

LECTURE SCHEDULE

	Date	Topic
1.	Wed 28.10.	Course Introduction & Short Review of the Elements
2.	Fri 30.10.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri 06.11.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Wed 11.11.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
5.	Fri 13.11.	Redox Chemistry
6.	Mon 16.11.	Transition Metals: General Aspects & Crystal Field Theory
7.	Wed 18.11.	Zn, Ti, Zr, Hf & Atomic Layer Deposition (ALD)
8.	Fri 20.11.	V, Nb, Ta & Metal Complexes and MOFs
9.	Mon 23.11.	Cr, Mo, W & 2D materials
10	Wed 25.11.	Mn, Fe, Co, Ni, Cu & Magnetism and Superconductivity
11.	Fri 27.11.	Resources of Elements & Rare/Critical Elements & Element Substitutions
12.	Mon 30.11.	Lanthanoids + Actinoids & Pigments & Luminescence & Upconversion
13.	Wed 02.12.	Inorganic Materials Chemistry Research

EXAM: Thu Dec 10, 9:00-12:00 (IN ZOOM)

PRESENTATION TOPICS/SCHEDULE

Wed 18.11. Ti: Ahonen & Ivanoff

Mon 23.11. Mo: Kittilä & Kattelus

**Wed 25.11. Mn: Wang & Tran
Ru: Mäki & Juopperi**

**Fri 27.11. In: Suortti & Räsänen
Te: Kuusivaara & Nasim**

**Mon 30.11. Eu: Morina
U: Musikka & Seppänen**

QUESTIONS: Lecture 12

- List all the possible lanthanoid ions that have 7 f electrons.
- List all the possible lanthanoid ions that have 14 f electrons.
- Why Eu has so low melting point?
- Which way you prefer to place the rare earth elements in the periodic table? Why?

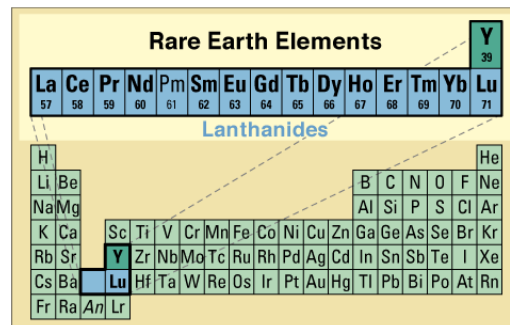
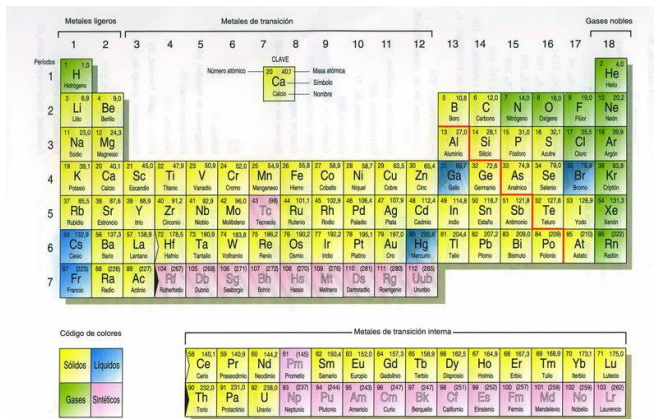
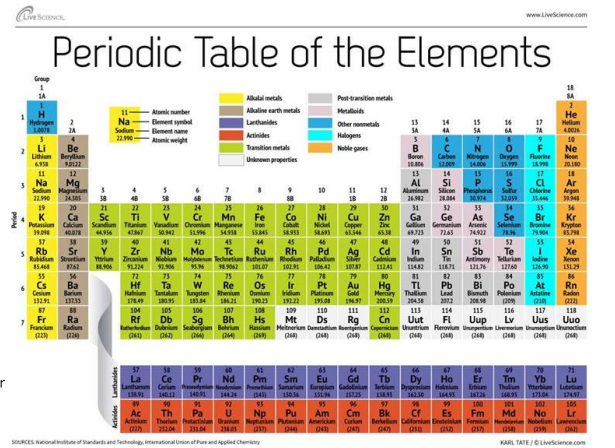


FIGURE 2. Chemical periodic table delineating the 16 rare earth elements (REE): the lanthanides, La through Lu, plus Y, whose geochemical behavior is virtually identical to that of the heavier lanthanides. Promethium has no long-lived isotopes and occurs naturally on Earth only in vanishingly small quantities. An represents the first 14 actinide elements; Lr is the last actinide.



1																	18
H ¹												B ⁵	C ⁶	N ⁷	O ⁸	F ⁹	Ne ¹⁰
Li ³	Be ⁴											Al ¹³	Si ¹⁴	P ¹⁵	S ¹⁶	Cl ¹⁷	Ar ¹⁸
Na ¹¹	Mg ¹²	3	4	5	6	7	8	9	10	11	12	Ga ³¹	Ge ³²	As ³³	Se ³⁴	Br ³⁵	Kr ³⁶
K ¹⁹	Ca ²⁰	Sc ²¹	Ti ²²	V ²³	Cr ²⁴	Mn ²⁵	Fe ²⁶	Co ²⁷	Ni ²⁸	Cu ²⁹	Zn ³⁰	In ⁴⁹	Sn ⁵⁰	Sb ⁵¹	Te ⁵²	I ⁵³	Xe ⁵⁴
Rb ³⁷	Sr ³⁸	Y ³⁹	Zr ⁴⁰	Nb ⁴¹	Mo ⁴²	Tc ⁴³	Ru ⁴⁴	Rh ⁴⁵	Pd ⁴⁶	Ag ⁴⁷	Cd ⁴⁸	Tl ⁸¹	Pb ⁸²	Bi ⁸³	Po ⁸⁴	At ⁸⁵	Rn ⁸⁶
Cs ⁵⁵	Ba ⁵⁶	La ⁵⁷	Hf ⁷²	Ta ⁷³	W ⁷⁴	Re ⁷⁵	Os ⁷⁶	Ir ⁷⁷	Pt ⁷⁸	Au ⁷⁹	Hg ⁸⁰						
Fr ⁸⁷	Ra ⁸⁸	Ac ⁸⁹	Rf ¹⁰⁴	Db ¹⁰⁵	Sg ¹⁰⁶	Bh ¹⁰⁷	Hs ¹⁰⁸	Mt ¹⁰⁹	Uun ¹¹⁰								

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	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

