Transparent Polymer Composite Coatings

Downconverting Composites

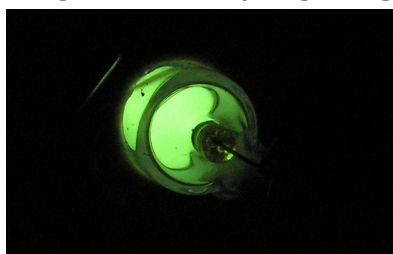


Upconverting Composites

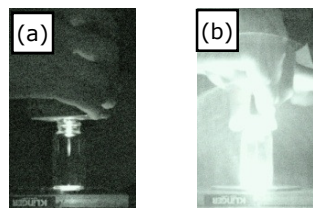


Applications

High Efficiency Lighting

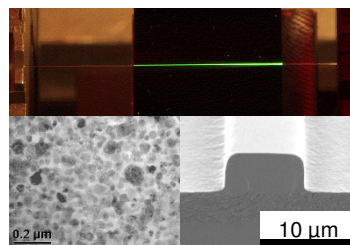


Night Vision Imaging

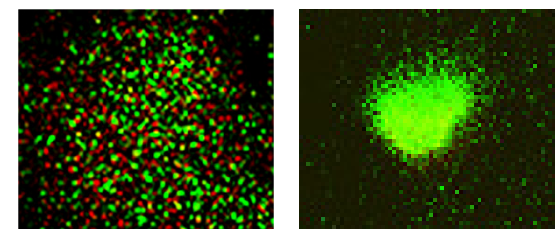


(a) Background (empty vial)
(b) Powder emission using handheld laser

Telecommunication



Biomedical Applications



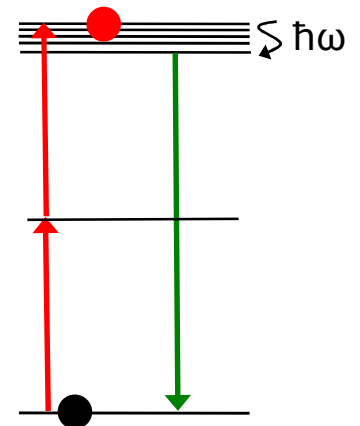
Images taken using confocal microscope

Types of Phosphors

- Classification based on energy conversion

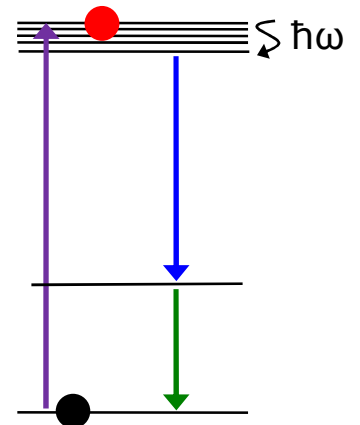
- Up-conversion phosphors

- emission of high energy photons upon excitation with low energy photon source
- maximum quantum efficiency $\sim 100\%$



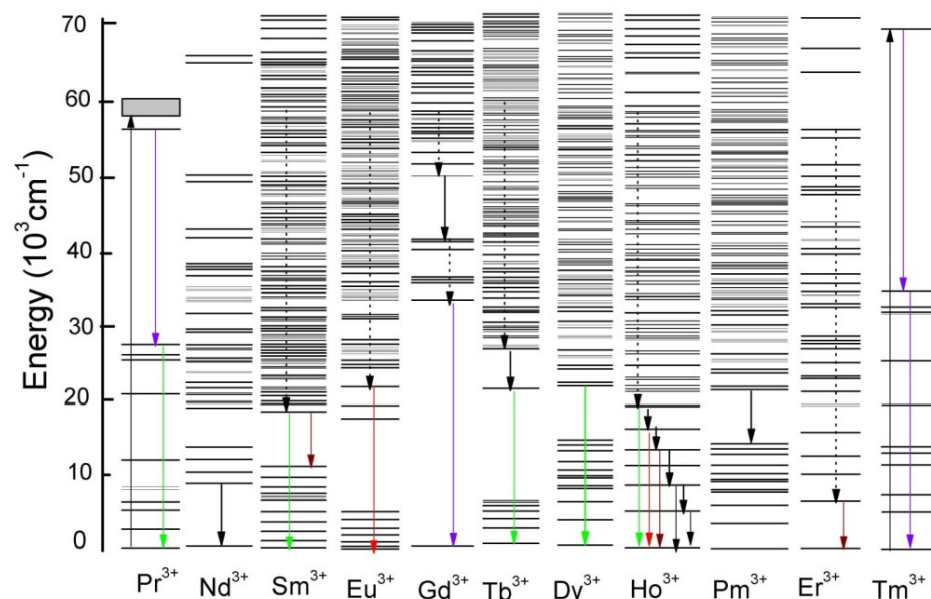
- Down-conversion phosphors

- emission of low energy photons upon excitation with high energy photon source
- maximum quantum efficiency $\sim 100\%$
- quantum cutting down-conversion:
1 vacuum ultraviolet photon ($\lambda < 200$ nm) absorbed, 2 visible photons emitted
- maximum quantum efficiency $\sim 200\%$



Optical Properties of Phosphors

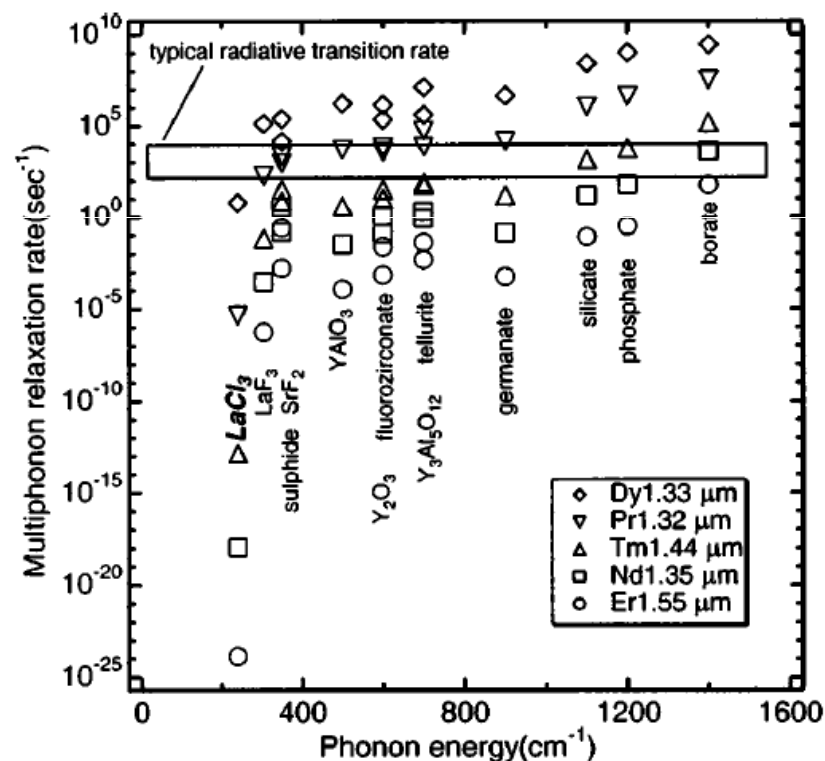
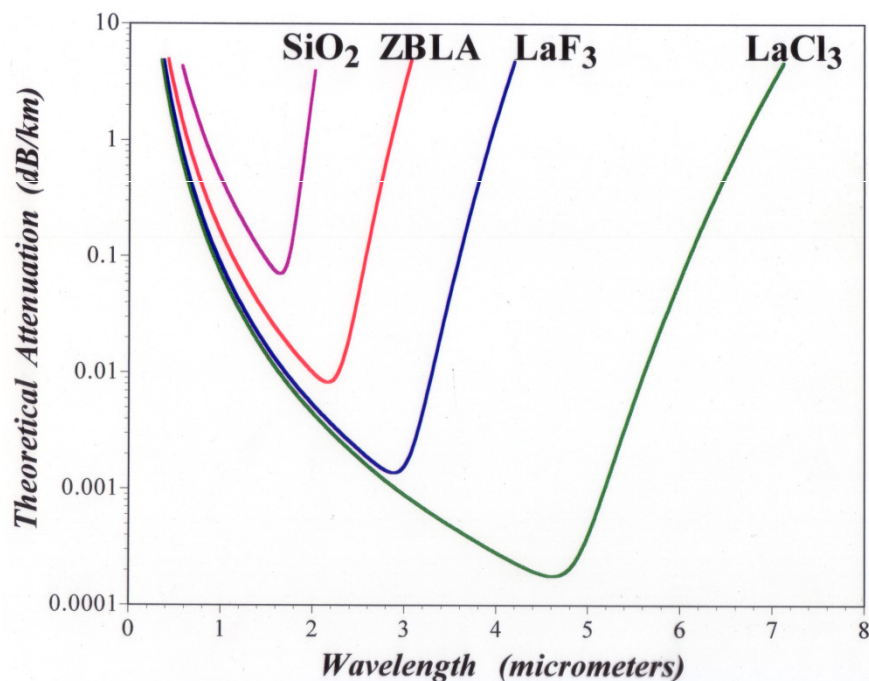
- Properties controlled by:
 - Dopant
 - radiative transitions predicted from electronic energy levels
 - Host lattice contributions
 - non-radiative losses, phonon energy, bond ionic character, symmetry of dopant site



- Desired properties
 - High absorption cross-section at exciting wavelength
 - High fluorescence decay time and emission cross-section
 - High quantum yield
 - High optical transparency in the emitting region
 - Low cost of production, non-toxic, high stability

Why Rare-Earth Doped Halides?

