Luminescent Nanoparticles of Metal Oxides

Yuanbing Mao, Ph.D.

Multifunctional Applications of Oxides (MAO) Laboratory
Department of Chemistry
Illinois Institute of Technology

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Building College-University Partnerships for Nanotechnology

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Assistant Professor
Penn State University
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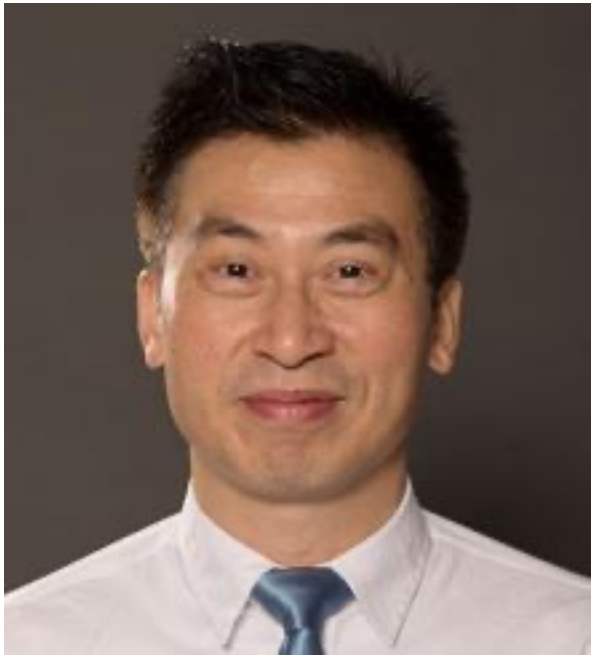
Introductions

Presenter



Yuanbing Mao, PhD
Professor and Chair
Department of Chemistry
Illinois Tech

ILLINOIS INSTITUTE OF TECHNOLOGY

Acknowledgements (2010 – present)

Visiting Scholars:
Dr. H Liu
Dr. W. Luo
Dr. L. Mao
Dr. L. Yi
Dr. L. Tian

Postdoctoral Fellows:
Dr. J. Ahmed
Dr. S. Gupta (Fulbright)
Dr. M. Pokhrel
Dr. B. Srivastava
Dr. Y. Tian
Dr. J. Zhao

Graduate Students:
Mr. S. Alaparthi (WV State U)
Ms. P. Kukkapalli (Guardian Drug Co.)
Mr. Q. Li (TAMU → Purdue U)
Ms. W. Lin (Iowa State U)
Ms. X. Sun (TAMU → Purdue U)
Ms. Christina Figueroa (UTRGV)
Mr. M. Hakim Marjuban (UTRGV)
Mr. O. Oriretan (UTRGV)
Ms. M. Penilla (UTRGV)
Mr. J. Zuniga (Moltex Energy, Canada)
Ms. F. Jahanbazi (Current)
Mr. T. Abeywickrama (Current)

Undergraduates (> 60):
Mr. A. Altecor (Rice U → DuPont)
Mr. A. Arguelles (TAMU)
Ms. J. Bravo (Iowa State U)
Ms. Y. Cantu (Texas State U)
Mr. H. Chirino (UTRGV)
Ms. D. Concha (Baylor C)
Mr. K. Diab (UT Medical School)
Ms. E. Garcia (Great Mills Co.)
Ms. B. Gonzalez (UTRGV)
Ms. A. Lopez (UTRGV)
Ms. Q. Lu (Sharyland ISD)
Mr. L. Lu (UTRGV)
Ms. D. Owens (McAllen ISD)
Ms. M. Palacios (UT Medical School)
Mr. J. Shaikh (Medical School)
Ms. M. Valdez (UTRGV)
Mr. E. Villarreal (Rice U, NSF GF)
Mr. K. Wahid (UT Medical School)
etc.

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High School Interns (> 18):
P. Aguirre (UTRGV), A. Flores, M. Gorena, S. Maldonado, A. Ramos, A. Rocha, M. Trejo, H. De Santiago (UTRGV), M. Valdez (UTRGV), C. Waters (TAMU), etc.

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Collaborators:

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Dr. B. Guiton (UKentucky)
Dr. E. Kelley (NIST)
Dr. K. Lozano (UTRGV)
Dr. K. Martirosyan (UTRGV)
Dr. J. Neuefeind (ORNL)
Dr. A. Puretzky (ORNL)
Dr. L. Sun (UConn)
Dr. M. Therien (Duke U)
Dr. D. Wall (WSU)

$$:

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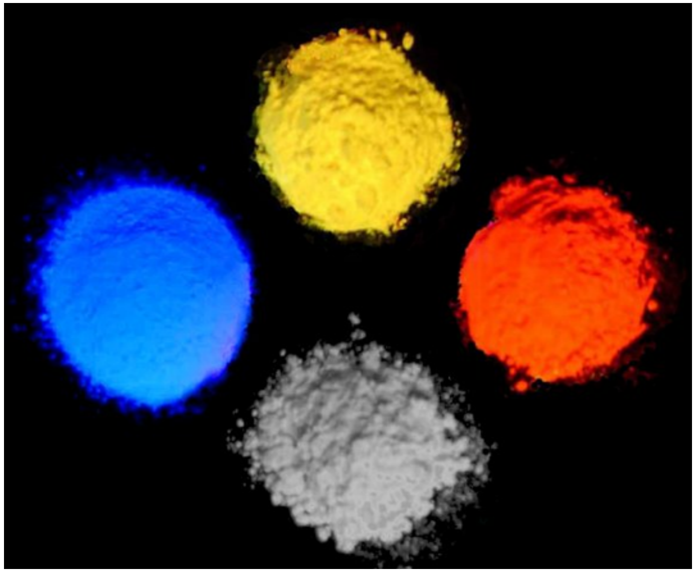
Bill & Melinda Gates foundation

Outline

- Intro
- PL and RL
- PerL
- UC
- Summary

Metal Oxides

Chemical compounds containing at least one oxygen atom as well as at least one metallic element.



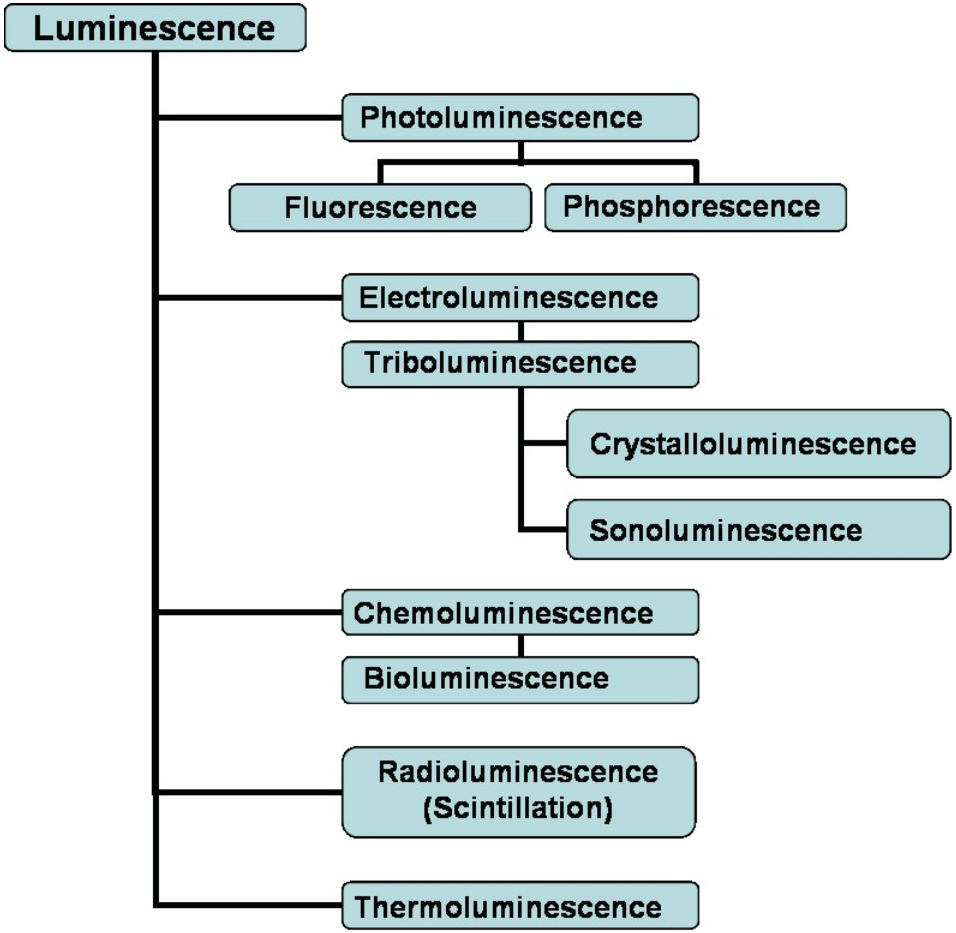
https://www.sigmaaldrich.com/materials-science/material-science-products.html?TablePage=112202335

Luminescence

A light emission which represents an excess over the thermal radiation and lasts for a time exceeding the period of electromagnetic oscillation.

A form of cold-body radiation *vs.* incandescent light.

Loses correlation between phases of absorbed and emitted light *vs.* reflected and stray light.

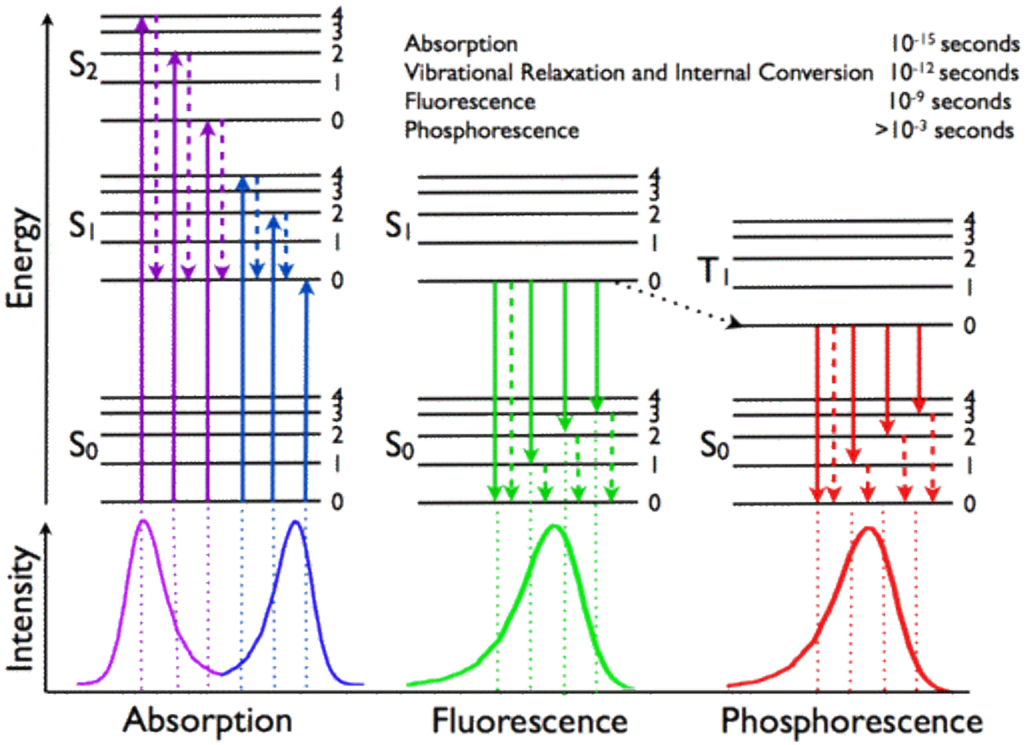


https://www.phenix.bnl.gov/phenix/WWW/publish/barish/publish/wasiko/Copy/Solar/Luminescence%20and%20Fluorescence%20Spectroscopy.htm

Brief history:

- ✓ 'Afterglow' traced back to ~1000 years
- ✓ First observed fluorescence from quinine by Sir J.F.W. Herschel in 1845
- ✓ G.G. Stokes coined the term 'fluorescence' in 1853
- ✓ E. Wiedemann used the term 'luminescence' in 1888
- ✓ Basic principles of fluorescence were mostly developed during the 1020's and 1930's:
  - Excited state lifetime (Gaviola)
  - Quantum yield (Wavilov)
  - Polarization of fluorescence (Weigert, F. Perrin)
  - Jablonski diagram (A. Jablonski)
- ✓ Fluorescence resonance energy transfer by T. Förster in the 1950's
- ✓ Upconversion by F. Auzel in the 1960's

Luminescence



Jablonski diagram and spectra showing the fundamental photophysical processes in organic molecules:

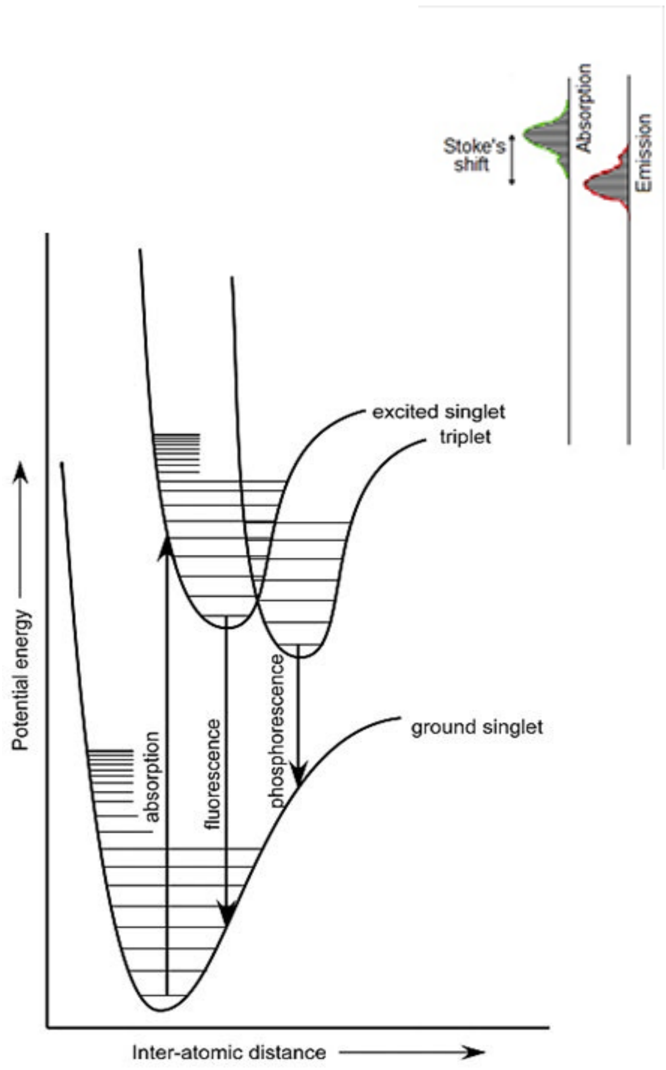
Absorption of a photon: $S_0 \rightarrow S_1, S_2$

Internal conversion: $S_2 \rightarrow S_1$ (non-radiative)

