Rare-earth upconversion luminescence for optical sensing

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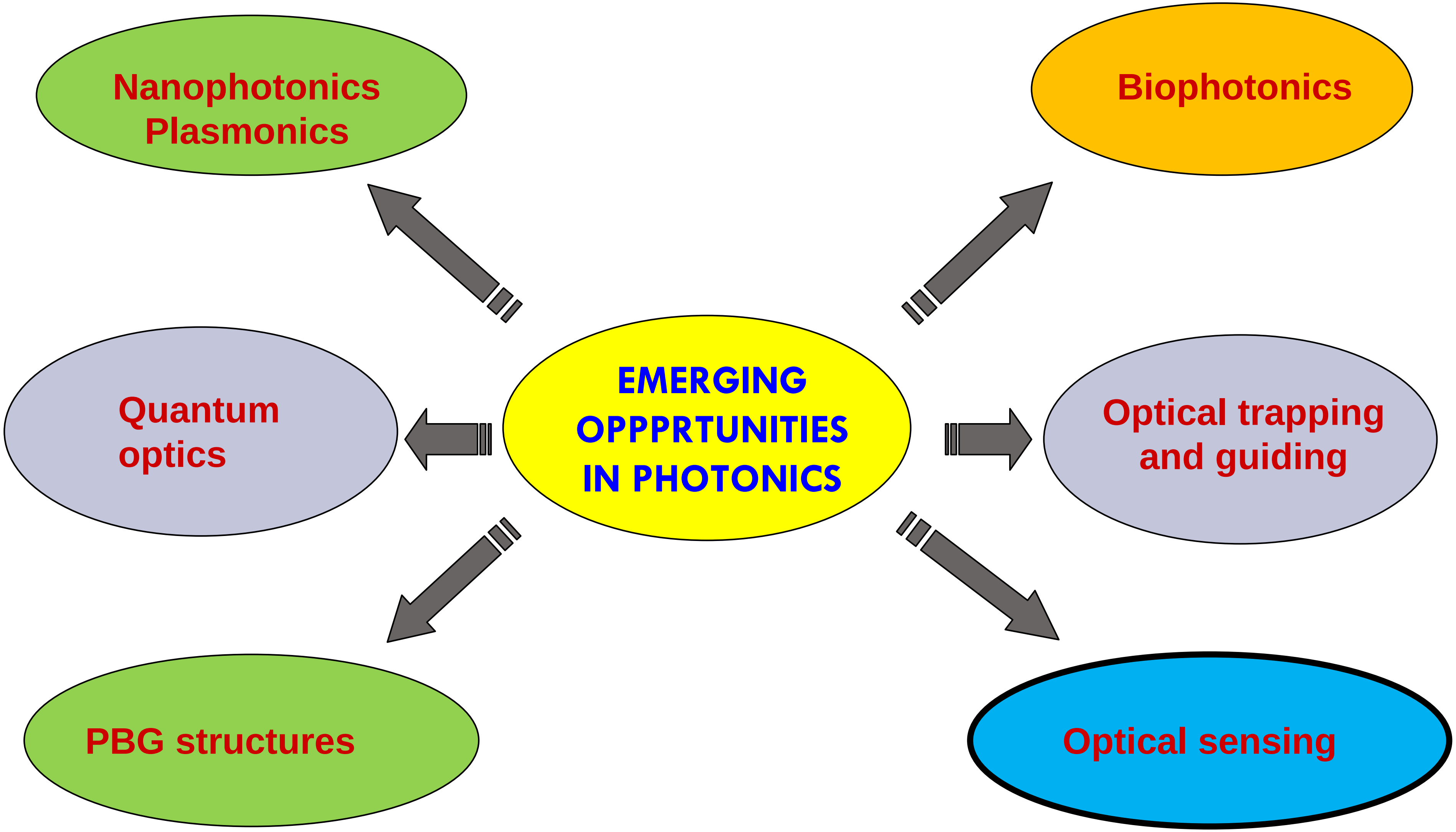
July 6, 2014 r.

Photonics



EMERGING OPPPRTUNITIES IN PHOTONICS

Nanophotonics
Plasmonics

Biophotonics

Quantum optics

Optical trapping and guiding

PBG structures

Optical sensing

Plan

- Luminescence
- Introduction to rare-earths
- Upconversion luminescence
- Sensing
    - sensing using RE-doped upconversion nanoparticles
    - upconversion phosphors as optical marker materials
    - temperature sensing
    - bio-applications

- Other examples

Luminescence

Luminescence is emission of light by a substance not resulting from heat; it is thus a form of cold body radiation.

- **Photoluminescence** { **fluorescence** / **phosphorescence**

- Chemi luminescence
- Tribo luminescence
- Electro luminescence
- Roentgeno luminescence
- Radio luminescence
- Bio luminescence

Natural fluorite (CaF_2) after UV irradiation

optoelectronics

Photoluminescence

Photoluminescence (PL) describes the phenomenon of light emission from any form of matter after the absorption of photons.

Fluorescence;	fast process 10^{-6} s,
Phosphorescence;	slow process (hours- days)

Gypsum crystal ($CaSO_4$ $2H_2O$) from Dobrzyn PL, which glows for several seconds after switching off excitation lamp.

Phosphor = synthetic material that manifests luminescence

History (short)

Sir George Stokes (1852) coined the term **fluorescence**. He showed that the fluorescence emission occurred at a higher wavelength (lower energy) than the excitation light. This displacement is now called the **Stokes Shift**

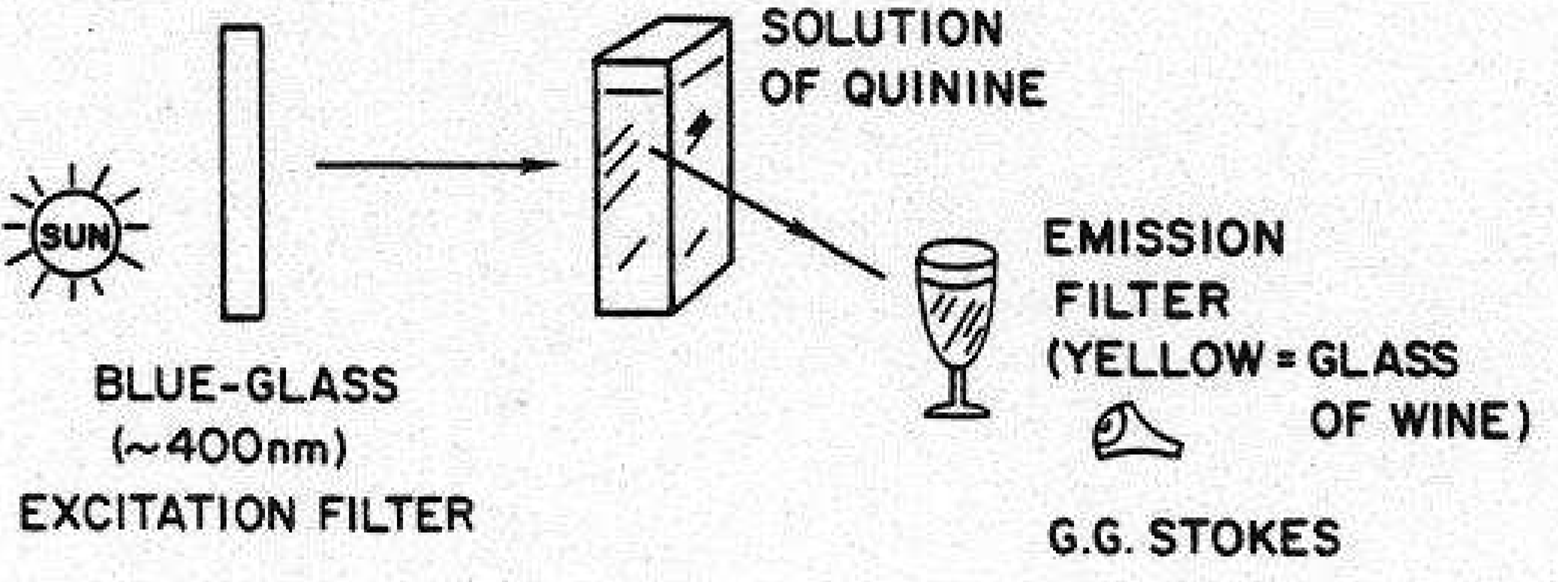


Figure 1.4. First detection of the Stokes' shift.

Fluorescence

***Fluorescence*:**

“an effect in which a substance releases electromagnetic radiation while absorbing another form of energy, but ceases to emit the radiation immediately upon cessation of the input energy”; “the light emission of a given wavelength by a substance that is activated by light of a different wavelength.”

***Academic Press Dictionary of Science and Technology*, 1992.**

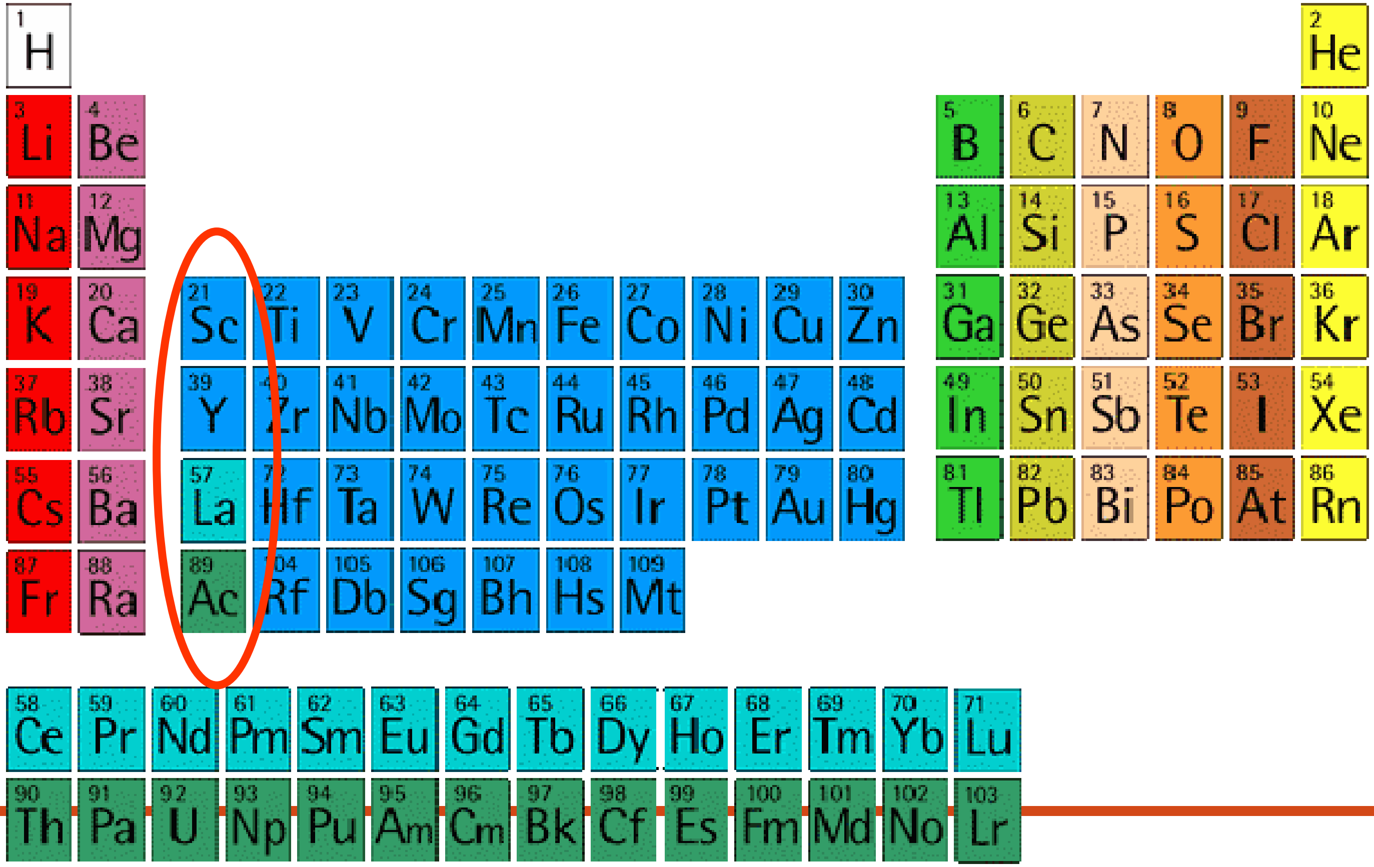
“The emission of a longer wavelength radiation by a substance as a consequence of absorption of energy from a shorter wavelength radiation, continuing only as long as the stimulus is present;” “distinguished from phosphorescence in that, in the latter, emission persists for a perceptible period of time after the stimulus has been removed”

***Stedman’s Medical Dictionary*, 24th ed., 1982.**

Rare -earths

Lanthanides = series of chemical elements compriseing 15 metallic chemical elements with atomic numbers 57 through 71, from lanthanum through lutetium.

These 15 lanthanide elements, along with the chemically similar scandium and yttrium, are known as the **rare earth** elements.



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									
58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu				
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr				

Rare –earths history – the very beginning

1787 Carl Axel Arrhenius, an artillery lieutenant and amateur geologist, finds a black mineral in a quarry near Ytterby, 30 km from Stockholm.

1788 B. R. Geijer (Stockholm) describes the mineral (d = 4.2) and names it ytterbite, presently known as gadolinite, with formula $Be_2FeY_2SiO_{10}$.