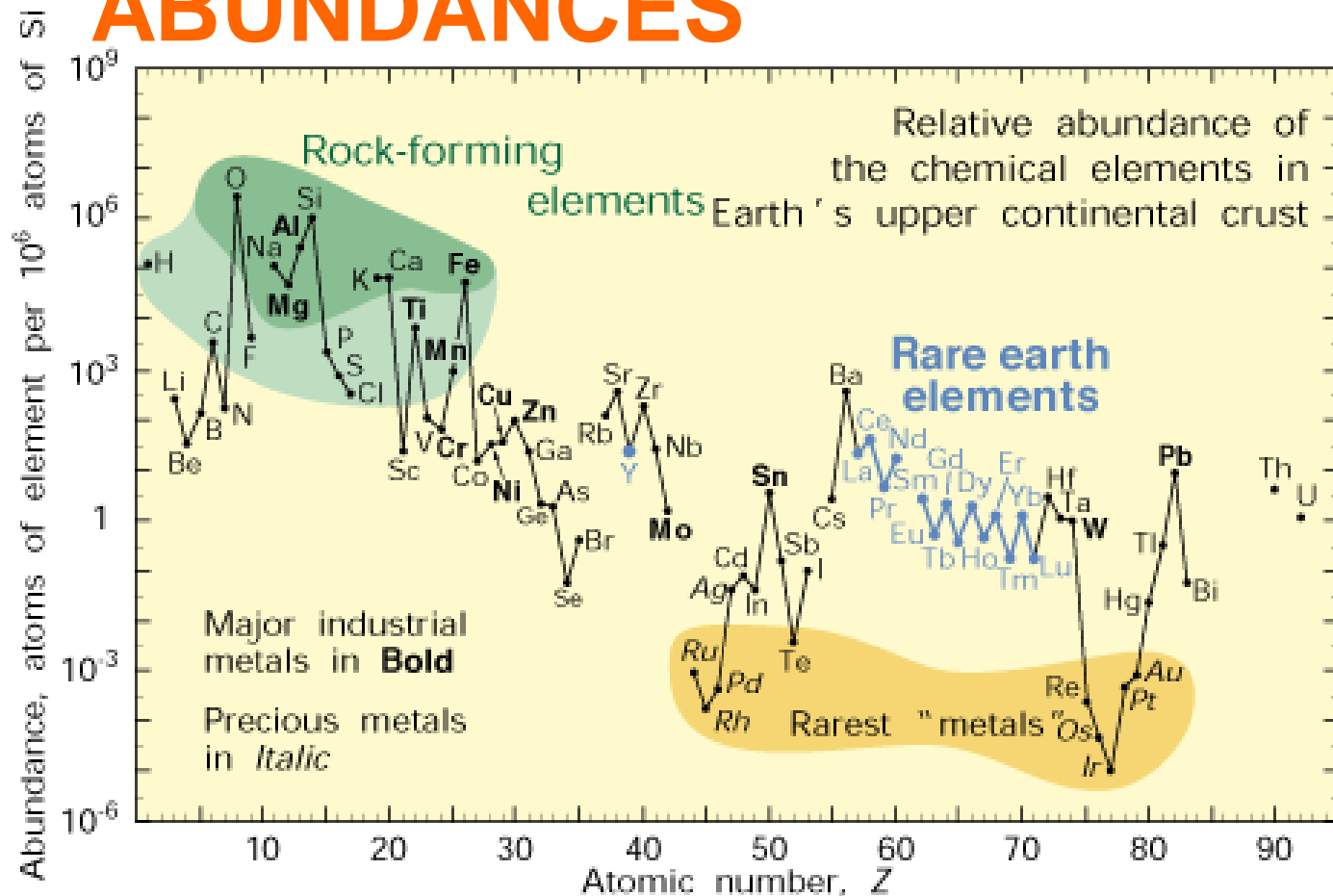


Figure 4. Abundance (atom fraction) of the chemical elements in Earth's upper continental crust as a function of atomic number. Many of the elements are classified into (partially overlapping) categories: (1) rock-forming elements (major elements in green field and minor elements in light green field); (2) rare earth elements (lanthanides, La–Lu, and Y; labeled in blue); (3) major industrial metals (global production $> \sim 3 \times 10^7$ 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:

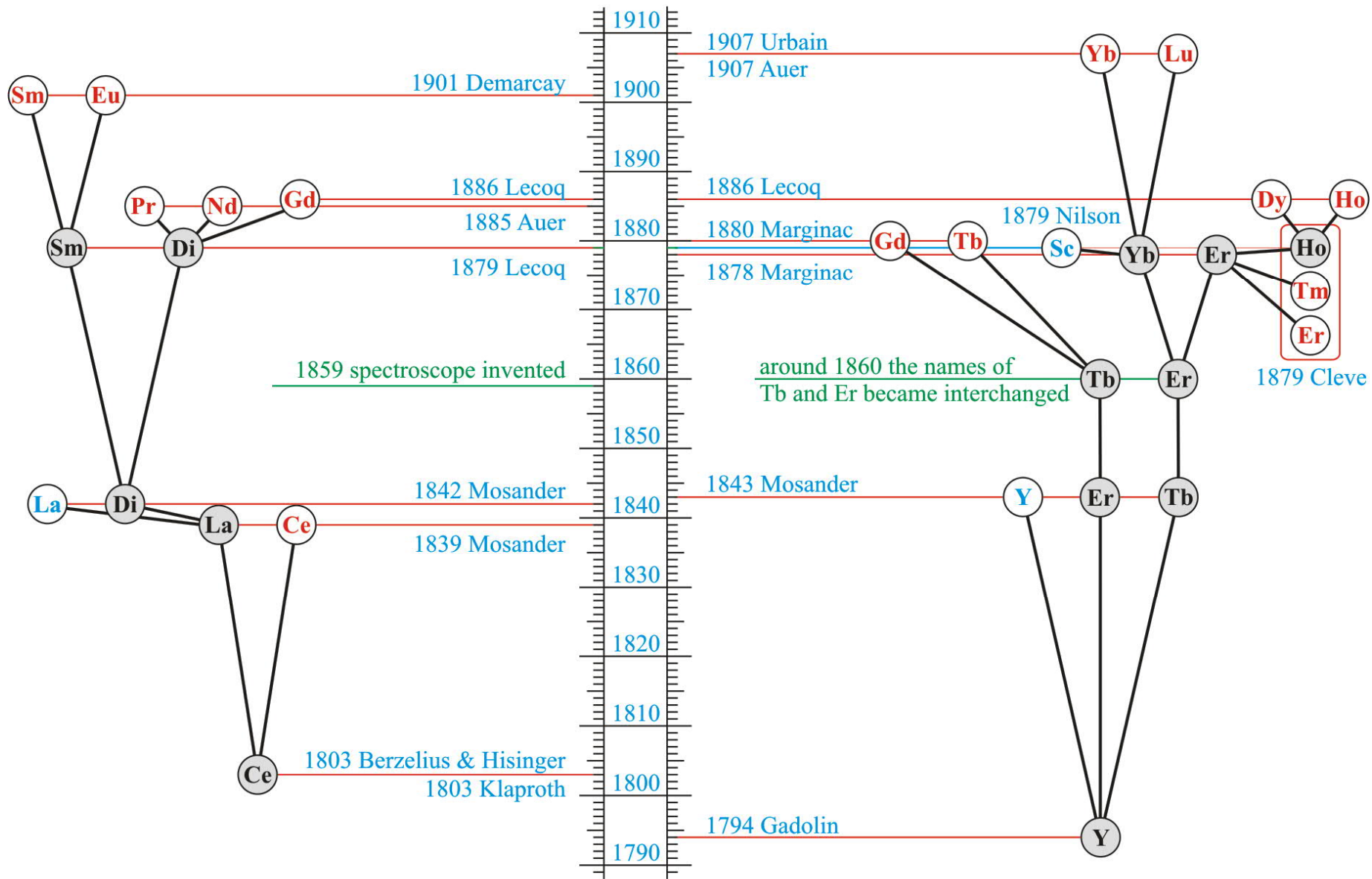
- Johan Gadolin (prof. at Univ. Turku) showed in 1794 that the new mineral found in Ytterby (near Stockholm) contained some new oxide (“earth”) of an unknown/new element → **yttrium**
- Olavi Erämetsä (inorg. chem. prof. at TKK) found in 1965 from nature small amounts of radioactive **promethium** (first 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 <i>lanthano</i> (= 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 <i>didymos</i> (= green twin)
Neodymium (Nd)	Welsbach 1885	Greek <i>neos didymos</i> (= new twin)
Dysprosium (Dy)	Boisboudran 1886	Greek <i>dysprositos prasio</i> (= difficult to reach)
Europium (Eu)	Demarcay 1896	Europe
Lutetium (Lu)	Urbain 1907	Lutetia (= Paris)



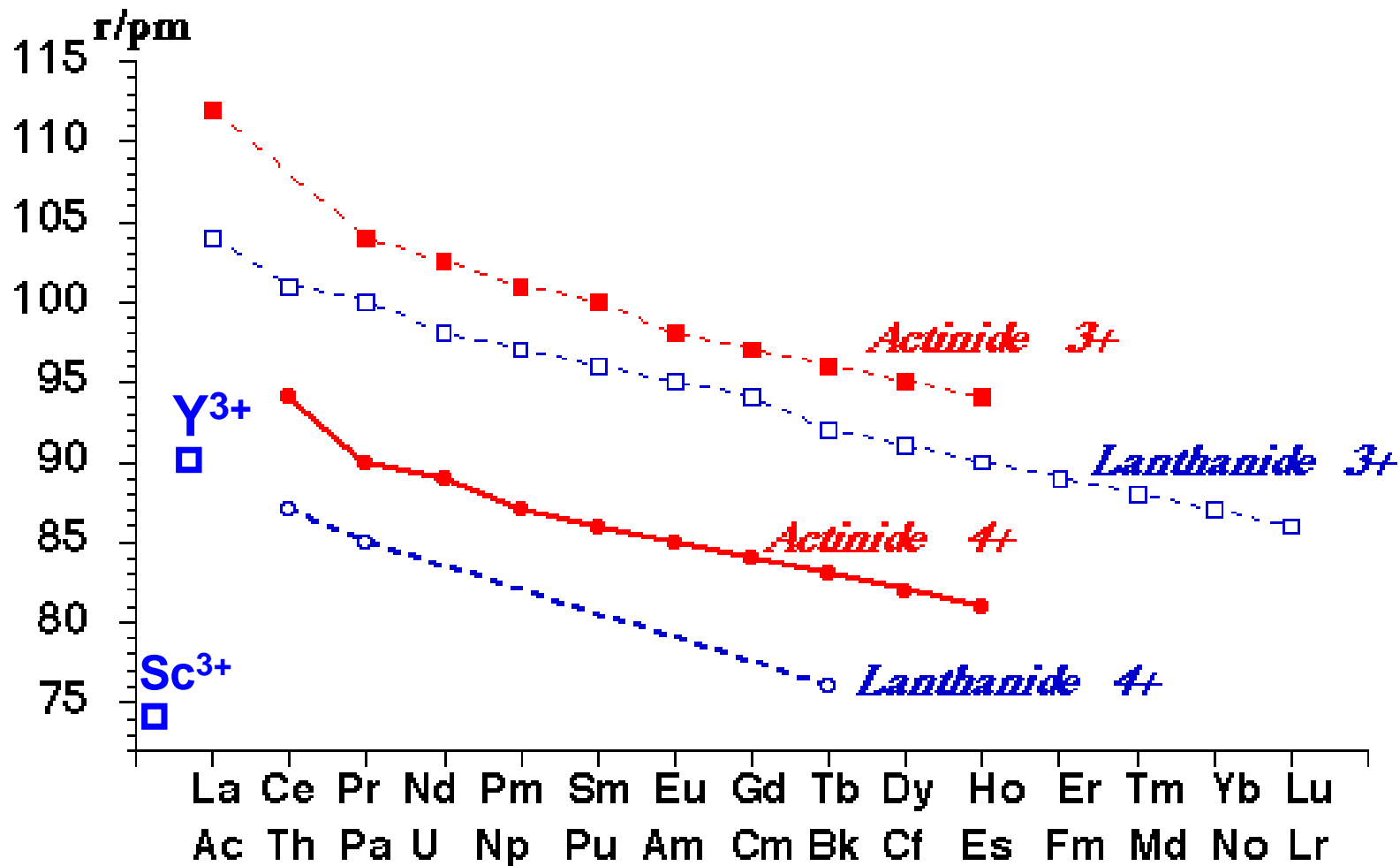
CERITE

$(\text{Ce,La,Ca})_9(\text{Mg,Fe}^{3+})(\text{SiO}_4)_6(\text{SiO}_3\text{OH})(\text{OH})_3$
 Bastnäs, Sweden