Fluorescence: $S_1 \rightarrow S_0$

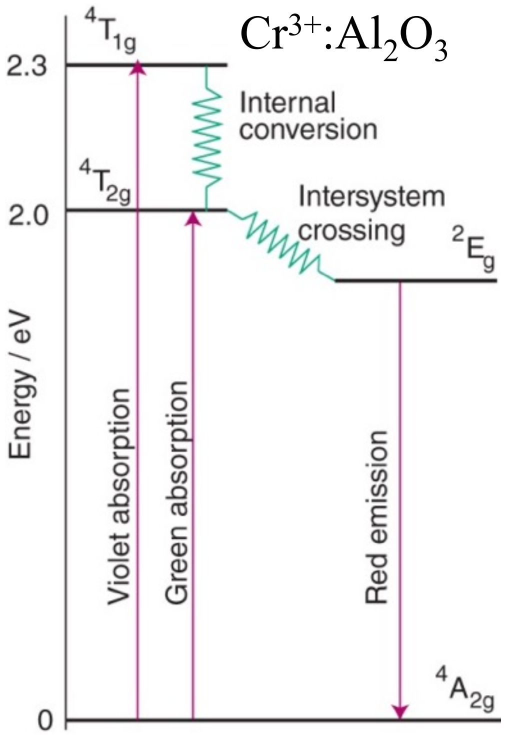
Intersystem crossing: $S_1 \rightarrow T_1$

Phosphorescence: $T_1 \rightarrow S_0$



https://www.lambertinstruments.com/technologies-1/2014/12/4/frequency-domain-flim-basic-equations

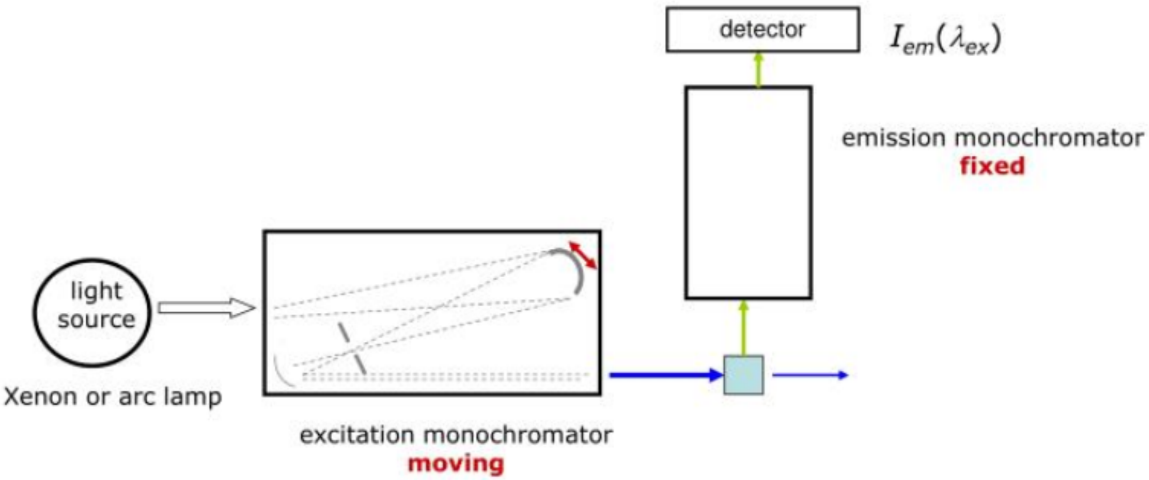
Luminescence

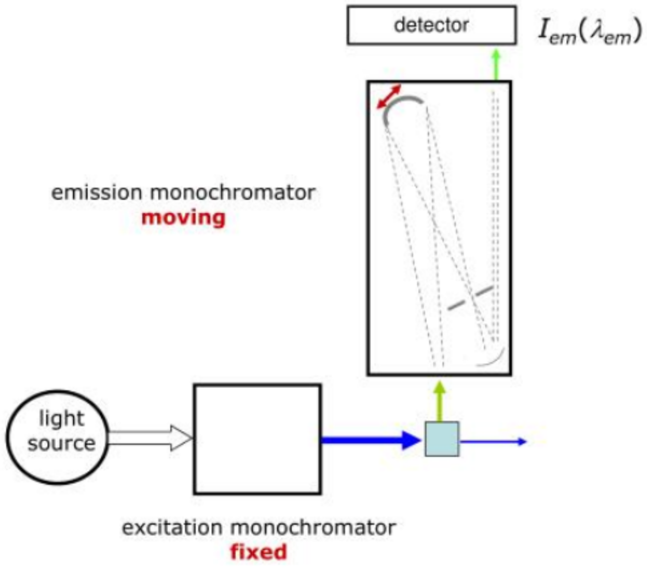


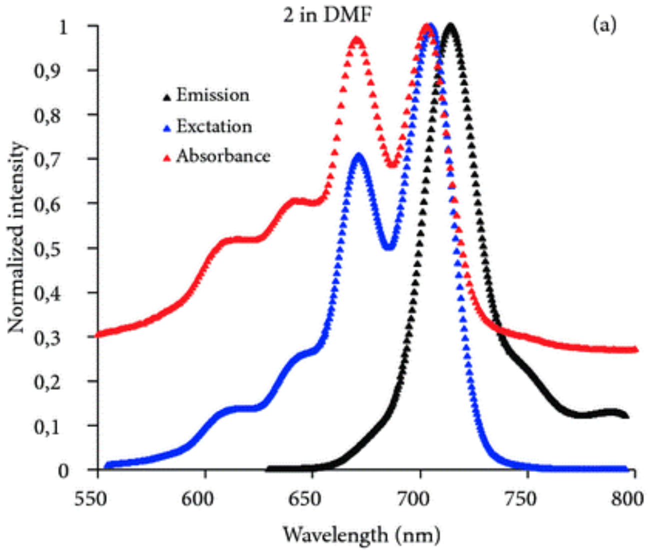
Luminescence Characterization:

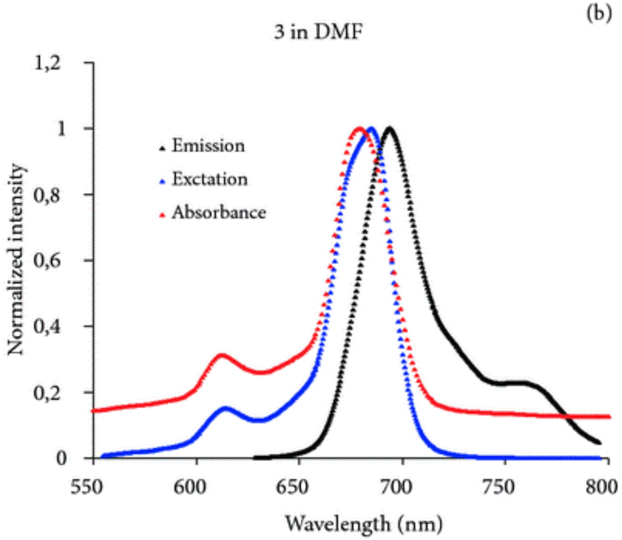
- ❑ Excitation spectroscopy
- ❑ Emission spectroscopy
- ❑ Quantum yield
- ❑ Lifetime
- ❑ ……

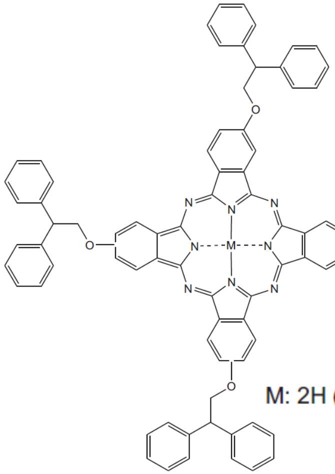
Excitation and Emission Spectra







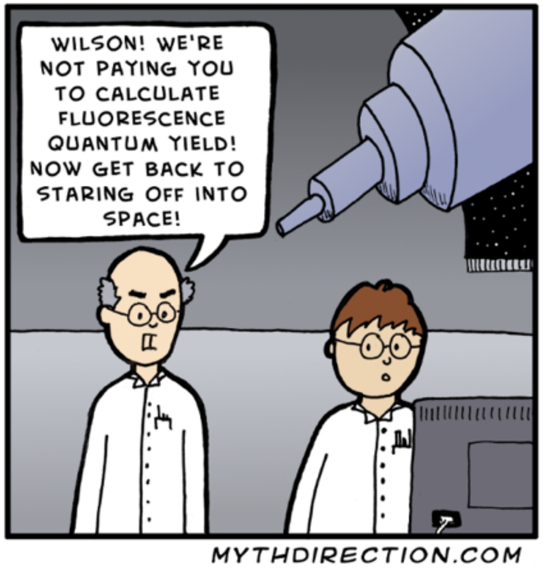


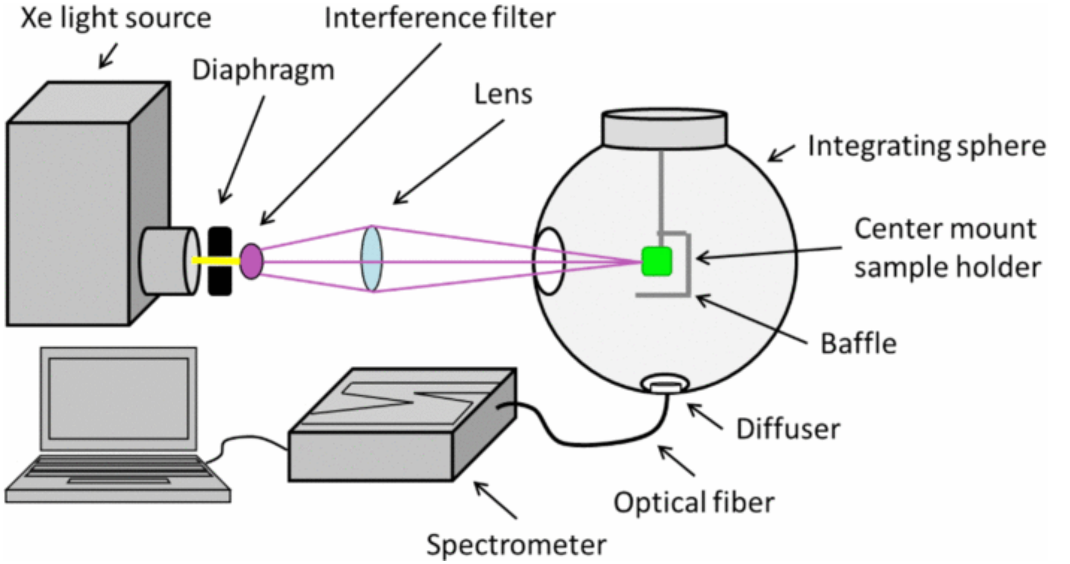


M: 2H (**2**), Zn(II) (**3**)

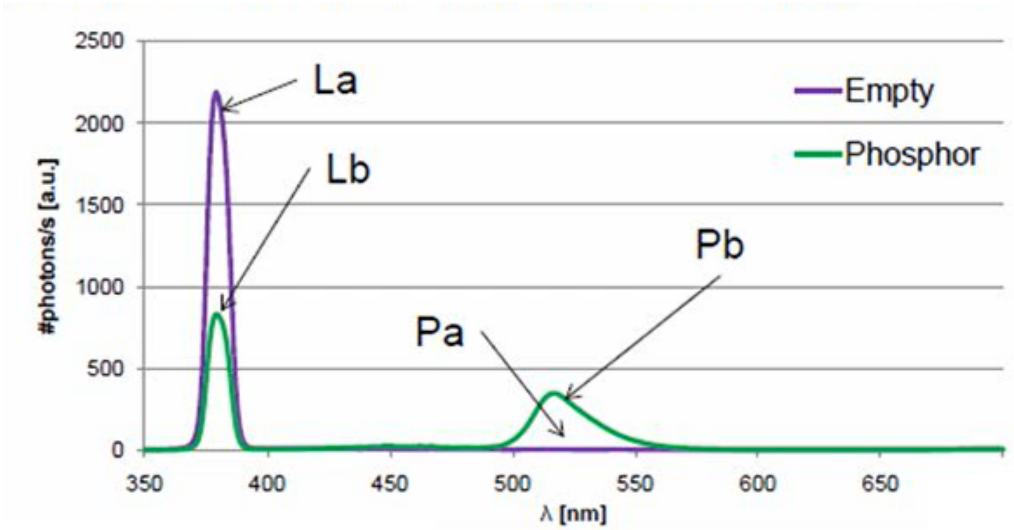
Turk. J. Chem. 38(6):1083-1093 (2014).

Luminescence Quantum Yield





Review of Scientific Instruments 85, 123115 (2014)



$$QE = \frac{\#\ \text{emitted photons}}{\#\ \text{absorbed photons}}$$

$$= \frac{Pb - Pa}{La - Lb}$$

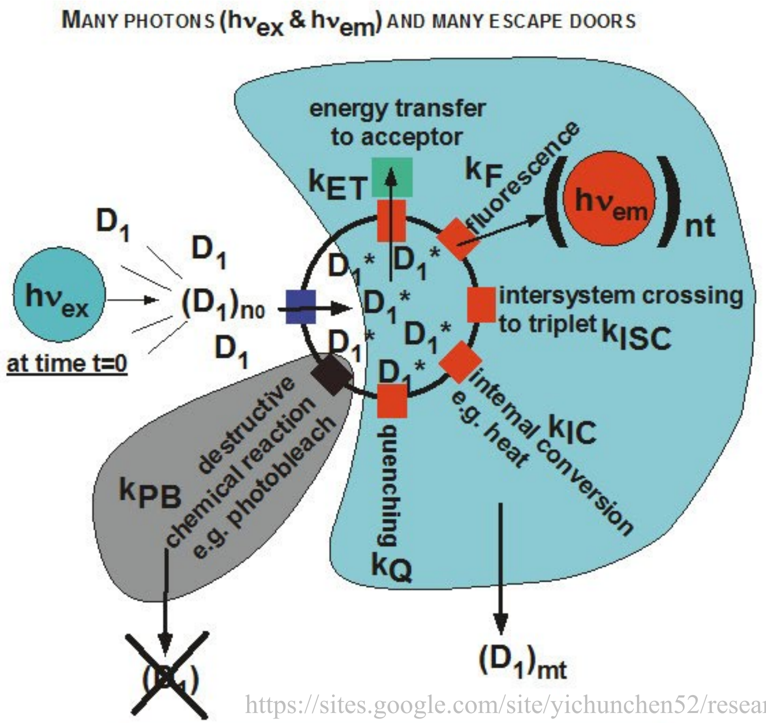
L_a: total # of incident photons

L_b: total # of photons not absorbed by the phosphor

P_a: dark signal in the emission wavelength area

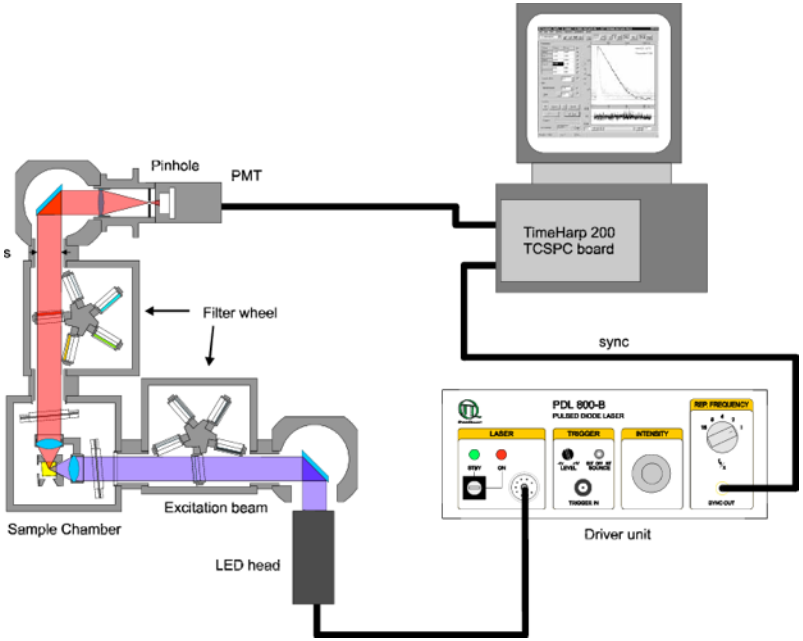
P_b: total # of photons emitted in emission wavelength area