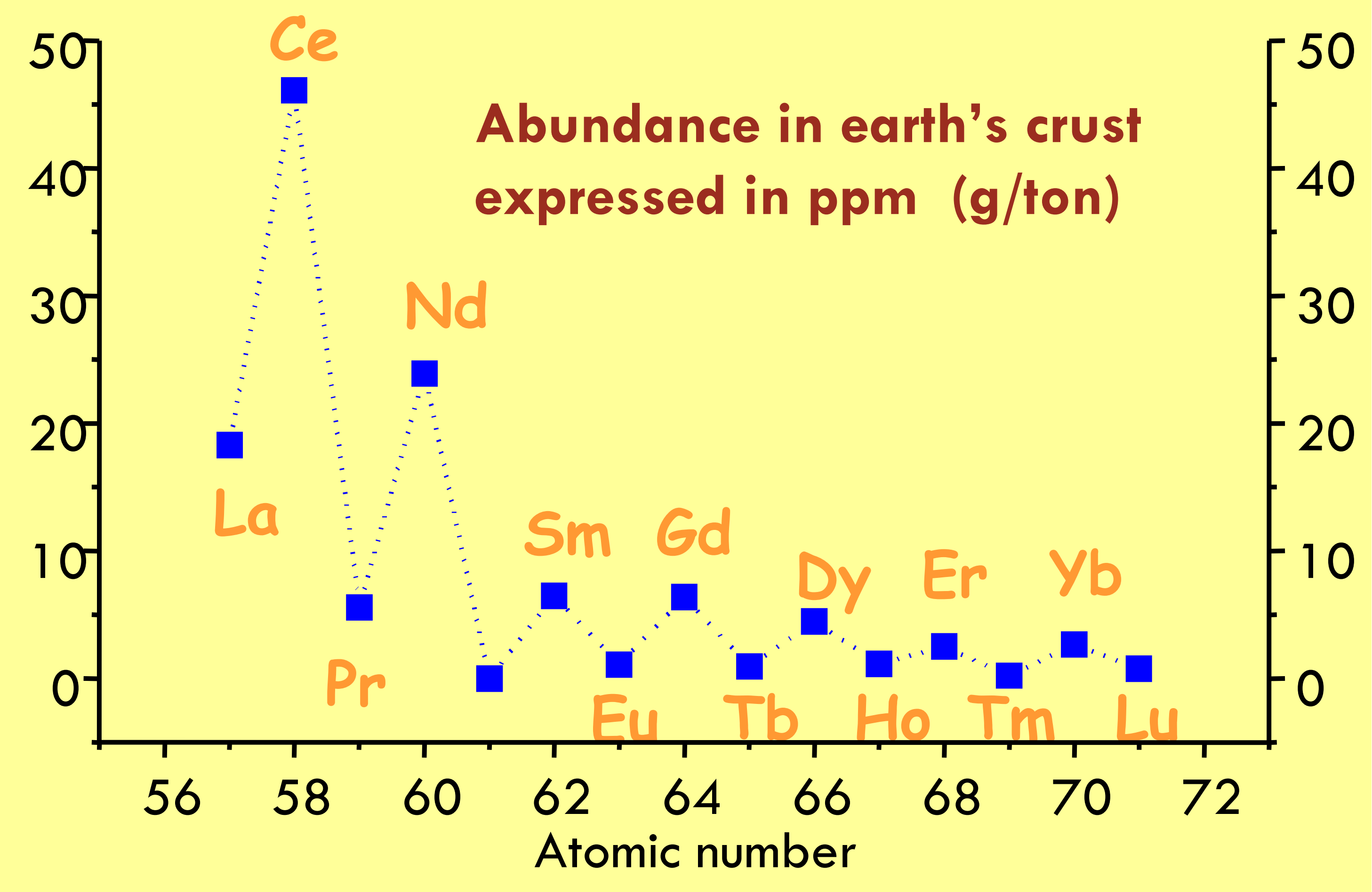
1792 J. Gadolin (1760-1852) studies the mineral and publishes a 19-page report in 1794 in the Proceedings of the Royal Swedish Academy of Sciences, concluding to the presence of a new "earth", which he names **yttrium**.

Rare –earths applications

17 elements from near the bottom of the periodic table

- Unique properties have led to a wide variety of applications and are important economically, environmentally and technologically
- Industrial applications: lighting, batteries, PV conversion, military weapons, TV & laptop screens, catalytic converters, magnets, semiconductors, ….
- Use of REs in high performance products has significantly increased over last 2 decades
- Toyota Prius uses about 1kg of Neodymium in each vehicle

Rare -earths natural abundance

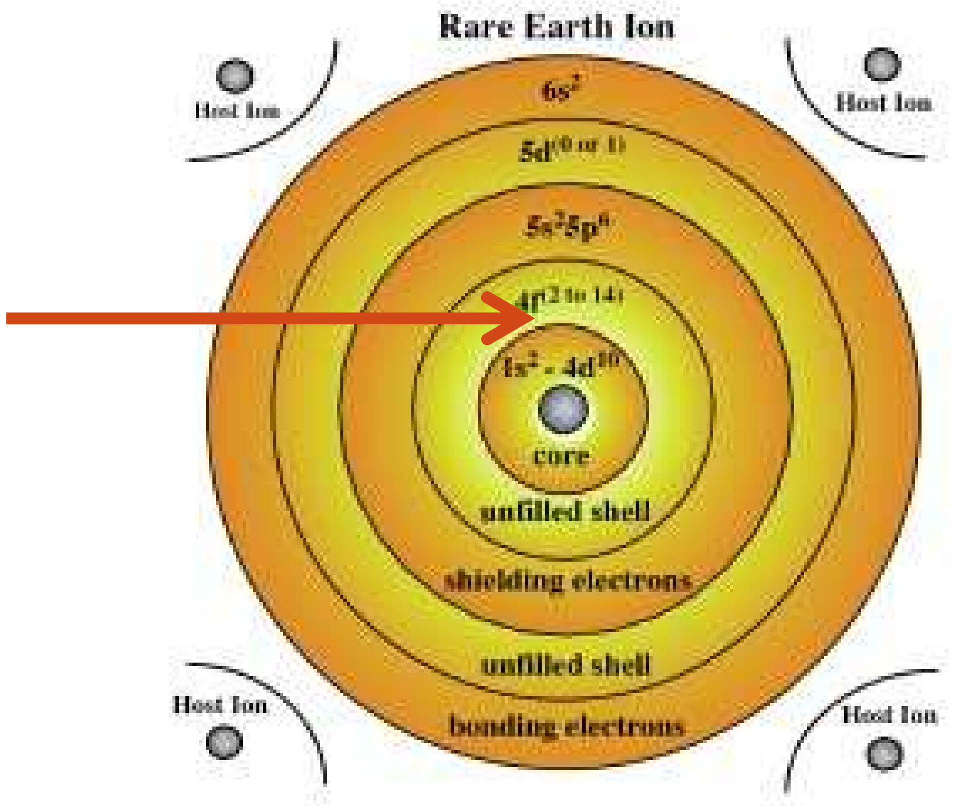


The elements are "rare" but not rarer than many others, such as Au, Pt, Pd, Rh, for instance

Atomic structure of RE ions in solids

Rare-earth ions

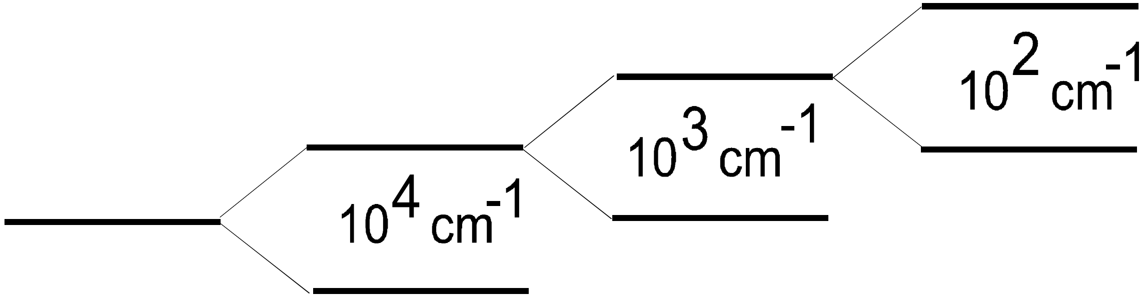
RE^{3+}	n
Ce^{3+}	1
Pr^{3+}	2
Nd^{3+}	3
Pm^{3+}	4
Sm^{3+}	5
Eu^{3+}	6
Gd^{3+}	7
Tb^{3+}	8
Dy^{3+}	9
Ho^{3+}	10
Er^{3+}	11
Tm^{3+}	12
Yb^{3+}	13



- 4f shell weakly affected by surrounding host ions,
- free ion ^{2S+1}L states split into $^{2S+1}L_J$ multiplets,
- narrow spectral lines, large cross sections,
- strong absorption and fluorescence.

Optical centers (= rare earths) in solids

Because of the shielding effect of the outer 5s and 5p shell electrons, the crystal- field interaction with inner 4f electrons is weak and can be treated as a perturbation (Stark effect) of the free-ions states. Accordingly, the energies of the corresponding levels of 4fn configuration are only weakly sensitive to the type of the crystal host.



Configurations 4f^n

Ho = central field
(Electrons in field
of the nucleus)

Terms ^{2S+1}L

Hc = Coulomb field
(Mutual repulsion
of electrons)

Levels $^{2S+1}L_J$

Hso = spin orbit
(Coupling between
spin and
Ho >Hc , Hso >Vo
orbital angular
momentum)

Stark Levels $^{2S+1}L_{J(\alpha)}$

Vo = crystal field
(Electric field of host)

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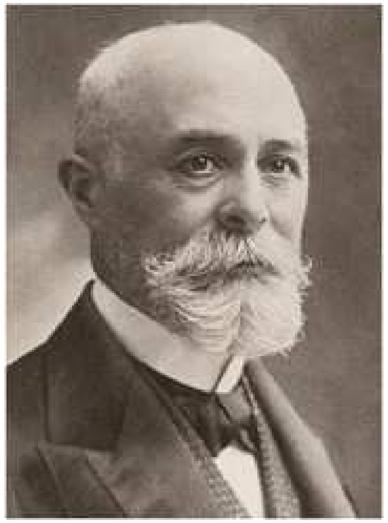
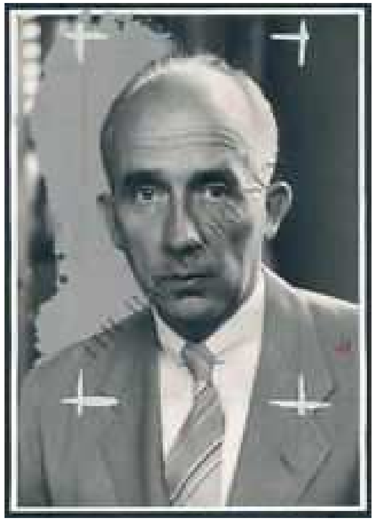
Optical centers (= rare earths) in solids



Henri Becquerel

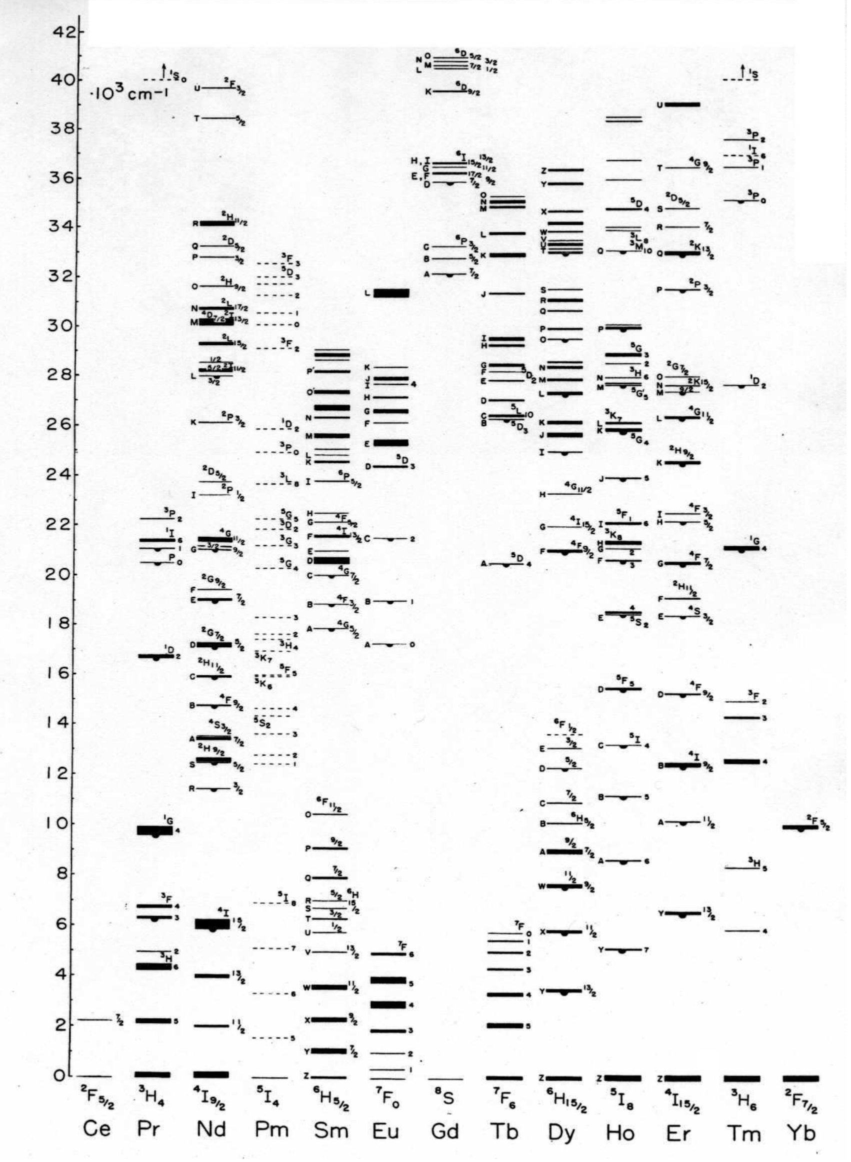
Becquerel, J&H Kamerlingh Onnes, „The absorption spectra of the compounds of the rare earths at the temperatures obtainable with liquid hydrogen, and their change by the magnetic field"

KNAW, Proceedings, 10 II, 1907-1908, Amsterdam, 1908, pp. 592-603



G.H. Dieke

Gerhard H. Dieke and Robert A. Satten Spectra and Energy Levels of Rare Earth Ions in Crystals Am. J. Phys. 38, 399 (1970)



