TENTATIVE LECTURE SCHEDULE

		Date	Topic
1.	Wed	07.09.	Course Introduction & Short Review of the Elements
2.	Fri	09.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Mon	12.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Fri	16.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Mon	19.09.	Transition Metals: General Aspects & Pigments
6.	Wed	21.09.	Redox Chemistry
7.	Fri	23.09.	Crystal Field Theory (Linda Sederholm)
8.	Mon	26.09.	V, Nb, Ta & Perovskites & Metal Complexes & MOFs & MLD
9.	Wed	28.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
10.	Fri	30.09.	Mn, Cu, Ru
11.	Mon	03.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
12.	Fri	07.10.	Lanthanoids + Actinoids & Luminescence
13.	Mon	10.10.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
14.	Wed	12.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
15.	Fri	14.10.	Inorganic Materials Chemistry Research

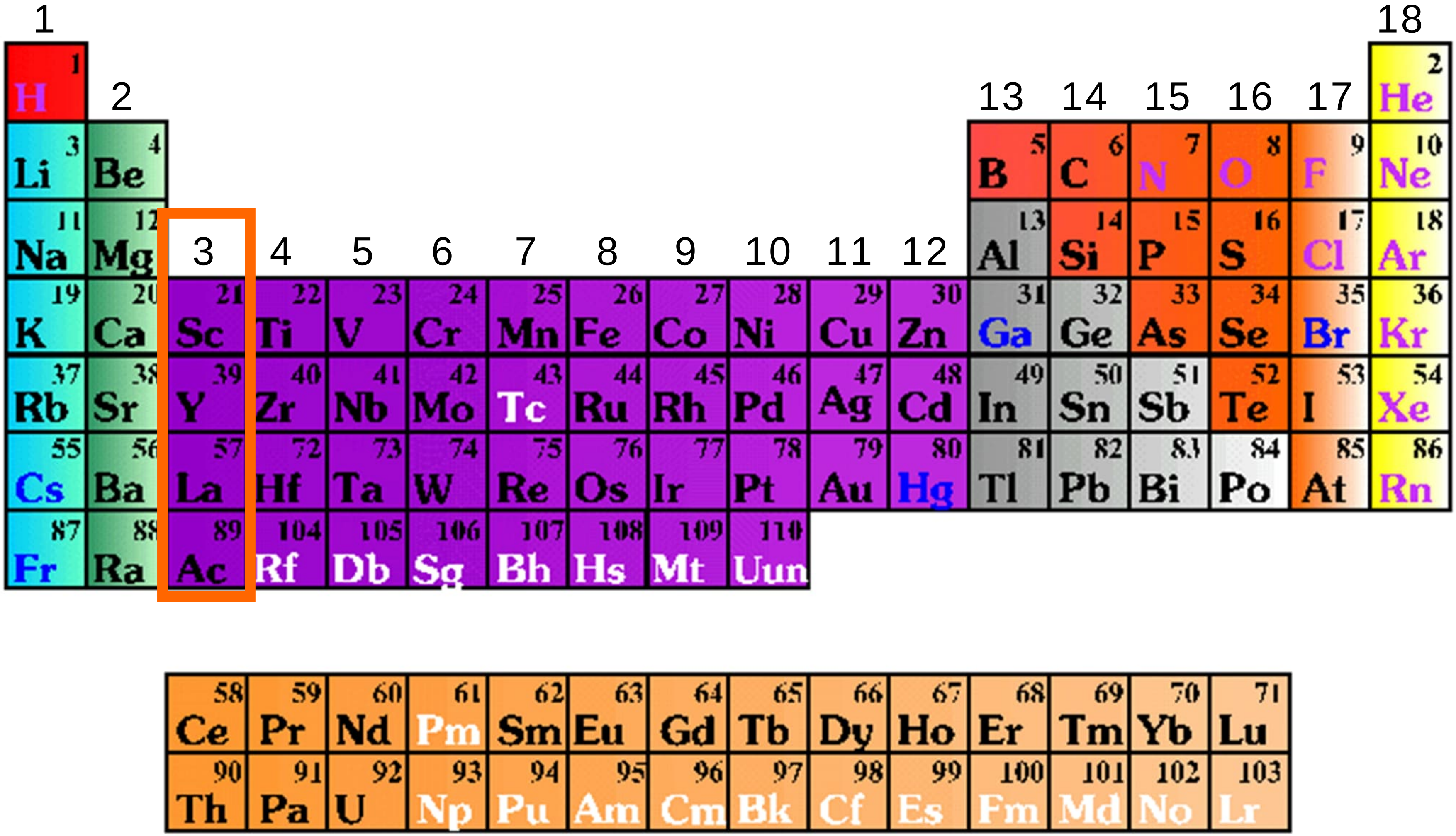
EXAM: Oct. 18, 9:00-12:00

PRESENTATION TOPICS/SCHEDULE

Fri 16.09.	Zn:	Rautakorpi, Stenbrink & Hyvärinen
Mon 26.09.	Nb:	Souza, Rahikka & Tong
Wed 28.09.	Mo:	Alimbekova & Tran (Nhi)
	Ti:	Mäki & Israr
Fri 30.09.	Mn:	Tao & Song (Zonghang)
	Cu:	Marechal, Weppe & Ishtiaq
	Ru:	Järvinen & Verkama
Fri 07.10.	Eu:	Bardiau, Wolfsberger & Klingerhöfer
	Nd:	Helminen, Olsio & Keskimaula
	U:	Airas & Holopainen
Wed 12.10.	Co:	Song (Yutong) & Lone
	In:	Antila & Wallius
	Te:	Peussa & Heylen

QUESTIONS: Lecture 12

- **List all the possible lanthanide ions that have 7 f electrons.**
- **List all the possible lanthanide ions that have 14 f electrons.**
- **Why Eu has so low melting point? Which other lanthanide has exceptionally low melting point?**



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
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	110 Uun								

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

f-BLOCK TRANSITION METALS

- lanthanides [elements after La: Ce ~ Lu]
- actinides [elements after Ac: Th ~ Lr]
- lanthanoids (Ln): La + Lanthanides
- rare earth elements (RE): Ln + Y + Sc

La	lanthanum	Tb	terbium
Ce	cerium	Dy	dysprosium
Pr	praseodymium	Ho	holmium
Nd	neodymium	Er	erbium
Pm	promethium	Tm	thulium
Sm	samarium	Yb	ytterbium
Eu	europium	Lu	lutetium
Gd	gadolinium	Y	yttrium