- Low phonon energy host
- Minimize non-radiative losses



Heavy Metal Fluoride Glass Formation

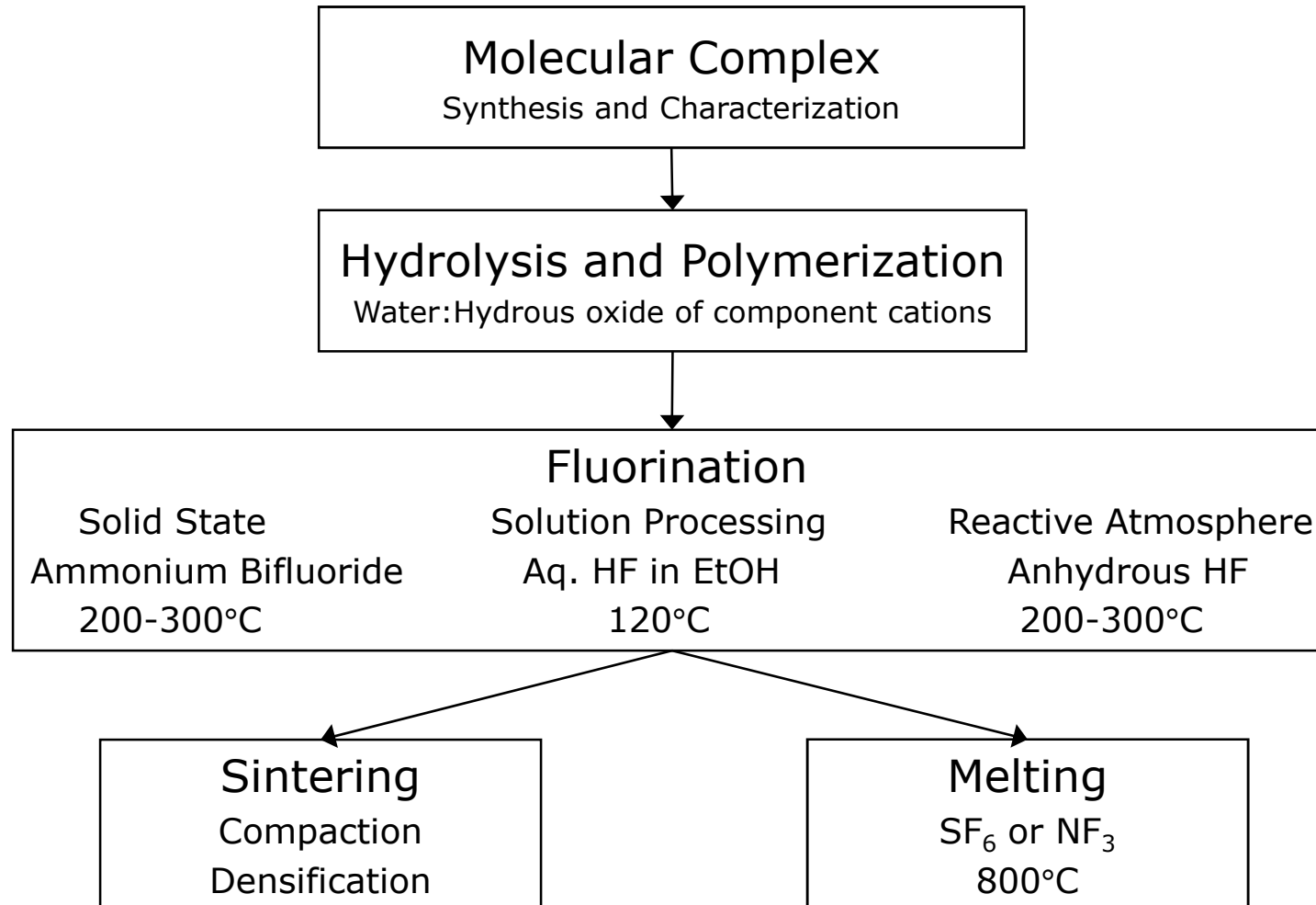
Material	T_g (°C)	T_{crys} (°C)	α (1×10^{-6}) (°C)
ZBLA	310	380	16
ZBLAN	260	360	17

- ZBLA and ZBLAN have better fiber drawing ability than other fluoride glasses
- Difficulties using conventional melt quenching method
 - Moisture sensitivity of precursors and liquid melt
 - ZrF_4 films were hygroscopic and contained other emission quenching contaminants like reduced Zr and oxide species
 - Segregation due to different vapor pressures of precursors
 - Glass stability - small difference in T_g and T_{crys}
 - high tendency for formation of crystalline regions
 - Low viscosity and coefficient of thermal expansion

Sol-Gel Synthesis of Halide Glasses

- Limitations of Conventional Processing
 - CVD: segregation problems due to different vapor pressures of component precursors
 - Melt: impurities and crystallization problems
- Advantages of Sol-Gel
 - Purity: purified alkoxide and organometallic precursors
 - Homogeneity: atomic scale mixing
 - Glass Stability: viscous sintering at low T
 - Compositional Versatility: Cations (Rare earths);
Anions (F, Cl, Br...)
 - Forms: Amenable to fibers, films and bulk optics

Schematic of Sol-Gel Synthesis



Sol-Gel Precursor Selection

- Metal organic precursors cause undesirable properties
 - “Foam” pellets and films on sintering
 - Optical blackening from residual free carbon
- To overcome drawbacks of metal organic precursors
 - Fluorinating/oxidizing atmospheres
 - Use inorganic precursors

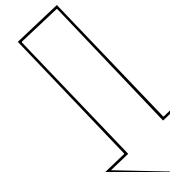
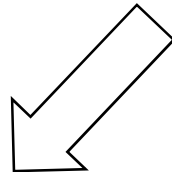
Samples	Wt% C	Wt% H	Temp. (°C)	Lifetime (ms)			
				ZHC N ₂	ZHC HF	ZBLA N ₂	ZBLA HF
Hydrous oxide gel – 50°C	22.67	3.69	100	0.73	1.12	0.38	0.70
Solution Fluorination			200	0.68	1.57	0.47	0.81
Fluorinated – 120°C, 1h	1.74	0.79	300	0.44	2.19	0.48	0.80
Vapor Phase Fluorination			325	0.40	2.15	0.49	0.96
Anhydrous HF – 200°C	0.23	0.12	400	0.26	2.75	0.34	1
Melt Processing			600	0.24		black	black
HF 200 → SF ₆ 800°C	0.00	0.00	800	0.18	3.80	black	4.73

Alternative Rare-Earth Systems?

Rare Earth Doped Glasses

Limitations:

- High purity raw materials
- Compositional uniformity
- Crystallization
- High cost of processing
- Limited processability



Rare-Earth Doped Polymer Systems

- dissolve rare-earth ions in polymers

Nanostructured Photonic Composites

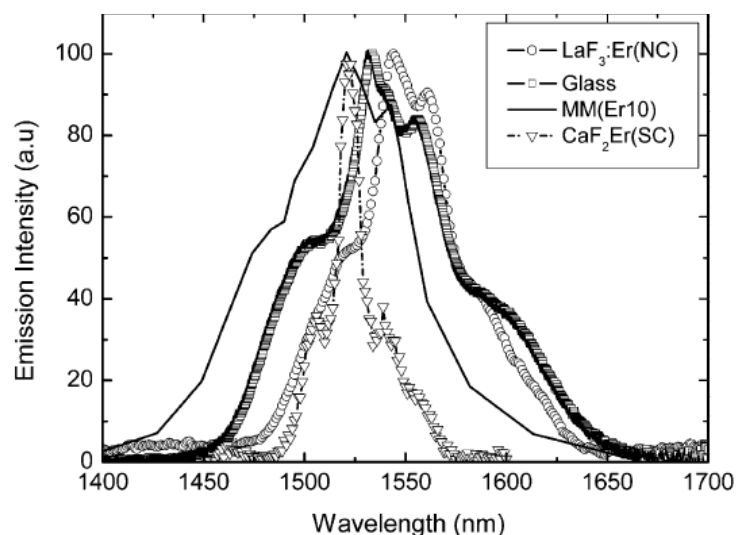
- dispersion of rare-earth doped nanocrystals in polymers