Luminescence Lifetime

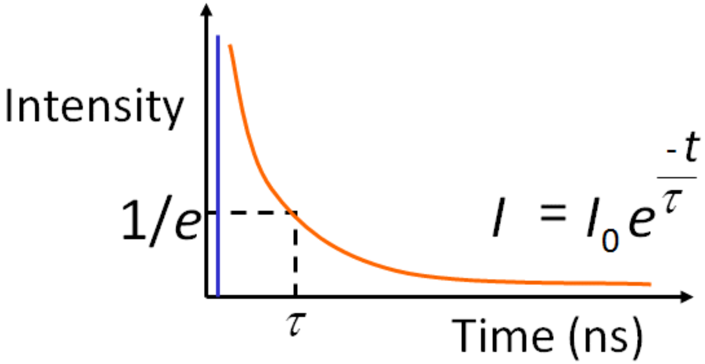


https://sites.google.com/site/yichunchen52/research

lifetime of the excited state:
$1/\tau = k_T + k_F + k_{ISC} + k_{IC} + k_Q + k_{PB} = \sum_j k_j$

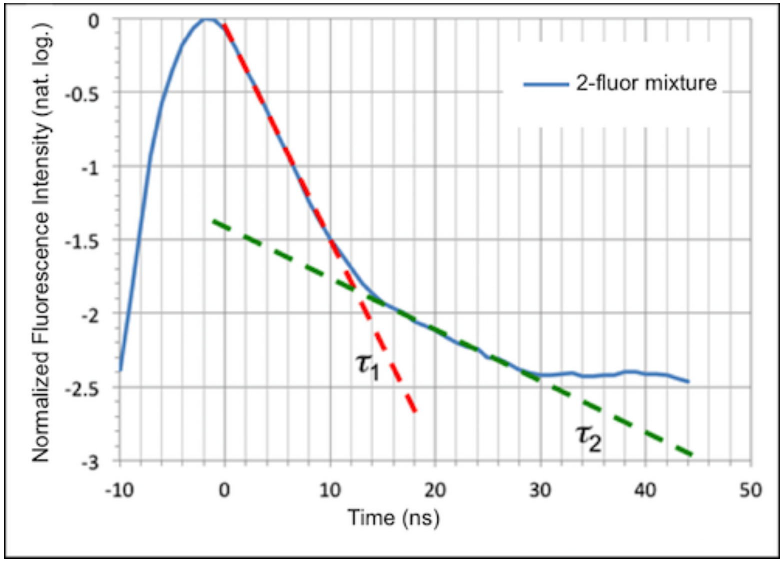


Proceedings of SPIE, 4648, April 2002. DOI: 10.1117/12.462651



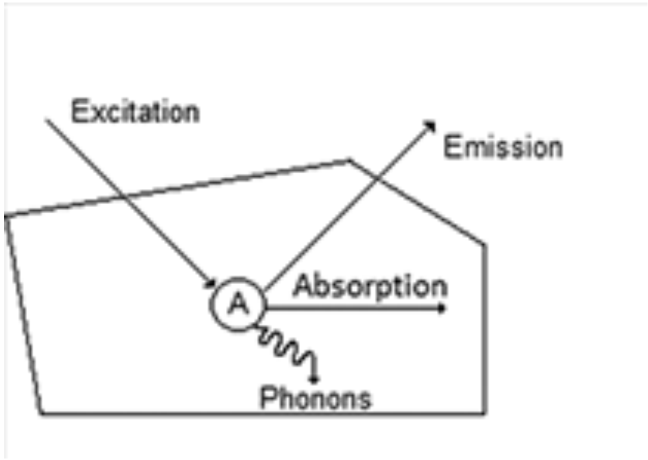
$I = I_0 e^{\frac{-t}{\tau}}$

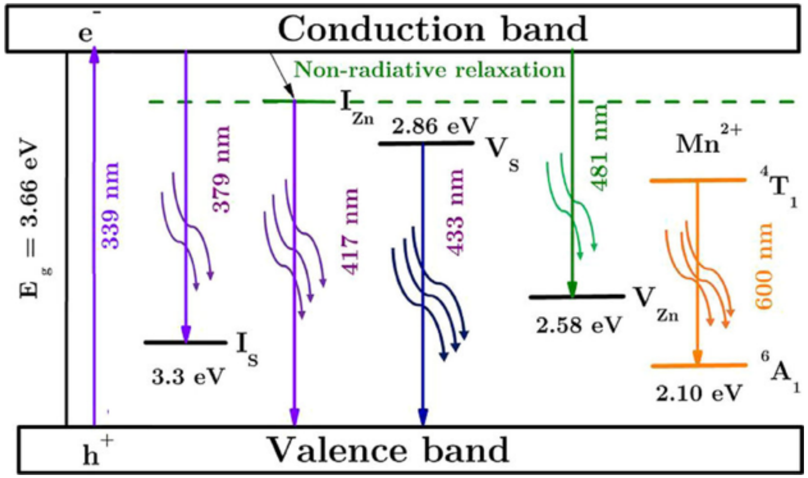
https://www.lambertinstruments.com/technologies-1/2014/12/4/fluorescence-lifetime-imaging-microscopy



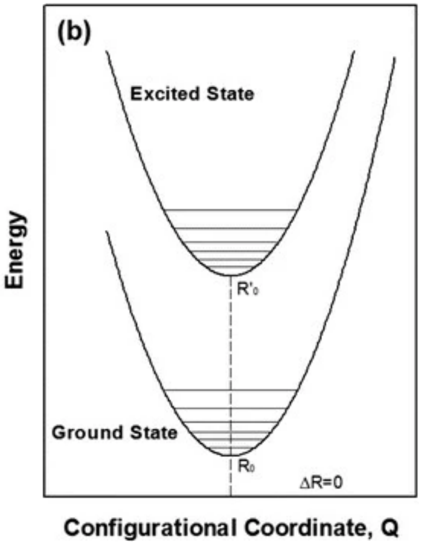
https://www.kineticriver.com/danube/

Luminescing Materials





Optik, 2018, 153, 31-42



Tian, J Solid State Lighting, 2014, 1, 11

Objectives:

- To search new host materials
- To develop nanoscopic light emitters
- To explore strategies to enhance luminescence
- To understand structured-related mechanisms

Luminescing Nanoparticles

In general and potentially:

High quantum efficiencies, sharp emission peaks, high photostability, emission wavelength tunability, and may emit light when irradiated by ionizing radiation

Bioimaging:

Organic dyes: suffer from photobleaching and broad emission

Quantum dots: exhibit toxicity

Lanthanide-doped NPs:

(1) wide excitation range: UV to NIR
(2) broad emission wavelengths
(3) enhanced photostability
(4) large Stoke's shift
(5) increased lifetimes (milliseconds)
(6) upconversion emission, and
(7) high water dispersibility, biocompatibility, stealthy nature and preferably targeting ability

minimizes the autofluorescence and scattering of light

due to parity forbidden transitions occurring within 4f shell shielded by 5s and 5p orbitals,

Outline

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- **PL and RL**
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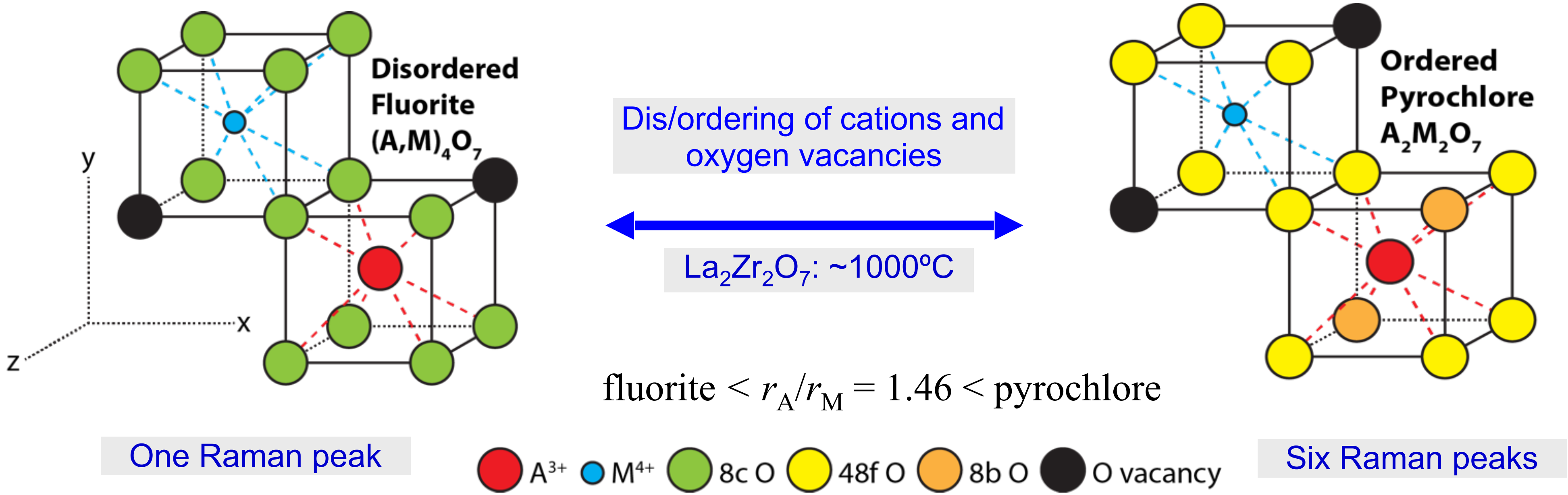
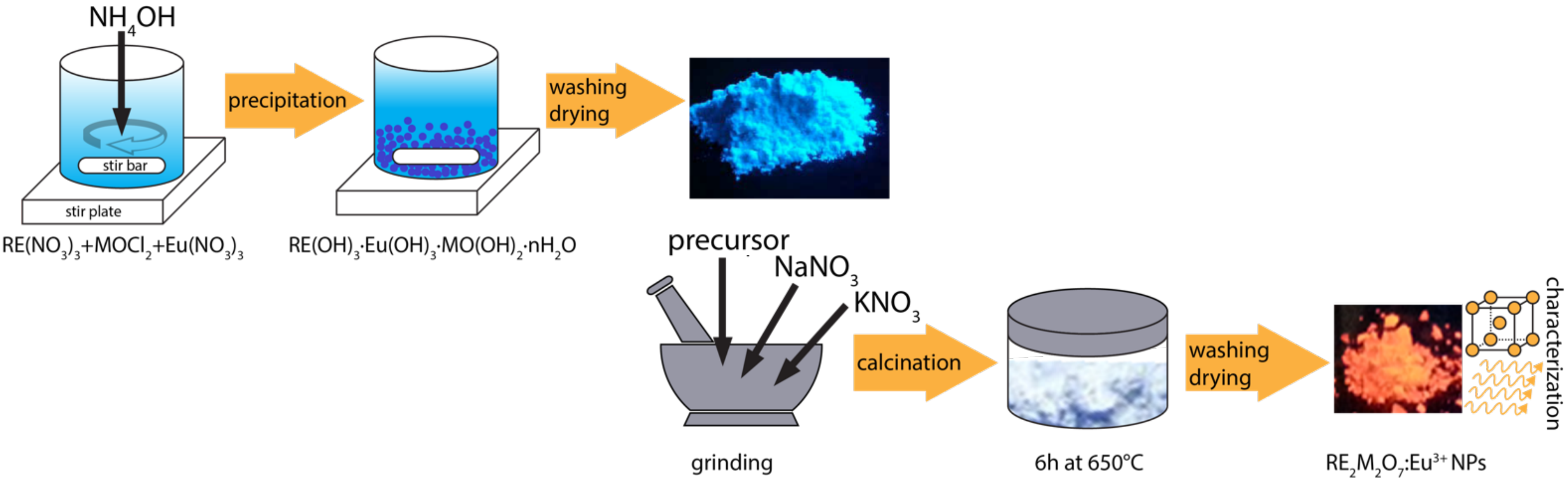
$A^{III}_2M^{IV}_2O_7$ Compounds



- ➢ Refractory with *m.p.* > 2500ºC
- ➢ Challenge to synthesize, especially @ nanodomain
- ➢ To make metastable phase if synthesis temp. is lower than phase transition temp.