YTTERBITE (GADOLINITE)

$(\text{Y,Ce,La,Nd})_2\text{FeBe}_2\text{Si}_2\text{O}_{10}$
 Ytterby, Sweden

LANTHANOID / ACTINOID CONTRACTION



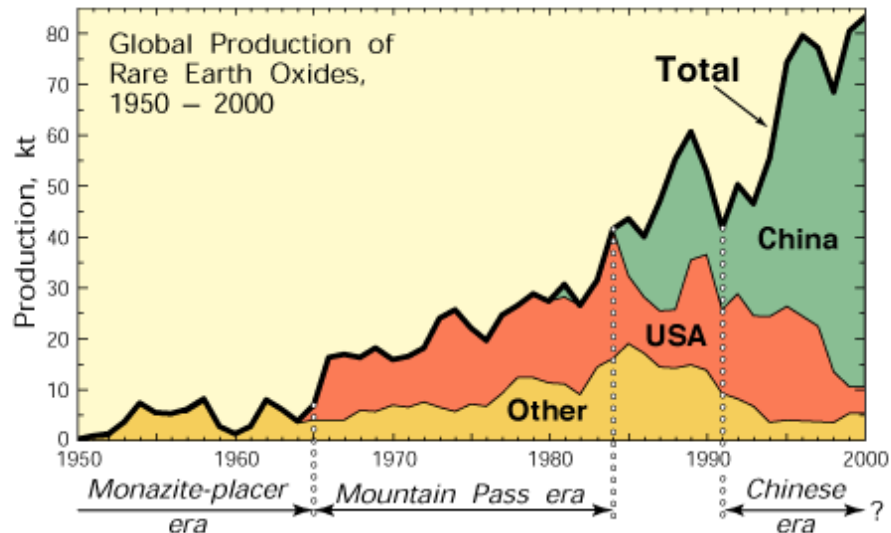
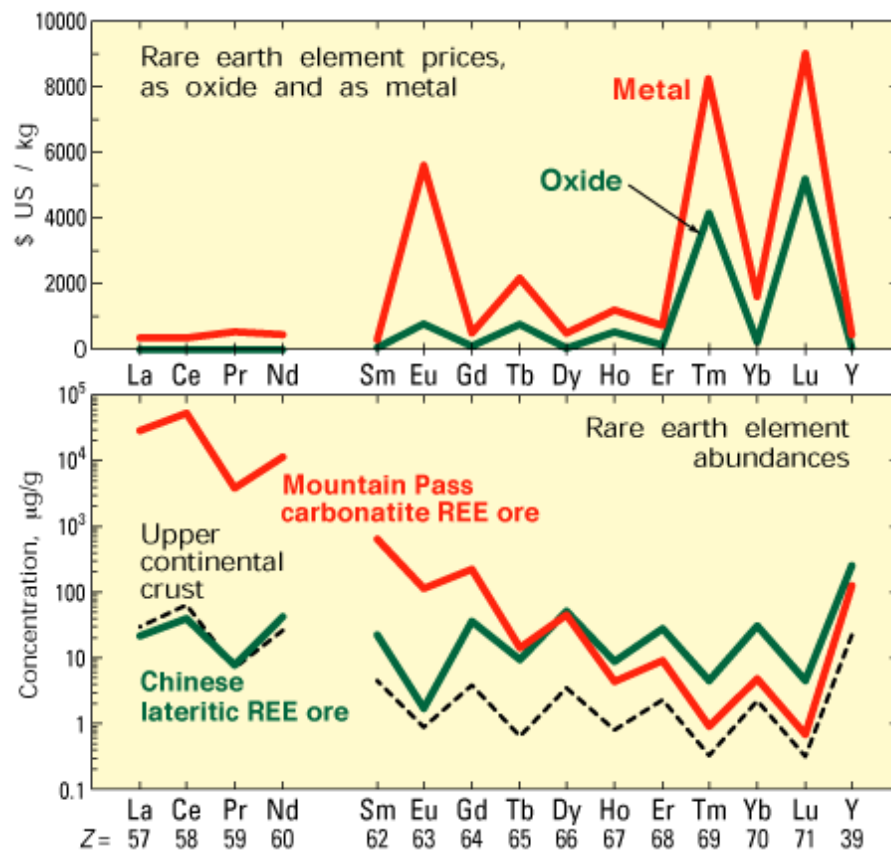


Figure 1. Global rare earth element production (1 kt=10⁶ kg) from 1950 through 2000, in four categories: United States, almost entirely from Mountain Pass, California; China, from several deposits; all other countries combined, largely from monazite-bearing placers; and global total. Four periods of 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 period from about 1984 to 1991; and the Chinese era, beginning about 1991.

**Currently:
China produces >95 %**



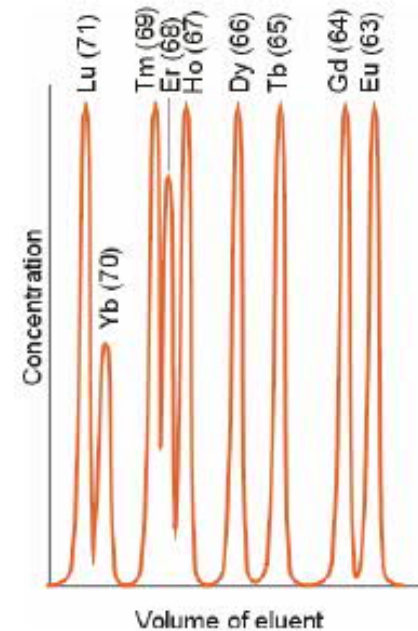
**Atomic numbers:
even more common than uneven**

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 $\text{Ce}(\text{IO}_3)_4$
 - reduction of Eu^{III} to Eu^{II} plus precipitation as EuSO_4
- Fractional crystallization (hundreds of steps):
e.g. $\text{RE}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$ or $\text{RE}(\text{BrO}_3)_3$
- Cation exchange
- Continuous solvent extraction (nonpolar organic solvent):
current large-scale separation technique

CATION EXCHANGE

- In the cation exchange column Na^+ ions are exchanged to RE^{3+} ions
- Elucidation with EDTA occurs in the order of: Lu, Yb, Tm, ...
(from smaller to larger)



re: Order of elution of separated lanthanoid ions

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 $(\text{Sc},\text{Y})_2\text{Si}_2\text{O}_7$ (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)	$4f^05d^16s^2$	+III
58	Cerium (Ce)	$4f^15d^16s^2$	+III, +IV
59	Praseodymium (Pr)	$4f^25d^16s^2$	+III
60	Neodymium (Nd)	$4f^35d^16s^2$	+III
61	Promethium (Pm)	$4f^45d^16s^2$	+III
62	Samarium (Sm)	$4f^55d^16s^2$	+III
63	Europium (Eu)	$4f^75d^06s^2$	+II, +III
64	Gadolinium (Gd)	$4f^75d^16s^2$	+III
65	Terbium (Tb)	$4f^75d^26s^2$	+III, +IV
66	Dysprosium (Dy)	$4f^95d^16s^2$	+III
67	Holmium (Ho)	$4f^{10}5d^16s^2$	+III
68	Erbium (Er)	$4f^{11}5d^16s^2$	+III
69	Thulium (Tm)	$4f^{12}5d^16s^2$	+III
70	Ytterbium (Yb)	$4f^{14}5d^06s^2$	+II, +III
71	Lutetium (Lu)	$4f^{14}5d^16s^2$	+III

MELTING POINTS (°C)