Rare-Earth Doped Polymer Systems

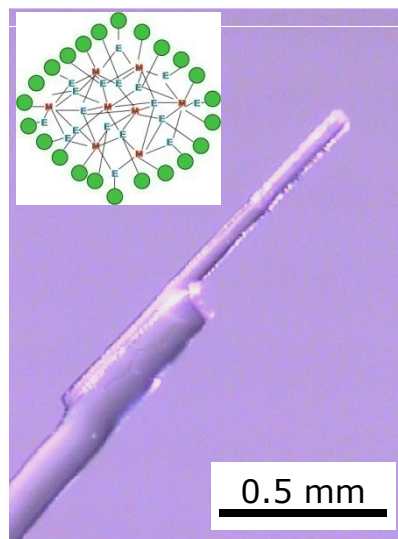
- Advantages of polymer systems
 - Lower processing costs
 - Excellent processability
 - Tunable optical performance with incorporation of multiple rare-earth systems
 - Low weight, flexible
- Limitations
 - Low solubility of rare earth ions
 - Quenching of emission from rare earth ions due to polymer functional groups (e.g. -OH and -CH)

Molecular Minerals

- Inorganic clusters with high solubility in polymers
- Surrounding ligands protect rare earth ions to reduce non-radiative losses and quenching
- Stability issues of inorganic clusters led to development of inorganic nanoparticle-polymer composites



Comparison of IR emission spectrum of Er10 molecular minerals with other Er-doped systems



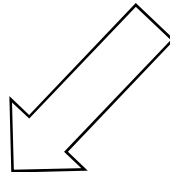
(THF)₃Er(SePh)₃ Molecular Minerals Single Crystals and Solutions

Alternative Rare-Earth Systems?

Rare Earth Doped Glasses

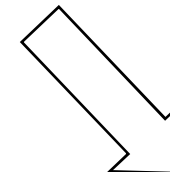
Limitations:

- High purity raw materials
- Compositional uniformity
- Crystallization
- High cost of processing
- Limited processability



Rare-Earth Doped Polymer Systems

- poor chemical and thermal stability



Nanostructured Photonic Composites

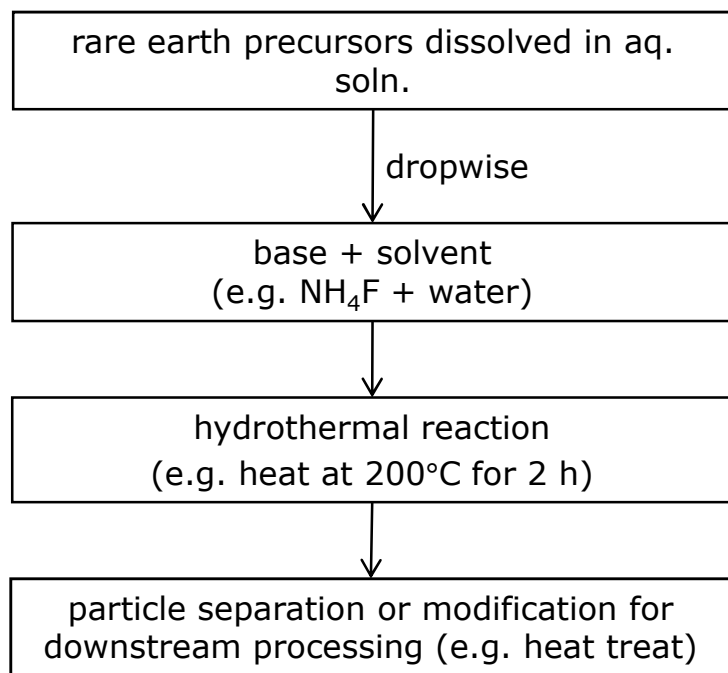
- dispersion of rare-earth doped nanocrystals in polymers

Nanostructured Photonic Composites

- Dispersion of rare-earth doped nanoparticles in IR-transparent polymer matrix
- Combine advantages of polymers and inorganic host
 - inorganic host: low phonon energy, intense emissions, good chemical resistance and high thermal stability
 - polymers: low weight, flexibility, good impact resistance and excellent processability
- Desired properties
 - High optical transparency (low scattering and absorption)
 - High solids loading → bright devices
- Suitable for device integration
 - LEDs
 - optical fibers
 - optical waveguides

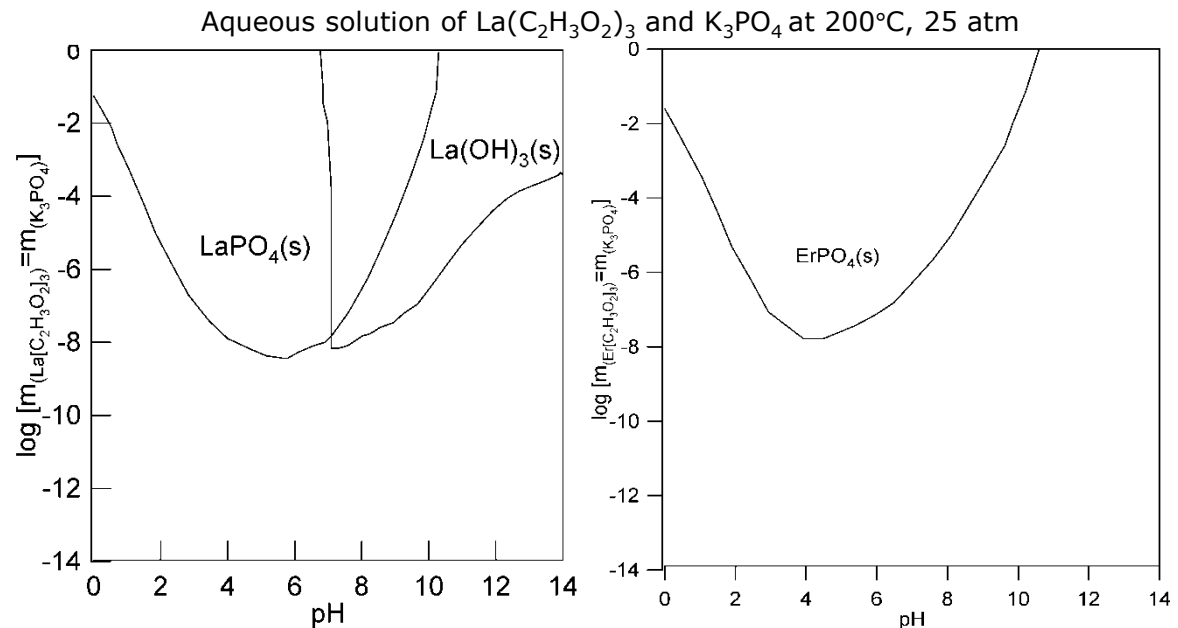
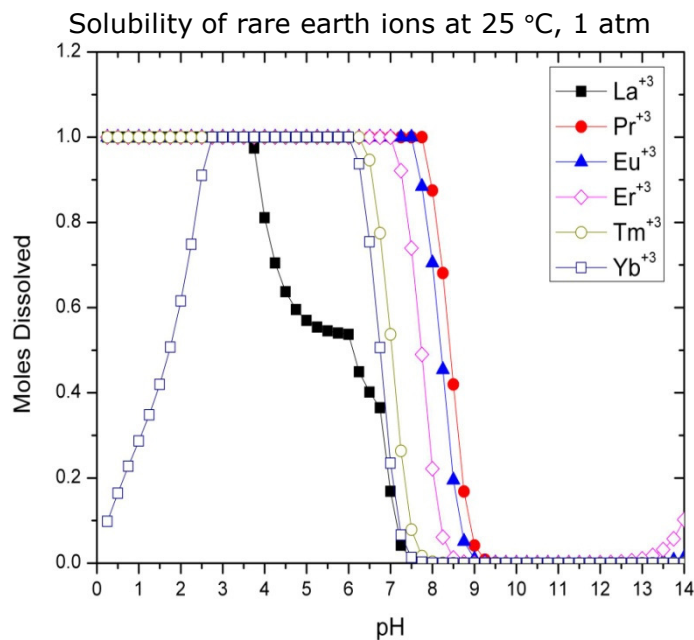
Hydrothermal Synthesis of Phosphors

- Reproducible with control of particle phase and size
- Versatile and applicable to various material systems
- Low-cost and easy to scale-up