Molten Salt Synthesis of $A_2M_2O_7$ NPs

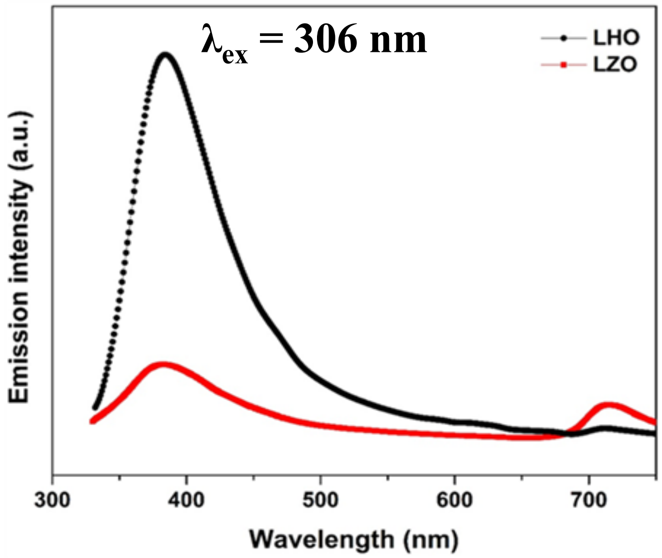


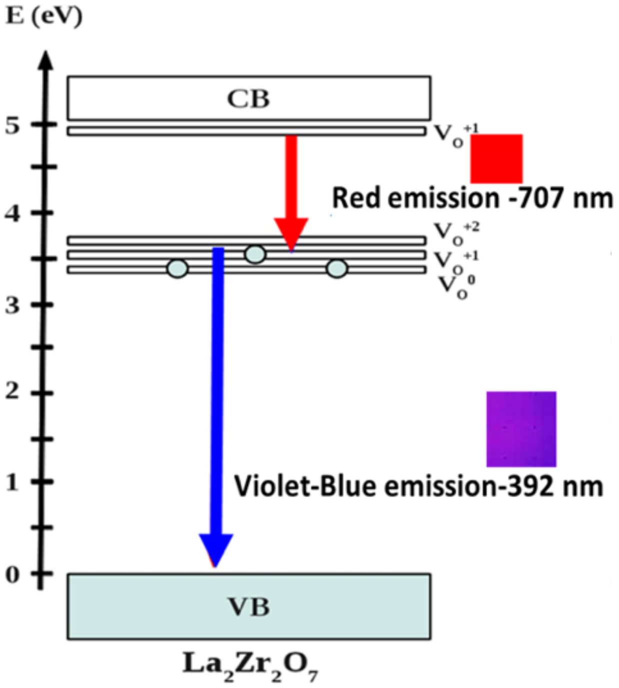
Benefits of the MSS Process

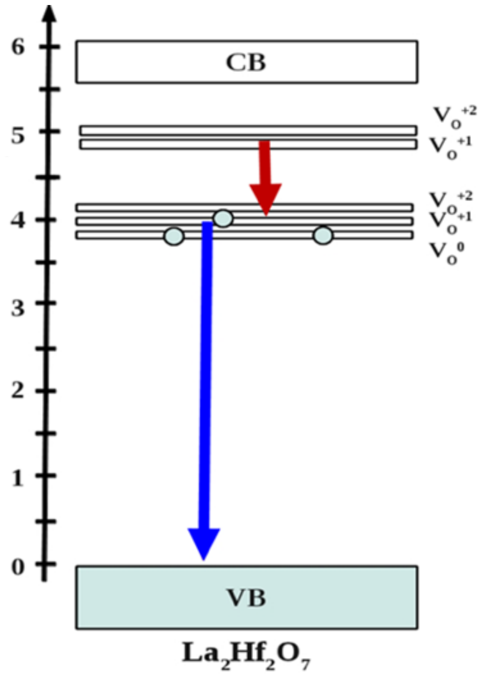
- Lower temp. + evener distribution: Solid-state synthesis *vs.* MSS
- Soft aggregates: sol-gel method *vs.* MSS
- Particle size reduction: flux method *vs.* MSS
- No milling or surface dead layer

Yuanbing Mao, Xia Guo, Jian Y. Huang, Kang L. Wang, and Jane P. Chang, Luminescent nanocrystals with $A_2B_2O_7$ composition synthesized by kinetically modified molten salt synthesis, Journal of Physical Chemistry C, 2009, 113(4), 1204-1208.

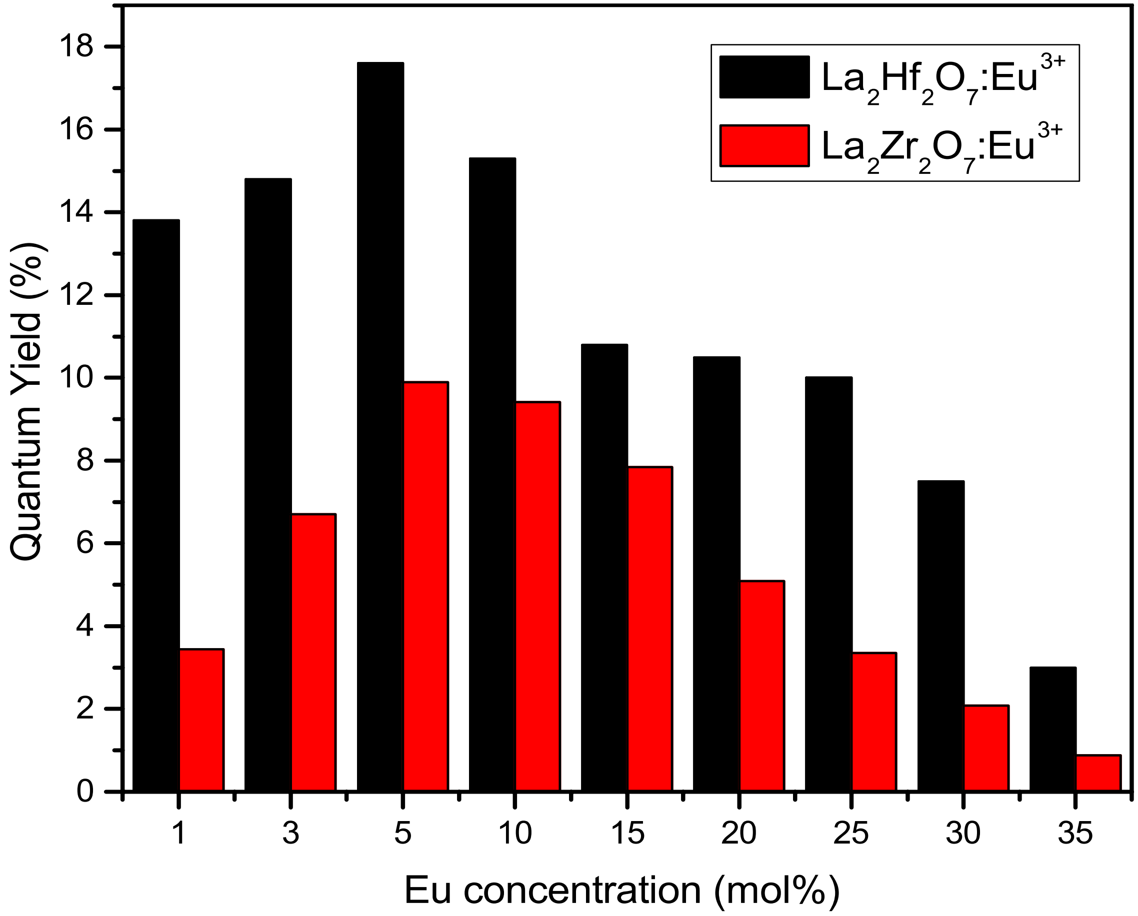
Cationic Variation: $La_2Zr_2O_7$ *vs* $La_2Hf_2O_7$ NPs







Cationic Variation: $Eu^{3+}:La_2Zr_2O_7$ *vs* $Eu^{3+}:La_2Hf_2O_7$



- ➢ PL: peak at ~5% Eu^{3+}.
- ➢ QY: $La_2Hf_2O_7 > La_2Zr_2O_7$.

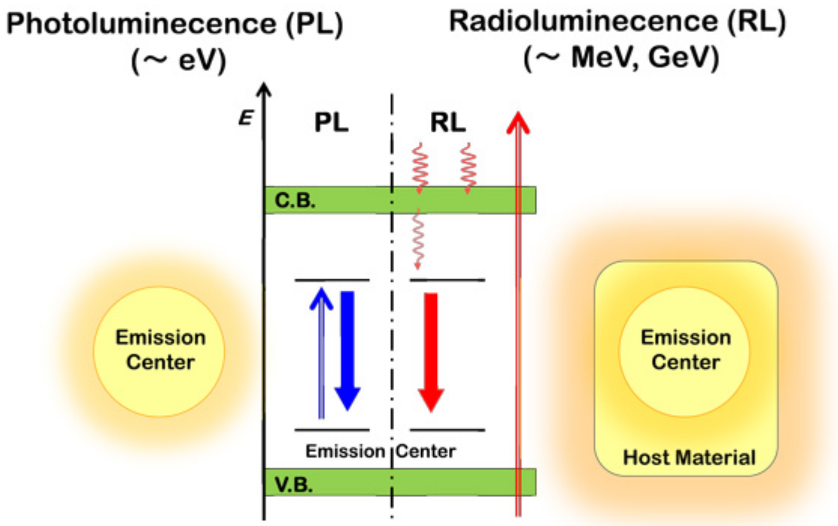
CN	6
^{40}Zr: $[Kr]4d^25s^2$	0.72
^{72}Hf: $[Xe]4f^{14}5d^26s^2$	0.71

Change of M^{4+} cations in ionic $A_2M_2O_7$ compounds:

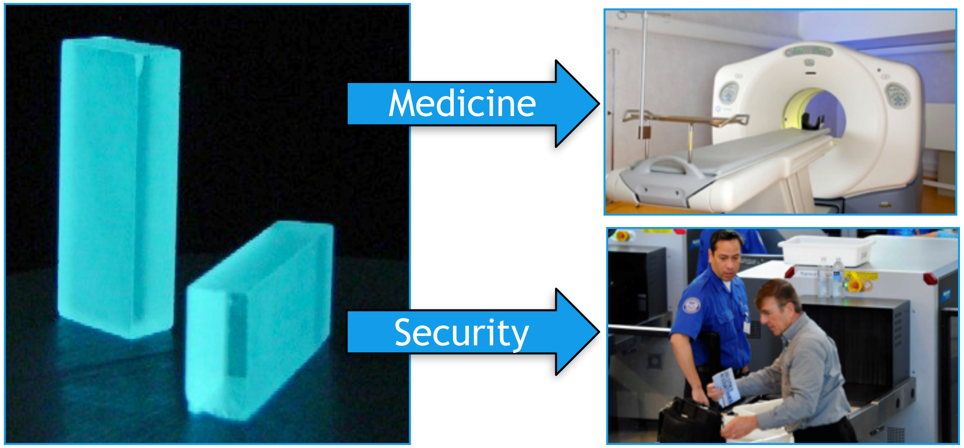
→ Affects crystal field splitting (CFS) of Eu^{3+} ions
→ Changes the charge cloud of Eu^{3+} ions
→ Varies QY

Kareen Wahid, Madhab Pokhrel, and Yuanbing Mao, Structural, Photoluminescence and Radioluminescence Properties of Eu^{3+} Doped $La_2Hf_2O_7$ Nanoparticles, Journal of Solid State Chemistry, 2017, 245, 89-97.

Photoluminescence *vs.* Radioluminescence

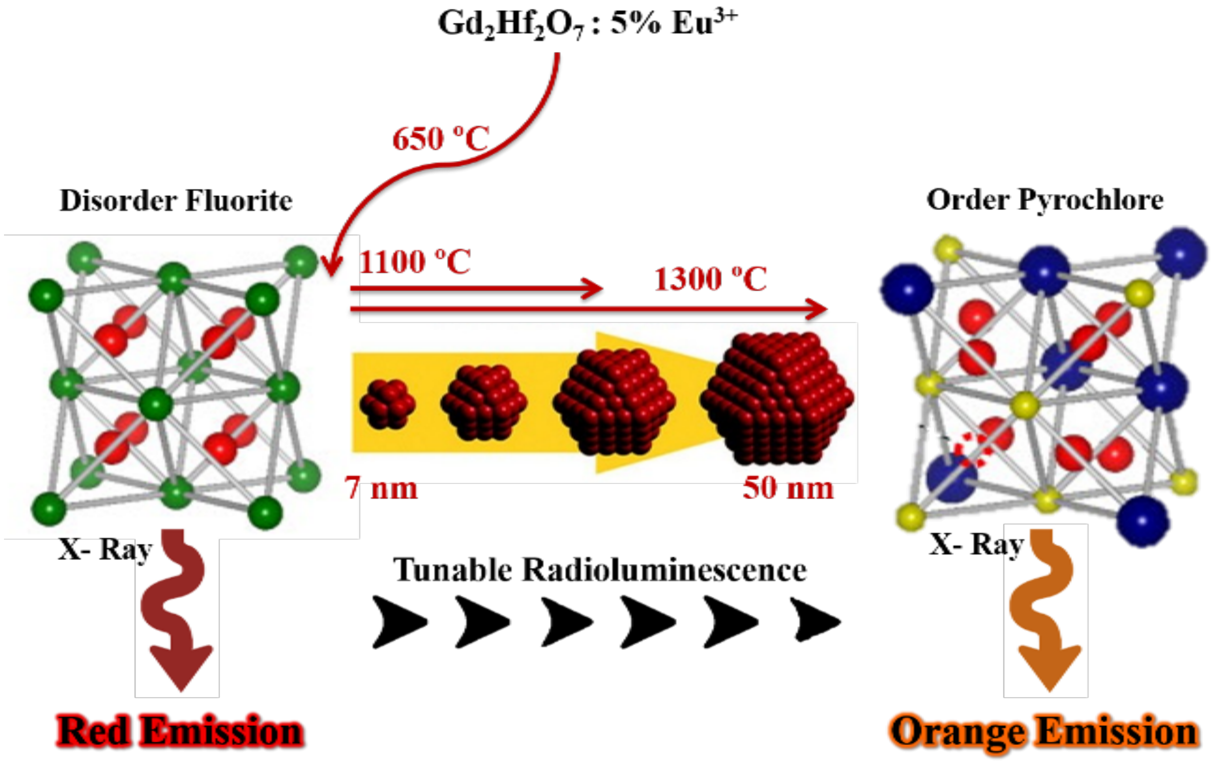


http://research.kyoto-u.ac.jp/service/topic/spirits/lists/h25list_e/sprits_h25en_68_masai/



- ➢ Expanding applications of ionizing radiation scintillation detectors
- ➢ The progress on new scintillators is slow
- ➢ The use of high quality single crystals is not the only way to achieve better scintillation properties

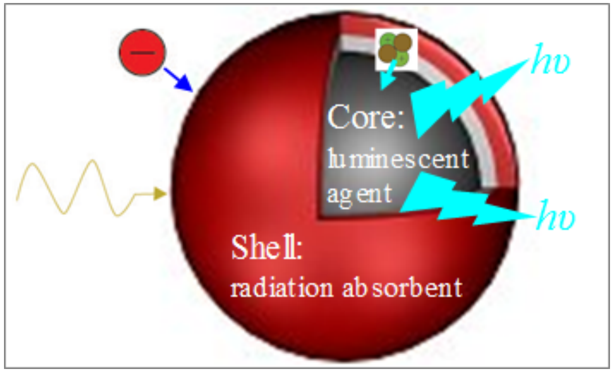
Particle Size & Crystal Structure Engineering

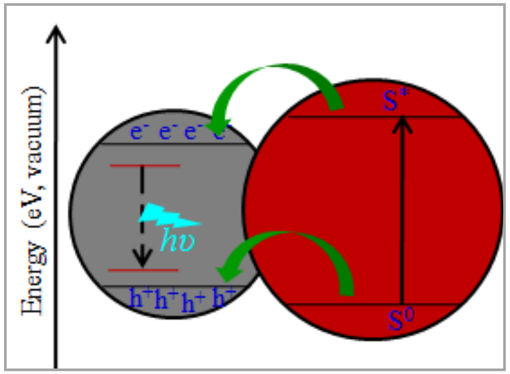


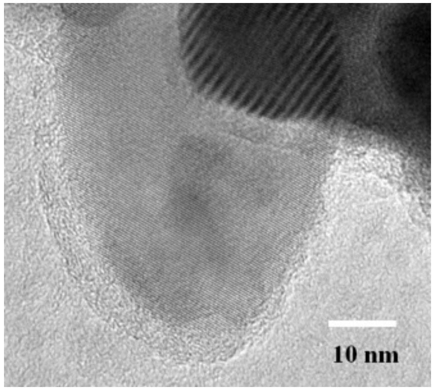
➢ Tunability of RL color: red → orange
➢ Strategy for designing advanced optoelectronic materials

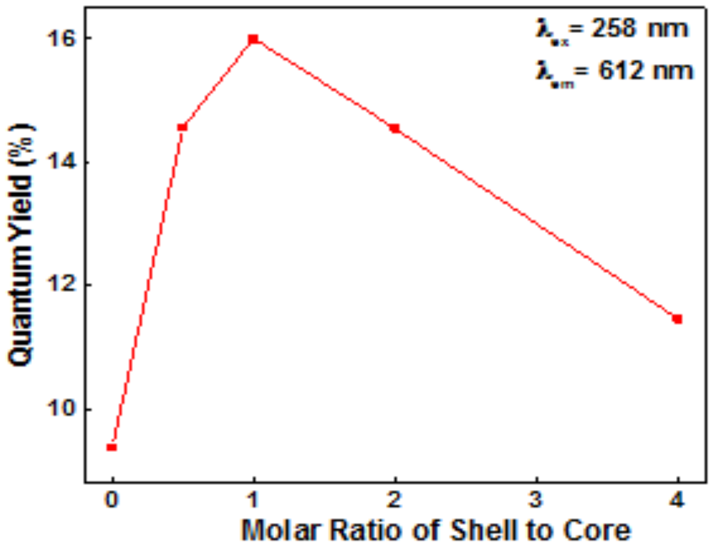
Santosh K. Gupta, Maya Abdou, Partha Sarathi Ghosh, Jose P. Zuniga, and Yuanbing Mao, Thermally Induced Disorder-Order Phase Transition of $Gd_2Hf_2O_7$:Eu^{3+} Nanoparticles and its Implication on Photo- and Radio-Luminescence, ACS Omega, 2019, 4, 2779-2791.