ABUNDANCES

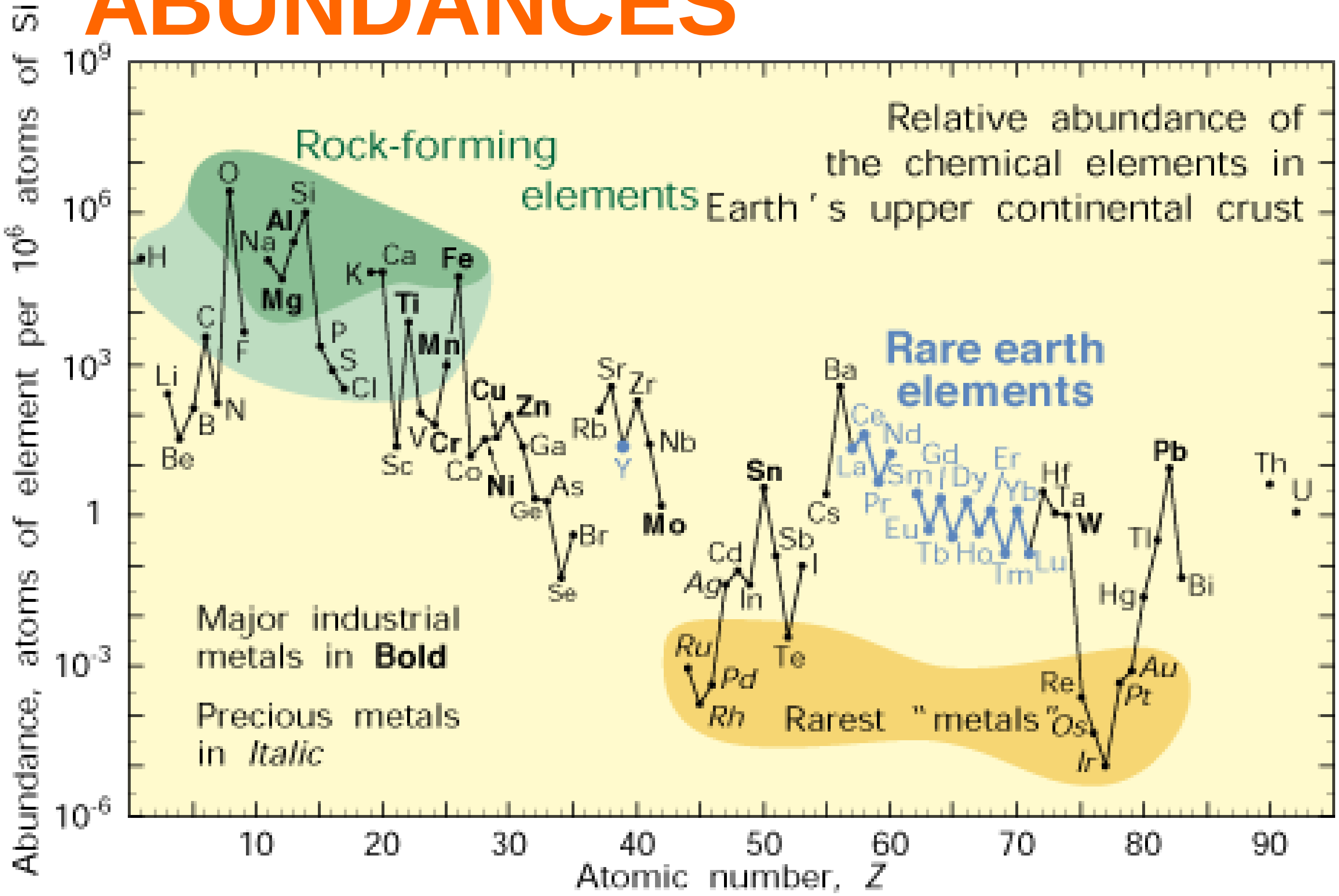


Figure 4. Abundance (atom fraction) of the chemical elements in Earth's upper continental crust as a function of atomic number. Many of the elements are classified into (partially overlapping) categories: (1) rock-forming elements (major elements in green field and minor elements in light green field); (2) rare earth elements (lanthanides, La–Lu, and Y; labeled in blue); (3) major industrial metals (global production $>\sim 3\times10^7$ kg/year; labeled in bold); (4) precious metals (italic); and (5) the nine rarest "metals"—the six platinum group elements plus Au, Re, and Te (a metalloid).

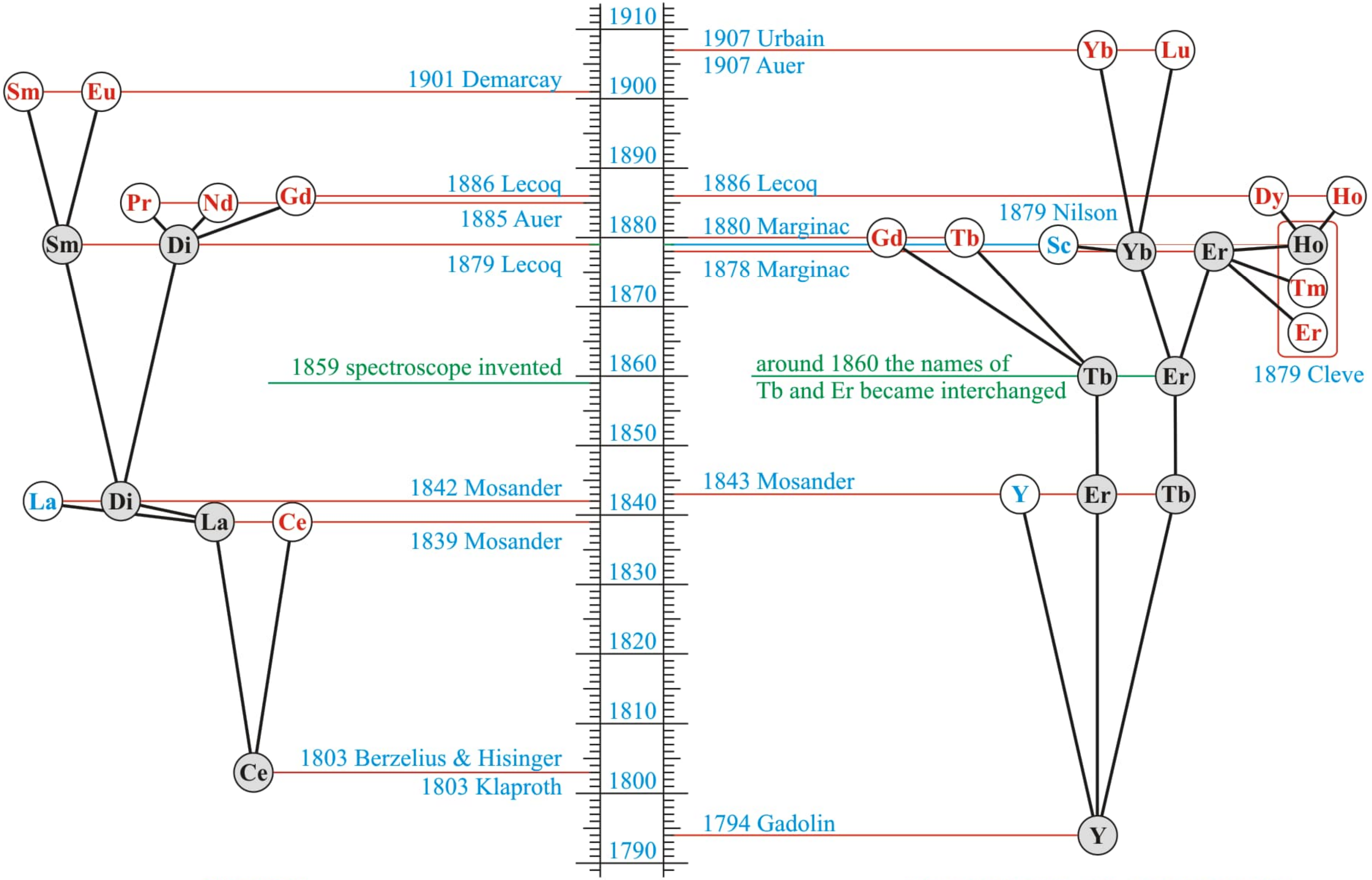
RARE EARTH ELEMENTS (= METALS)

- **Discovery history starts from and ends in Finland:**

  - Johan Gadolin (prof. at Univ. Turku) showed in 1794 that the new mineral found in Ytterby (near Stockholm) contained some new oxide (“earth”) of an unknown/new element → yttrium

  - Olavi Erämetsä (inorg. chem. prof. at TKK) found in 1965 from nature small amounts of radioactive promethium (first discovered in USA in 1940s as a fission product in nuclear reactions)

Element	Discoverer	Origin of name
Cerium (Ce)	Klaproth 1803	Ceres (asteroid)
Lanthanum (La)	Mosander 1839	Greek *lanthano* (= to hide)
Terbium (Tb)	Mosander 1843	Ytterby
Erbium (Er)	Mosander 1843	Ytterby
Ytterbium (Yb)	Mariqnac 1878	Ytterby
Holmium (Ho)	Cleve 1878	Holmia (= Stockholm)
Thulium (Tm)	Cleve 1879	Thule (= Nothern country)
Scandium (Sc)	Nilson 1879	Scandinavia
Samarium (Sm)	Boisboudran 1879	Samarskite (mineral)
Gadolinium (Gd)	Marignac 1880	Johan Gadolin
Praseodymium (Pr)	Welsbach 1885	Greek *didymos* (= green twin)
Neodymium (Nd)	Welsbach 1885	Greek *neos didymos* (= new twin)
Dysprosium (Dy)	Boisboudran 1886	Greek *dysprositos prasios* (= difficult to reach)
Europium (Eu)	Demarcay 1896	Europe
Lutetium (Lu)	Urbain 1907	Lutetia (= Paris)