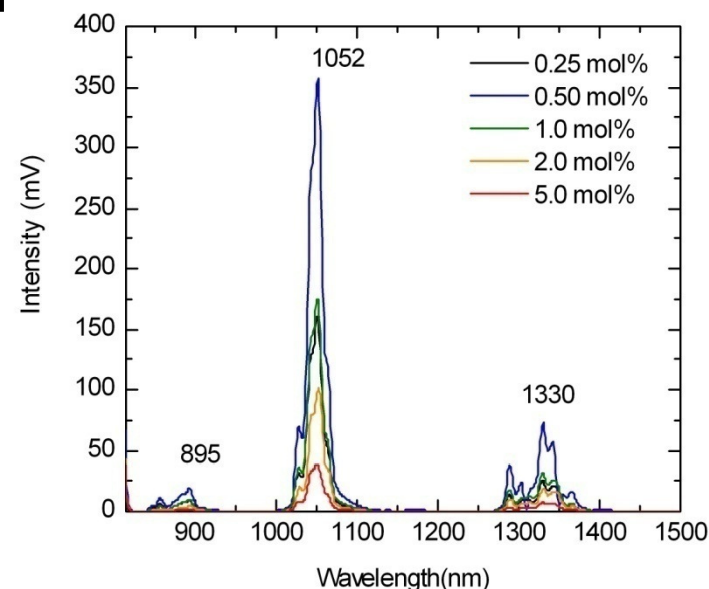
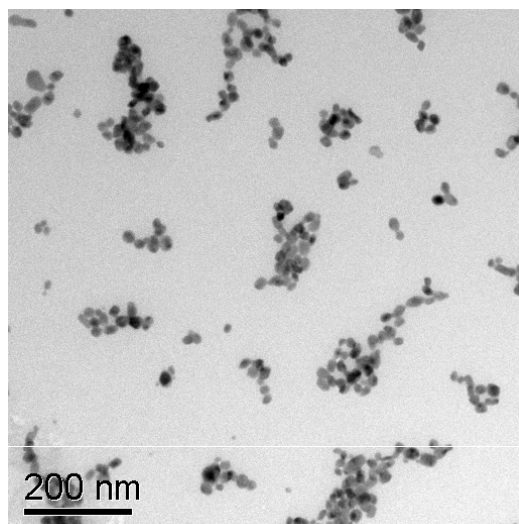
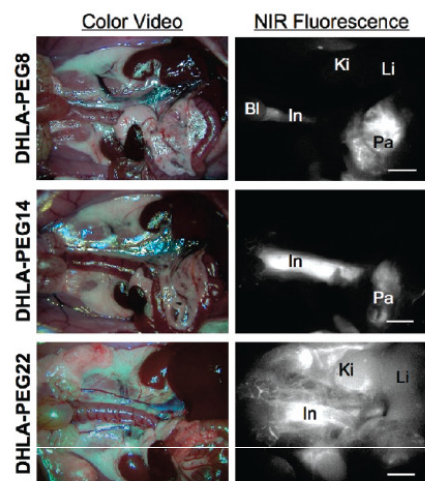


Thermochemical Engineering and Design

- Tool for solvothermal reaction design
- Phase pure products from simulated equilibrium yield diagrams
- Analyze dopant incorporation into host lattice and crystal growth problems



IR-emitting $\text{YF}_3\text{:Nd}$ nanoparticles



HS Choi et al. Nano Lett., *in press*.

- Emerging application in diagnosis and imaging
 - low tissue-penetrating visible emission from conventional fluorescent probes inadequate for deep tissue imaging
 - imaging sensitivity potentially improve by $\geq$ tenfold
- NIR-emitting rare earth doped phosphors
 - narrow excitation and emission bandwidth
 - tunable over longer NIR range

Radiative Properties of YF₃:Nd

- Energy level calculations from Hamiltonian equation
 - $H = H_{FI} + H_{CF}$, where H_{FI} and H_{CF} is the free ion and crystal field contributions, respectively
- Judd-Ofelt intensity parameters, Ω_t (t=2,4 and 6)
 - strength and nature of crystal field acting on rare-earth ion
 - $\Omega_2 = 0.87 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 1.56 \times 10^{-20} \text{ cm}^2$ and $\Omega_6 = 3.53 \times 10^{-20} \text{ cm}^2$
 - $\Omega_4 > \Omega_6$ to maximize intensity of $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition (i.e. 895 nm)
 - $\Omega_4 < \Omega_6$ to maximize intensity all other transitions from $^4F_{3/2}$ (e.g. 1052 nm)
 - Ω_4/Ω_6 (YF₃:Nd) = 0.44 compared with Ω_4/Ω_6 (YAG:Nd) = 0.54
 - calculate theoretical oscillator strength for any $J \rightarrow J'$ transition

$$\text{oscillator strength, } f = \frac{2m\bar{\omega}_o}{3\hbar(2J+1)} \times \sum_{t=2,4,6} \Omega_t \times \left| \left\langle \alpha J \parallel U^{(t)} \parallel \alpha' J' \right\rangle \right|^2$$

where $\left| \left\langle \alpha J \parallel U^{(t)} \parallel \alpha' J' \right\rangle \right|$ is reduced matrix with rank t ,
 α and α' are quantum numbers for J and J' states, respectively
 - determine radiative transition probability, A_{rad} for $J \rightarrow J'$ transition

Quantum Efficiency of YF₃:Nd

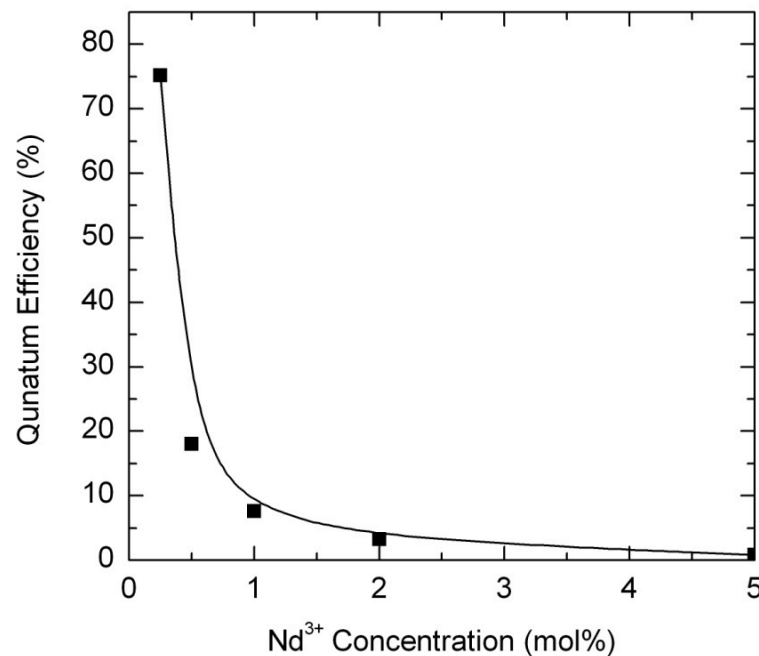
- Quantum efficiency, η : percent photons emitted from desired transition

$$\eta = \frac{\Sigma A_{rad,i}}{\Sigma A_{rad,i} + \Sigma A_{non-rad}} = \frac{\tau_{lum}}{\tau_{rad}} \quad \text{and} \quad \Sigma A_{non-rad} = A_{ET} + A_{MPR} + A_{OH}$$