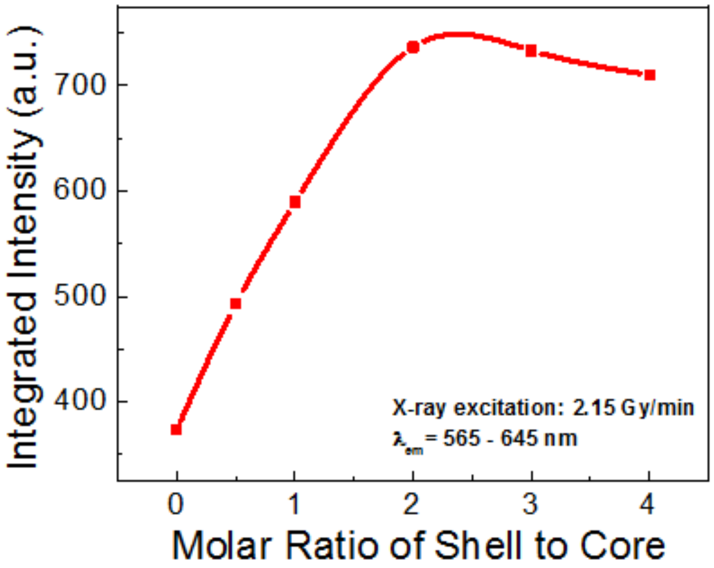
Core@Shell Strategy







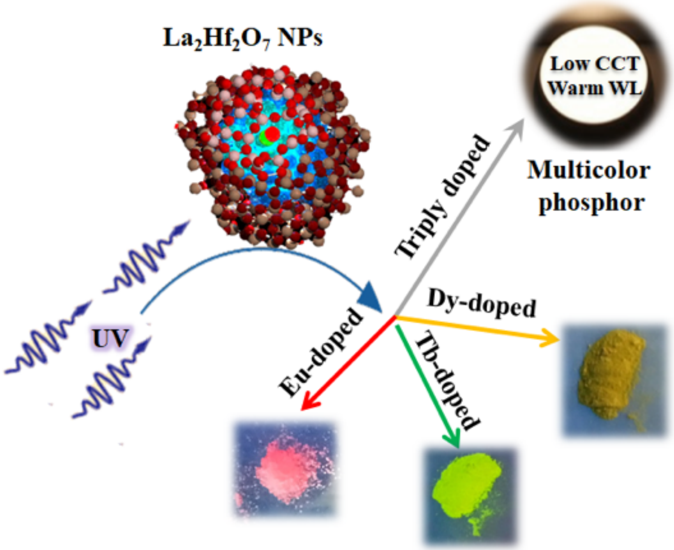




Eu:$La_2Zr_2O_7$@YBO_3 NPs

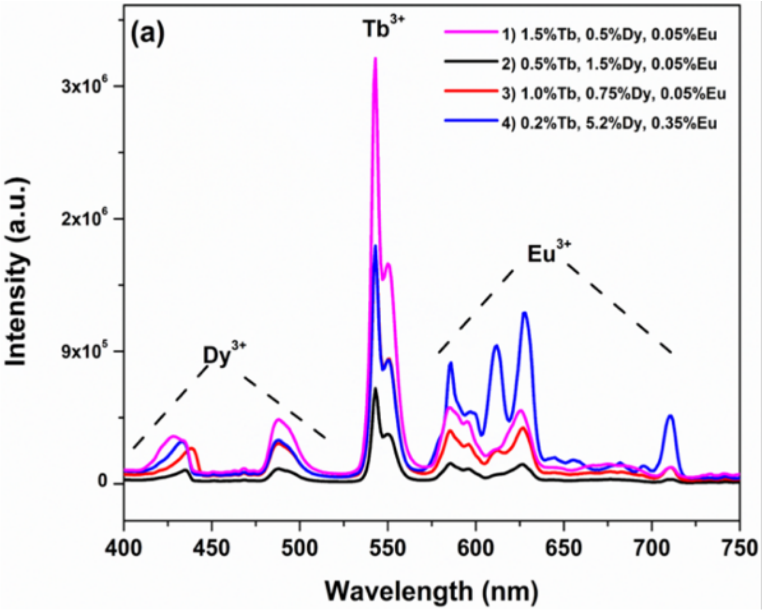
- ➢Shell: eliminates surface defects
- ➢Charge carriers: transfer from shell to core
- ➢PL & RL: increased ~2 times

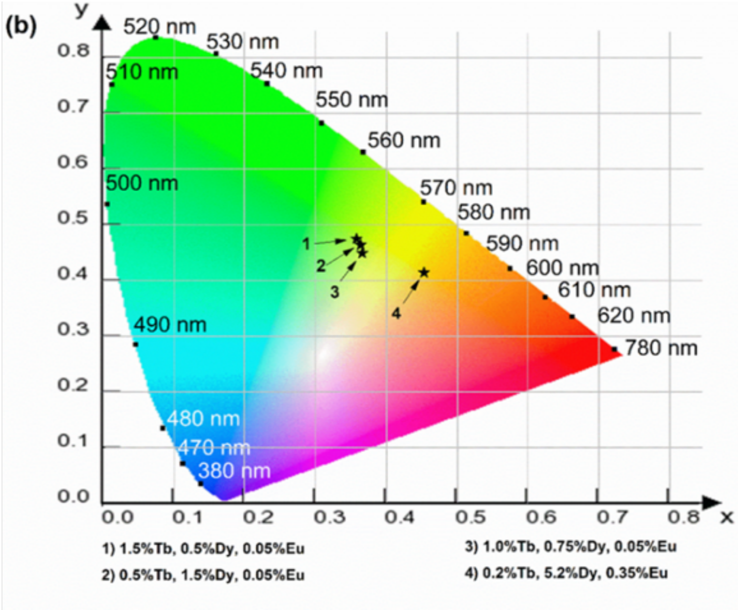
Warm White Lighting



- ➢ DOE: WLEDs will save >20% electricity (2010-30)
- ➢ Deficiency of the red light component in commercial phosphors

Dy,Tb,Eu:$La_2Hf_2O_7$ NPs

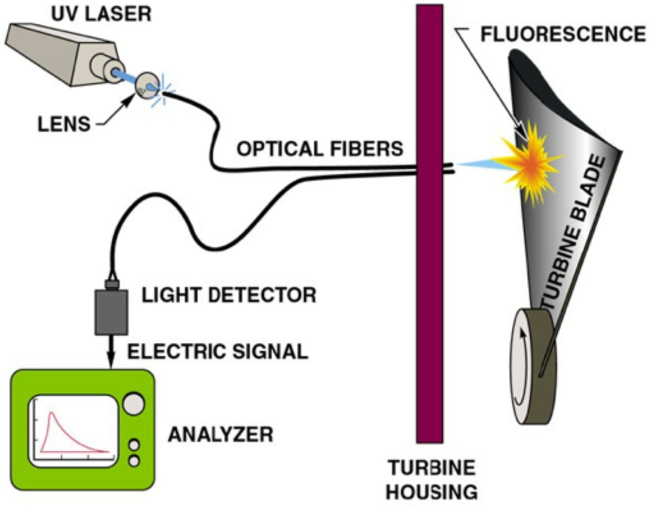


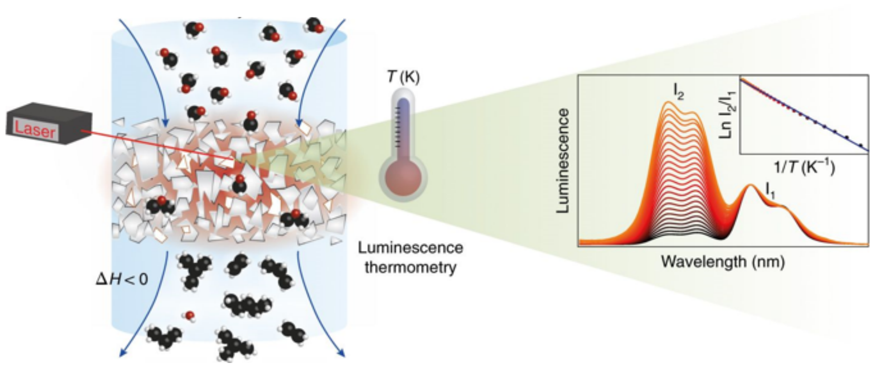


Luminescence Thermometry

- For harsh environments
- High spatial resolution
- Rapid response
- Non-invasive operation
- To reduced areas
- Offering sub-micrometric resolution
- High accuracy

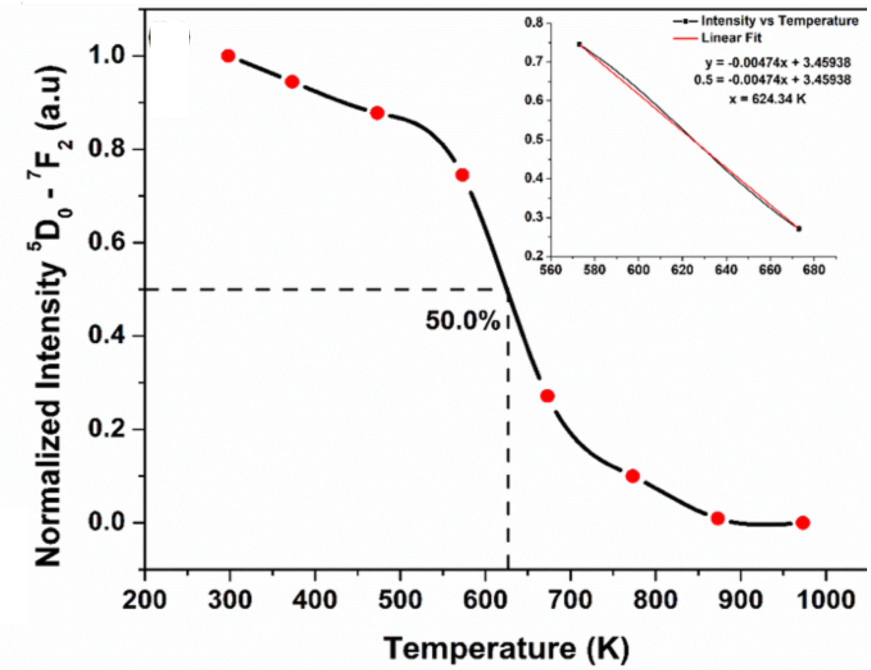
Current thermographic phosphors are restricted to bulk samples with moderate sensitivity and intermediate temperature range





Luminescence Thermometer

$La_2Hf_2O_7$:5%Eu NPs



Materials	Maximum S_r (%K^{-1})	Temp. range (K)
$Gd_2O_3:Er^{3+}/Yb^{3+}$	0.39	300-900
$NaLuF_4:Ho^{3+}/Yb^{3+}$	0.12	350-750
$Yb_3Al_5O_{12}:Er^{3+}$	0.48	295-973
$NaLuF_4:Gd^{3+}$	0.29	298-523
$Y_2MgTiO_6:Mn^{4+}$	0.14	10-513
$GdVO_4:Sm^{3+}$	1.41	393-603
$La_2Hf_2O_7:Eu^{3+}$	**3.53**	**298-973**

- High activation energy: 0.425 eV
- Highest relative temperature sensitivity (S_r)
- Contributions: high QY, good PL and RL properties, high lifetime, and excellent thermal stability.

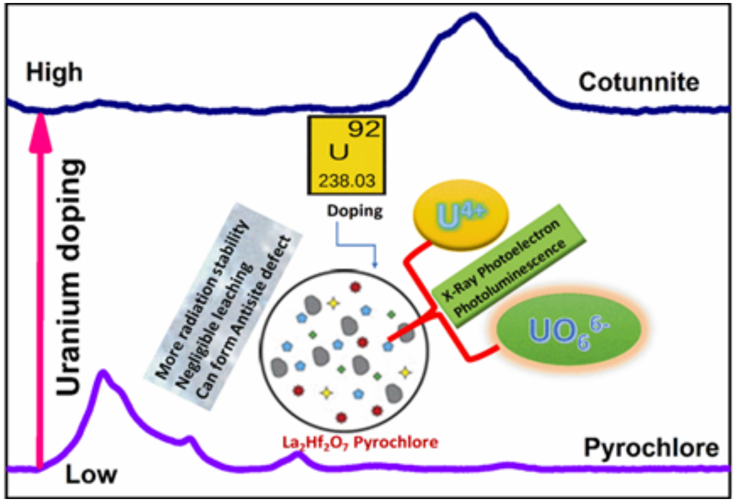
Collaborative work with Dr. Alex Puretzky at ORNL

Santosh K. Gupta, Jose Zuniga, P.S. Ghosh, Maya Abdou, and Yuanbing Mao, Correlating Structure and Luminescence Properties of Undoped and Eu^{3+} doped $La_2Hf_2O_7$ Nanoparticles Prepared with Different Co-Precipitating pH Values through Experimental and Theoretical Studies, Inorganic Chemistry, 2018, 57(18), 11815-11830.

Nuclear Waste Immobilization

Suitable properties of nuclear waste hosts:

- large containing capability
- high thermal stability
- good radiation stability
- high chemical stability
- resistance to radiation-induced amorphization
- negligible leaching
- etc.