CERITE

$(Ce,La,Ca)_9(Mg,Fe^{3+})(SiO_4)_6(SiO_3OH)(OH)_3$

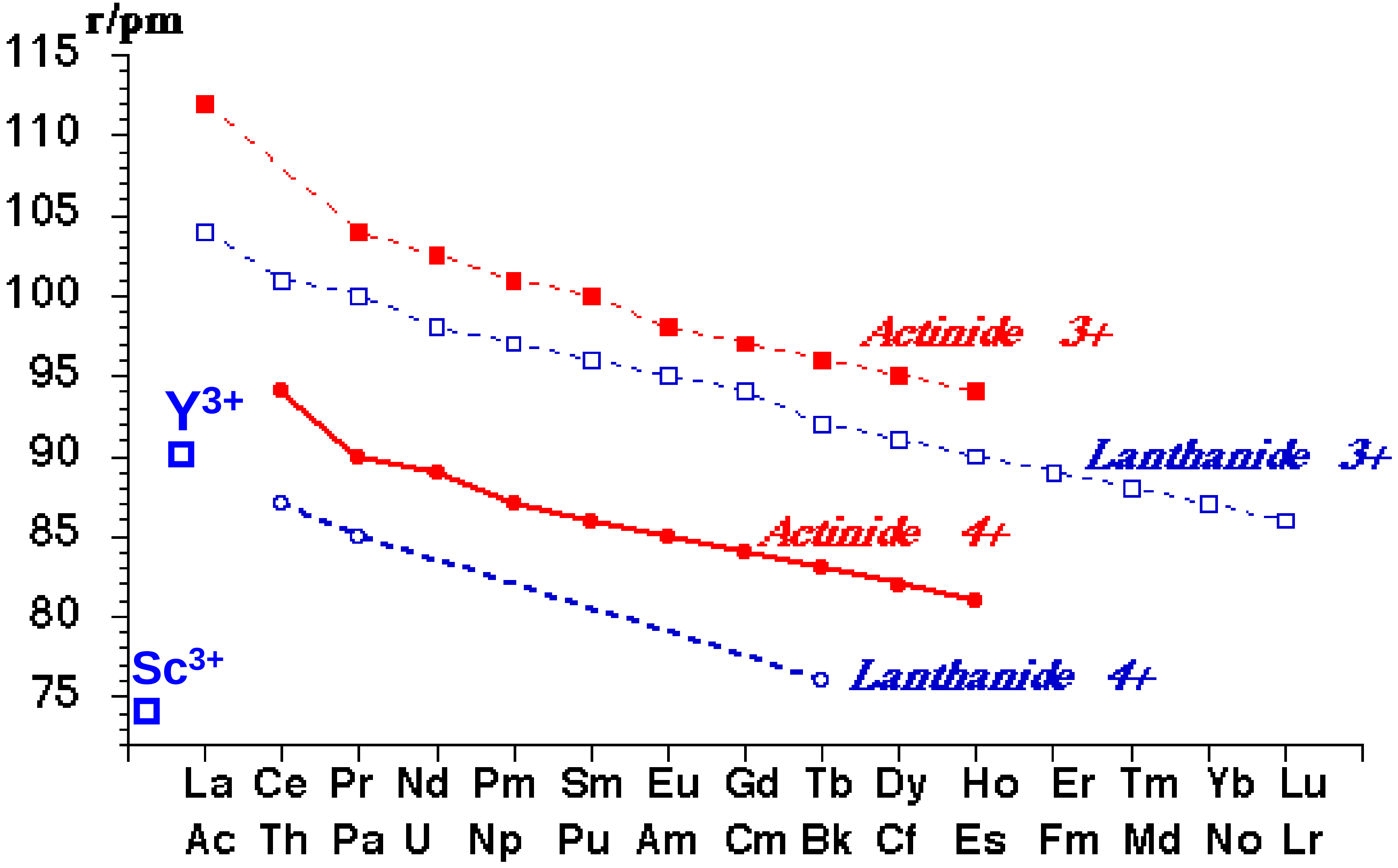
Bastnäs, Sweden

YTTERBITE (GADOLINITE)

$(Y,Ce,La,Nd)_2FeBe_2Si_2O_{10}$

Ytterby, Sweden

LANTHANIDE / ACTINIDE CONTRACTION



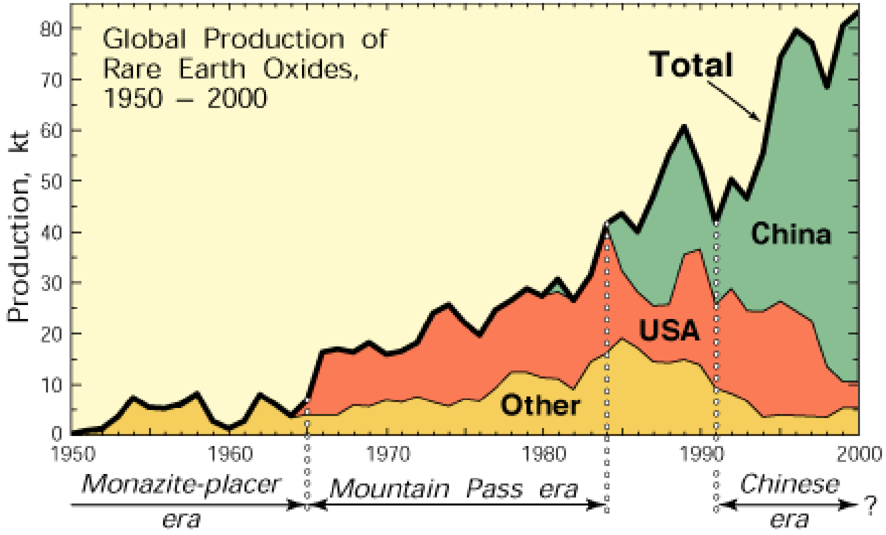
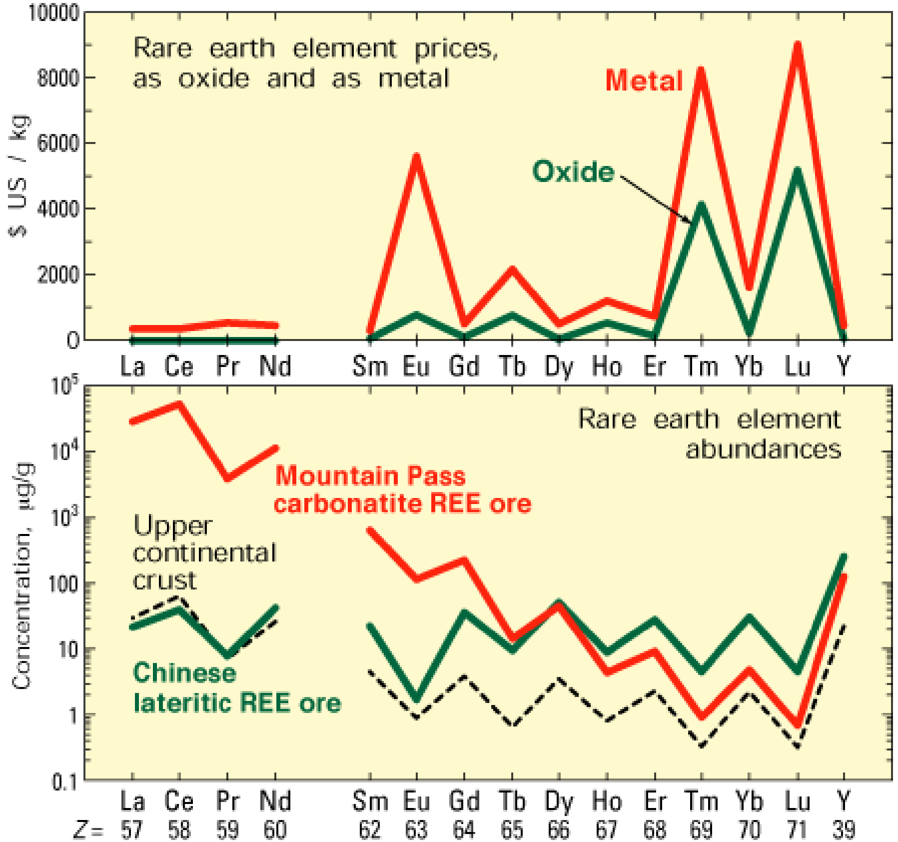


Figure 1. Global rare earth element production (1 kt=10^6 kg) from 1950 through 2000, in four categories: United States, almost entirely from Mountain Pass, California; China, from several deposits; all other countries combined, largely from monazite-bearing placers; and global total. Four periods of production are evident: the monazite-placer era starting in the late 1800s and ending abruptly in 1964; the Mountain Pass era, starting in 1965 and ending about 1984; a transitional perioc from about 1984 to 1991; and the Chinese era, beginning about 1991.