Carnall, Goodman, Rajnak, Rana. *J. Chem. Phys.*, 90 (1989) 3445

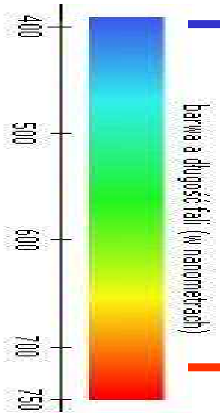
Optical centers (= rare earths) in solids

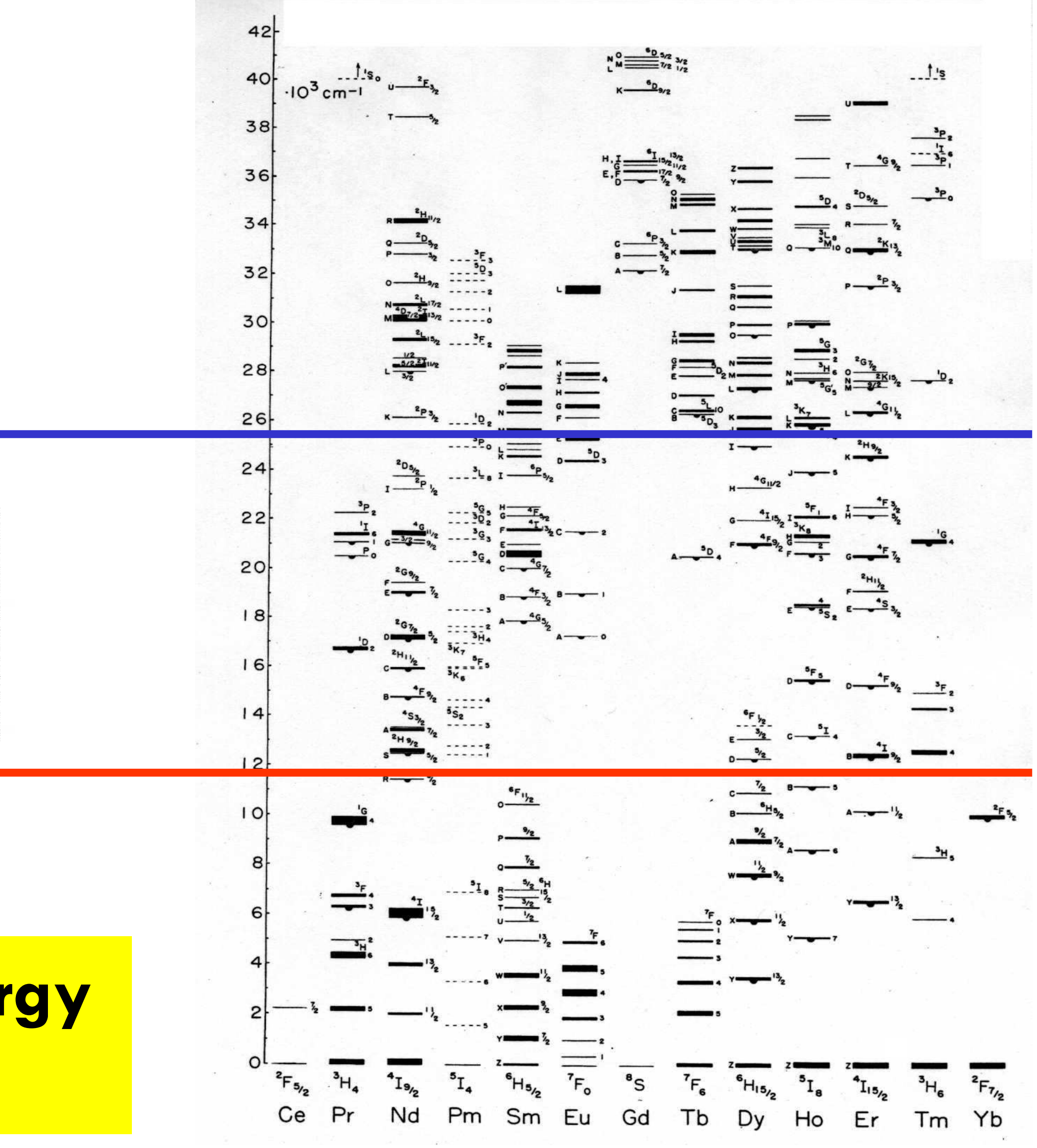
1988

Carnall, Goodman

Rajnak, Rana

Ln^{3+}





Dieke diagram for the energy levels of trivalent RE ions

From fascination to boredom

The richness and complexity of lanthanide optical spectra are reflected in an article published in 1937 by J.H. van Vleck:
„The Puzzle of Rare Earth Spectra in Solids”

Other perspective:

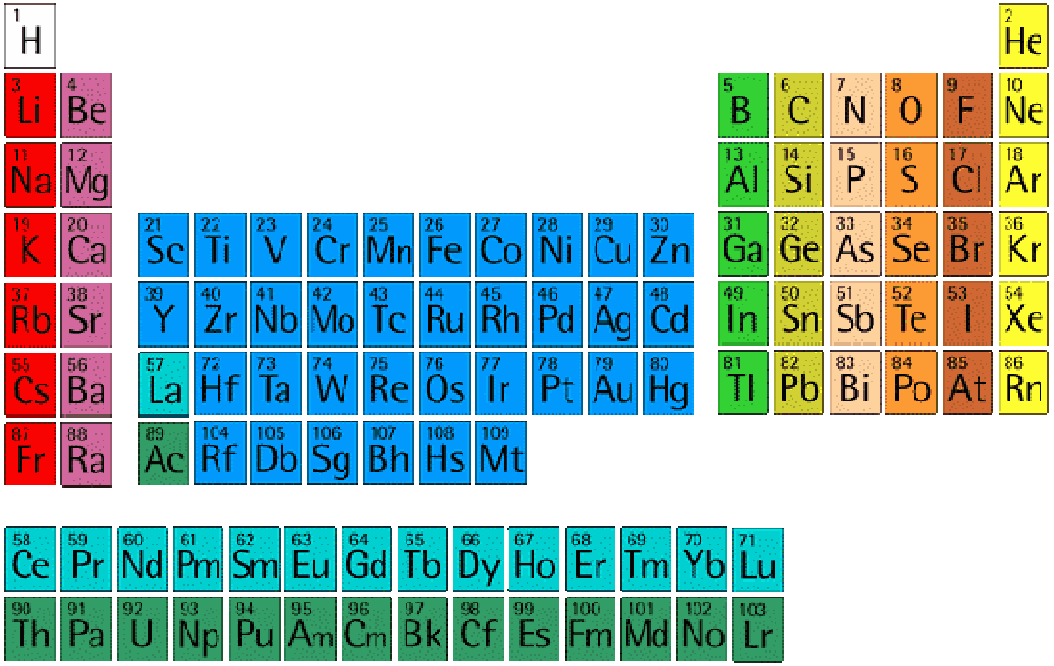
Pimentel and Sprately in the book *Understanding Chemistry* 1971:
"Lanthanum has only one important oxidation state in aqueous solution, the +3 state. With few exceptions, this tells the whole boring story about the other 14 elements"

Optical centers (= rare earths) in solids

Phosphors

Centers:

lanthanides
(Z=58–71)
rare-earths (RE) →



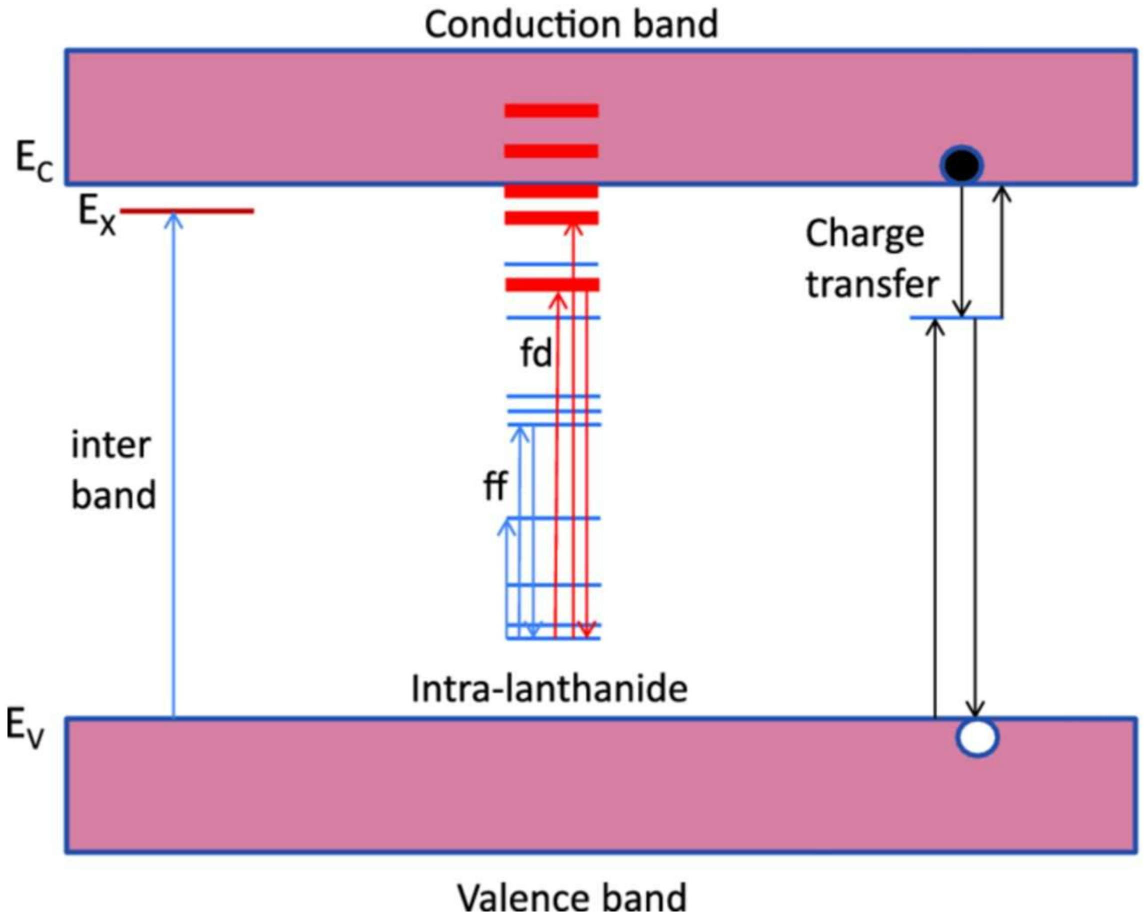
Matrixes:

- crystals,
- glasses,
- ceramics,
- polymers,

} oxides, fluorides, semiconductors, nano-sized, waveguides

Optical centers (= rare earths) in solids

Electronic transitions of RE in solid matrixes. Bands and discrete levels



Dorenbos P ECS J. Solid State Sci. Technol. 2013;2:R3001-R3011

Optical centers (= rare earths) in solids

Rare-earth ions

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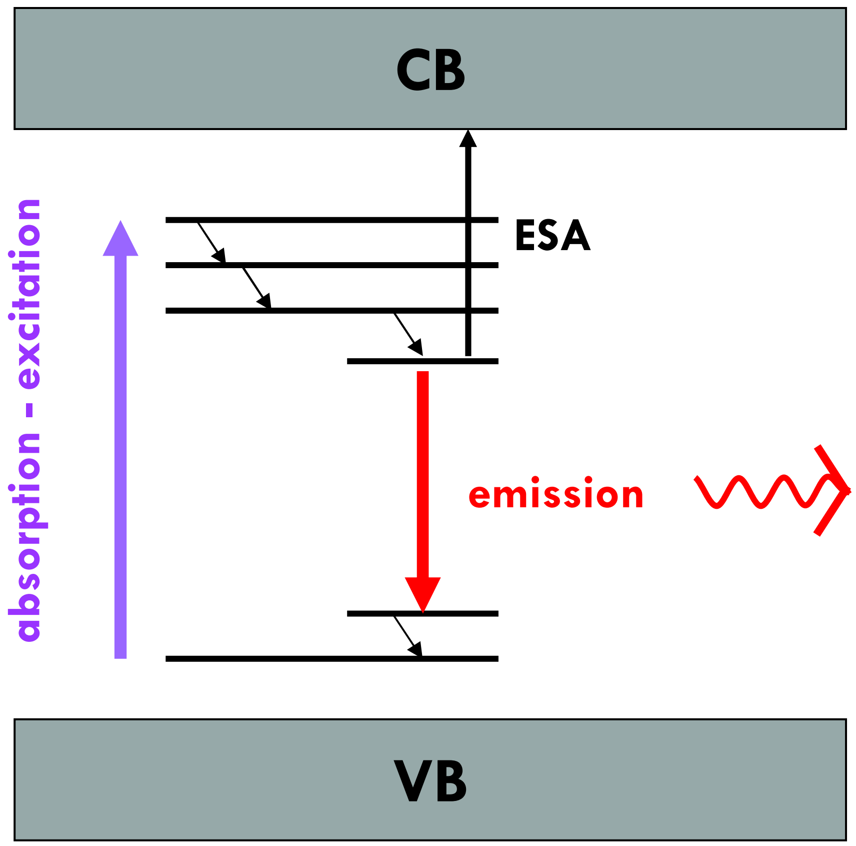
Tb^{3+}	8
Dy^{3+}	9
Ho^{3+}	10
Er^{3+}	11
Tm^{3+}	12
Yb^{3+}	13

- Electronic configuration: [Xe] $4f^n\ 5s^2\ 5p^6$ (n=1-13)
- Incomplete inner $4f^n$ orbital
- Weak crystal field
- Splitting of levels by crystal field



electron-photon-phonon interaction

Transitions and selection rules

Not all transitions between atomic states that are energetically feasible **are allowed**.

Wavefunctions must have correct parity (Laporte rule).