COLOURS OF IONS

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

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

OXIDES

Ln_2O_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

LnO_2

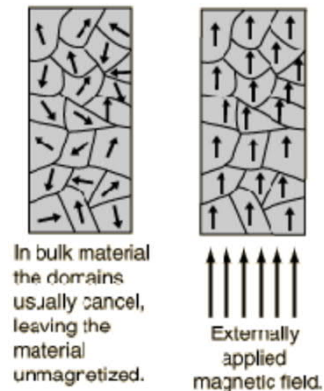
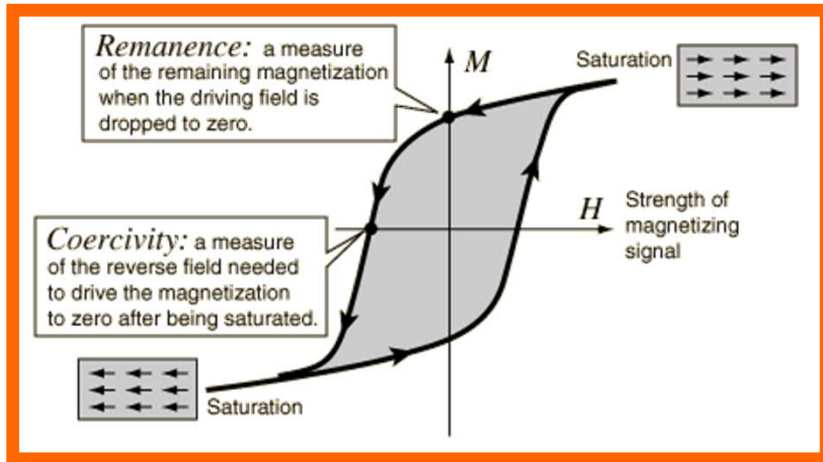
- CeO_2
- Pr_6O_{11} , Tb_4O_7

LnO

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

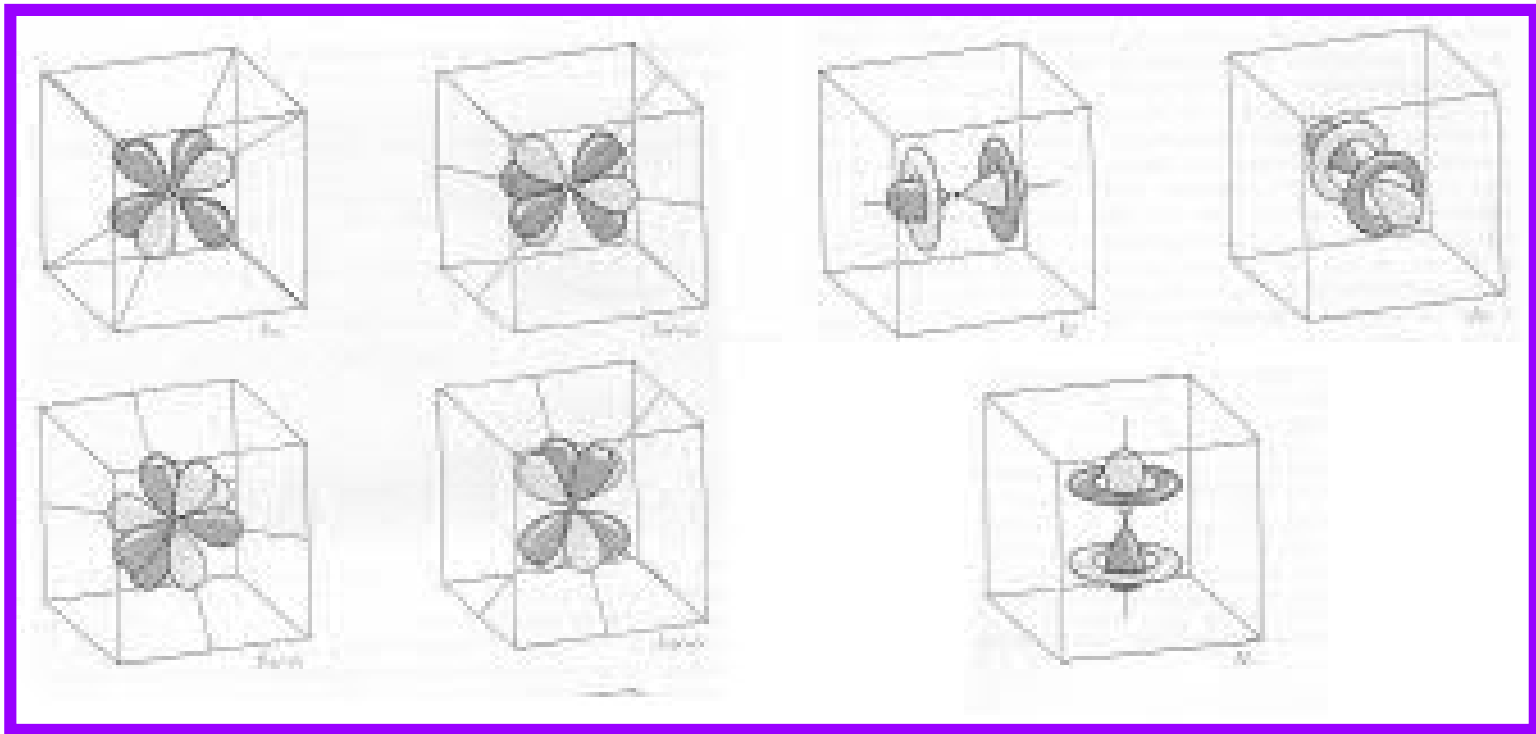
PERMANENT MAGNETS (ferromagnets)

- 1970s: SmCo_5 , $\text{Sm}_2\text{Co}_{17}$
- 1980s: $\text{Nd}_2\text{Fe}_{14}\text{B}$ (= neomagnets; very strong)
- With neomagnets smaller electric motors (e.g. in car industry)



Material	Coercivity [T]	Remanence [T]
$\text{BaFe}_{12}\text{O}_{19}$	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
$\text{Ce}(\text{CuCo})_5$	0.45	0.7
SmCo_5	1.0	0.83
$\text{Sm}_2\text{Co}_{17}$	0.6	1.15
$\text{Nd}_2\text{Fe}_{14}\text{B}$	1.2	1.2

4f orbitals

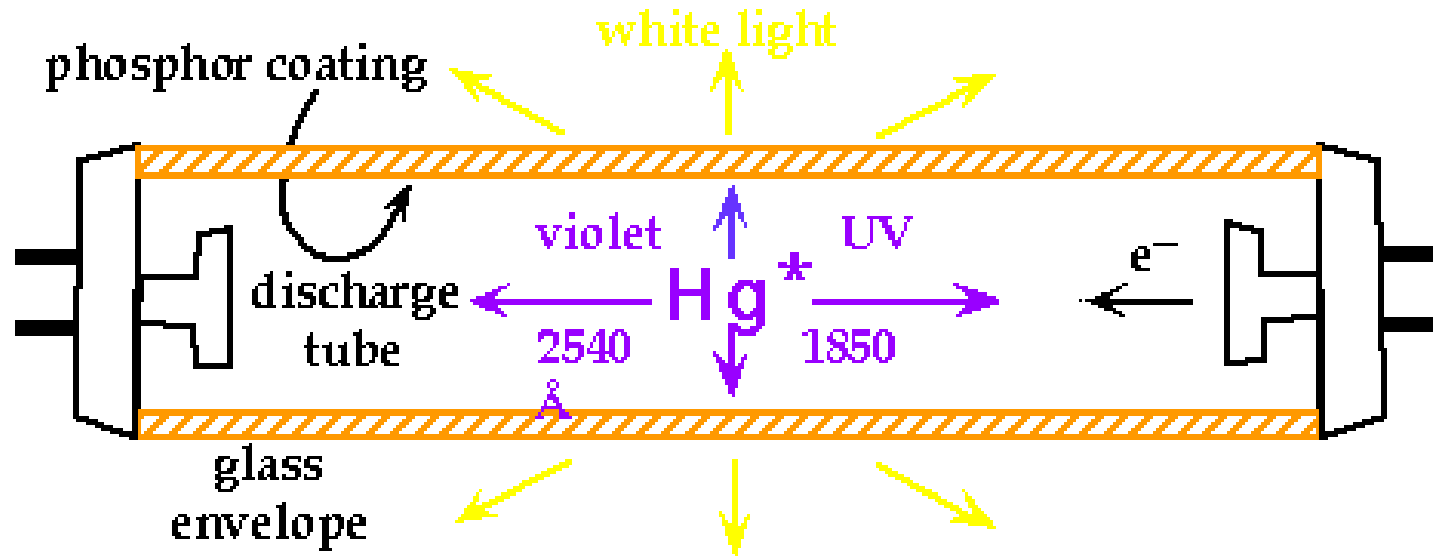


SPECTROSCOPIC PROPERTIES

- 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
→ lanthanoids have unique optical properties
- **Fluorescent lamps:**
from UV (254 nm)
to visible light
 - $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ red
 - $\text{CeMgAl}_{11}\text{O}_{19}:\text{Tb}^{3+}$ green
 - $(\text{Ce},\text{Gd})\text{MgB}_5\text{O}_{10}:\text{Tb}^{3+}$ green
 - $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ blue
 - $\text{Sr}_5(\text{PO}_4)_3(\text{F},\text{Cl}):\text{Eu}^{2+}$ blue
- **EL displays:**
from electric energy
to visible light
 - $\text{ZnS}:\text{Mn}^{2+}$ yellow
 - $\text{SrS}:\text{Ce}^{3+}$ bluishgreen
 - $\text{ZnS}:\text{Tb}^{3+}$ green
- **Lasers:**
 $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Nd}^{3+}$ 1064 nm