Currently:
China produces >95 %



Atomic numbers:
even more common than uneven

SEPARATION OF RARE EARTH ELEMENTS FROM EACH OTHER

- **Very difficult due to the similarities in chemistry**
- **Cerium and Europium chemically:**

  - oxidation of Ce^{III} to Ce^{IV} plus precipitation as CeO_2 or $Ce(IO_3)_4$

  - reduction of Eu^{III} to Eu^{II} plus precipitation as $EuSO_4$
- **Fractional crystallization (hundreds of steps):**

  e.g. $\mathit{RE}(NO_3)_3 \bullet 2NH_4NO_3 \bullet 4H_2O$ or $\mathit{RE}(BrO_3)_3$
- **Current large-scale separation technique:**

  Continuous solvent extraction (nonpolar organic solvent)

Misch-metal

- German: *Mischmetall* = mixed metal
- Metal alloy of rare earth elements
- Rare earth elements in natural portions (varies)
- Typical composition: 50% Ce + 45% La + Nd, Pr traces
- Use:
  - in lighter: alloyed with Fe and Mg oxides → ferrocerium
  - in production of FeSiMg alloy to remove free oxygen and sulphur

Scandium (Sc)

- discovered in 1879 by spectral analysis of the minerals euxenite and gadolinite from Scandinavia
- preparation of metallic Sc in 1937
- own rare mineral thortveitite $(Sc,Y)_2Si_2O_7$ (Norway 1911)
- produced as a by-product of rare-earth and uranium production; yearly trade of scandium (oxide) is only 10 tonnes
- first applications for scandium developed in the 1970s
- main use in aluminium alloys
- oxidation state +3; oxide Sc_2O_3
- chemical properties of Sc are intermediate between those of Al and Y
- diagonal relationship between Sc and Mg (ref. Al-Be)

Electronic configurations and oxidation states of lanthanoids

Z	Element	Electronic configuration	Oxidation states
57	Lanthanum (La)	$4f^{0}5d^{1}6s^{2}$	+III
58	Cerium (Ce)	$4f^{1}5d^{1}6s^{2}$	+III, +IV
59	Praseodymium (Pr)	$4f^{2}5d^{1}6s^{2}$	+III
60	Neodymium (Nd)	$4f^{3}5d^{1}6s^{2}$	+III
61	Promethium (Pm)	$4f^{4}5d^{1}6s^{2}$	+III
62	Samarium (Sm)	$4f^{5}5d^{1}6s^{2}$	+III
63	Europium (Eu)	$4f^{7}5d^{0}6s^{2}$	+II, +III
64	Gadolinium (Gd)	$4f^{7}5d^{1}6s^{2}$	+III
65	Terbium (Tb)	$4f^{7}5d^{2}6s^{2}$	+III, +IV
66	Dysprosium (Dy)	$4f^{9}5d^{1}6s^{2}$	+III
67	Holmium (Ho)	$4f^{10}5d^{1}6s^{2}$	+III
68	Erbium (Er)	$4f^{11}5d^{1}6s^{2}$	+III
69	Thulium (Tm)	$4f^{12}5d^{1}6s^{2}$	+III
70	Ytterbium (Yb)	$4f^{14}5d^{0}6s^{2}$	+II, +III
71	Lutetium (Lu)	$4f^{14}5d^{1}6s^{2}$	+III

MELTING POINTS (^{o}C)

La	920
Ce	795
Pr	935
Nd	1010
Pm	-
Sm	1072
Eu	822
Gd	1311
Tb	1360
Dy	1412
Ho	1470
Er	1522
Tm	1545
Yb	824
Lu	1656

COLOURS OF IONS

- **No strong colours**
  - **colourless: La^{III}, Ce^{IV}, Gd^{III}, Eu^{II} , Yb^{II}, Lu^{III}**
  - **green: Pr^{III}, Tm^{III}**
  - **violet: Nd^{III}, Er^{III}**
  - **yellowish pink: Pm^{III}, Ho^{III}**
  - **yellow: Sm^{III}, Dy^{III}, Yb^{III}**
  - **light pink: Eu^{III}, Tb^{III}**

OXIDES

Ln$_2$O$_3$

- trivalent oxide most common *Ln* oxide (for all *Ln*)
- strongly basic
- absorbs water/carbon dioxide from air → hydroxide/carbonate salts
- Similarities with alkali earth metal oxides

*Ln*O$_2$

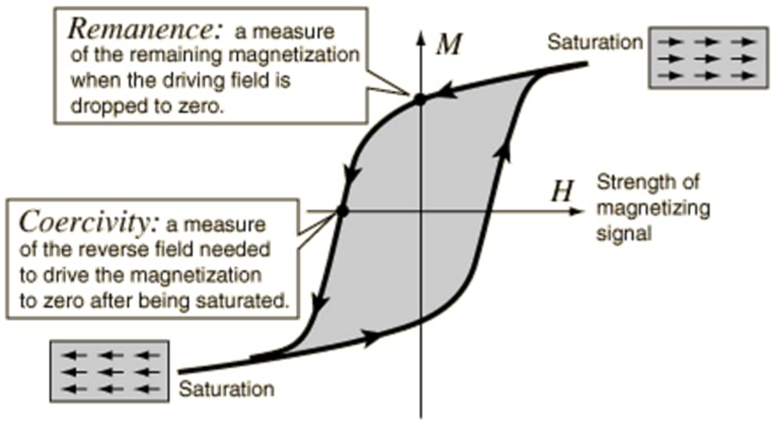
- CeO_2
- Pr_6O_{11}, Tb_4O_7

*Ln*O

- EuO, YbO: electrical insulators (Ln^{2+} O^{2-})
- EuO ferromagnetic
- NdO, SmO: electrical conductors (Ln^{3+} O^{2-} e^-)

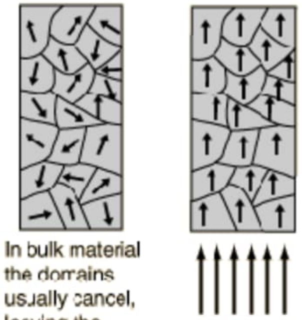
PERMANENT MAGNETS (ferromagnets)

- 1970s: $SmCo_5$, Sm_2Co_{17}
- 1980s: $Nd_2Fe_{14}B$ (= neomagnets; very strong)
- With neomagnets smaller electric motors (e.g. in car industry)



Remanence: a measure of the remaining magnetization when the driving field is dropped to zero.

Coercivity: a measure of the reverse field needed to drive the magnetization to zero after being saturated.

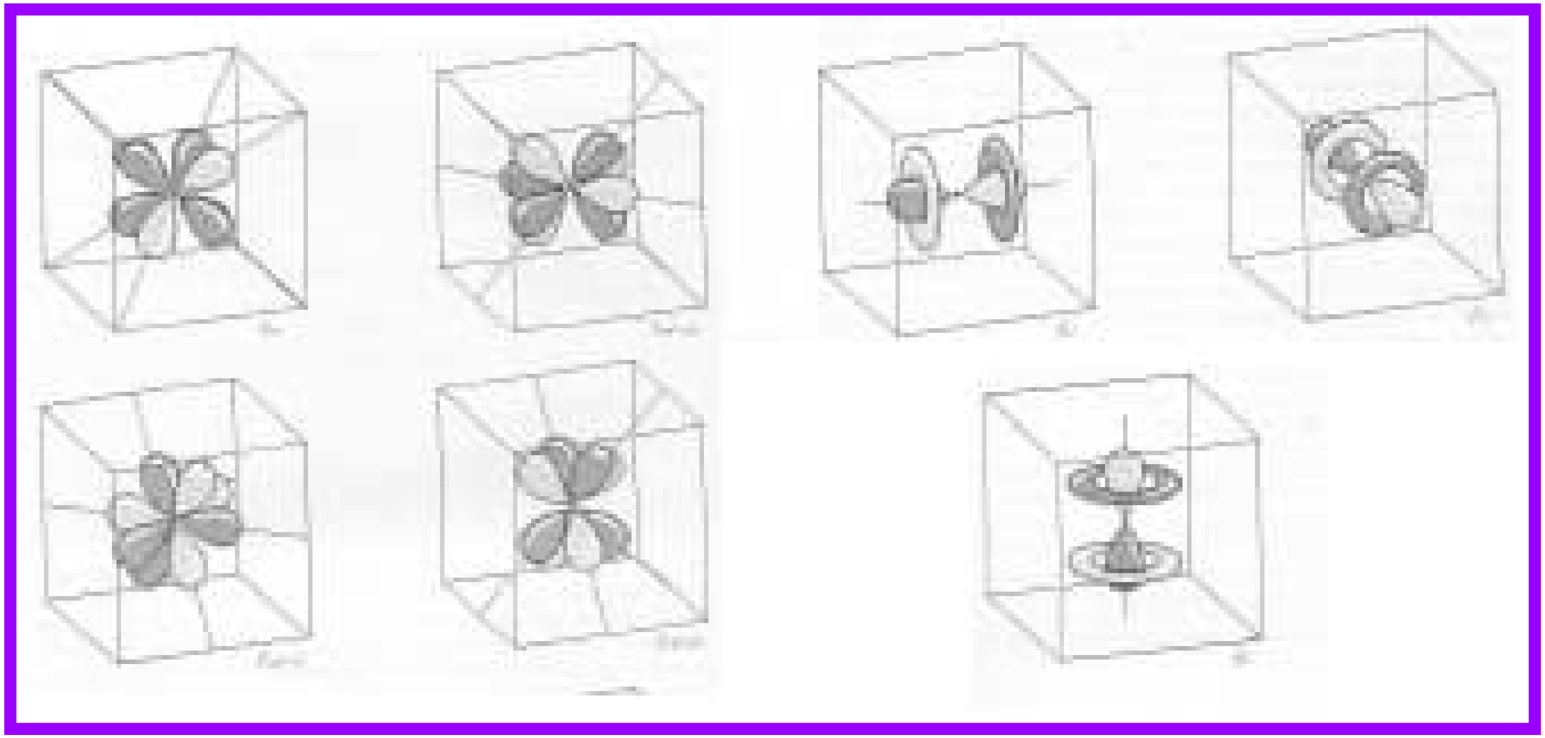


In bulk material the domains usually cancel, leaving the material unmagnetized.