Laporte's parity selection rule implies that states with the same parity cannot be connected by electric dipole transitions; as a consequence f–f transitions are forbidden by the ED mechanism.
Forbidden transitions may occur in practice but with low probabilities

Multiple selection rules

Selection rules for transitions depend on type of transitions, ED, EQ or MD

$$P = -e\sum_i \vec{r}_i$$

Electric-dipole operator (odd)

$$M = -\frac{e\hbar}{2mc}\sum_i \vec{I}_i + 2\vec{s}_i$$

Magnetic-dipole operator (even)

$$Q = -\frac{1}{2}\sum_i \left(\vec{k}\cdot\vec{r}_i\right)\times\vec{r}_i$$

Quadrupole operator (odd)

	S	L	J (no 0⇔0)	Parity
Electric dipole	ΔS=0	ΔL=0,±1	ΔL=0,±1	opposite
Magnetic dipol	ΔS=0	ΔL=0	ΔL=0,±1	same
Electric quadrupole	ΔS=0	ΔL=0,±1,±2	ΔL=0,±1,±2	opposite

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Electronic transitions of RE in solids.

- **Intraconfiguration transition: $4f^n$-$4f^n$ transition**

Forbidden transition, longer life time (ms - μs), sharp line, low intensity, the influence of environment on the 4f levels is weak because the 4f electrons are shielded from external electric fields by the outer $5s^2$ and $5p^6$ electrons.

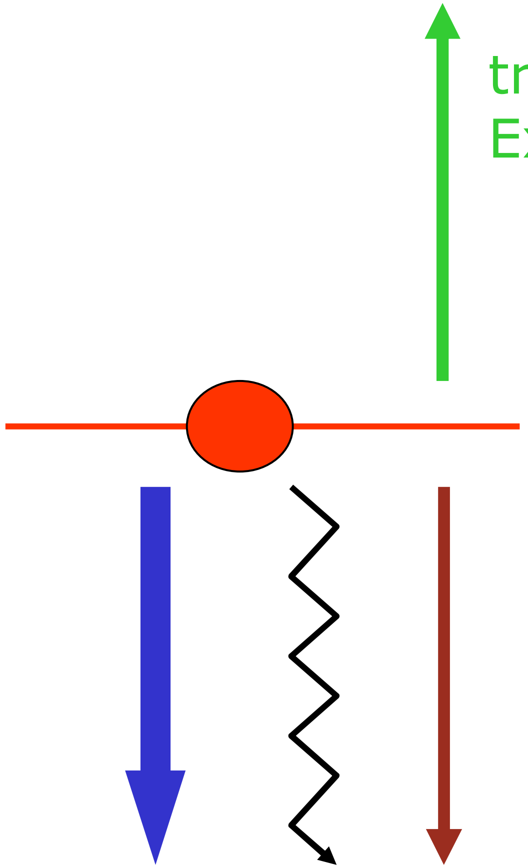
- **Interconfiguration transition:**

(1) **$4f^n$-$4f^{n-1}5d$ transition**, for example: Ce^{3+}, Pr^{3+}, Eu^{2+};

(2) **charge transfer transition:** $4f^n \rightarrow 4f^{n+1}L^{-1}$, (where L = ligand), for example: Eu^{3+}, Sm^{3+}, Yb^{3+}.

Allowed transition, short life time (~ns), broad band, stronger intensity. the influence of environment on the 5d levels is strong because they are located at outer orbits.

Relaxation of excited RE^{3+} ion



transfer
Excited State Absorption ESA

Excited state

Radiative decay **- photon**

Nonradiative decay - phonons

transfer, diffusion of excitation

Relaxation of excited RE^{3+} ion

Major Nonradiative Processes:

1. Multiphonon relaxation (W_{mp})
2. Energy transfer between ions (W_T)
3. Hydroxyl content/High frequency vibrational groups (W_{OH})
4. Impurity (W_{imp})

$$W_{nr} = W_{mp} + W_T + W_{0H} + W_{imp}$$

$$\tau_{fl} = 1/\left(W_r + W_{nr}\right)$$

W_r=radiative decay rate
W_{nr}=nonradiative decay rate

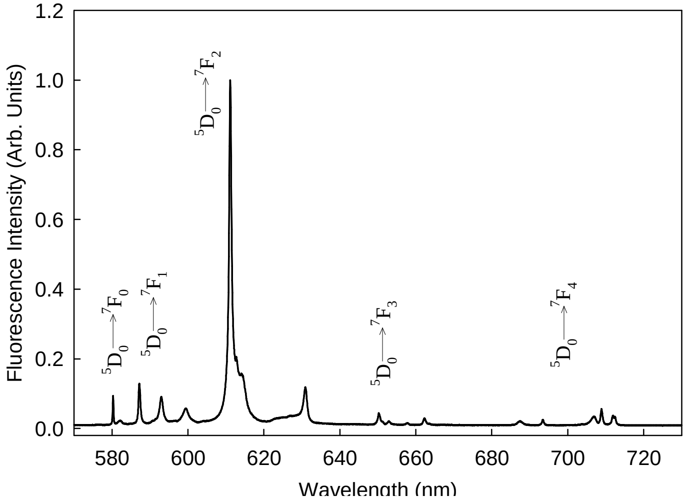
Radiative Quantum Efficiency:

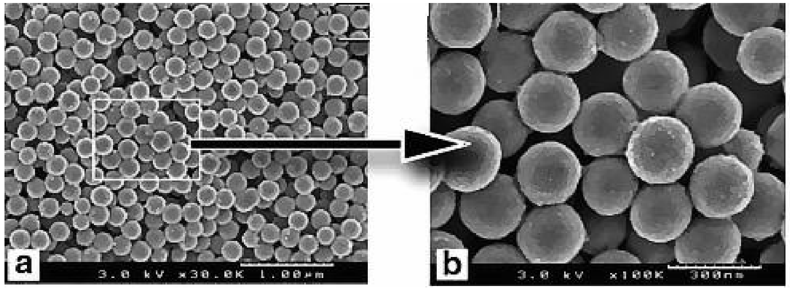
$$\eta = \frac{\tau_{fl}}{\tau_r} = \frac{W_r}{W_r + W_{nr}}$$

Examples of emission optical spectra

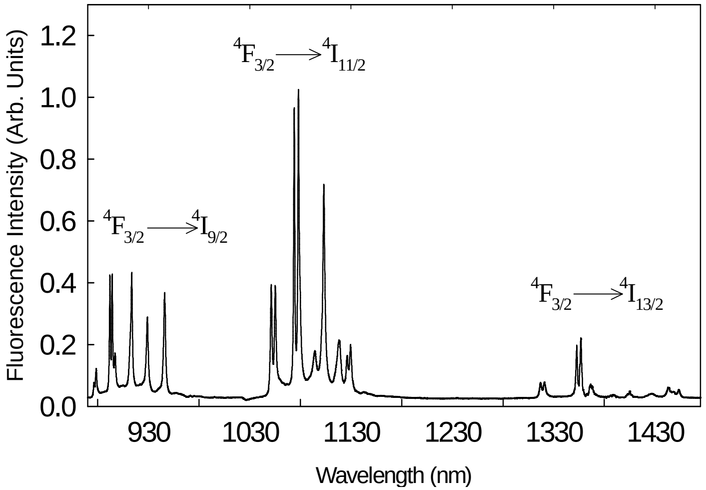
$Eu^{3+}:Y_2O_3$

nanocrystals





$Nd^{3+}:Y_3Al_5O_{12}$



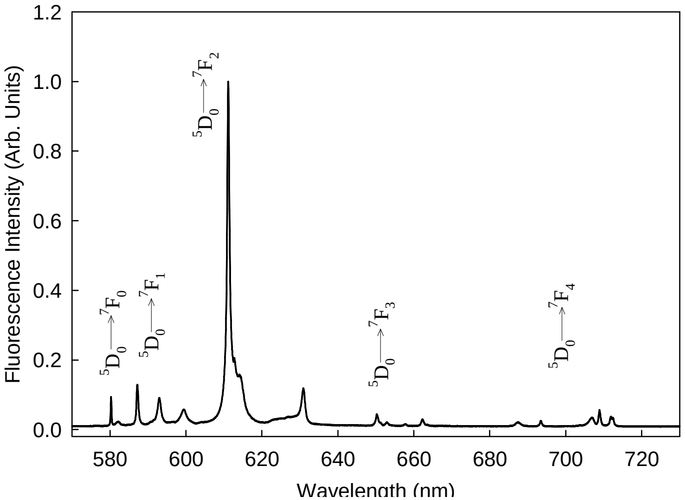
From Dhiraj Sardar Department of Physics University of Texas at San Antonio

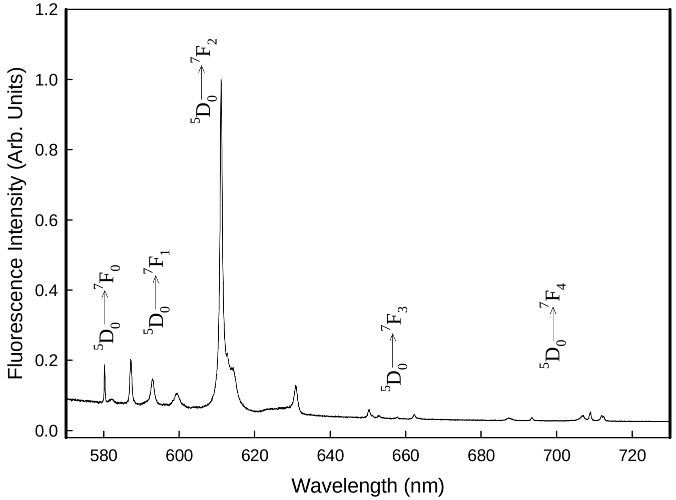
Examples of emission optical spectra

Nanoparticles

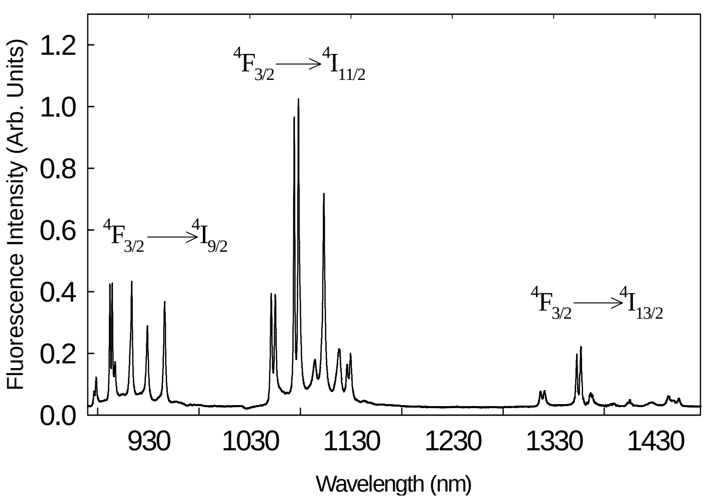
Epoxy embedded

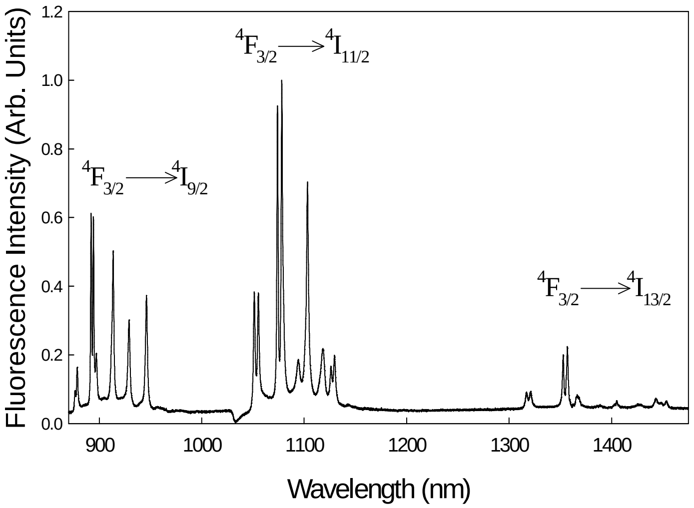
$Eu^{3+}:Y_2O_3$





$Nd^{3+}:Y_2O_3$





Brian Judd, George Ofelt and Brian Wybourne in Lądek Zdrój together for the first time
June 22, 2003 *4th International Spring Workshop on Spectroscopy, Structure and Synthesis of Rare Earth Systems*

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Rare-Earth-Activated Optical Materials

- Efficient, High-Power, Long-Lived IR, Visible, & UV Lasers
  - Nd^{3+}:YAG and Yb^{3+}:YAG lasers for high power
  - Nd^{3+}:YAG doubled for green pointers
  - $Nd^{3+}:YVO_4$ doubled for watts of green
  - Ho^{3+}, Er^{3+}, Tm^{3+}, … medical, dental, and industrial devices, …
- Phosphors, Displays, Hg-Free Lamps, Solid-State Lighting
  - Red $Eu^{3+}:Y_2O_2S$, a critical factor in success of color TV
  - Blue Eu^{2+} phosphors
  - Green $Tb^{3+}:(Ln, Ce)PO_4$ phosphor
  - White light by phosphors & diodes
  - Electroluminescent semiconductors with rare-earth ions
- Scintillators, Digital X-Ray Imaging, CAT and PET Scans, Particle Physics, and Oil Exploration, …
  - Lu^{3+} provides high density for efficient absorption
  - Some of the fastest and most efficient scintillator materials such as CeF_3, $Ce^{3+}:YAlO_3$, and $Ce^{3+}:Lu_2SiO_5$
- Spectral Hole Burning Devices
  - High bandwidth analog signal processing
  - Lasers stabilized to 2 parts in 10^{13}
  - Stabilized lasers for local oscillator in atomic clock
  - Optical data storage
- Quantum Information Devices
  - $Eu^{3+}:Y_2SiO_5$, $Pr^{3+}:Y_2SiO_5$, $Er^{3+}:Y_2SiO_5$, Tm^{3+}:YAG, $Tm^{3+}:LiNbO_3$, $Er^{3+}:LiNbO_3$
  - Er-doped optical fiber

