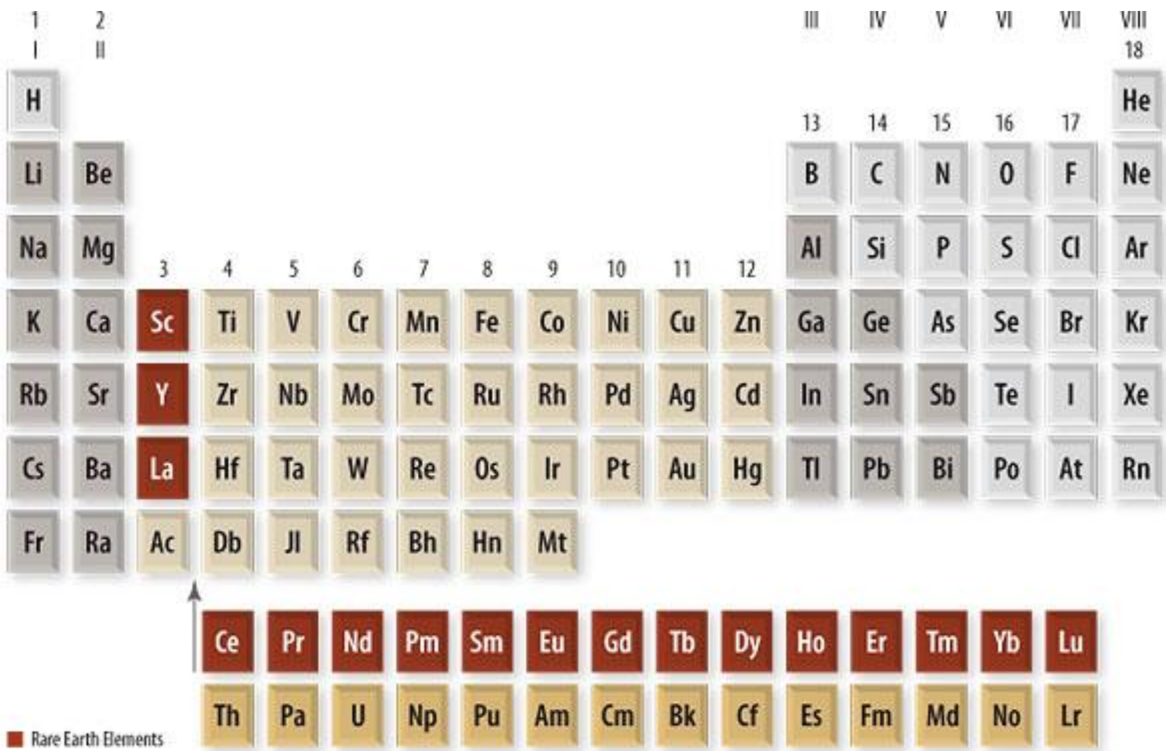
Rare earths and their applications

Koen Binnemans

KU Leuven - University of Leuven (Belgium)