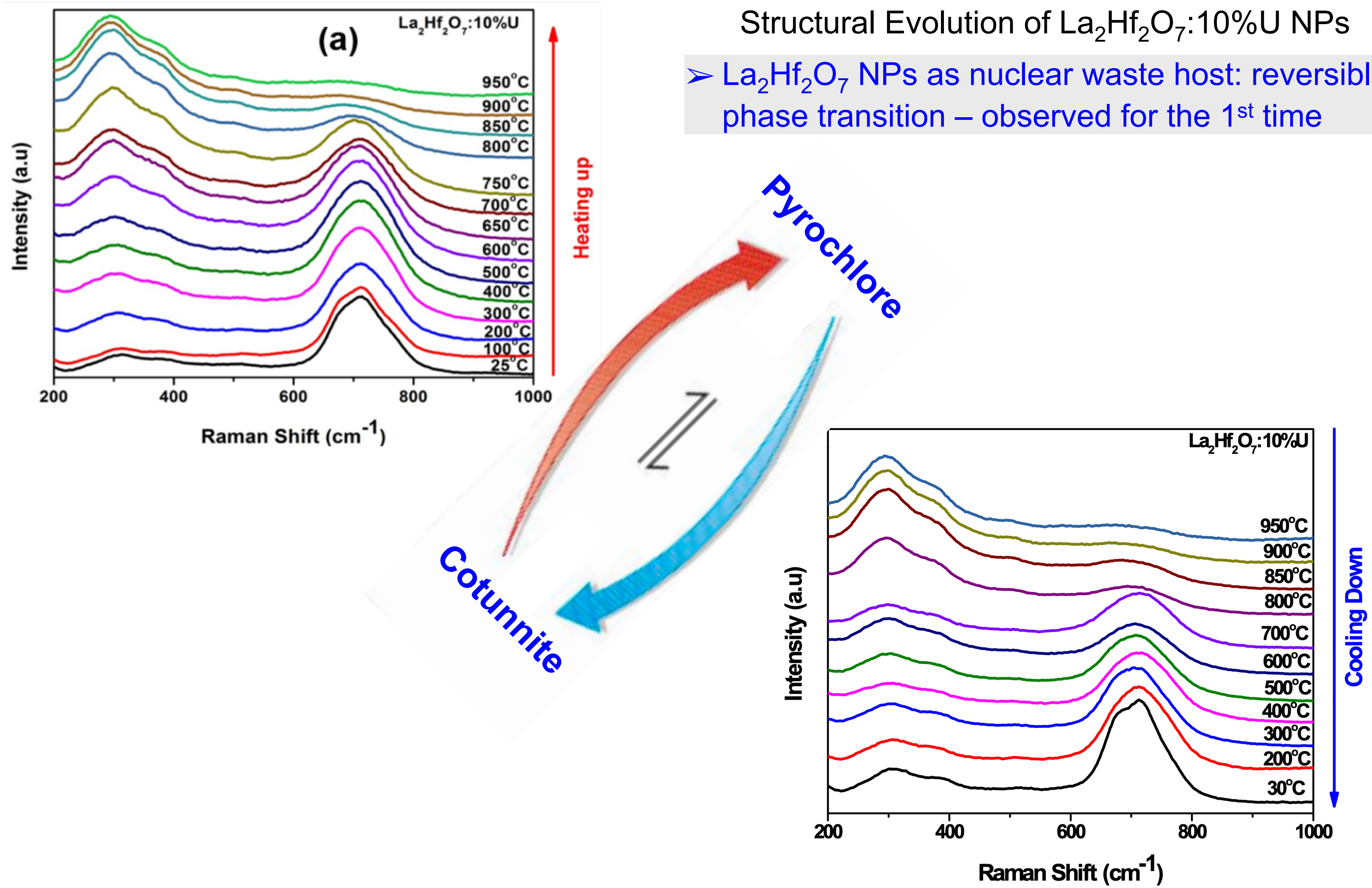
- ➢ Uranium and its radioactive isotopes: a high-level of nuclear waste
- ➢ $La_2Hf_2O_7$ NPs: U-doping induced phase transformation
- ➢ Speciation studies of uranium ion in $A_2M_2O_7$ compounds: uncharted and vague

Maya Abdou, Santosh K. Gupta, Jose Zuniga, and Yuanbing Mao, On Structure and Phase Transformation of Uranium Doped $La_2Hf_2O_7$ Nanoparticles as an Efficient Nuclear Waste Host, Materials Chemistry Frontiers, 2018, 2, 2201 - 2211 (cover).

Nuclear Waste Immobilization

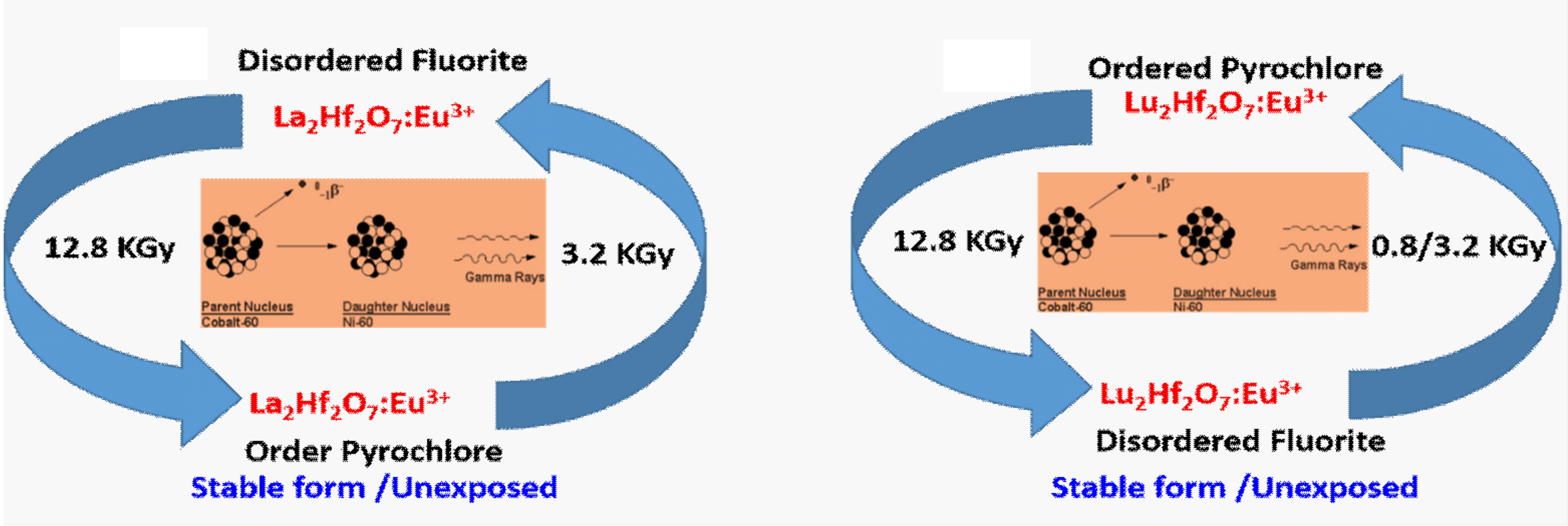
Structural Evolution of $La_2Hf_2O_7$:10%U NPs

➢ $La_2Hf_2O_7$ NPs as nuclear waste host: reversible phase transition – observed for the 1st time



Collaborative work with Dr. Alex Puretzky at ORNL

Nuclear Waste Immobilization



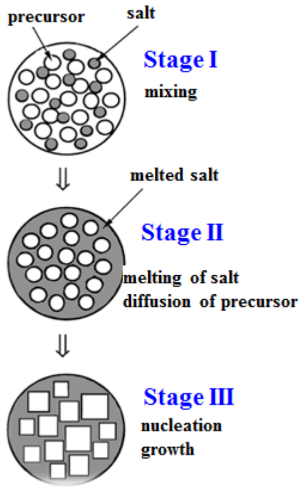
γ-ray irradiation impact on $A_2Hf_2O_7$:5%Eu NPs

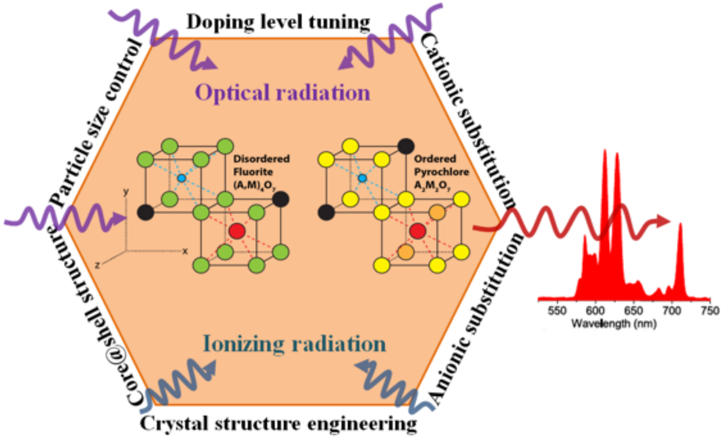
- Fascinating behavior from lanthanum (f^0) hafnate and lutetium (f^{14}) hafnate
- Two extreme compositions with the maximum and minimum ionic radius ratio r_{RE}/r_{Hf} of the studied $RE_2Hf_2O_7$:5%Eu NPs
- Beneficial for fundamental U chemistry and nuclear industry

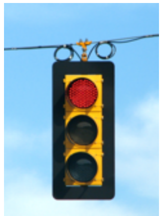
Collaborative work with Dr. Don Wall group at WSU

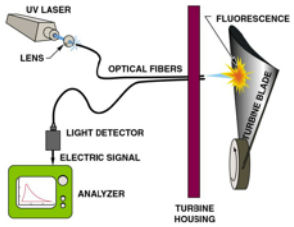
Victoria Trummel, Santosh K. Gupta, Madhab Pokhrel, Donald Wall, and Yuanbing Mao, Investigating the impact of gamma radiation on structural and optical properties of Eu^{3+} doped rare-earth hafnate pyrochlore nanocrystals, *Journal of Luminescence*, **2019**, *207*, 1-13.

Summary on Luminescence Studies of $A_2M_2O_7$ NPs







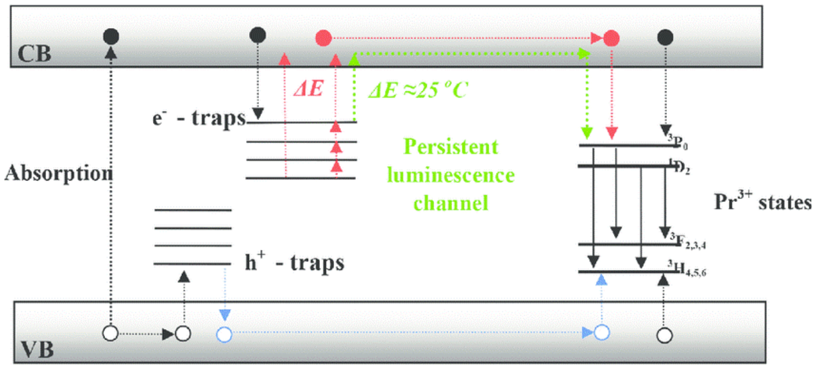


- Molten-salt synthesis method for $A_2M_2O_7$ NPs with different doping levels, compositions and crystal structures
- Several strategies to tune the spectral features of these NPs
- Explored both PL and RL of these phosphors and scintillators
- Have great potentials for broad optical applications

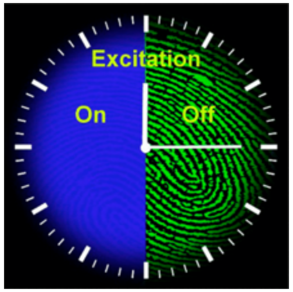
Outline

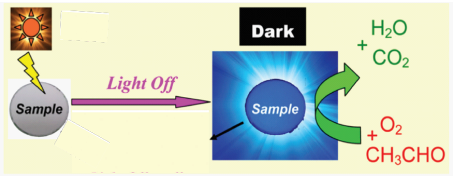
- Intro
- PL and RL
- **PerL**
- UC
- Summary

Persistent Luminescent Materials



- Materials which emit in the UV, VIS and/or NIR spectral regions for minutes, hours or even days after ceasing the excitation irradiation





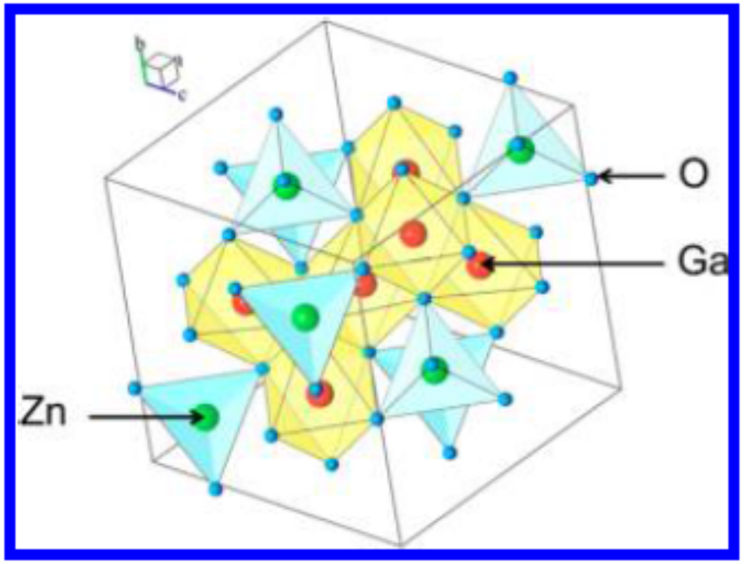
J. Phys. Chem. C 2017, 121, 5539–5550
Anal. Chem. 2017, 89, 12764–12770

- New applications spontaneously set more requirements on design methodology, morphology, and functionalization of PLMs
- New applications also promote the development of new PLMs

Bioimaging/Diagnostics

- ➢ Need to avoid tissue autofluorescence and weak tissue penetration
- ➢ Urgent need for PLM NPs with bright luminescence and long afterglow
- ➢ To understand their biodistribution *in vivo*

Red Long-Lasting Phosphor $Cr:ZnGa_2O_4$



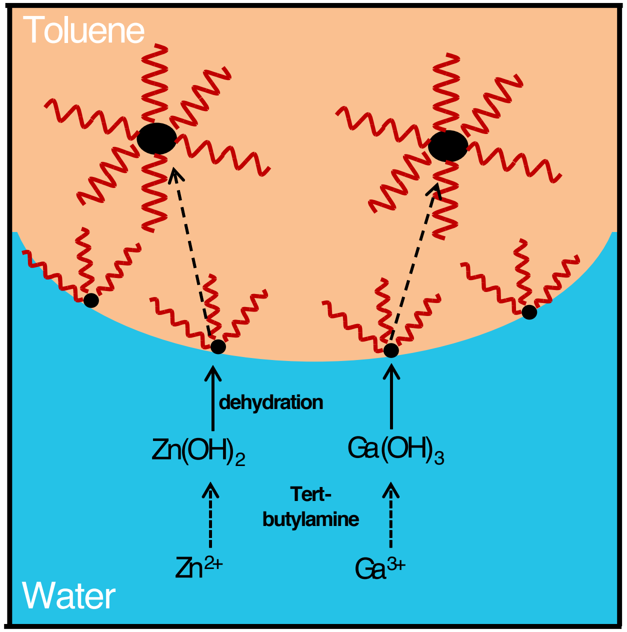
- Conveniently excited through its bandgap by UV light
- Emit s around 695 nm via the $^2E \rightarrow\ ^4A_2$ transition of Cr^{3+}
- Matches the optical window of biological tissues
- Use of a small dopant concentration (0.5%) and similar dopant size (Cr^{3+} *vs* Ga^{3+}) → reduce the occurrence of defects and avoid potential loss centers
- AB_2O_4 compound, spinel structure
- Zn^{2+} and Ga^{3+} ions occupy tetrahedral A and octahedral B sites, respectively