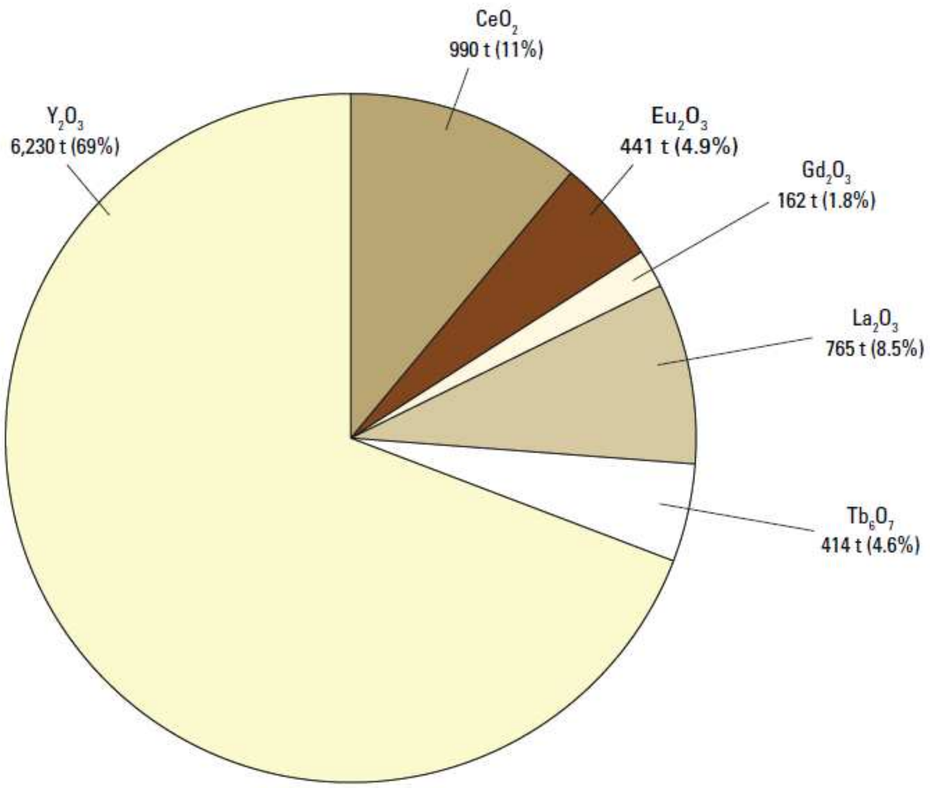
Average Rare Earth content - phosphors

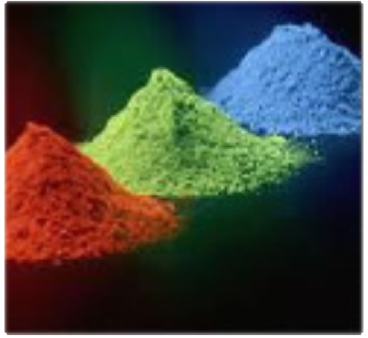
	Red 60%		Green 30%		Blue 10%		**White** **(R60%G30%B10%)**
	5% EU **95% Y**	**+**	**20% Ce** **38% La** **12% Tb** **30% Other**	**+**	**2% Eu** **98% Other**	**=**	**3% Eu** **57% Y** **6% Ce** **11.4% La** **3.6% Tb** **19% others**
RE%	**100%**		**70%**		**2%**		**100%**

REs comprise 65% of lamp phosphors

Rare Earths market

Global market: 9,000 ton of REOs was used in LED category



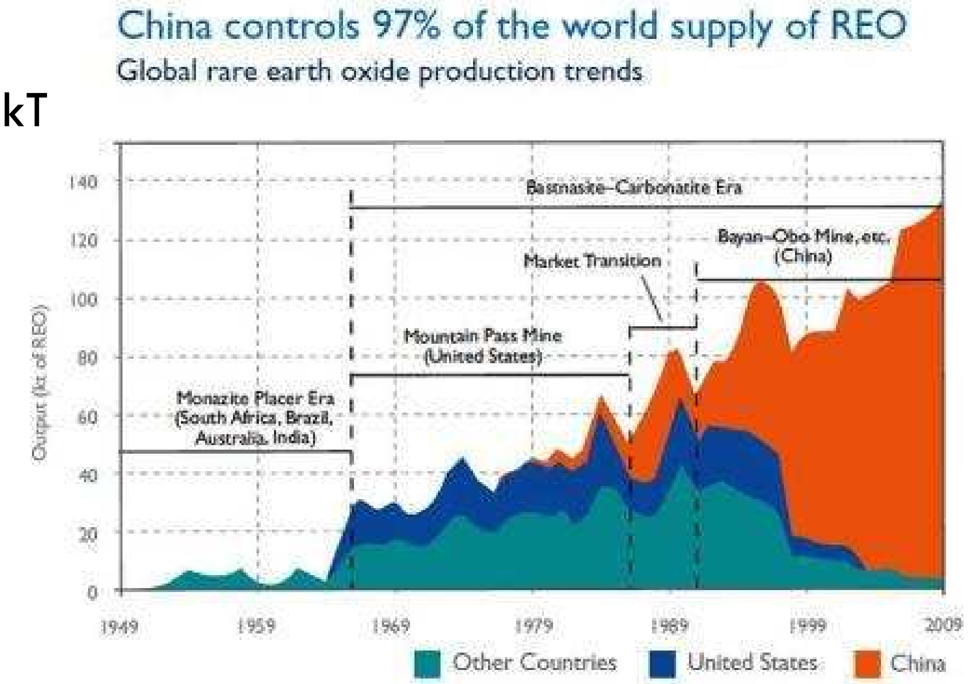


RE Fine Chemicals

RE Phosphor

LED
Products

Rare Earths market - production



China controls 97% of the world supply of REO

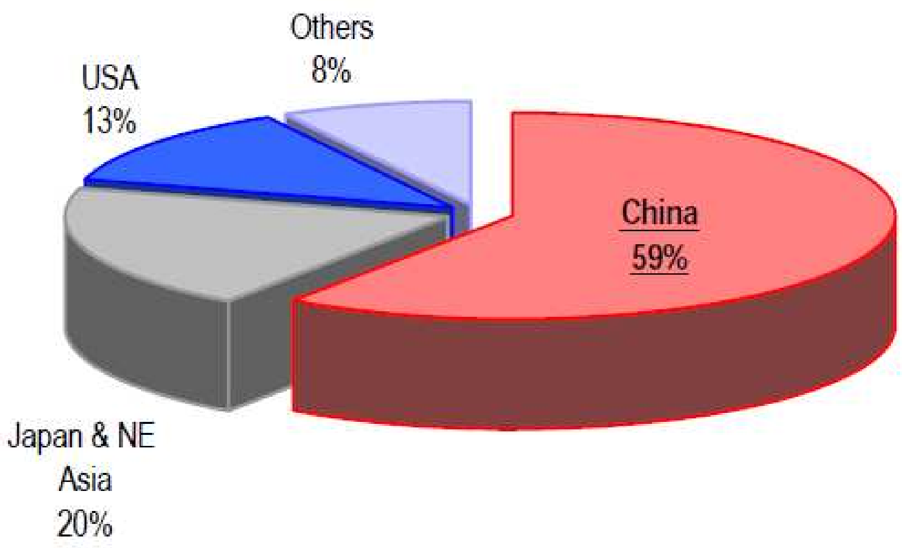
Global rare earth oxide production trends

kT

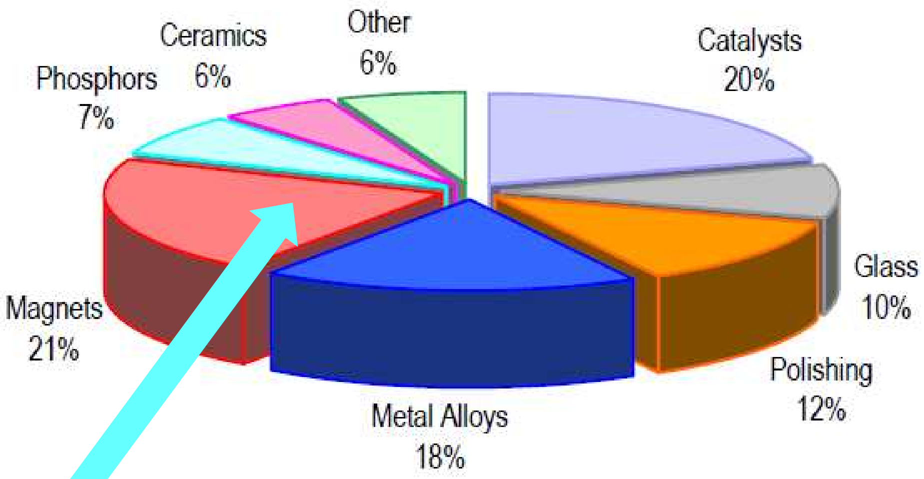
- Global production of REs reached 129,000 tones (market value of US$17.5 billion)
- Demand on raw REs is forecasted to increase by 56% each year in the next five years
- China alone constitutes 92% of global production of raw REs in 2011
- Manufacturing of high-tech products require the use of refined and purified REs-based specialty intermediate materials

Consumption

REE Consumers by Country/Region

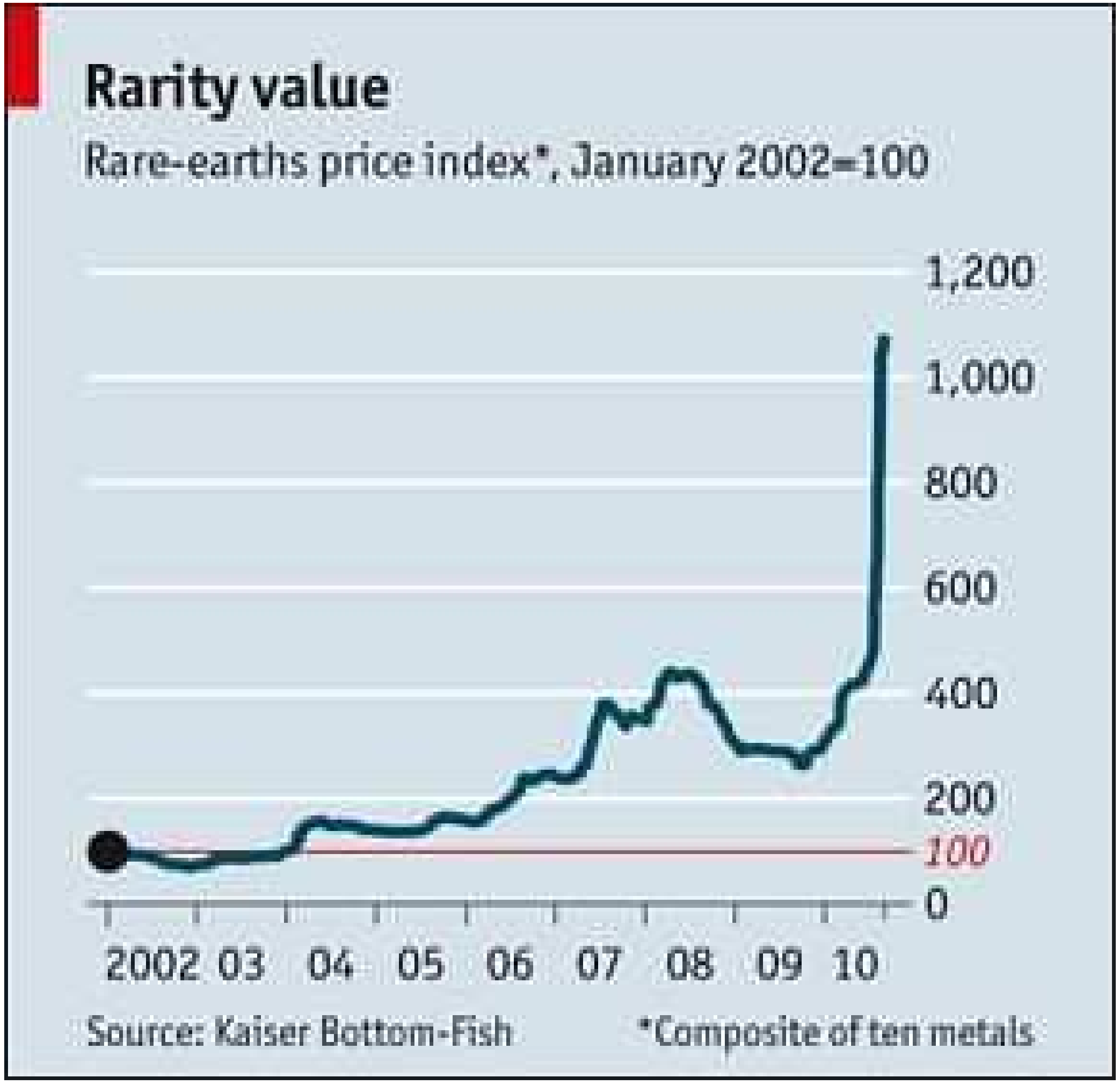


REE Consumers by End Use



phosphors

Rare Earths Price Index 2002-2010



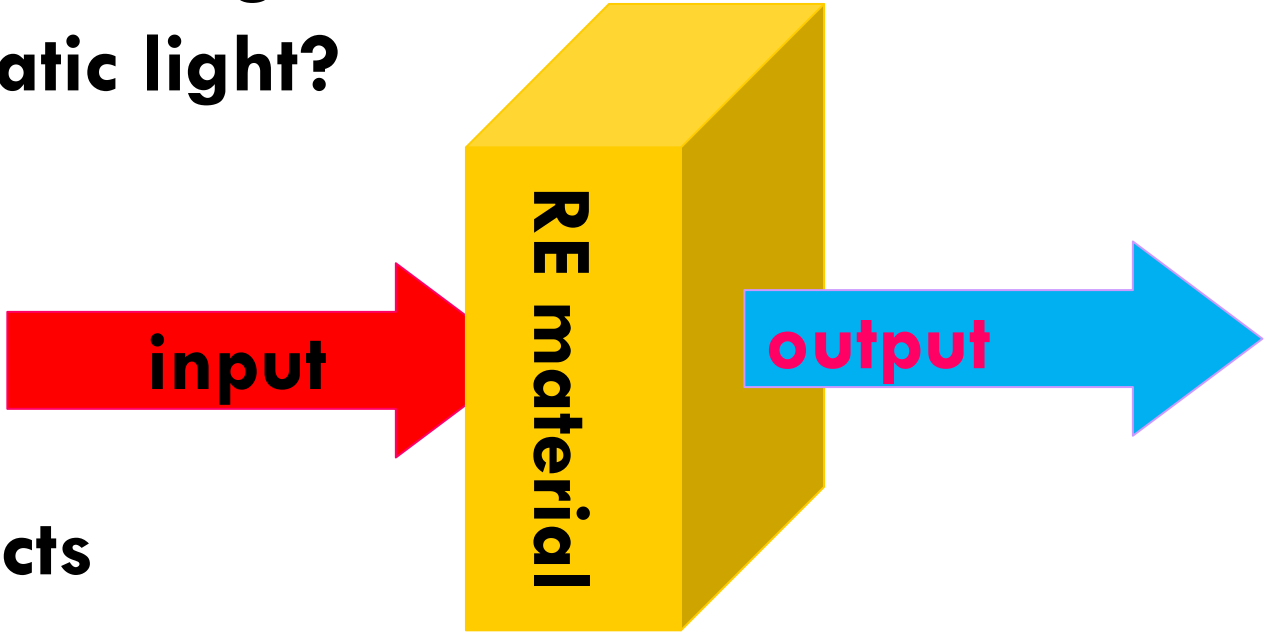
Source: *The Economist*

- Luminescence
- Introduction to rare-earths
- Upconversion luminescence
- Sensing
  - sensing using RE-doped upconversion nanoparticles
  - upconversion phosphors as optical marker materials
  - temperature sensing
  - bio-applications

Upconversion luminescence

Question:

Is it possible to change the color of a monochromatic light?