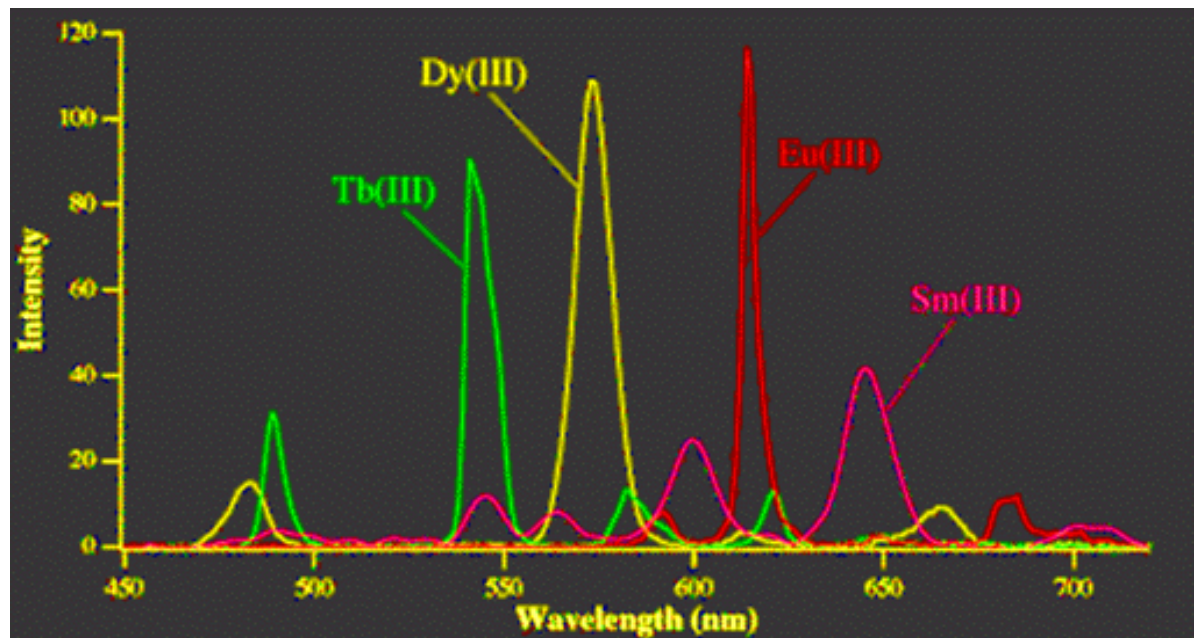


Fluorescence lamp

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

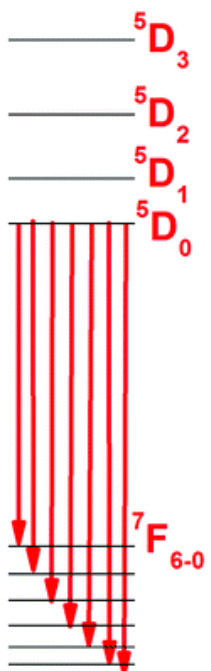




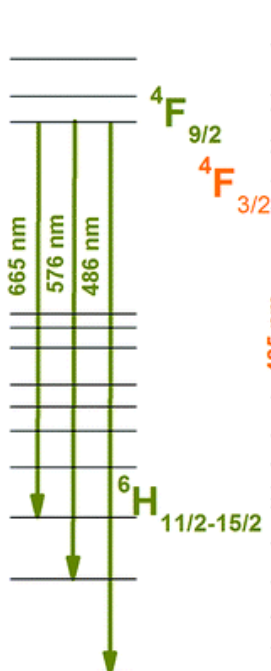
5D_3



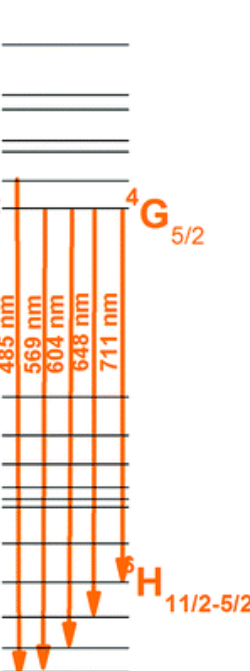
Tb^{3+}



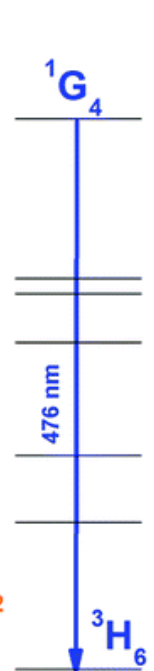
Eu^{3+}