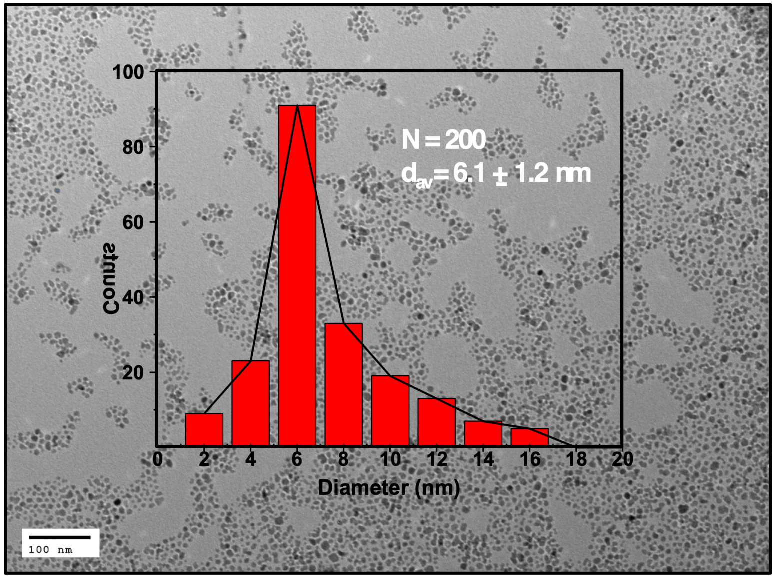
➢ The currently synthesized $Cr:ZnGa_2O_4$ NPs: 40–150 nm, polydisperse

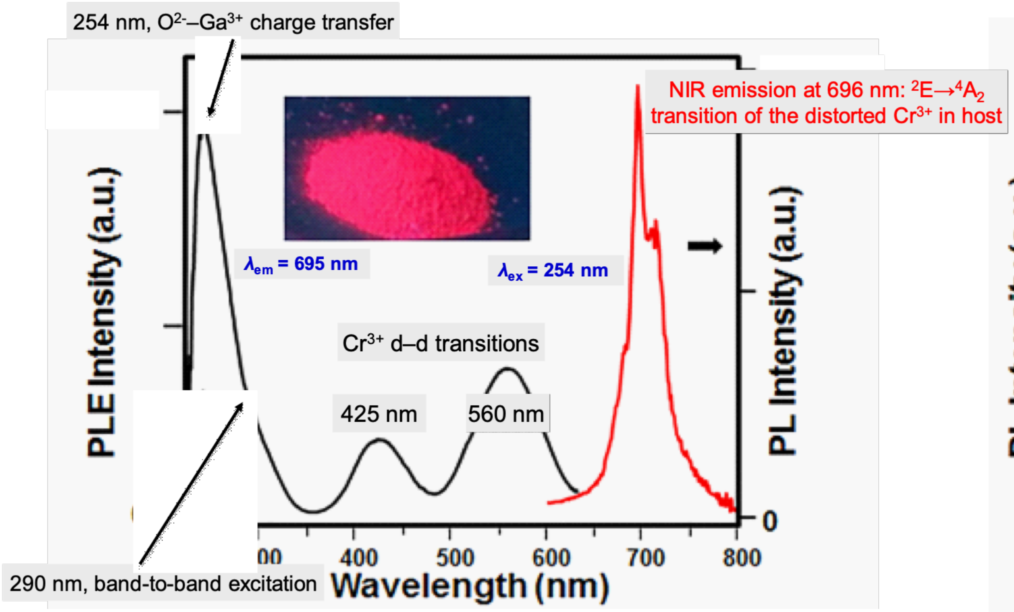
➢ No sub-10-nm persistent nanophosphors synthesized yet

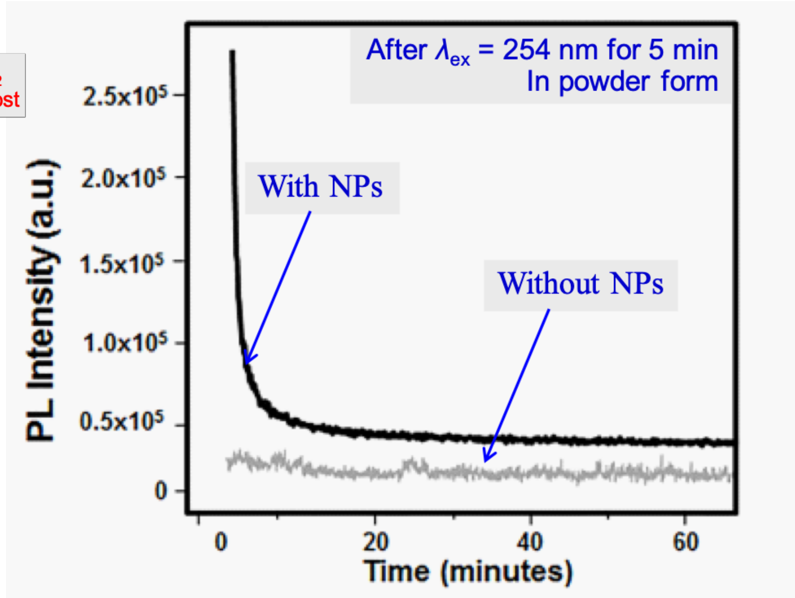
T. Maldiney, et al., Nat. Mater., 2014, 13, 418. A. Abdukayum, et al. JACS, 2013, 135, 14125.

PerL $Cr:ZnGa_2O_4$ NPs by Bi-Phasic Synthesis

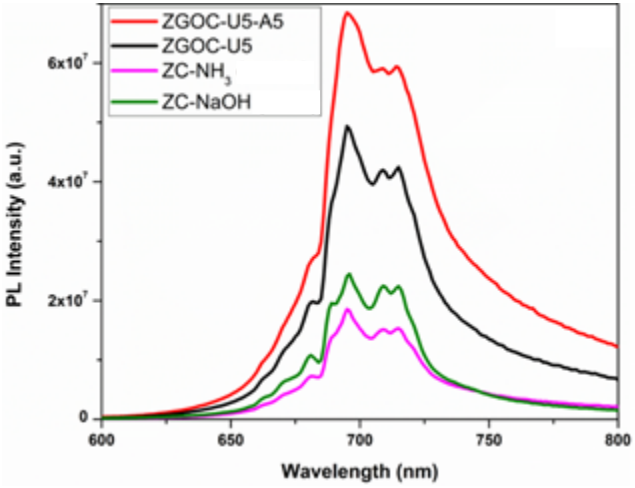


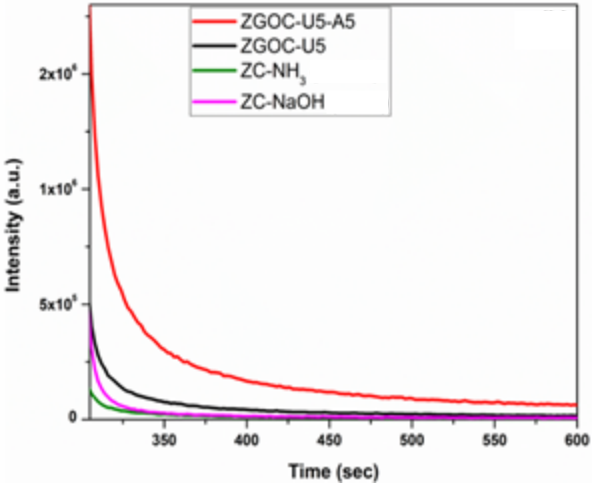




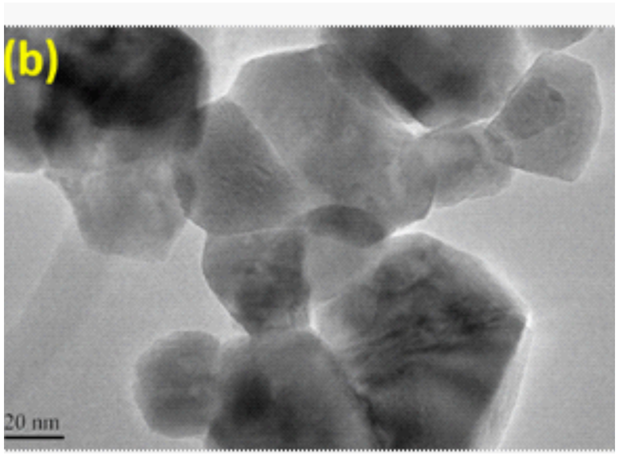


Enhancing PerL of $Cr^{3+}:ZnGa_2O_4$ NPs

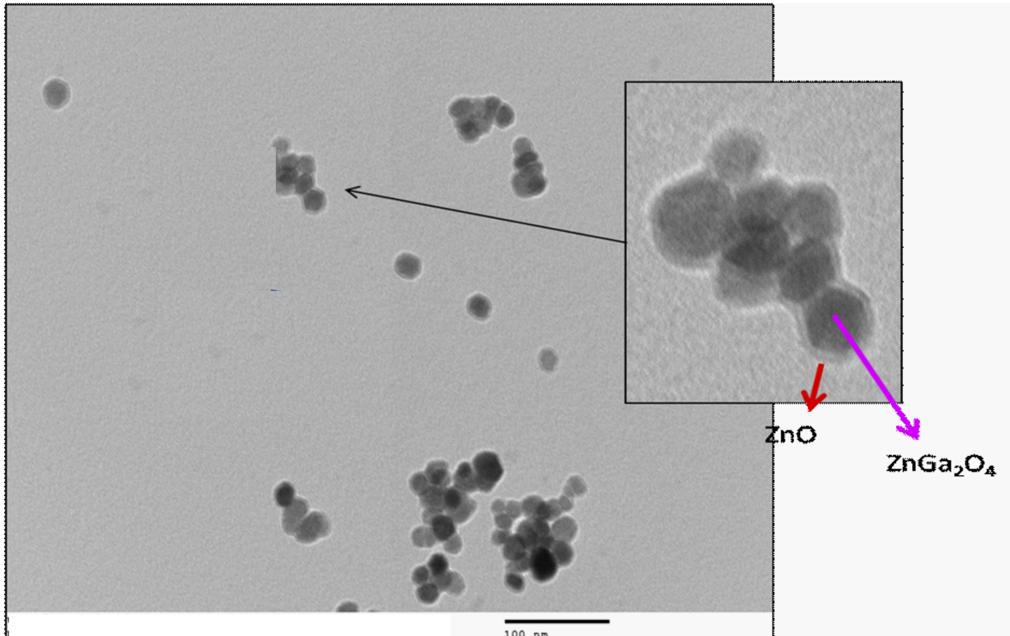




Hydrothermal Synthesis



Urea



Urea + NH_4NO_3

Outline

- Intro
- PL and RL
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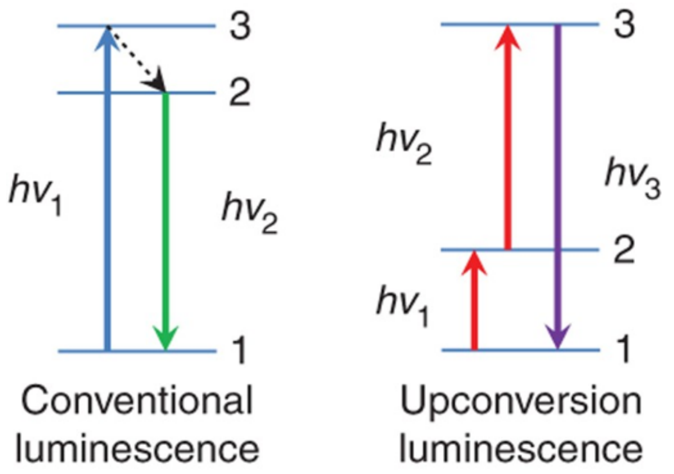
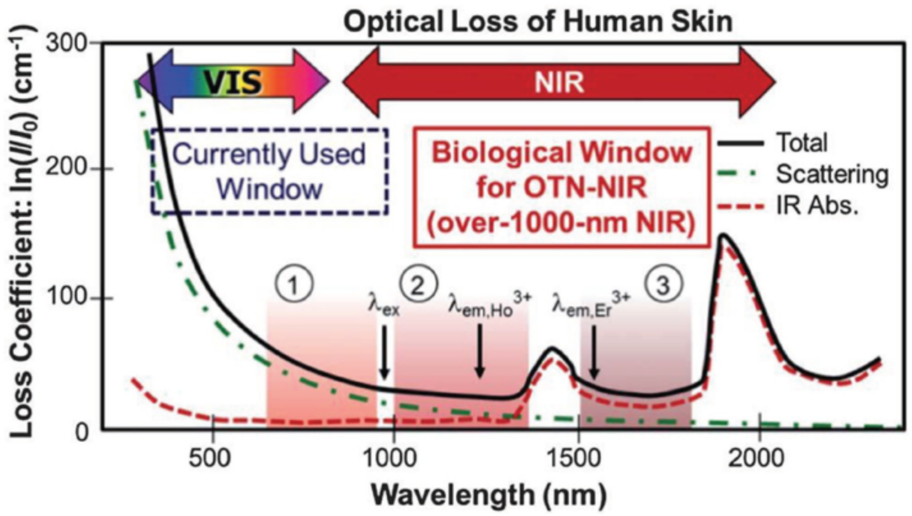
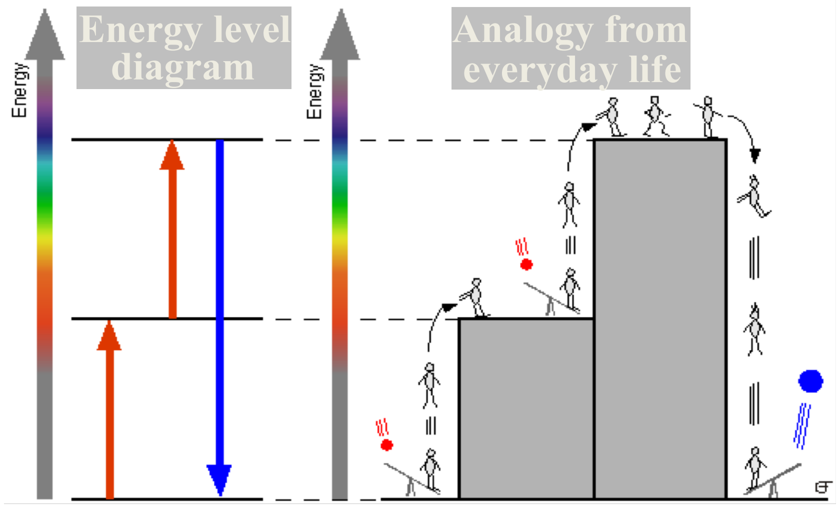
Upconversion Luminescence

An optical process that emits high-energy photons by absorbing two or more low-energy photons, which is caused by anti-Stokes luminescence