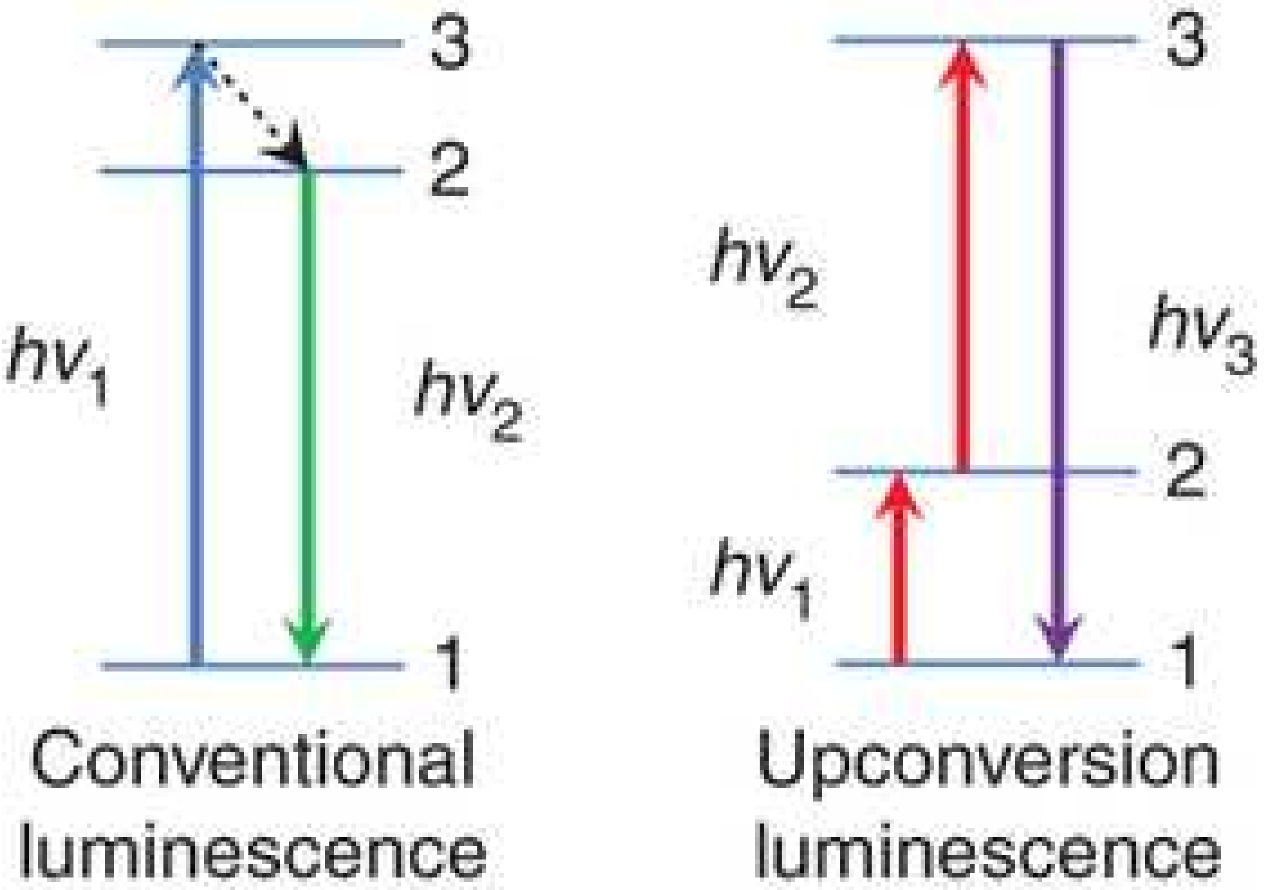


Answer:

Yes:

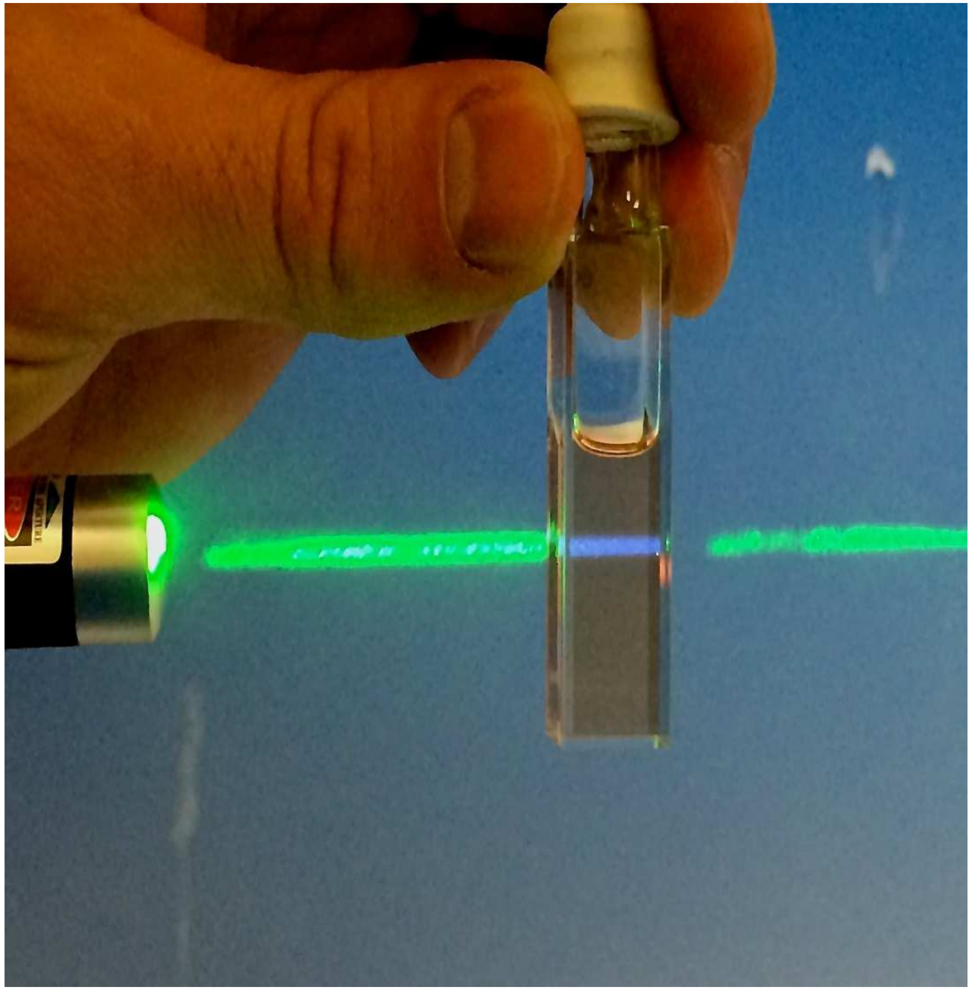
- nonlinear effects
- upconversion (or downconversion)

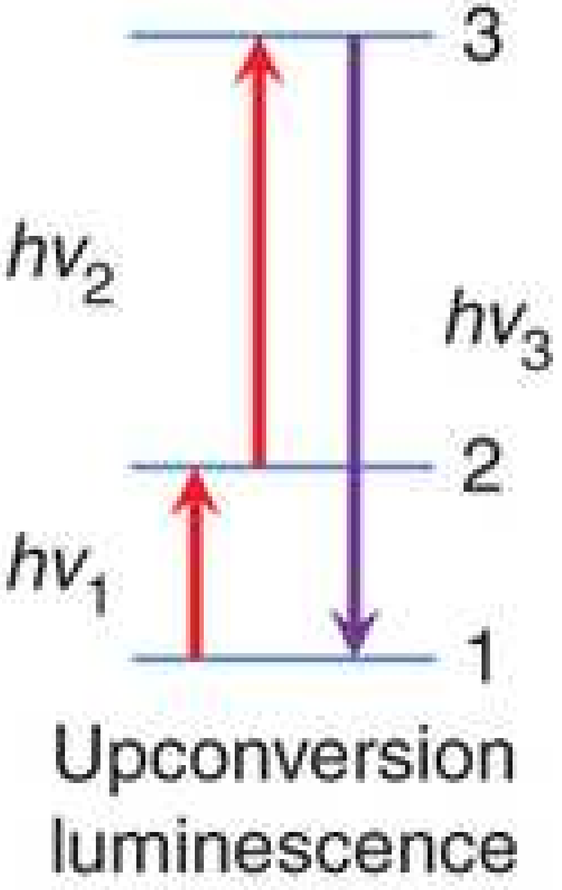
Upconversion luminescence



Up conversion luminescence or **anti-Stokes fluorescence** is the re-emission of **shorter** wavelength photons (higher frequency or energy) by a material that has absorbed photons of **longer** wavelengths (lower frequency or energy)

Upconversion luminescence





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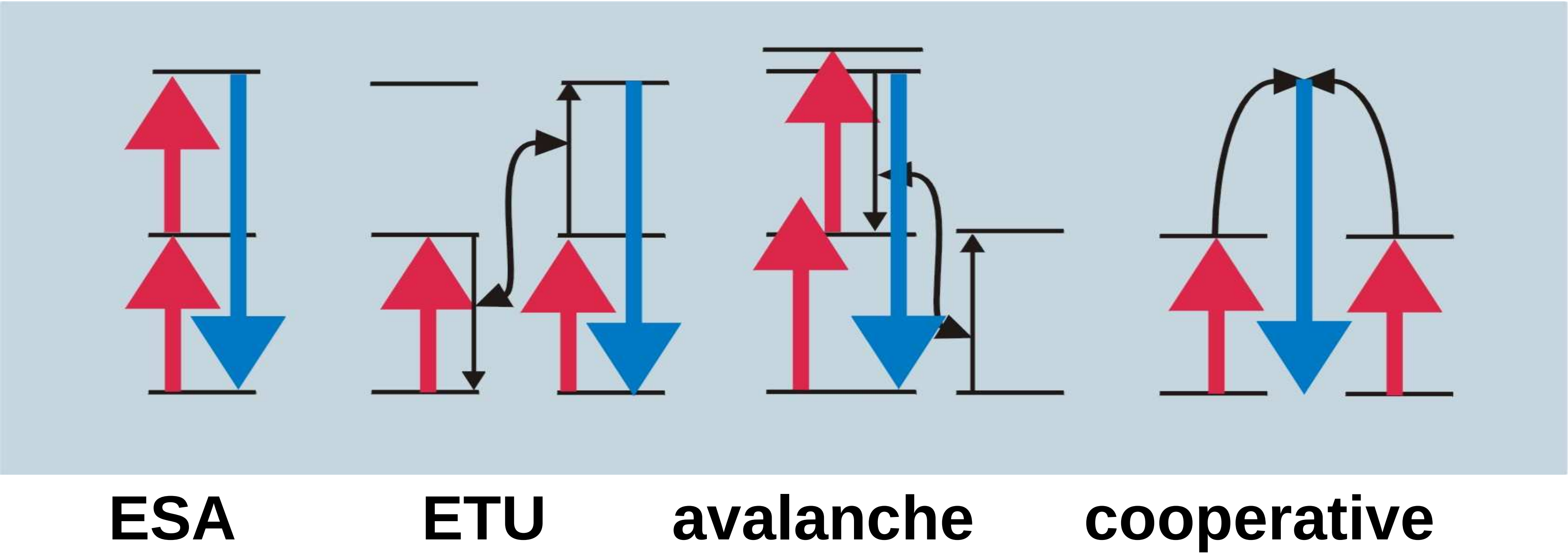
Upconversion luminescence

multi-photon and multi-ion processes and interactions could result in:

- **down-conversion; quenching or photon cutting,**
- **up-conversion; anti-Stokes emission, …**



•S.M. Kirkpatrick, S. R. Bowman, L. B. Shaw, J. Ganem „Cross relaxation and upconversion coefficients of the mid-infrared transitions of Pr^{3+}:$LaCl_3$" J. Appl. Phys. 82, 2759 (1997)

•J.S. Chivian, W.E. Case, D.D. Eden „The photon avalanche: A new phenomenon in Pr^{3+}-based infrared quantum counters" Appl. Phys. Lett. 35, 124 (1979)