Externally applied magnetic field.

Material	Coercivity [T]	Remanence [T]
$BaFe_{12}O_{19}$	0.36	0.36
Alnico IV	0.07	0.6
Alnico V	0.07	1.35
Alcomax I	0.05	1.2
MnBi	0.37	0.48
$Ce(CuCo)_5$	0.45	0.7
$SmCo_5$	1.0	0.83
Sm_2Co_{17}	0.6	1.15
$Nd_2Fe_{14}B$	1.2	1.2

4f orbitals



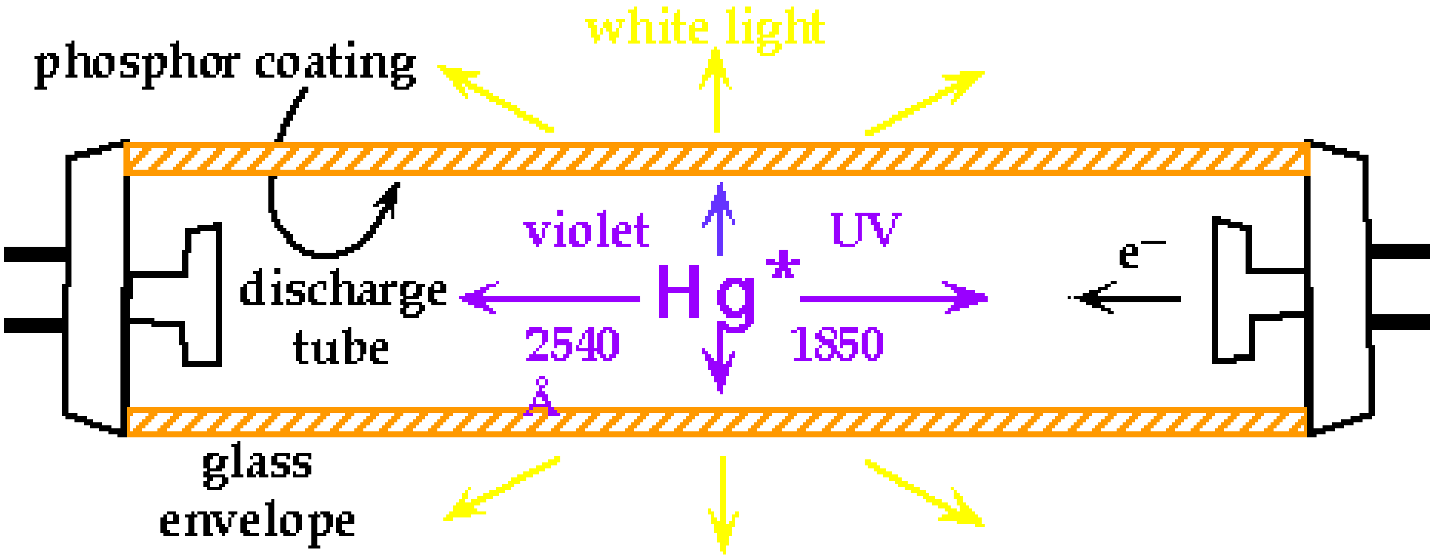
SPECTROSCOPIC PROPERTIES

- Energies of 4f orbitals splitted in crystal/ligand field (ref. d orbitals)
- More complicated splitting scheme than in the case of the d orbitals

LANTHANOIDS in OPTOELECTRONICS

- Electron transitions within 4f orbitals and between 4f and 5d orbitals
  → lantanoids have unique optical properties

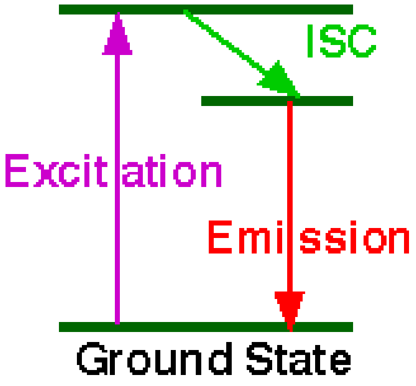
Fluorescent lamps:	$Y_2O_3:\mathbf{Eu^{3+}}$	**red**
from UV (254 nm)	$CeMgAl_{11}O_{19}:\mathbf{Tb^{3+}}$	**green**
to visible light	$(Ce,Gd)MgB_5O_{10}:\mathbf{Tb^{3+}}$	**green**
	$BaMgAl_{10}O_{17}:\mathbf{Eu^{2+}}$	**blue**
	$Sr_5(PO_4)_3(F,Cl):\mathbf{Eu^{2+}}$	**blue**
EL displays:	$ZnS:Mn^{2+}$	yellow
from electric energy	$SrS:\mathbf{Ce^{3+}}$	**bluishgreen**
to visible light	$ZnS:\mathbf{Tb^{3+}}$	**green**
Lasers:	$Y_3Al_5O_{12}:\mathbf{Nd^{3+}}$	**1064 nm**