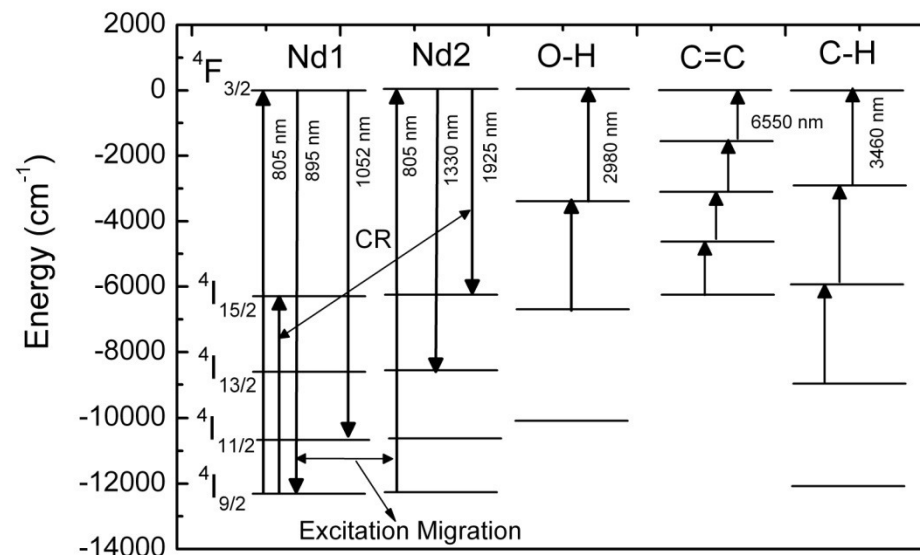
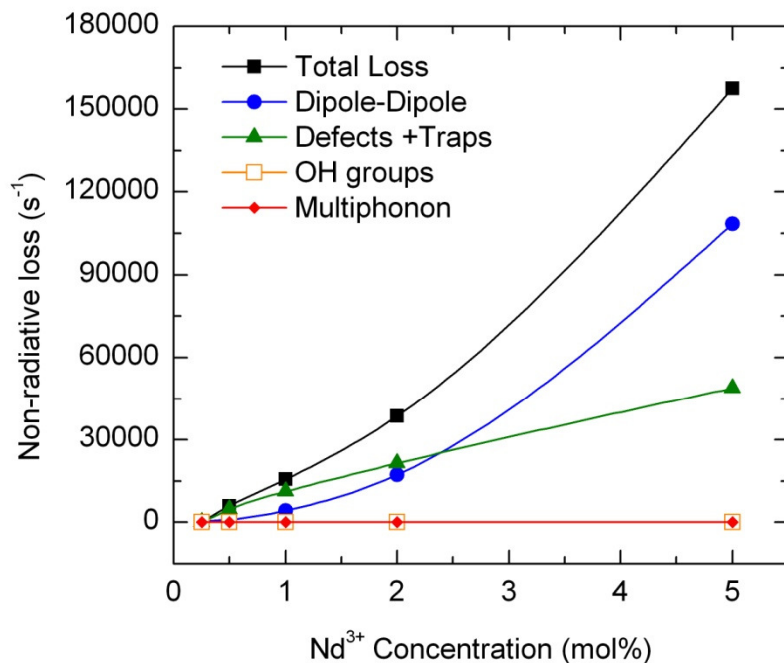
A_{ET} : losses from energy transfer (mainly dipole-dipole, dep. on RE-ion spacing)

A_{MPR} : multiphonon relaxation losses (surface defects, traps)

A_{OH} : losses from -OH quenching



Non-Radiative Losses of $\text{YF}_3:\text{Nd}$

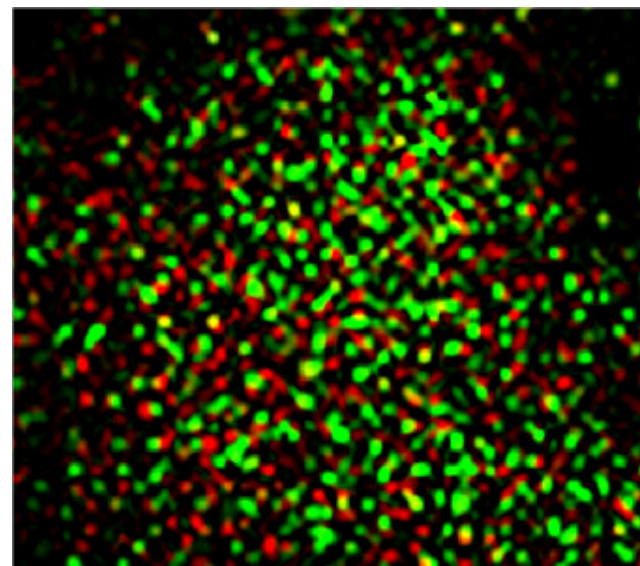
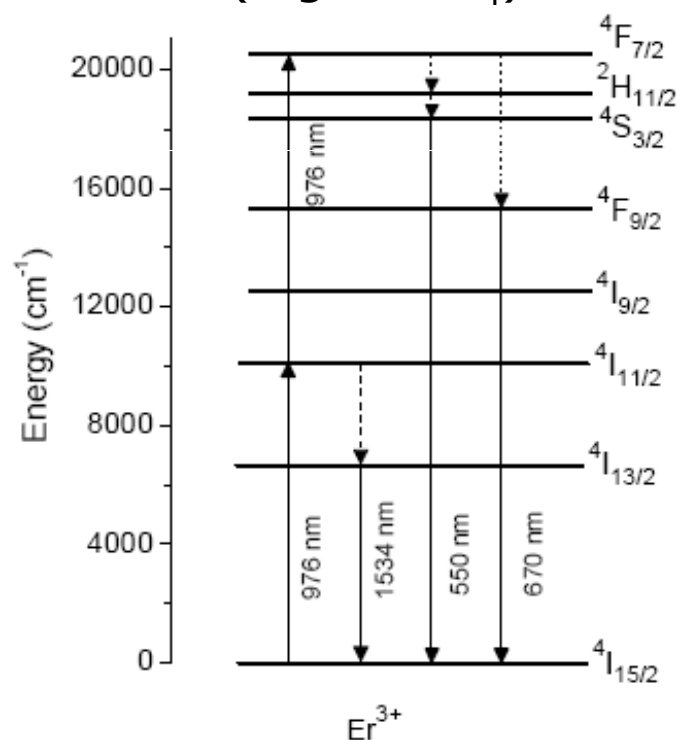


- Dipole-dipole interactions dominate non-radiative losses
- C-H resulted in reduced efficiency of 1052 nm emission
- O-H, C=C and C-H quenchers of 1925 nm emission

Other Losses → Upconversion!

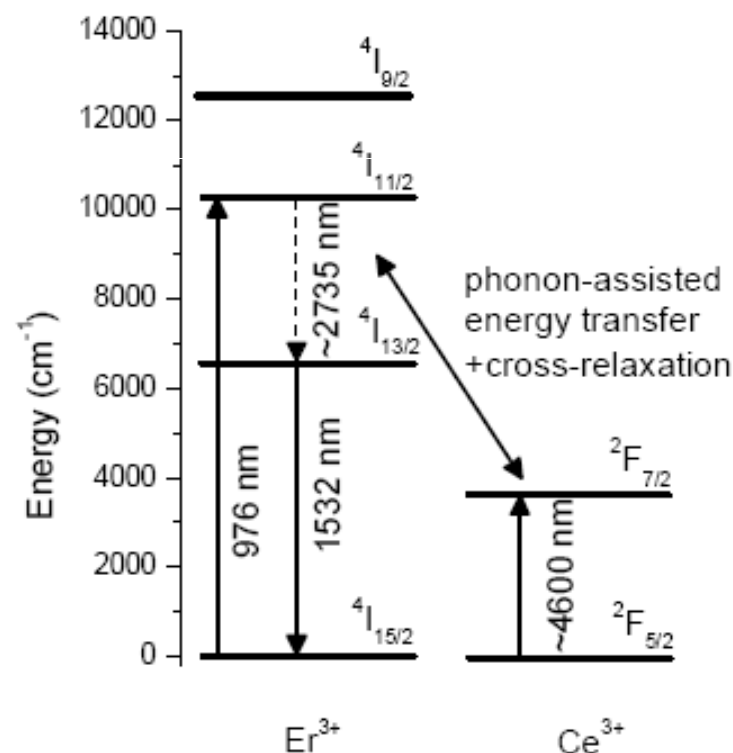
- Despite reducing non-radiative losses, infrared-to-visible upconversion reduces intensity of IR emission

Typical halide hosts
(e.g. NaYF₄)