Dy^{3+}

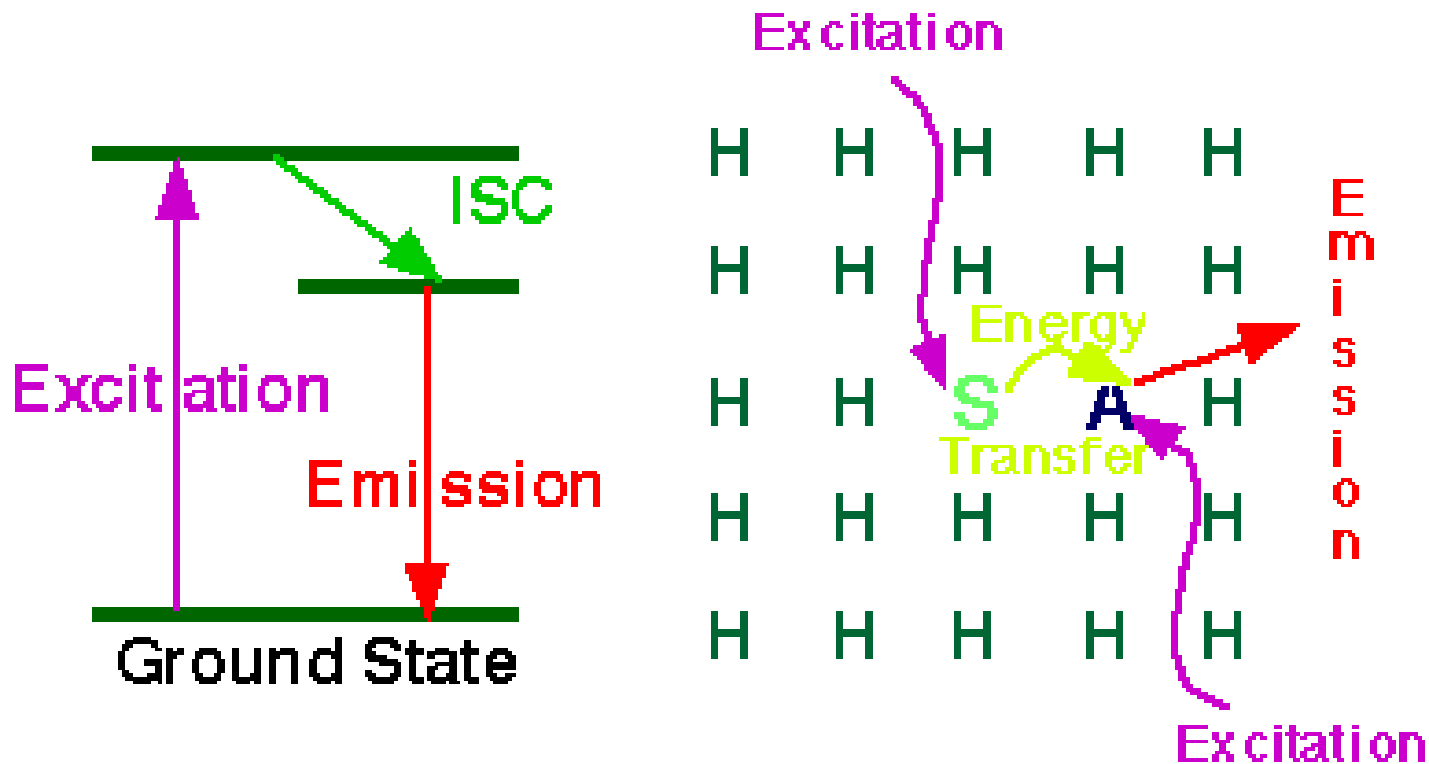


Sm^{3+}

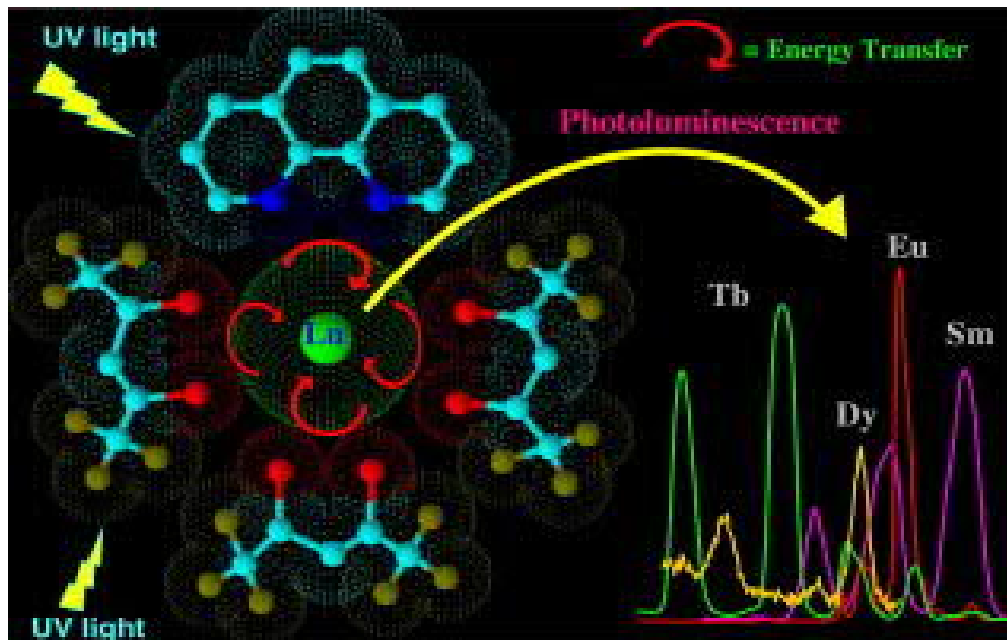
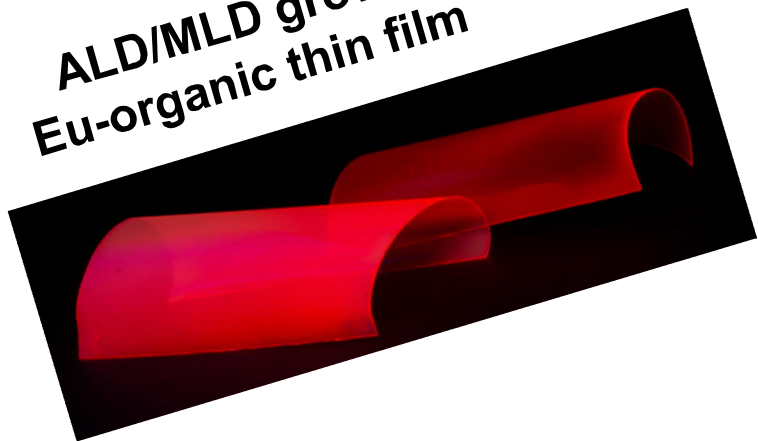


Tm^{3+}

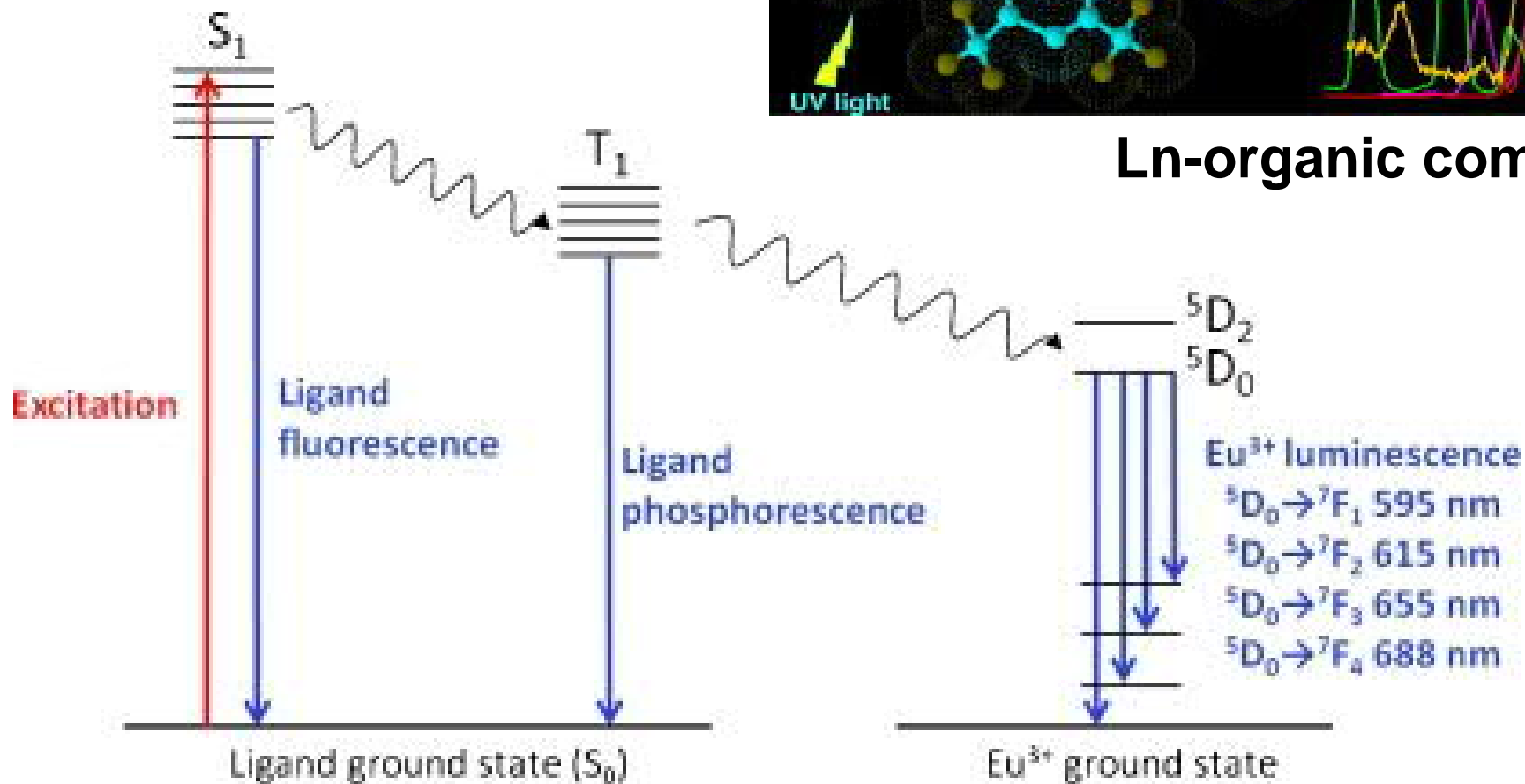
ENERGY TRANSFER: Sensitizer → Activator

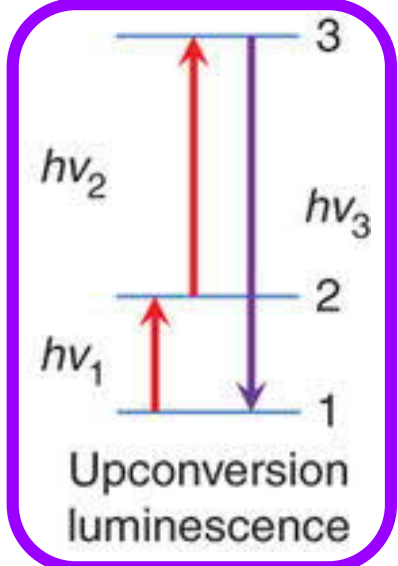
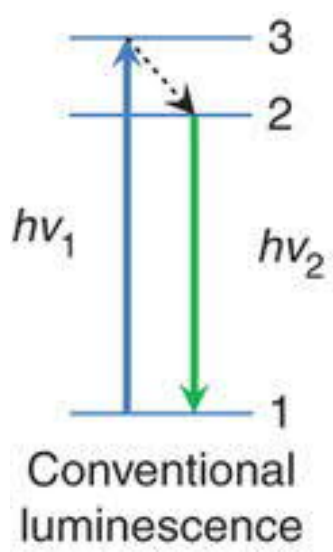