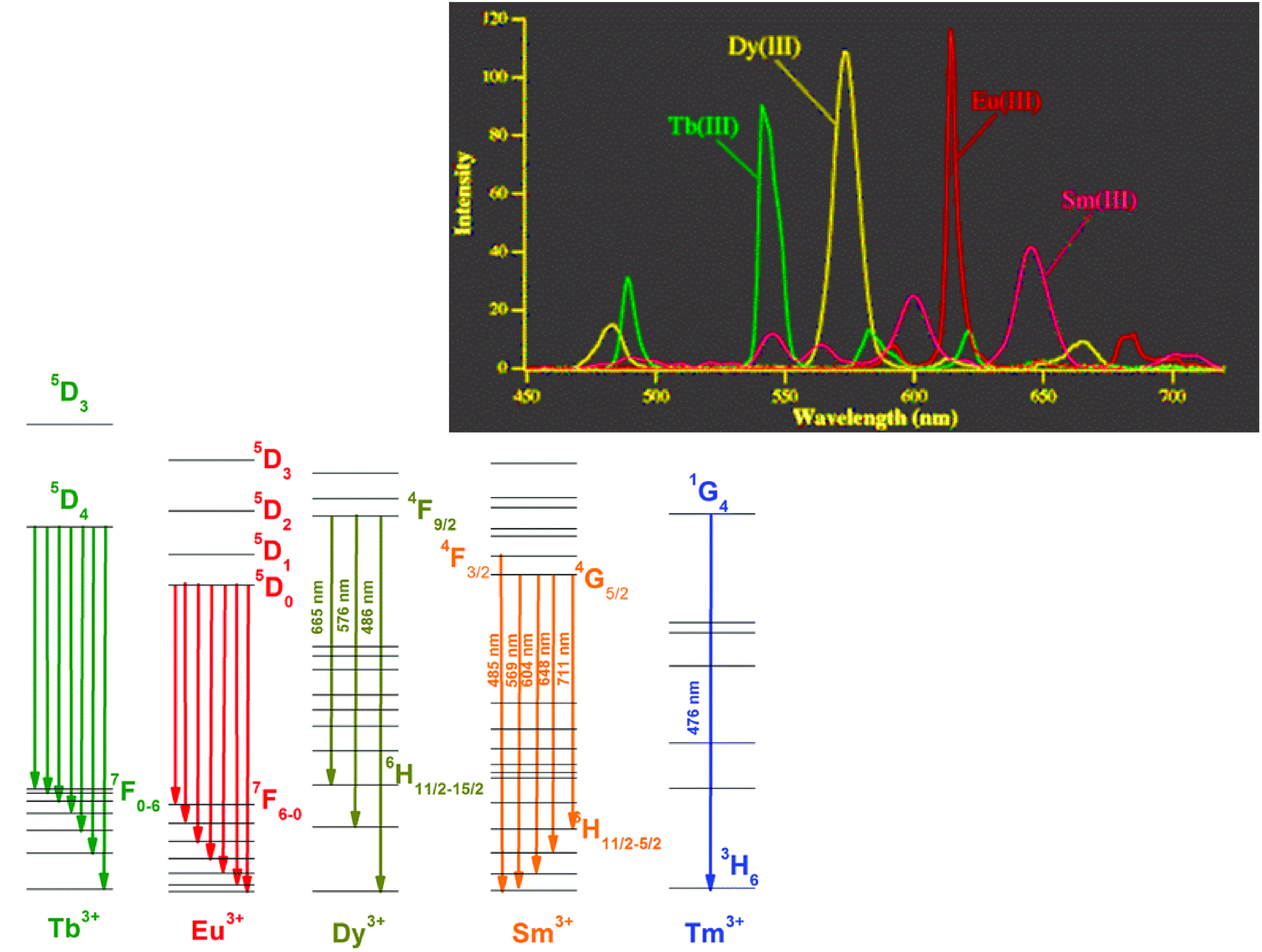


Fluorescence lamp

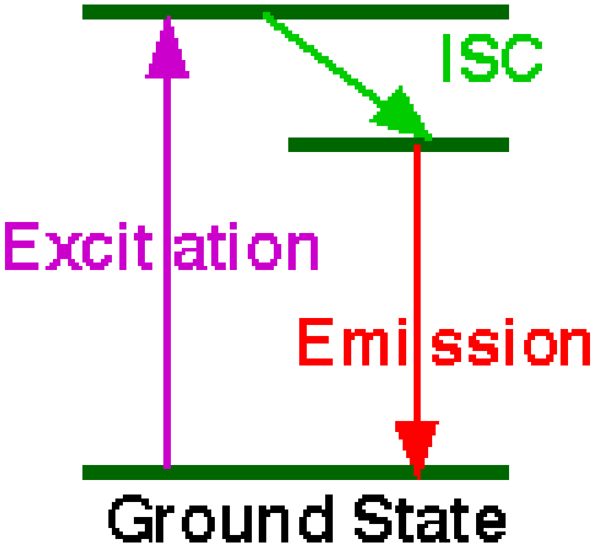
LUMINESCENCE (= fluorescence)

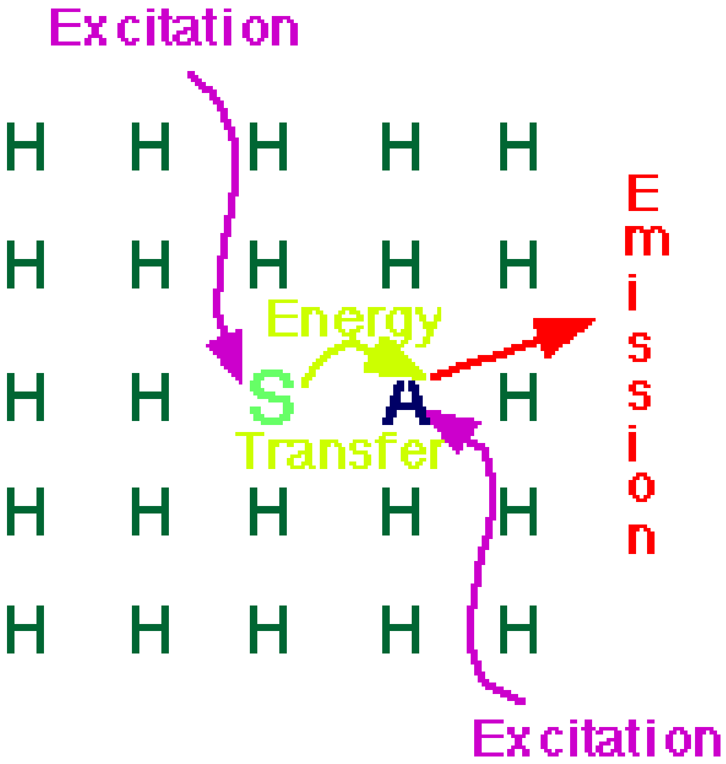
- **Material absorbs higher-energy photon and emits smaller-energy photon (shorter-to-longer wavelength; UV → Vis)**
- **Energy difference → lost as heat**
- **Different ways to excite luminescence:**
    - **- photoluminescence**
    - **- electroluminescence**
    - **- thermoluminescence**
    - **- chemiluminescence**
    - **- triboluminescence**
    - **- bioluminescence**



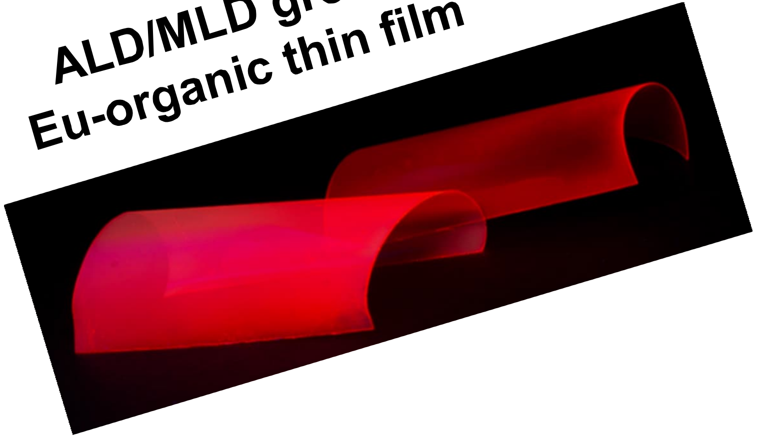

Dy(III)
Eu(III)
Tb(III)
Sm(III)
Intensity
0
20
40
60
80
100
120
450
500
550
600
650
700
Wavelength (nm)
⁵D₃
⁵D₄
⁷F₀₋₆
Tb³⁺
⁵D₃
⁵D₂
⁵D₁
⁵D₀
⁷F₆₋₀
Eu³⁺
⁴F₉/₂
665 nm
576 nm
486 nm
⁶H₁₁/₂₋₁₅/₂
Dy³⁺
⁴F₃/₂
⁴G₅/₂
485 nm
569 nm
604 nm
648 nm
711 nm
⁶H₁₁/₂₋₅/₂
Sm³⁺
¹G₄
476 nm
³H₆
Tm³⁺