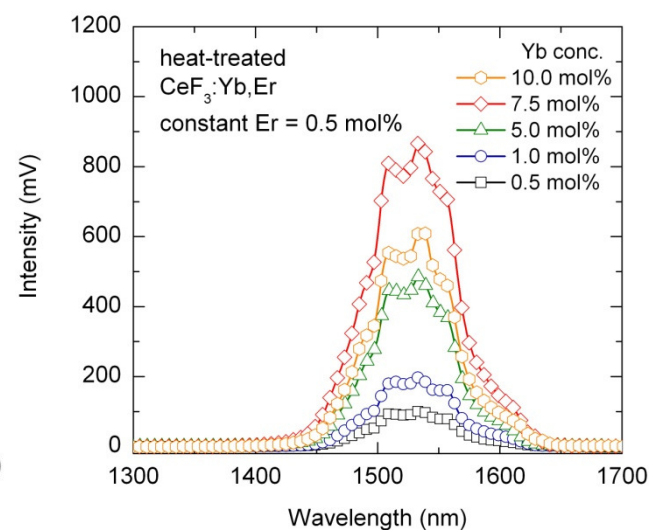
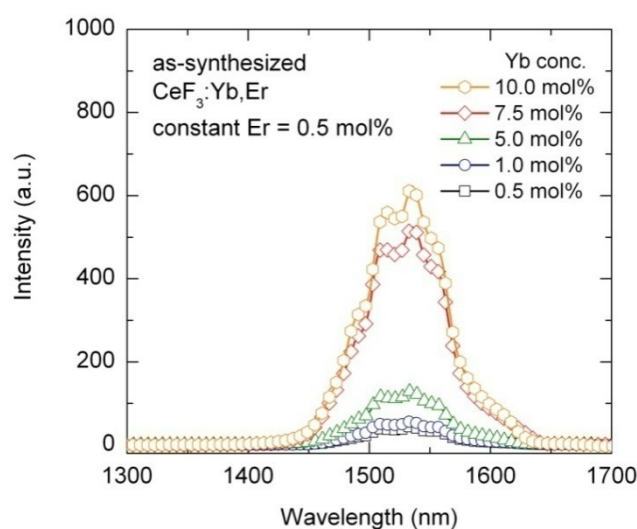
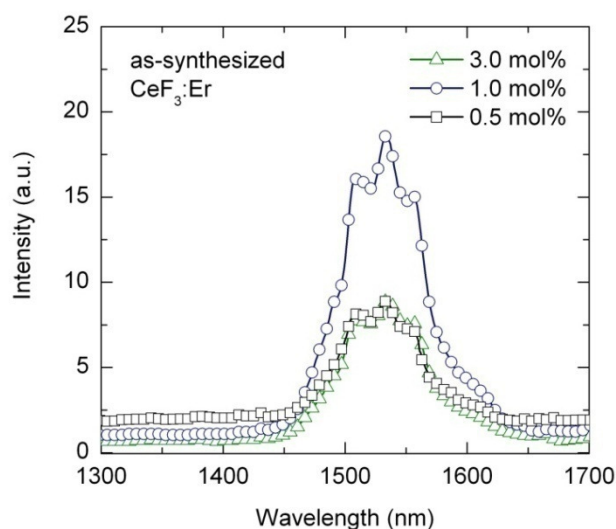
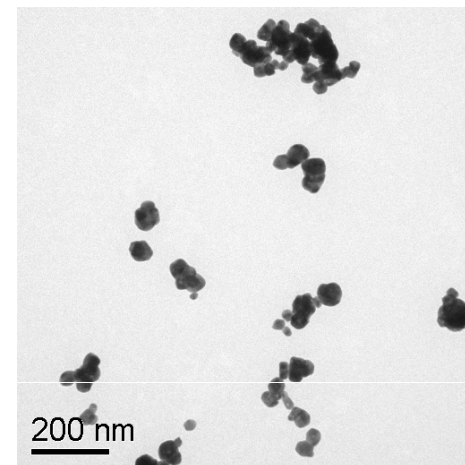
IR Emission Without Upconversion

- Rare earths doped within interactive CeF_3 host enabled intense IR emission without upconversion



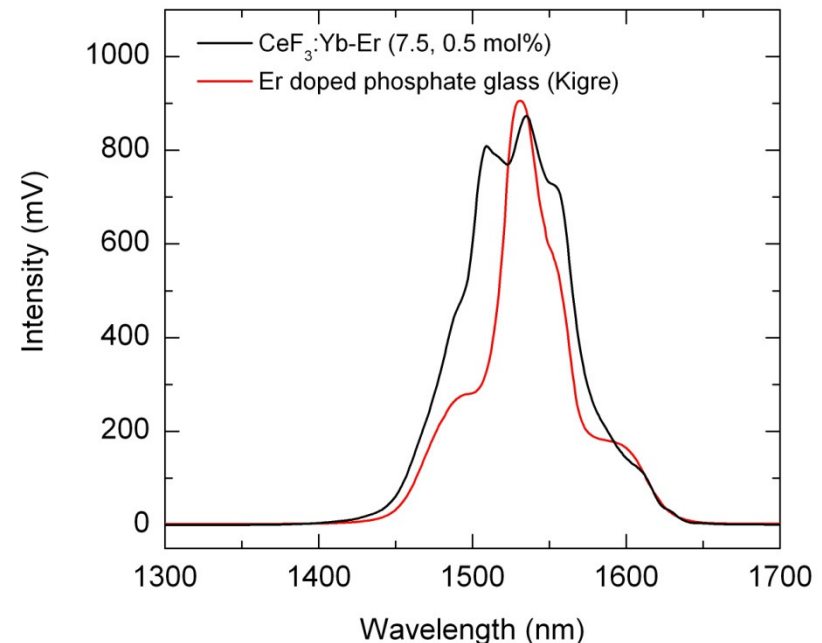
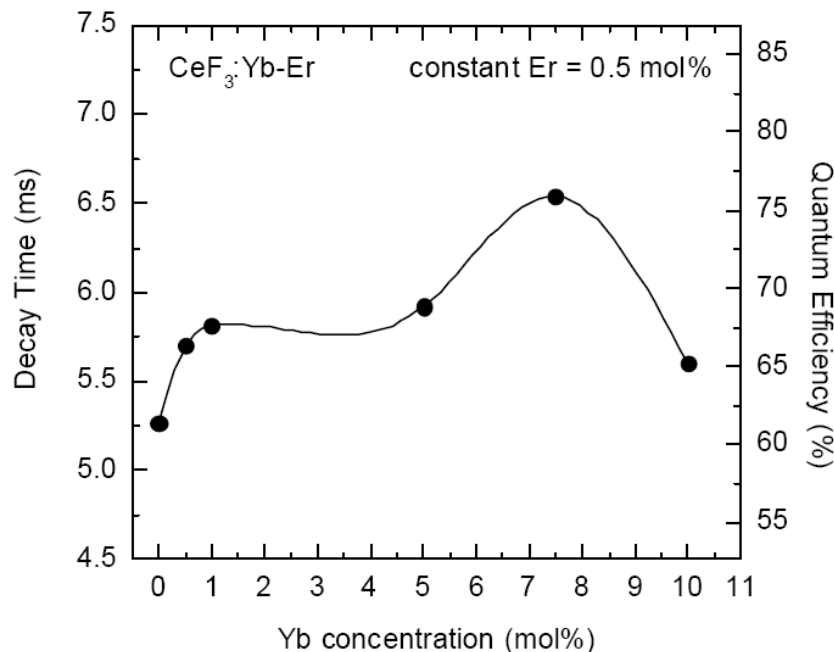
Er & Yb-Er Doped CeF₃ Nanoparticles

- Intense IR emission-no visible emission!
 - 980 nm excitation light source
 - Increased IR branching ratio via phonon-assisted energy transfer to Ce³⁺
 - Yb co-doping increased 980 nm absorption efficiency, resulting in ~25X increase in emission intensity
 - Further increase in emission (~2 times) after heat treatment

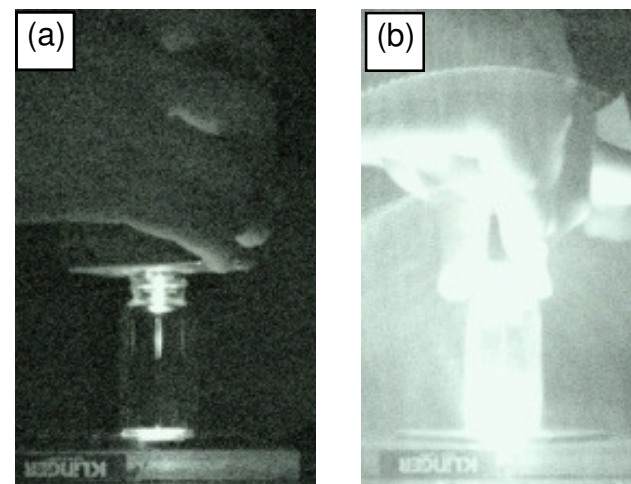
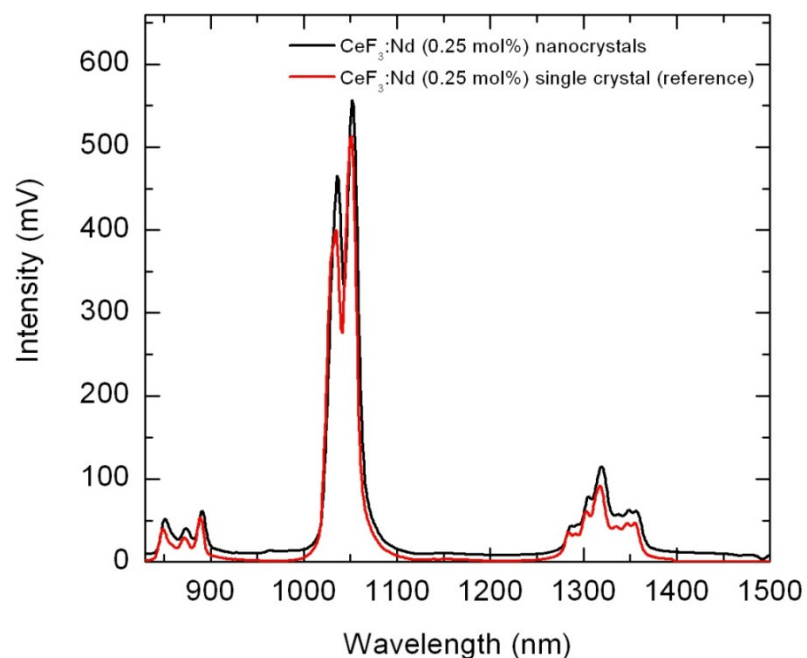