ALD/MLD grown
Eu-organic thin film



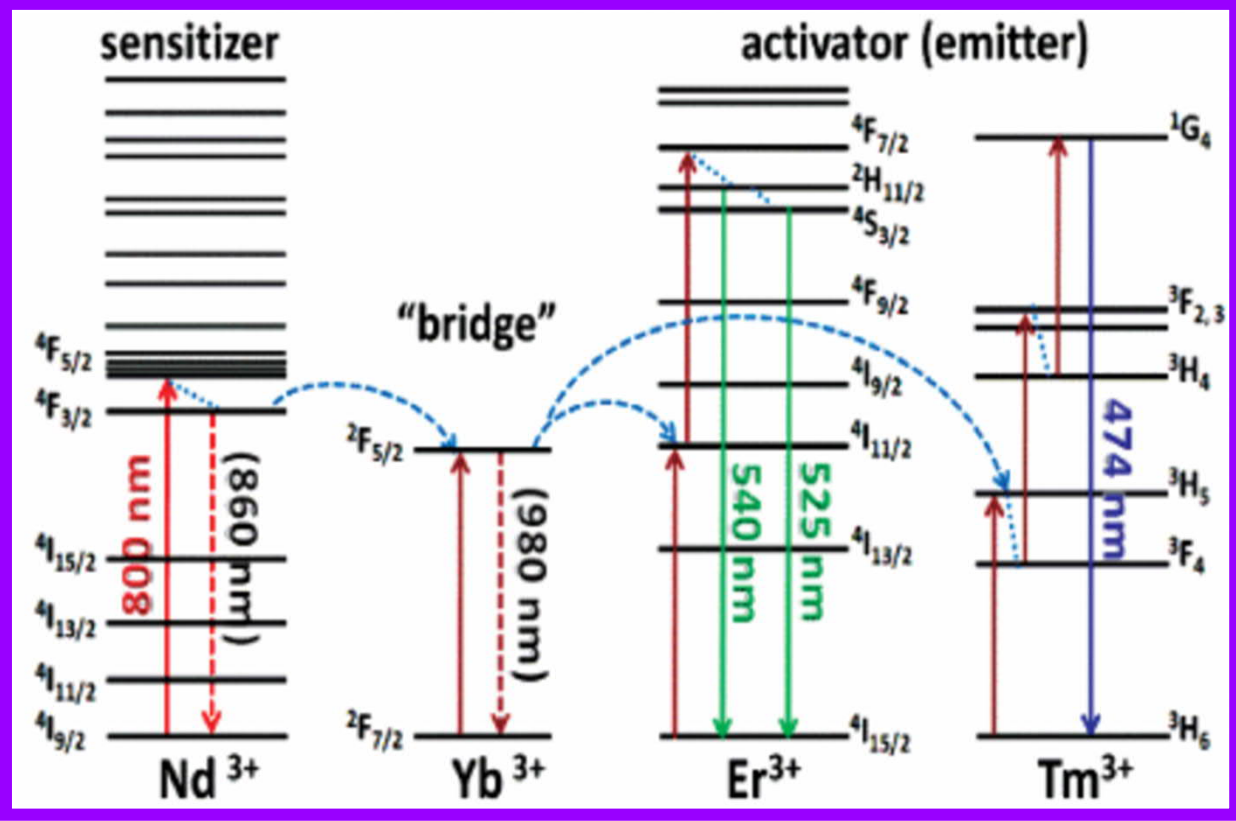
Ln-organic complex



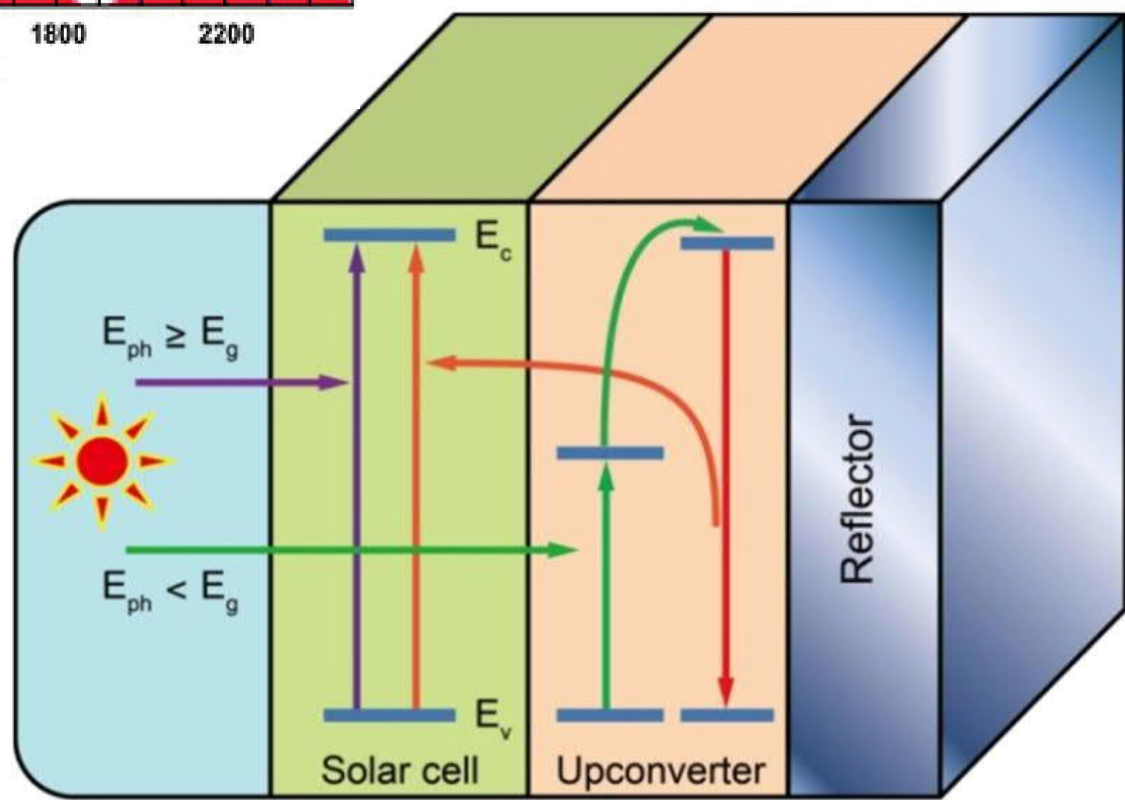
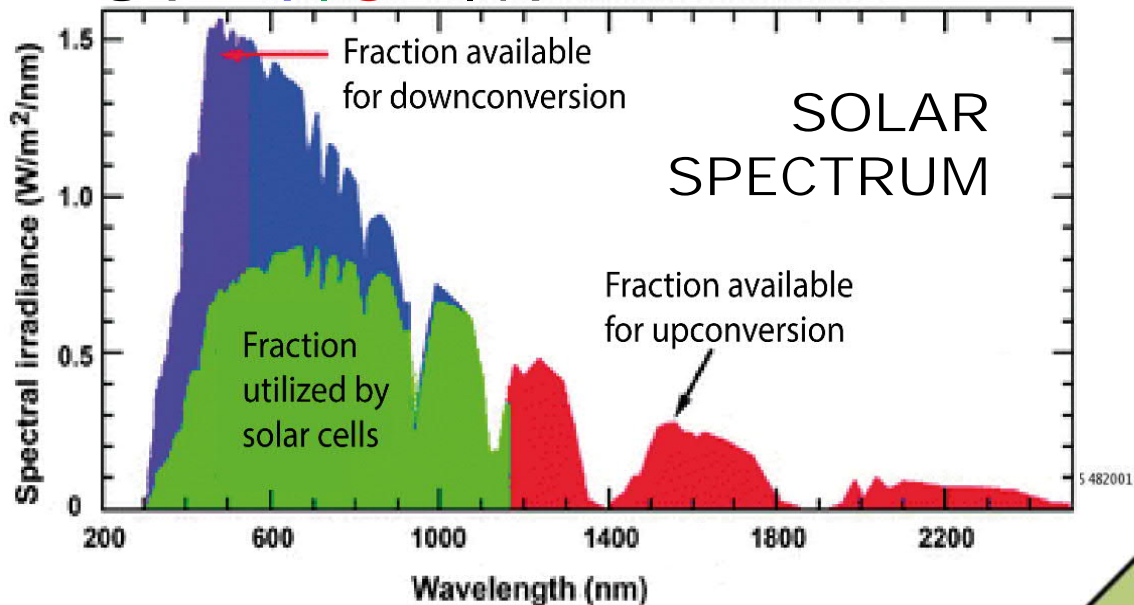


UPCONVERSION EMISSION

- for example from IR to Visible

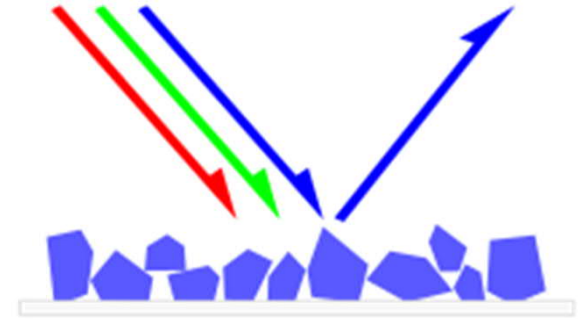


← UV VIS IR →



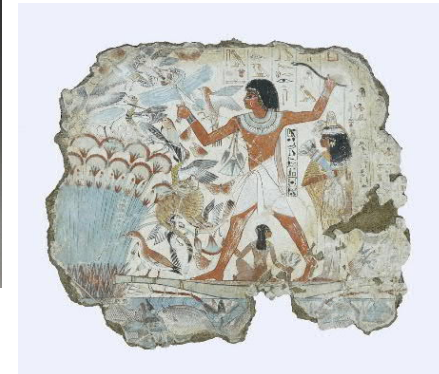
PIGMENT

- Material with wavelength-selective absorption
- Usable pigment must have a high tinting strength; used in paints, inks, plastics, fabrics, cosmetics, food, etc.
- For applications in industry and arts
→ insoluble in water and stable in light and heat
- Naturally occurring pigments such as ochres and iron oxides have been used as colorants since prehistoric times
- April 2018 by *Bloomberg Businessweek*:
 - global value of pigment industry \$30 billion
 - TiO_2 (white) has the largest share