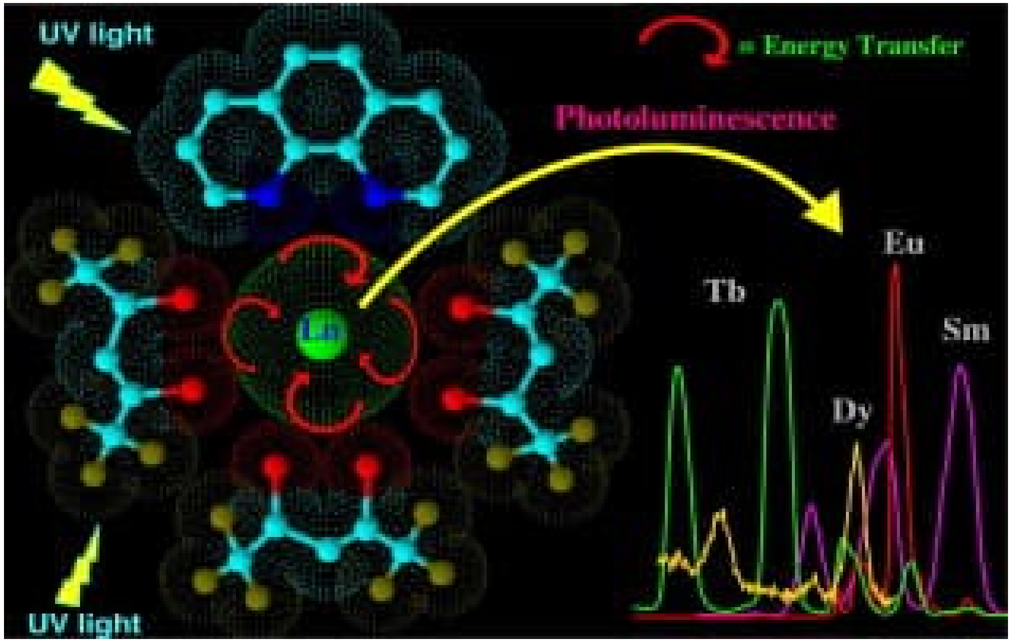
ENERGY TRANSFER: Sensitizer → Activator



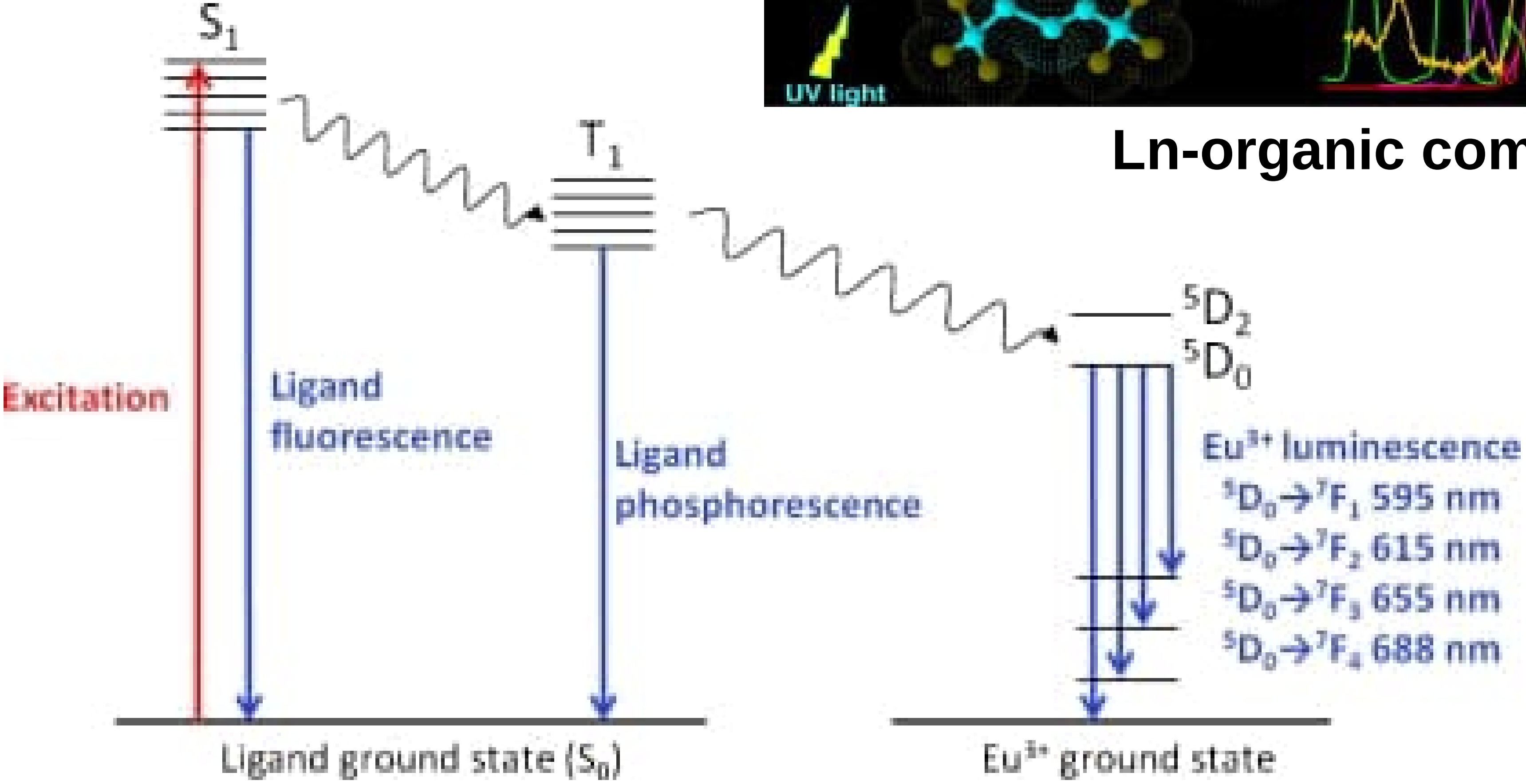


ALD/MLD grown Eu-organic thin film



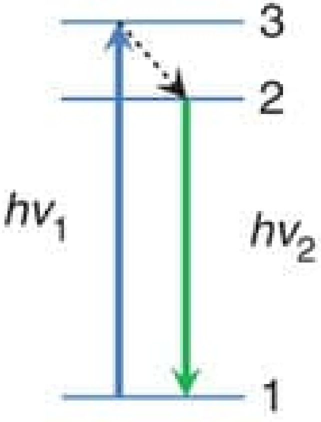


Ln-organic complex

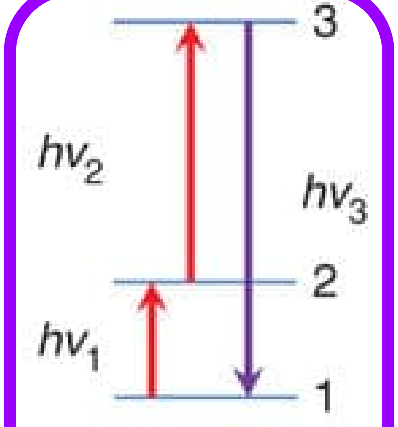


UPCONVERSION EMISSION

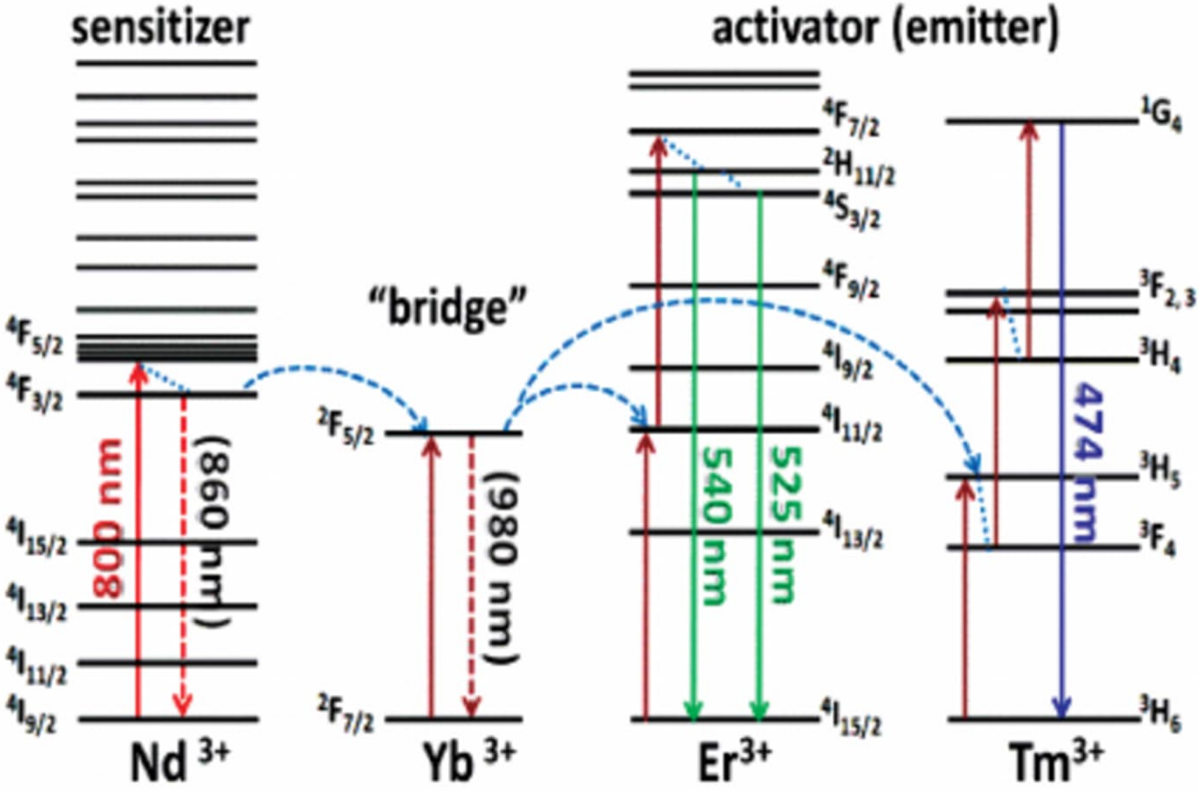
- for example from IR to Visible



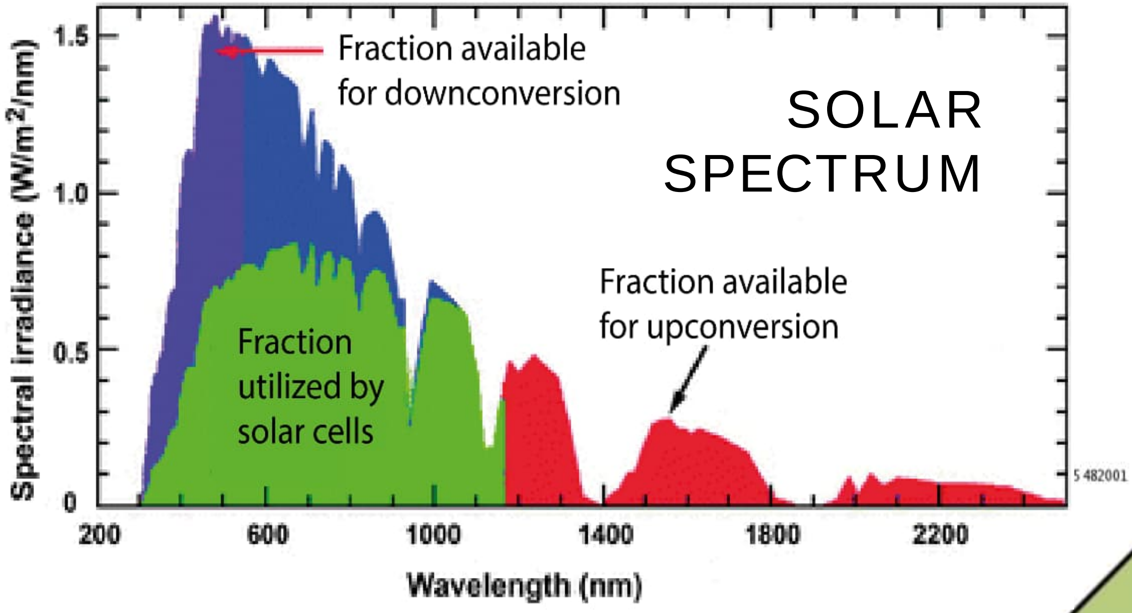
Conventional luminescence



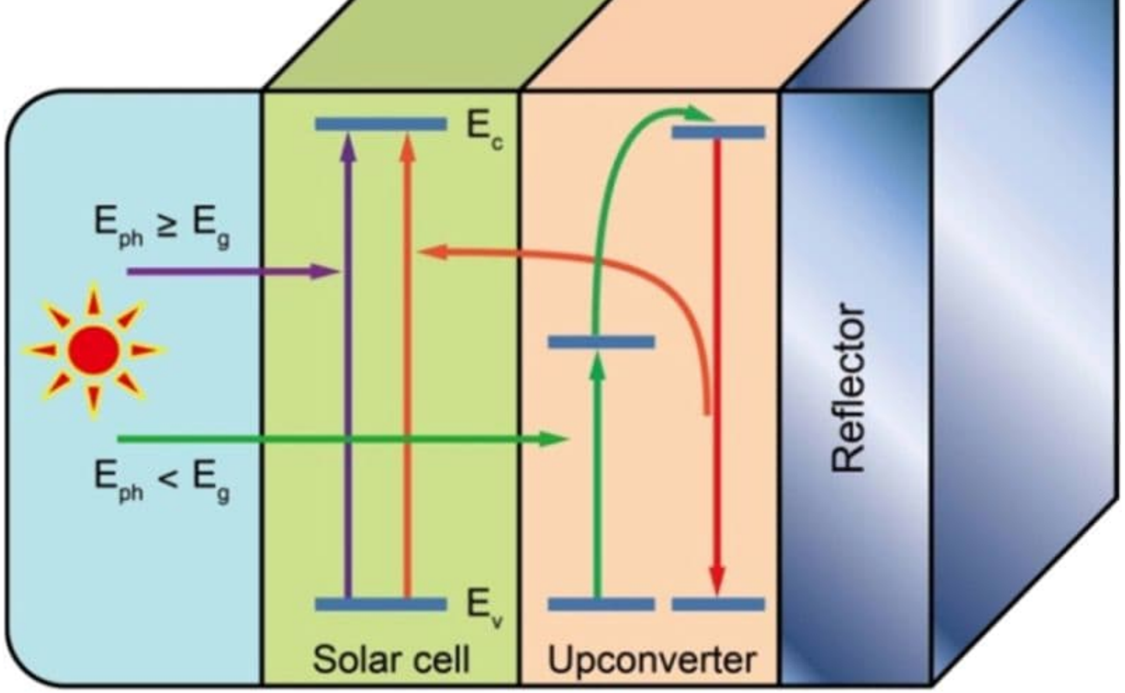
Upconversion luminescence



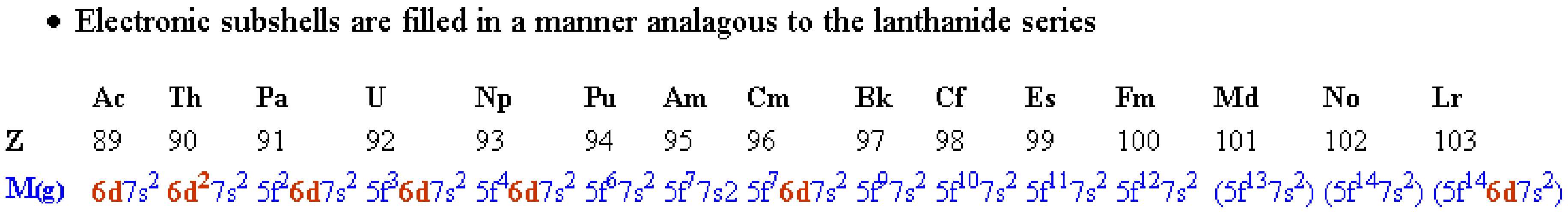
← UV VIS IR →



SOLAR SPECTRUM



ACTINOIDS



- Electronic subshells are filled in a manner analagous to the lanthanide series

	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
Z	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
M(g)	$6d7s^2$	$6d^2 7s^2$	$5f^2 6d7s^2$	$5f^3 6d7s^2$	$5f^4 6d7s^2$	$5f^6 7s^2$	$5f^7 7s2$	$5f^7 6d7s^2$	$5f^9 7s^2$	$5f^{10} 7s^2$	$5f^{11} 7s^2$	$5f^{12} 7s^2$	$(5f^{13} 7s^2)$	$(5f^{14} 7s^2)$	$(5f^{14} 6d7s^2)$

Occurrence of Uranium & Transuranoids

- only Ac, Th, Pa and U found in nature
- transuranoids exist only artificially

  (trace amounts of Np and Pu in uranium minerals)