Upconversion luminescence

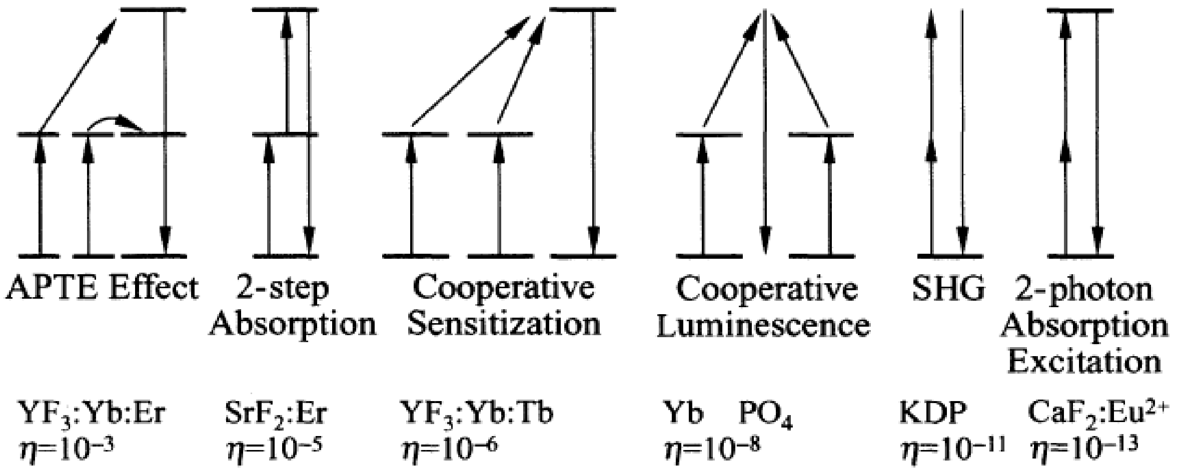
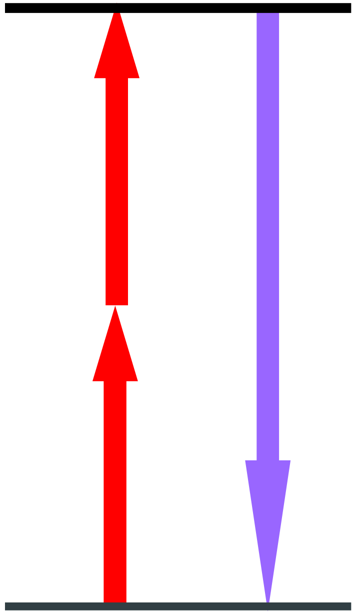


Figure 5.3 Various two-photon up-conversion processes with their relative efficiency in considered materials



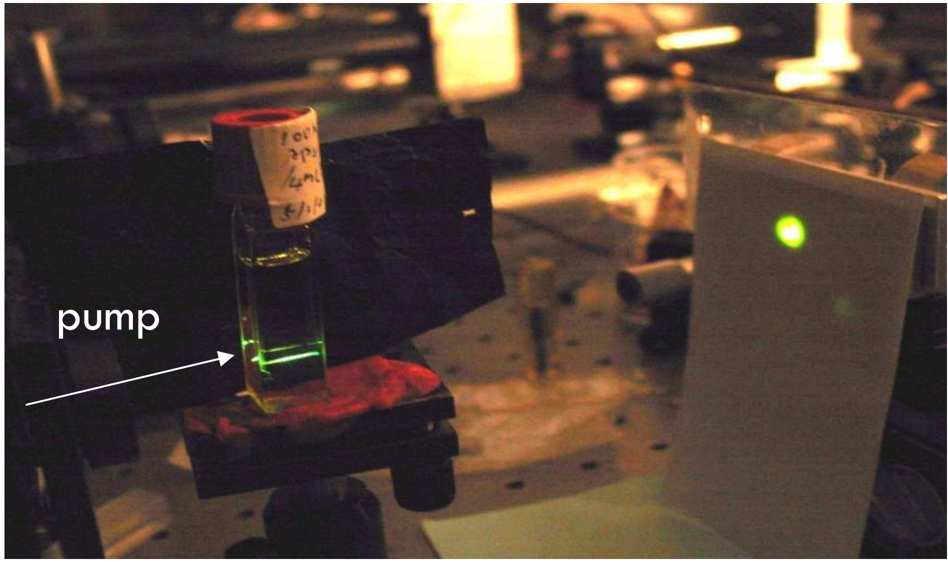
F. Auzel „Upconversion and Anti-Stokes Processes with f and d Ions in Solids" Chem. Rev. 2004, 104, 139-173

Two-photon laser spectroscopy has been used as an important complementary technique in studying optical materials containing RE ions as it has a different parity selection rule, allows access to higher energy states, and has a greater variety of possible polarizations than linear spectroscopy.

- T.R. Badder, A. Gold, „Polarization dependence of two-photon absorption in solids", Phys. Rev. 171 (1968) 997
- D.S. McClure „Two-photon spectroscopy using infrared photons" in Advanced Solid State Lasers, OSA Technical Digest (Optical Society of America, 1986) WA1-1
- M.C. Downer „The puzzle of two-photon rare-earth spectra in solids", in *Laser Spectroscopy of Solids*, ed. W.M. Yen Spriger Verlag vol. 65 (1989) p.29

Upconversion luminescence

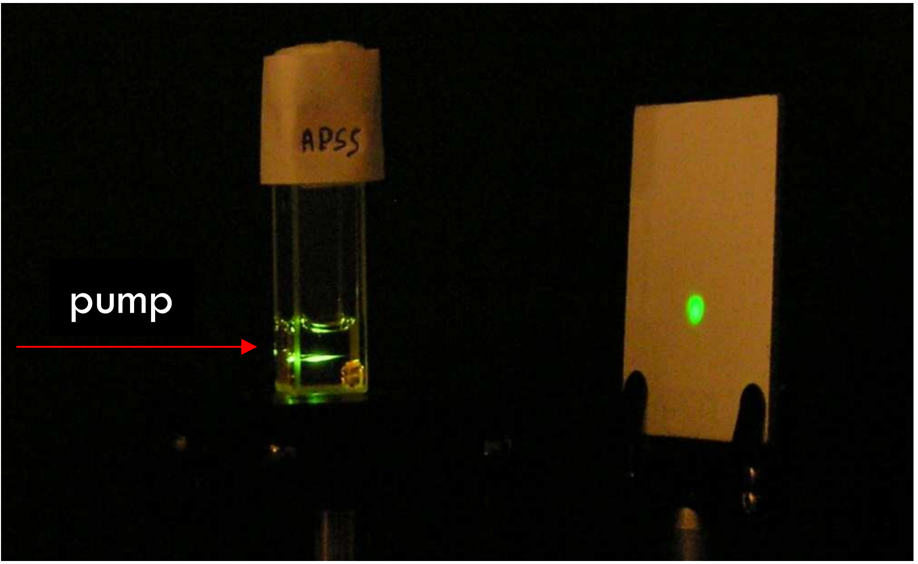
Three- Photon Excited Amplified Emission



λ_{pump}=1300nm

λ_{em}^{max}=553nm

Four-Photon Excited Amplified Emission

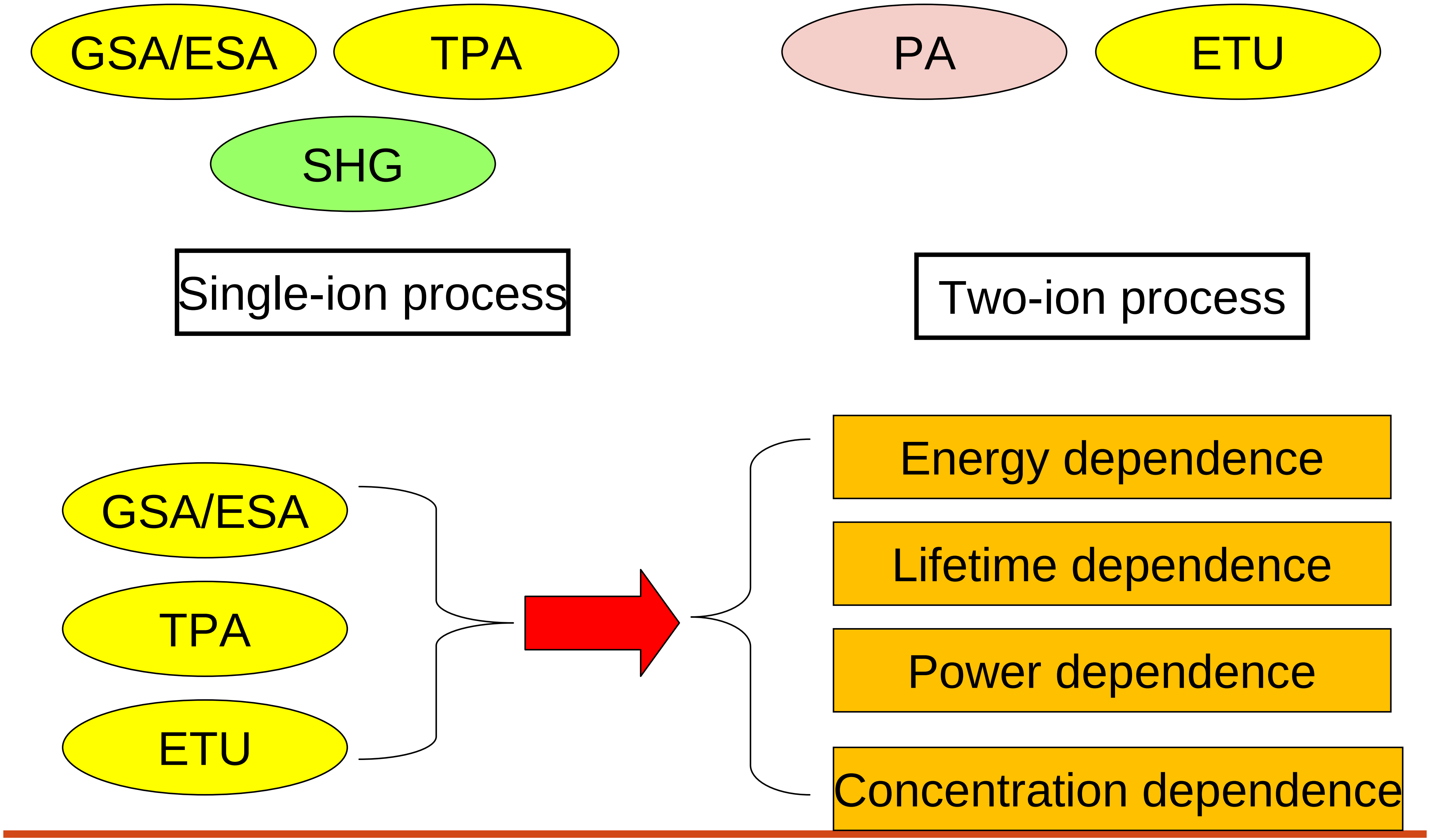


λ_{pump}=1770nm

λ_{em}^{max}=553nm

He *et al.*, Nature 415, *767* (2002)

multi-photon and multi-ion processes and interactions



GSA/ESA

TPA

SHG

Single-ion process

PA

ETU

Two-ion process

GSA/ESA

TPA

ETU

Energy dependence

Lifetime dependence

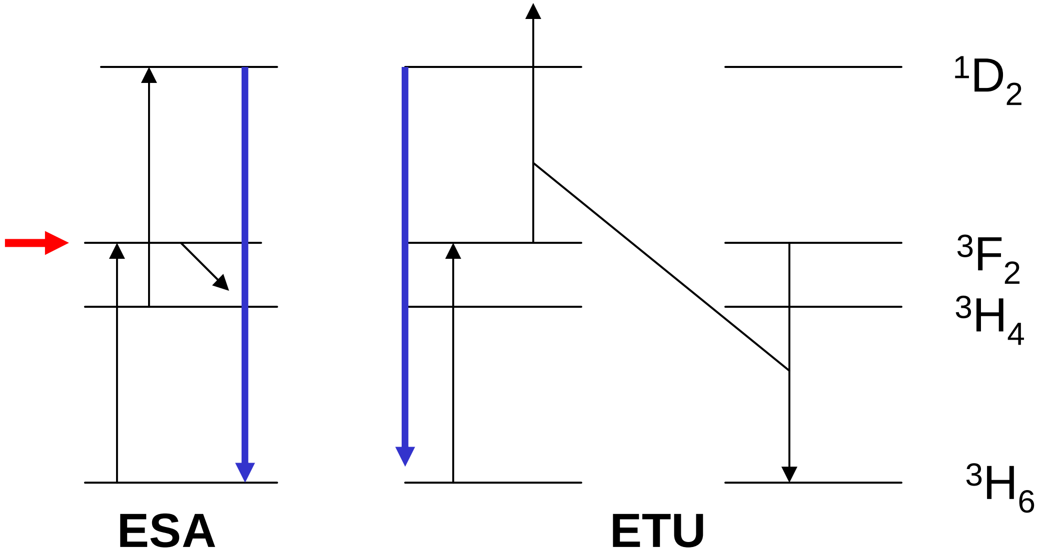
Power dependence

Concentration dependence

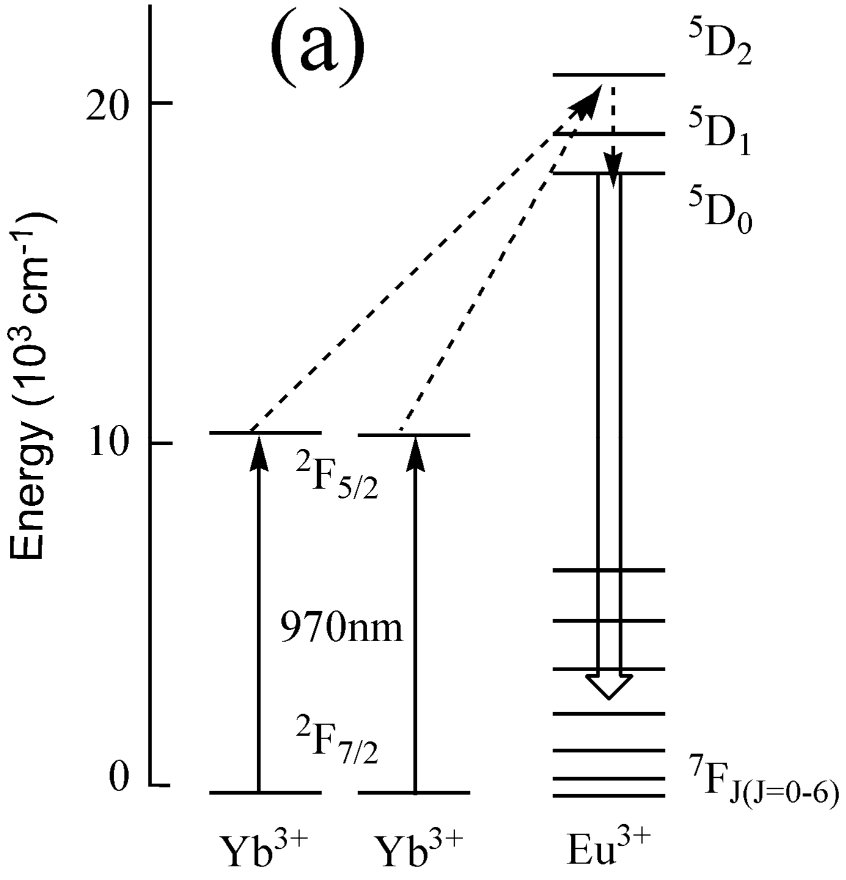
ESA/ETU

Distinguish mechanism by:

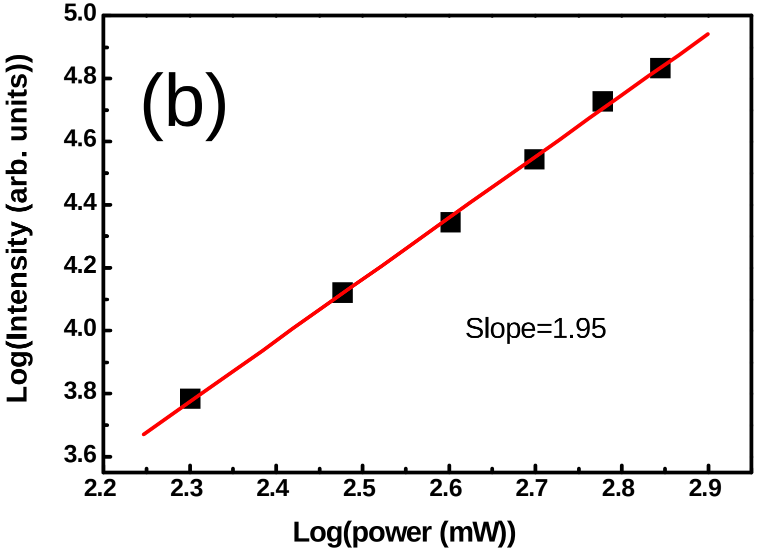
1. **Upconversion excitation spectrum.**
2. **Risetime of lifetime.**
3. **Concentration.**



Many body (cooperative) processes



Y_2O_3:Yb^{3+},Eu^{3+} upconversion

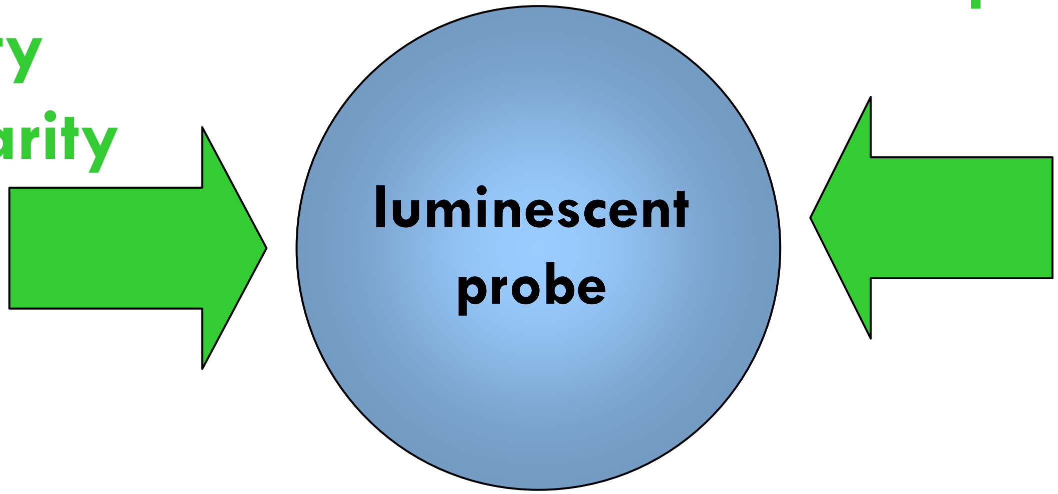


Yb^{3+} often employed for upconversion since it has absorption band ~10000 cm^{-1} and no higher levels.

Applications of two-photon induced luminescence

- microscopy
- micro-fabrications
- three-dimensional data-storage and display
- optical power limiting
- up-converted lasing
- up-converted sensing
- photodynamic therapy
- localized release of bio-active species

RE^{3+} ion as a fluorescent probe



- other ions
- electric fields
- viscosity
- pH polarity

- temperature
- pressure

luminescent probe

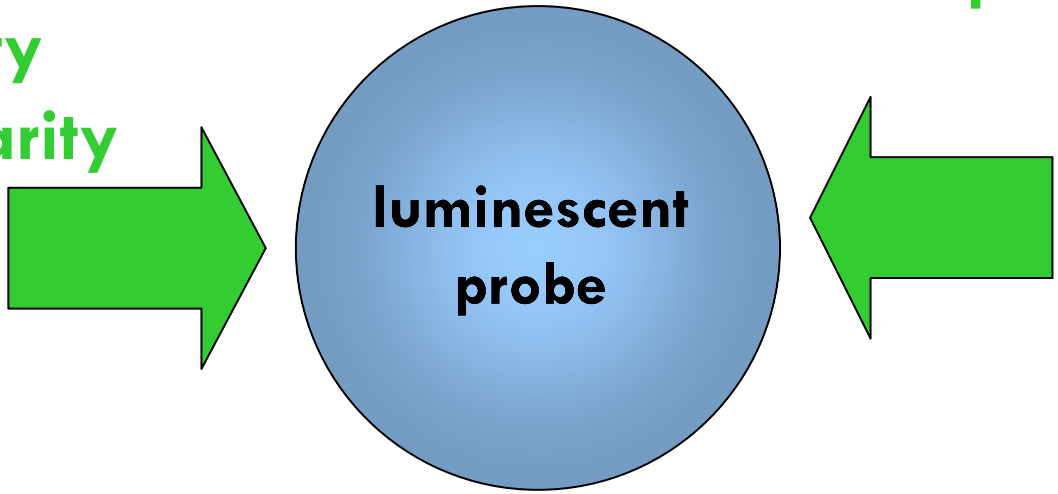
The specific spectroscopic properties of RE^{3+} ions make them ideal luminescent probes:

- easily recognizable line-like spectra
- long lifetimes of excited states
- large Stokes' shift upon ligand excitation

RE^{3+} ion as a fluorescent probe

- other ions
- electric fields
- viscosity
- pH polarity

- temperature
- pressure



Lanthanide-containing luminescent probes can be used as:

- **structural probe (site symmetry)**
- **analytical probes (mainly for bio-analyses)**
- **imaging probe for medical diagnosis (tumor imaging)**

RE^{3+} ion as a fluorescent probe

Various phosphor characteristics are affected by external interactions:

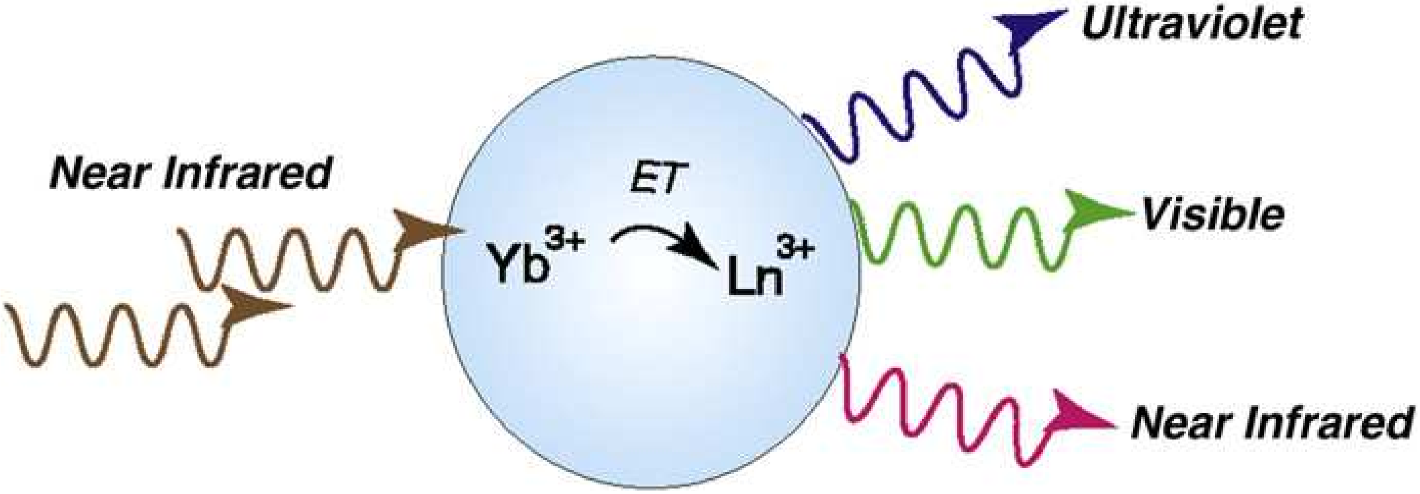
- Decay Time
- Line shift and broadening
- Ratio of emission lines
- Emission distribution
- Absorption band-width and position
- Excitation band-width and position
- Rise time

RE^{3+} ion as a fluorescent probe

what is UCNP?

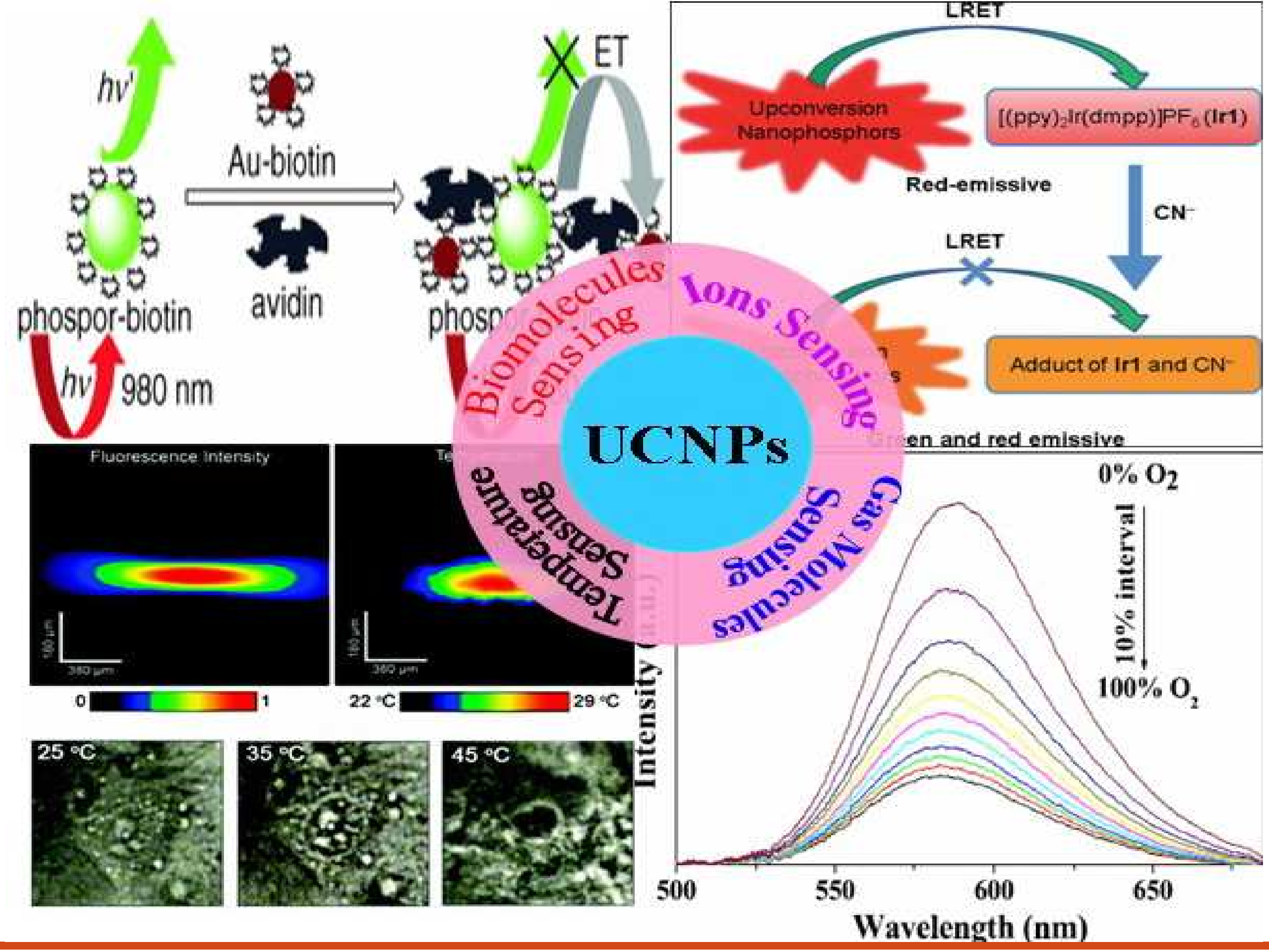
UCNP = upconverting nanoparticle

Rare earth (RE)-doped upconversion nano-phosphors (UCNPs) can efficiently convert near-infrared (NIR) light into visible or ultraviolet (UV) luminescence



fluoride, oxide, oxyfluoride, vanadates, oxysulfide, etc

RE^{3+} ion as a fluorescent probe



Shuwei Hao et. al. *Theranostics* 2013, Vol. 3, Issue 5