Comparison with Commercial Laser Glass

- Er-doped phosphate laser glass (Kigre Inc., South Carolina)
- Glass up-converts, difficult to make and is very expensive
- Our emission properties match those of the world's best Er-doped glass!
 - $\text{CeF}_3\text{:Yb-Er}$: Max. intensity ~ 870 mV and decay time ~ 6.5 ms
 - Kigre Glass: Max. intensity ~ 900 mV and decay time ~ 8 ms



Nd- and Pr- doped CeF_3 Nanoparticles

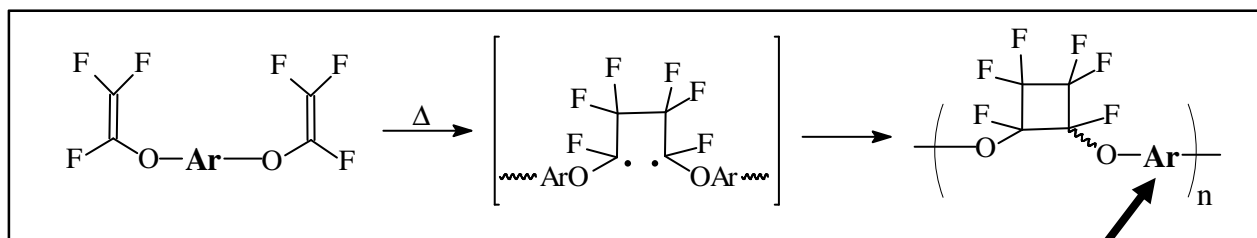


(a) Background (empty vial)
(b) Powder emission using handheld laser

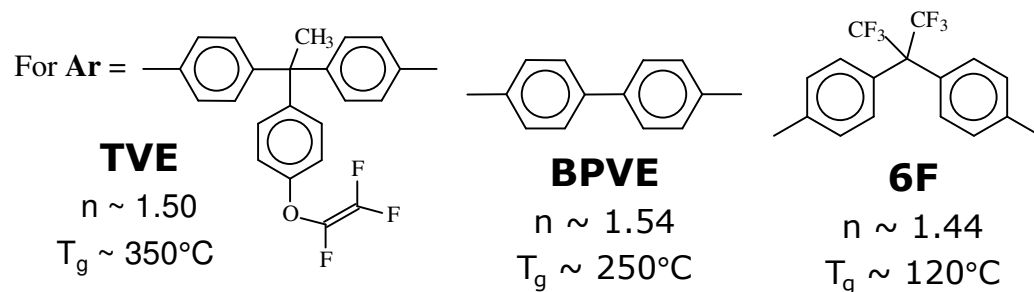
- No visible emissions from upconversion observed
- $\text{CeF}_3:\text{Nd}$ nanoparticles as bright as its standard bulk single crystal
- Emission from $\text{CeF}_3:\text{Pr}$ nanoparticles easily captured using commercial night vision camera

Polymers Selection

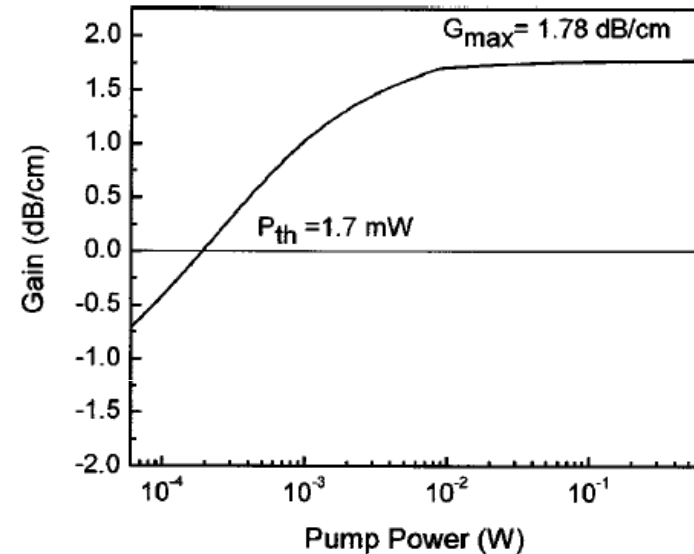
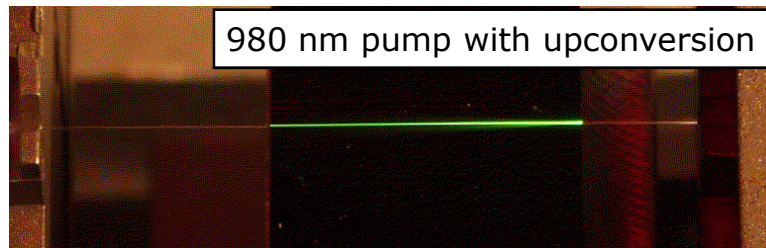
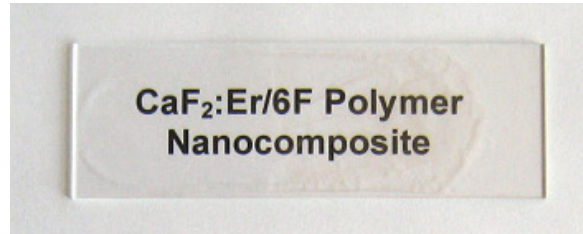
- Replace –CH and –OH groups to prevent quenching
- Suitable candidates:
 - Fluoracrylates (Allied Chemical), Teflon AF (Dupont), Ultradel (Amoco), CYTOP (Asahi Chemical), PFCB (Tetramer Technologies, Inc.)
- Most are costly and difficult to process (e.g. Teflon AF)
- Selecting PFCB



Perfluorocyclobutyl (PFCB) ring



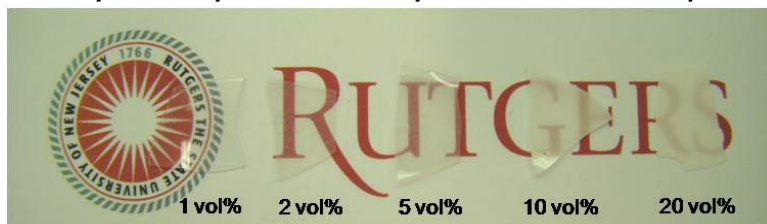
CaF₂:Er Fluoropolymer Nanocomposites



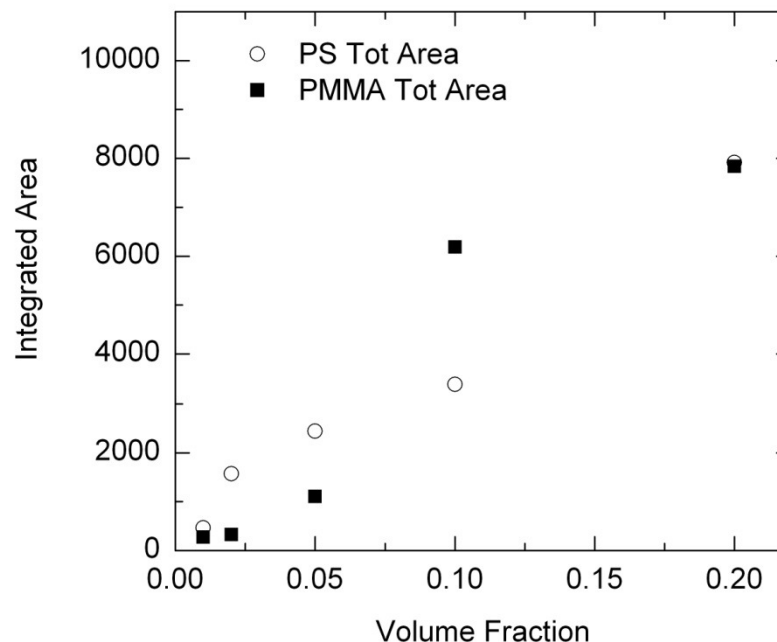
- Transparent CaF₂:Er/6F fluoropolymer composites showed IR emission together with visible upconversion
- Predicted maximum gain of 1.78 dB/cm
- Potential applications as waveguides and optical amplifiers