- ca. 100 different uranium minerals, most important being uraninite (pikivälke) UO_x ($x = 2-2.67$) and carnotite $K_2(UO_2)_2(VO_4)_2 \bullet 3H_2O$
- U ca. 500 times more common than Au:

  earth crust 2.1 ppm, ocean water 0.002 - 0.003 ppm
- occasionally U content may be high enough to create a natural nuclear reactor, e.g. Oklo in Africa billions years ago
- 15 isotopes (^{226}U - ^{240}U):

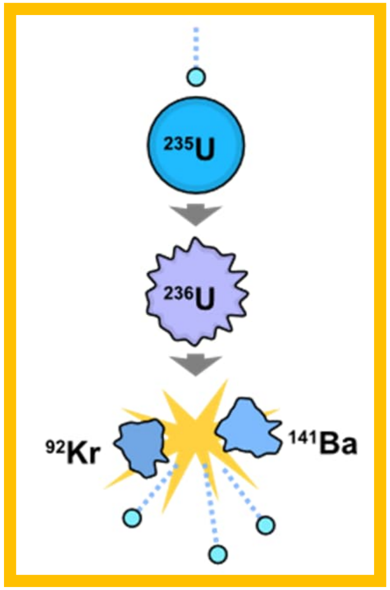
  ^{238}U 99.275 %

  ^{235}U 0.720 %

  ^{234}U 0.005 %
- all U isotopes unstable

ENRICHMENT OF URANIUM

- **Small carbonate content in ore → acid dissolution/extraction**
- **Large carbonate content in ore → basic dissolution/extraction**



- **Concentration after filtering**
- **Precipitation → yellow cake**
  acid solution: $(NH_4)_2U_2O_7$ or MgU_2O_7
  carbonate solution: $Na_2U_2O_7$
- **Reduction → UO_2**
- **Green salt UF_4**
- **For isotope enrichment: $UF_4(s) + F_2(g) \rightarrow UF_6(g)$**
- **Isotope enrichment: gas diffusion process, centrifugal separation, electromagnetic separation, laser exitation, jet/spray separation**
- **Use as a fuel in nuclear reactors: ^{235}U, $^{235}UO_2$, $^{235}UC_2$**