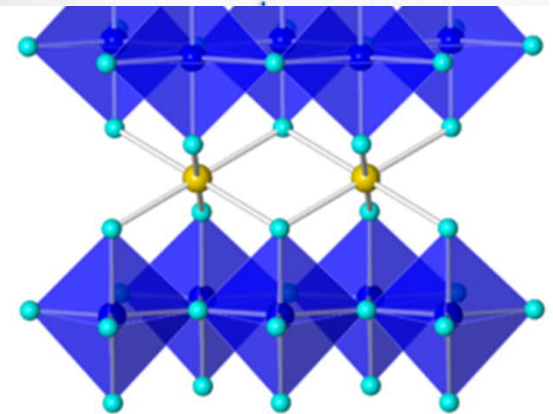


Inorganic BLUE PIGMENTS

- **6 000 years ago, *Ultramarine*:**
“true blue” made from semiprecious gemstone lapis lazuli mined in e.g. Afghanistan
- **1826 *French Ultramarine*:**
synthetic ultramarine
- **4 000 years ago, *Egyptian Blue*:**
“turquoise”, first synthetic pigment (calcium copper tetrasilicate) made by heating sand and copper together
- **1704 *Prussian Blue*:** $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
(other names: e.g. Berlin, Turnbull, midnight blue)
- **1802 *Cobalt Blue*:** CoAl_2O_4
- **2009 *Mas or YInMn Blue*:** $\text{Y}(\text{In},\text{Mn})\text{O}_3$



- **Prof. Mas Subramanian** received 2008 National Science Foundation grant to explore **novel materials for electronics applications**
- Main aim: **multiferroic (FM + FE)** materials
- He directed his PhD student Andrew Smith to synthesize a mixture of two oxides:
YInO₃ (ferroelectric; white)
YMnO₃ (antiferromagnetic; black)
- The result was NOT multiferroics, but blue material
- Subramanian has experience in chemical industry (DuPont) and recognized the value of the new **blue pigment** (filed a patent)
- Color adjusted by In/Mn ratio: Y(In_{0.8}Mn_{0.2})O₃ strongest
- First blue pigment discovered since 1802 (cobalt blue)
- **Huge interest:**
 - industry: Nike, Crayola, etc.
 - media: New York Times, Time Magazine, National Geographic, Businessweek, etc.
 - arts: Harvard Art Museum, etc.

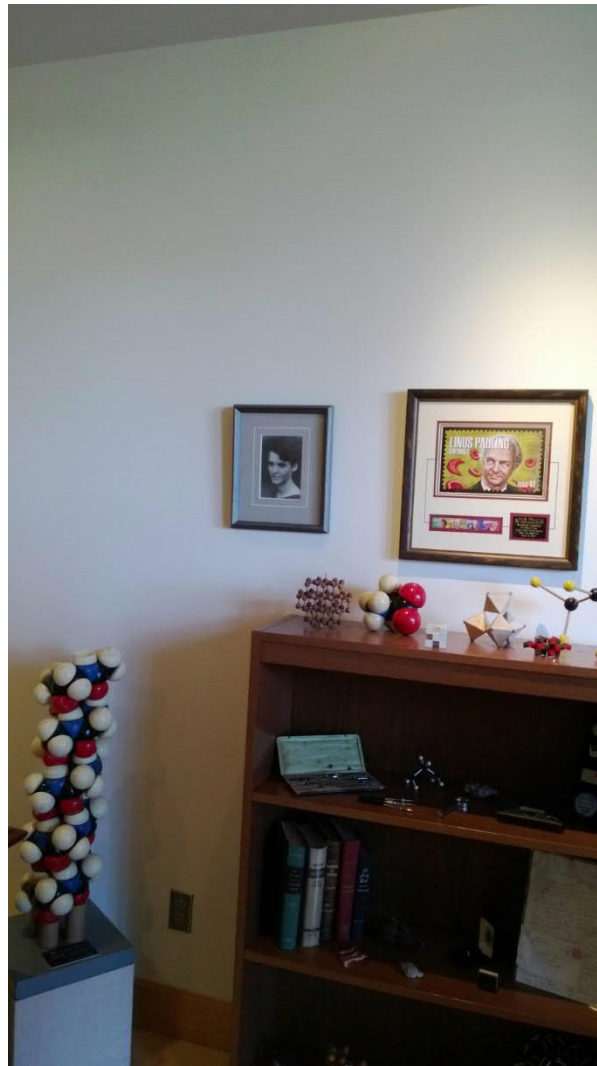
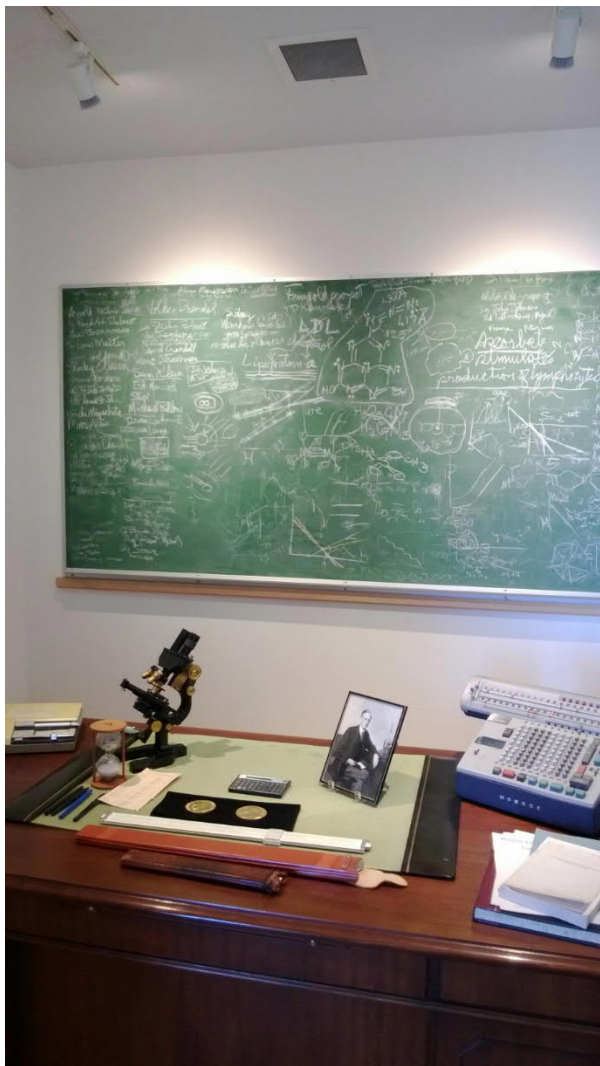


Mas Subramanian

- Born: 1954, Chennai, India
- MSc. 1977 (Inorganic Chemistry: clays and minerals) University of Madras 1977
- PhD 1982 (Solid State Chemistry: pyrochlore oxides) Indian Institute of Technology, Madras
- 1982-1984 PostDoc, Texas A&M University, USA
- 1984-2006 DuPont, USA:
 - ceramics, superconductors, dielectrics, catalysis, thermoelectrics, multiferroics, ionic conductors, etc.
- 2006-now Professor at Oregon State University: design and synthesis of novel functional materials for emerging applications in energy, environment & electronics
- 2009: novel durable blue pigment: **YInMn Blue**



Mount Hood (Oregon)
by Aquarelles de Mas Blue
by Ms. Rajeevi Subramanian



Linus Carl Pauling (1901–1994) was an American chemist, biochemist, peace activist, author, and educator, graduated at Oregon State University. He published more than 1200 papers and books, 850 on scientific topics. *New Scientist* rated him in 2000 the 16th most important scientist in history. Pauling was one of the founders of the fields of quantum chemistry and molecular biology. For his scientific work, Pauling was awarded the Nobel Prize in Chemistry in 1954. In 1962, for his peace activism, he was awarded the Nobel Peace Prize. Pauling is one of only two people who have received Nobel Prizes in different fields, the other being Marie Curie.

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)	$6d7s^2$	$6d^27s^2$	$5f^26d7s^2$	$5f^36d7s^2$	$5f^46d7s^2$	$5f^67s^2$	$5f^77s^2$	$5f^76d7s^2$	$5f^97s^2$	$5f^{10}7s^2$	$5f^{11}7s^2$	$5f^{12}7s^2$	$(5f^{13}7s^2)$	$(5f^{14}7s^2)$	$(5f^{14}6d7s^2)$

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 $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$
- 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 ($^{226}\text{U} - ^{240}\text{U}$):
 - ^{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: $(\text{NH}_4)_2\text{U}_2\text{O}_7$ or MgU_2O_7
carbonate solution: $\text{Na}_2\text{U}_2\text{O}_7$
- Reduction → UO_2
- Green salt UF_4
- For isotope enrichment: $\text{UF}_4(\text{s}) + \text{F}_2(\text{g}) \rightarrow \text{UF}_6(\text{g})$
- Isotope enrichment: gas diffusion process, centrifugal separation, electromagnetic separation, laser excitation, jet/spray separation
- Use as a fuel in nuclear reactors: ^{235}U , $^{235}\text{UO}_2$, $^{235}\text{UC}_2$