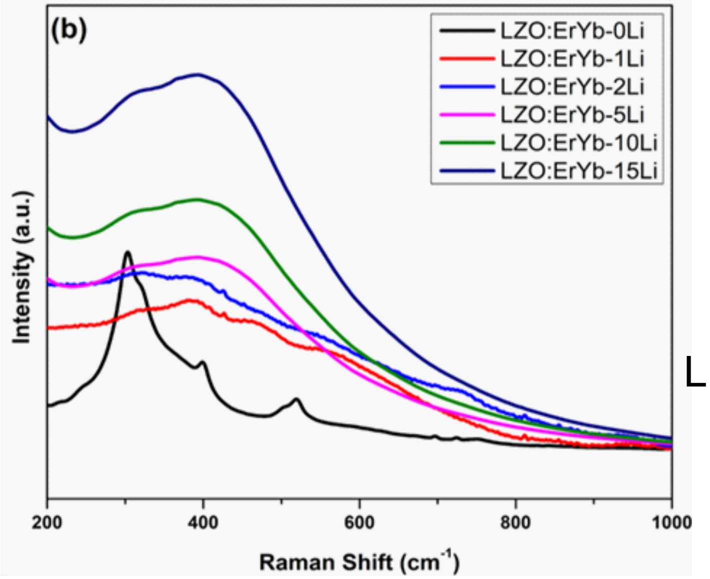


Small **2018**, *14*, 1801882



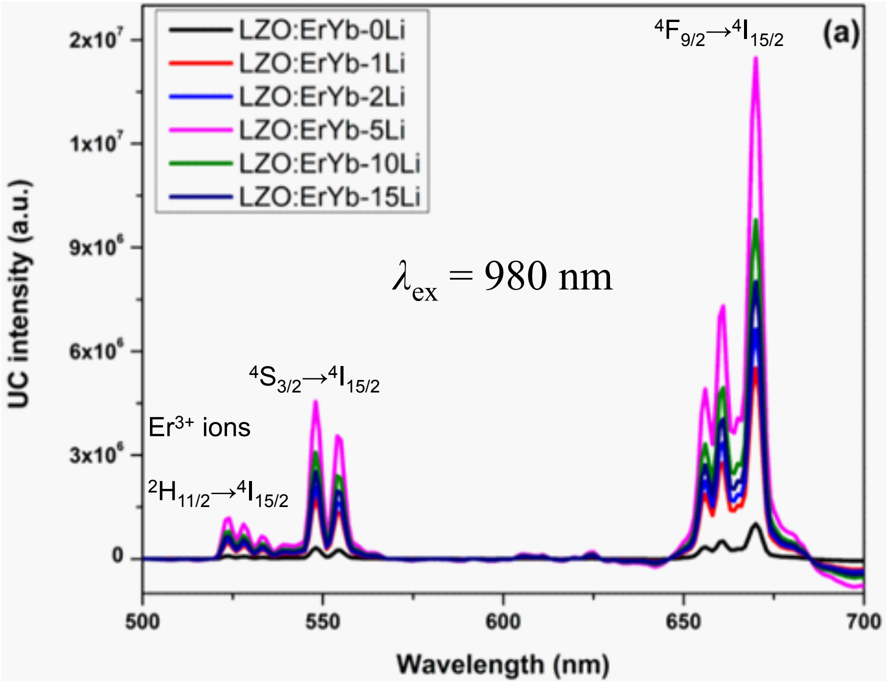
http://dcbwww.unibe.ch/groups/guedel/images/res/upc.GIF

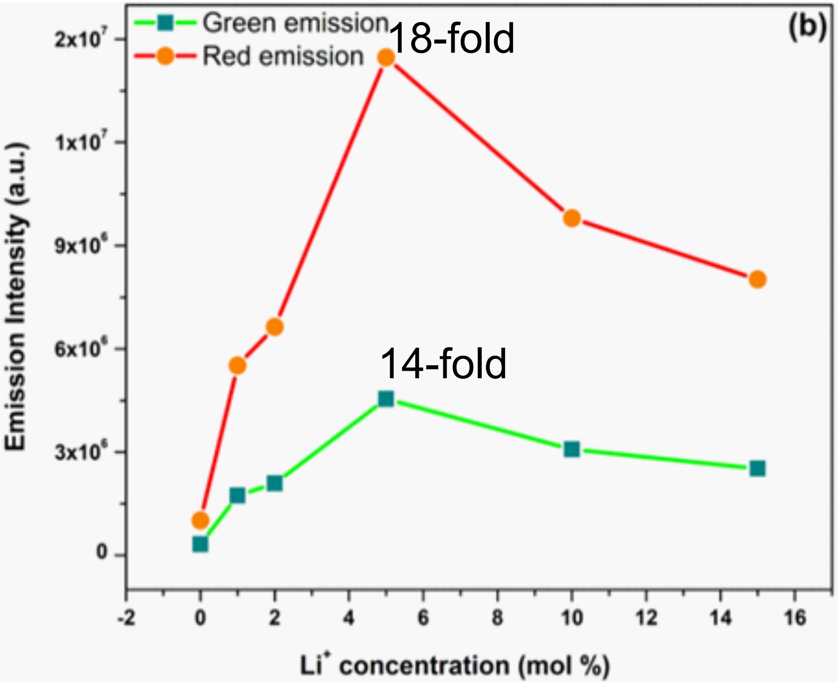
Enhanced Upconversion



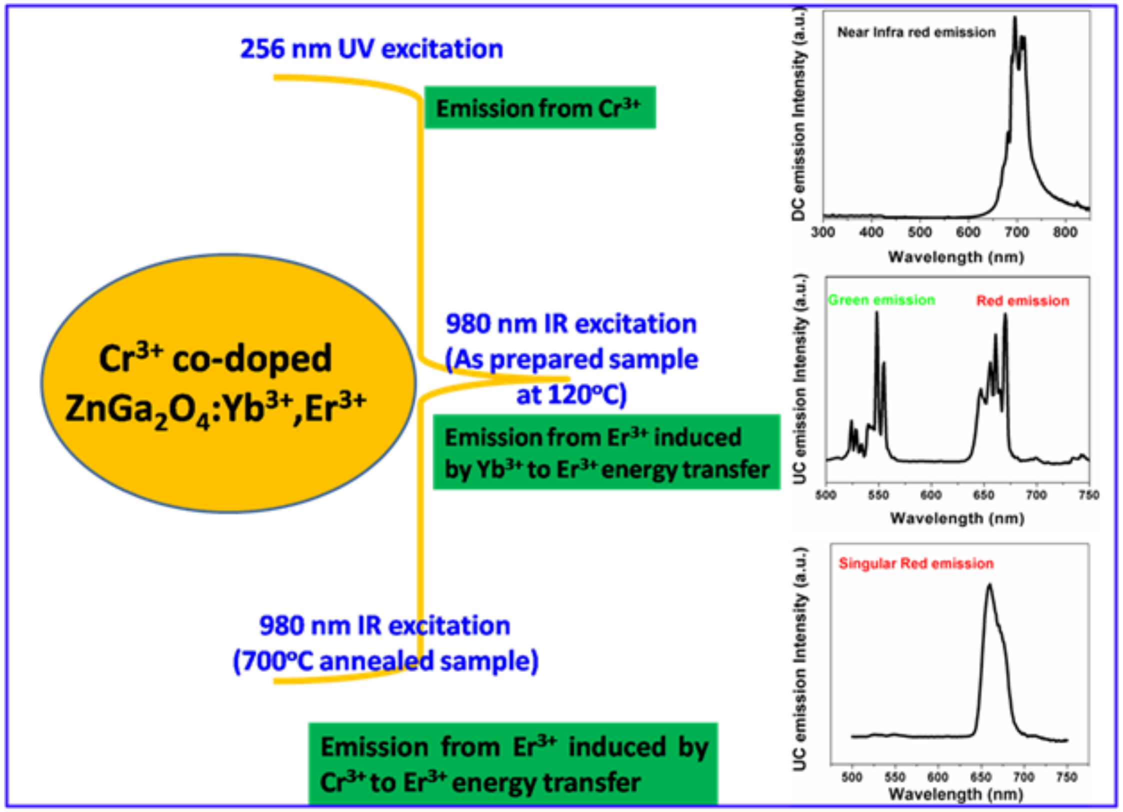
Er,Yb:$La_2Zr_2O_7$ NPs

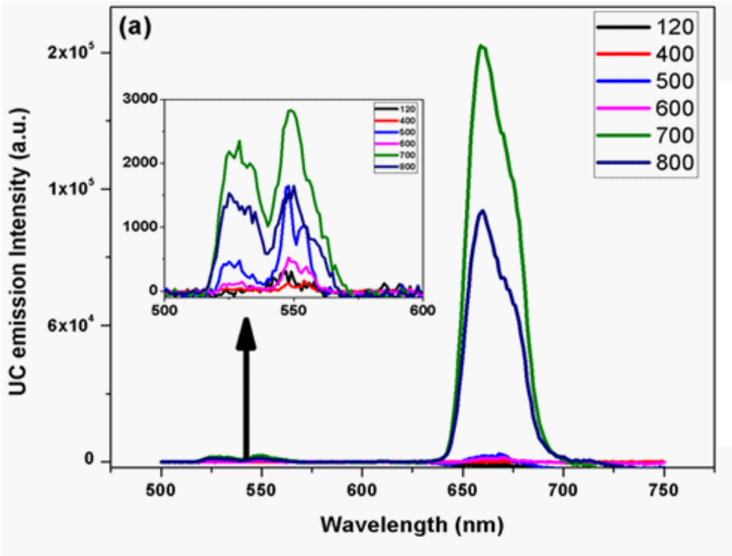
Li^+ co-doping induced phase transition

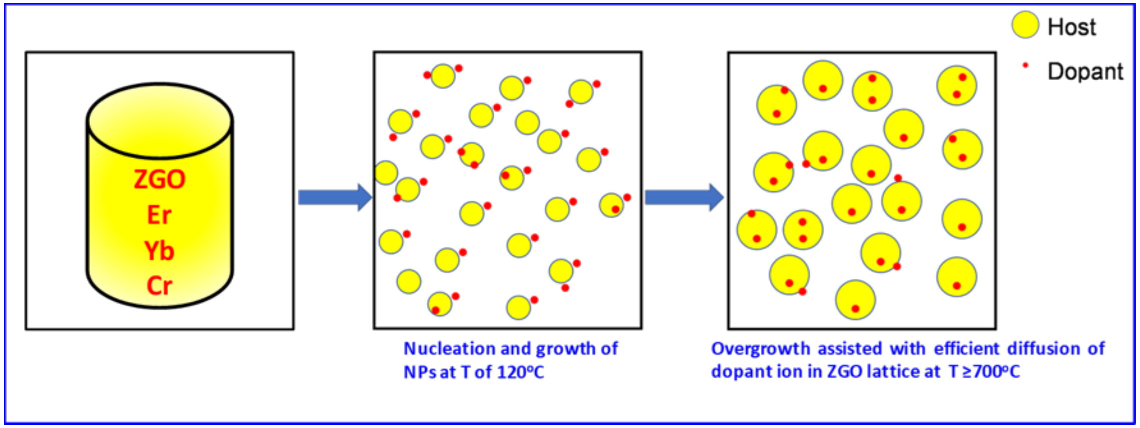


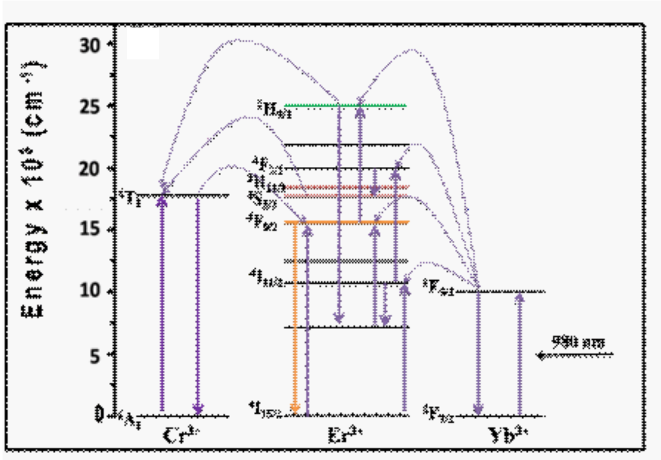


Upconverting Singular Red Emission

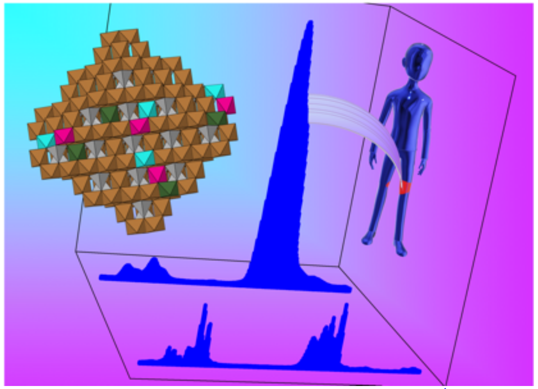








Summary



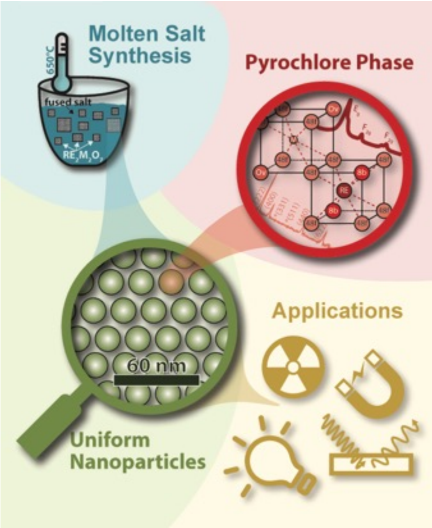
Upconversion

$Er,Yb:La_2Zr_2O_7$ NPs:
Li^+-co-doping
Phase-transition induced UC enhancement
$Cr,Er,Yb:ZnGa_2O_4$ NPs:
Thermal-treatment induced even distribution
Singular red emission

Photo- & Radio-Luminescence

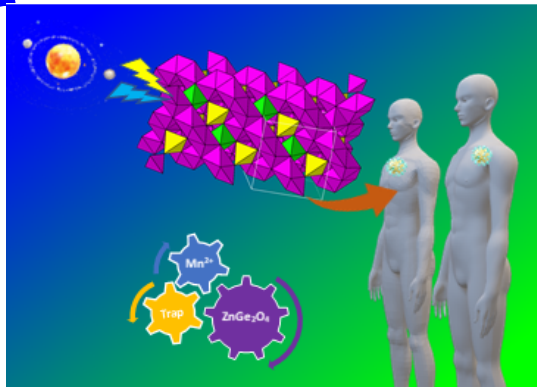
$A_2M_2O_7$ NPs:
Molten-salt synthesis
6 Spectral tuning strategies
Warm white light
Luminescence thermometry
Actinide Immobilization

Luminescent NPs of Metal Oxides



Persistent Luminescence

$Cr:ZnGa_2O_4$ NPs:
Bi-phasic synthesis
Hydrothermal synthesis
Smallest particles
Red persistent PL
Bioimaging



Thank you for your attention!

Any questions/comments?