Transparent IR-emitting Nanocomposites

Polymethyl methacrylate nanocomposites

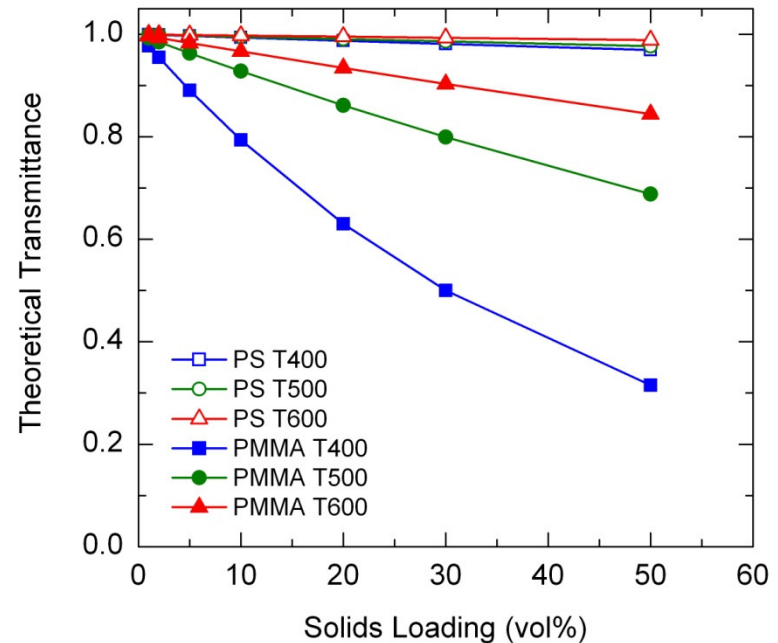
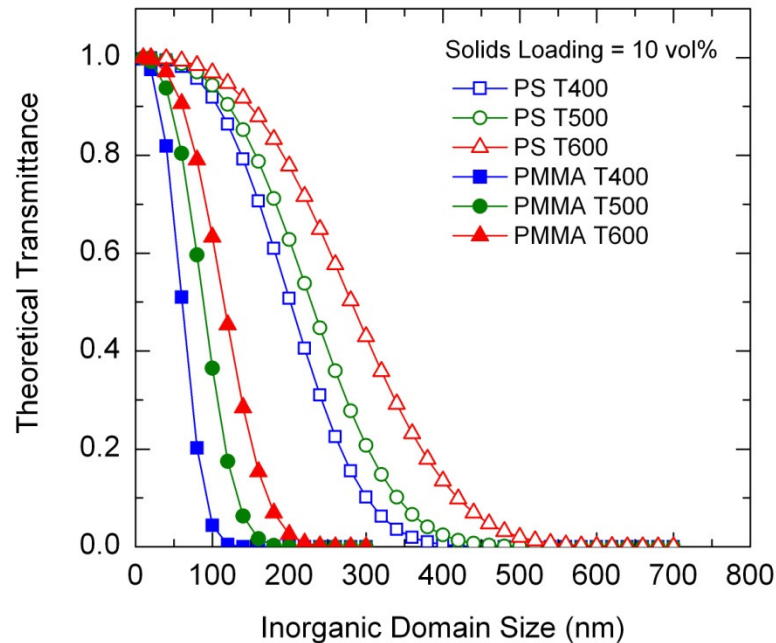


Polystyrene nanocomposites



- Used low cost commodity polymers
 - Polymethyl methacrylate (PMMA) and Polystyrene (PS)
- Obtained transparent composites of rare-earth doped CeF_3 nanoparticles with high solid loading

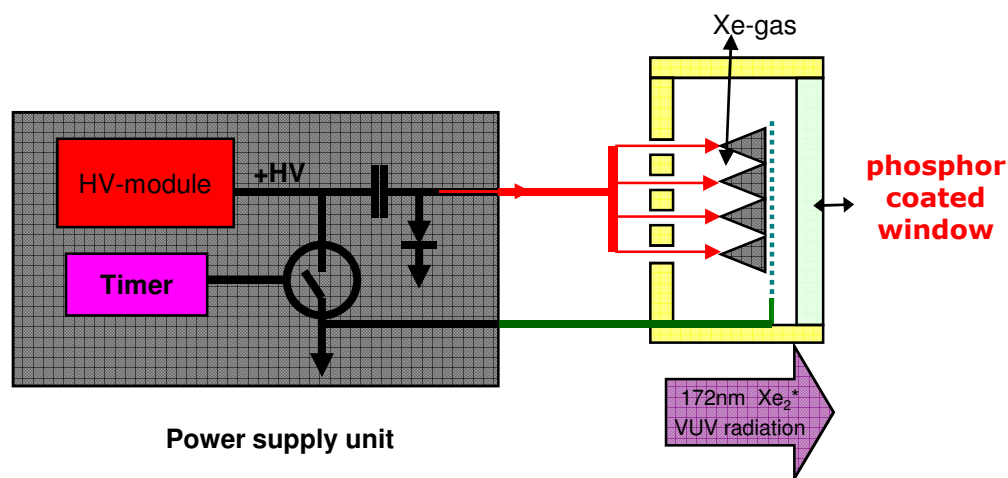
Index Matching!



- At 1.5 μm , $n_{\text{PS}} \sim 1.57$, $n_{\text{PMMA}} \sim 1.48$; $n_{\text{part}} \sim 1.60$
 - Δn (Particle:PMMA) ~ 0.12 ; Δn (Particle:PS) ~ 0.03
- Index matching allows more tolerance to dispersion quality (agglomerates, solid loading)

Phosphors for Efficient Hg-free Lighting

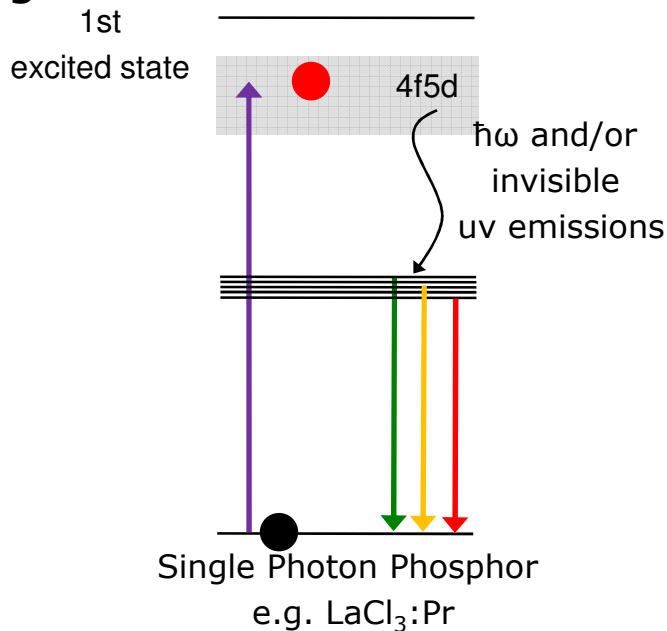
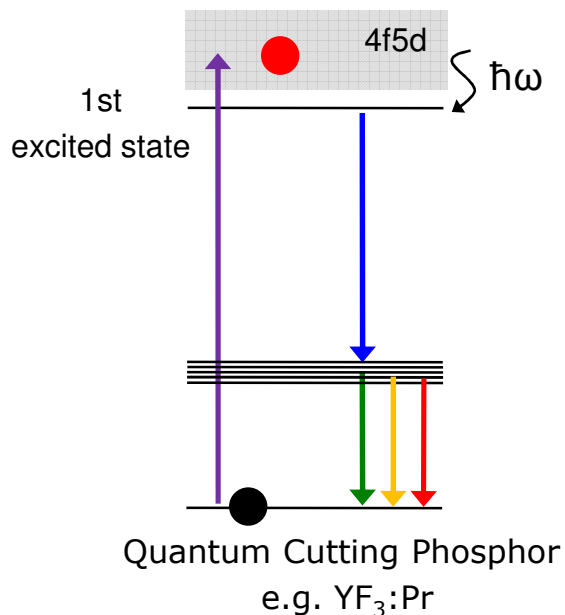
- Xe₂ excimer source (emission at 172 nm) and quantum cutting downconversion rare-earth halides
- Potential quantum efficiency at 200% with ~30% output
- Limitations to overcome:
 - light output (lumens/W) of Xe₂ lamps lower than Hg lamps
 - quantum cutting phosphor with high energy efficiency for VUV conversion by minimizing large losses by nonradiative relaxation



Schematic Courtesy of UV Solutions

Quantum Cutting Phosphors

- Emits >1 photons for each absorbed photon
- Max. potential quantum efficiency $>100\%$
- Basic requirements
 - Energy band gap of the material $E_g > 7\text{eV}$
 - First excited state should lie below the $4f5d$ state
 - Low non-radiative loss which reduces the emission intensity
 - Strong absorption at the exciting radiation



Green Quantum Cutting Phosphor