Rare earths in the periodic table



Source: www.tre-ag.com

Lanthanides = series of elements La-Lu

Rare earths = lanthanides + Y + Sc

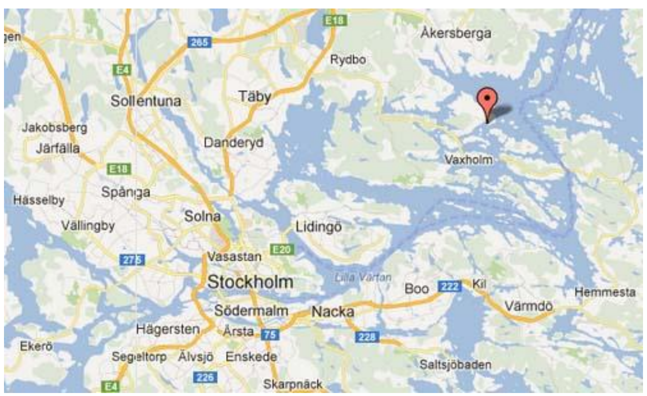
REEs = rare-earth elements

LREE = La-Sm HREE = Eu-Lu, Y

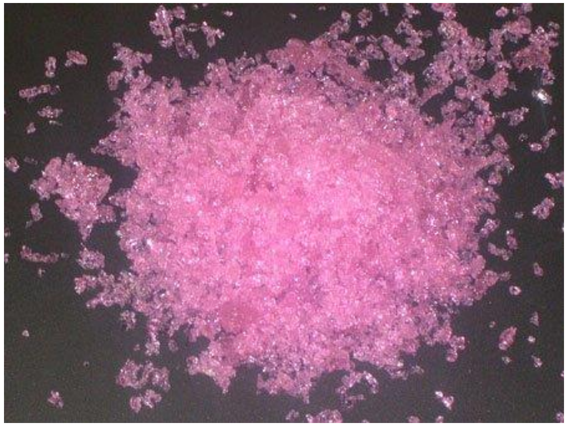
Rare earths: names and symbols

Name	Chemical Symbol	Atomic Number (Z)
Scandium	Sc	21
Yttrium	Y	39
Lanthanum	La	57
Cerium	Ce	58
Praseodymium	Pr	59
Neodymium	Nd	60
Promethium	Pm	61
Samarium	Sm	62
Europium	Eu	63
Gadolinium	Gd	64
Terbium	Tb	65
Dysprosium	Dy	66
Holmium	Ho	67
Erbium	Er	68
Thulium	Tm	69
Ytterbium	Yb	70
Lutetium	Lu	71

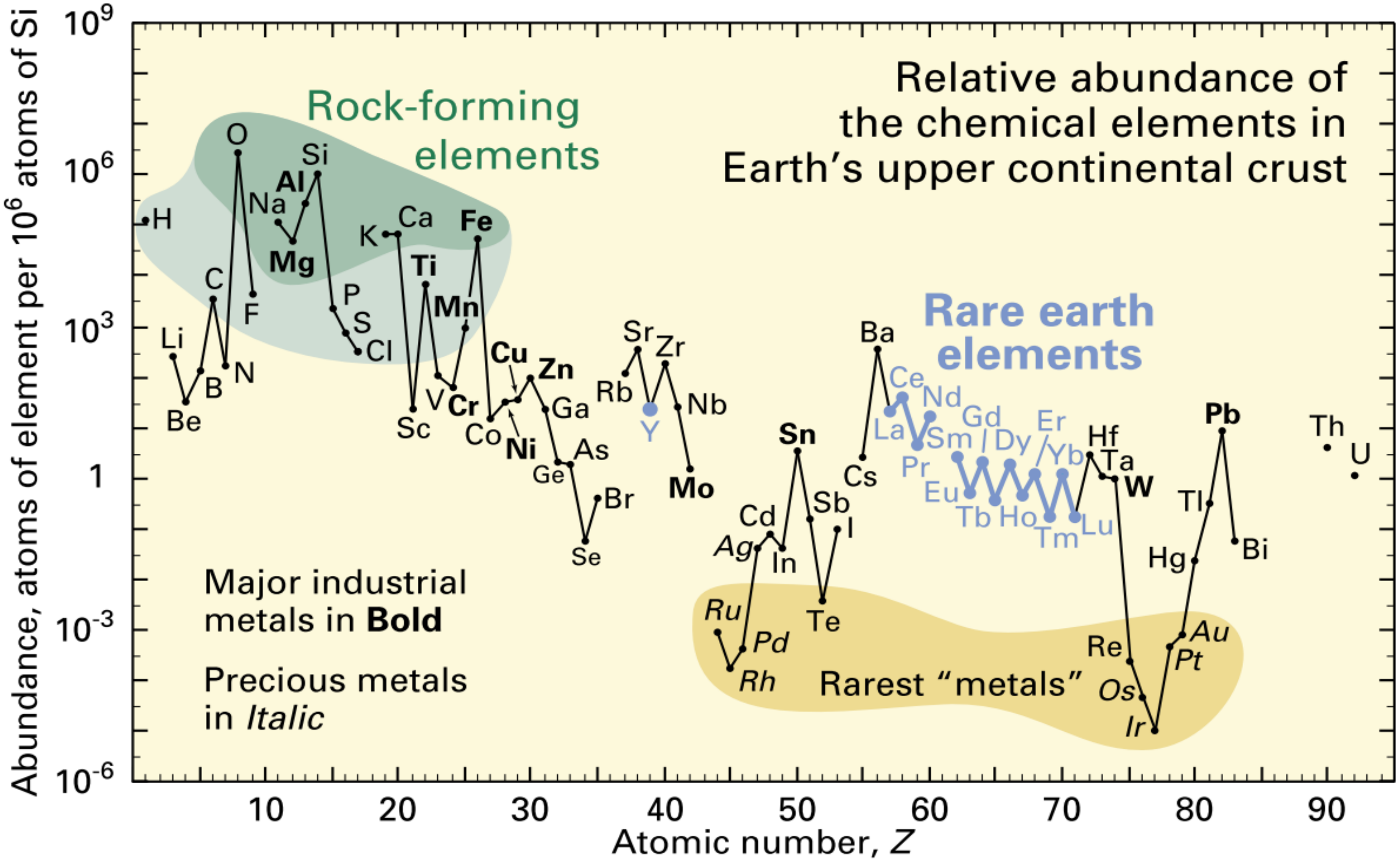
Ytterby (Sweden)



Rare earths: How do they look like?



Rare earths are not very rare!



Source: US Geological Survey

Rare-earth ore minerals

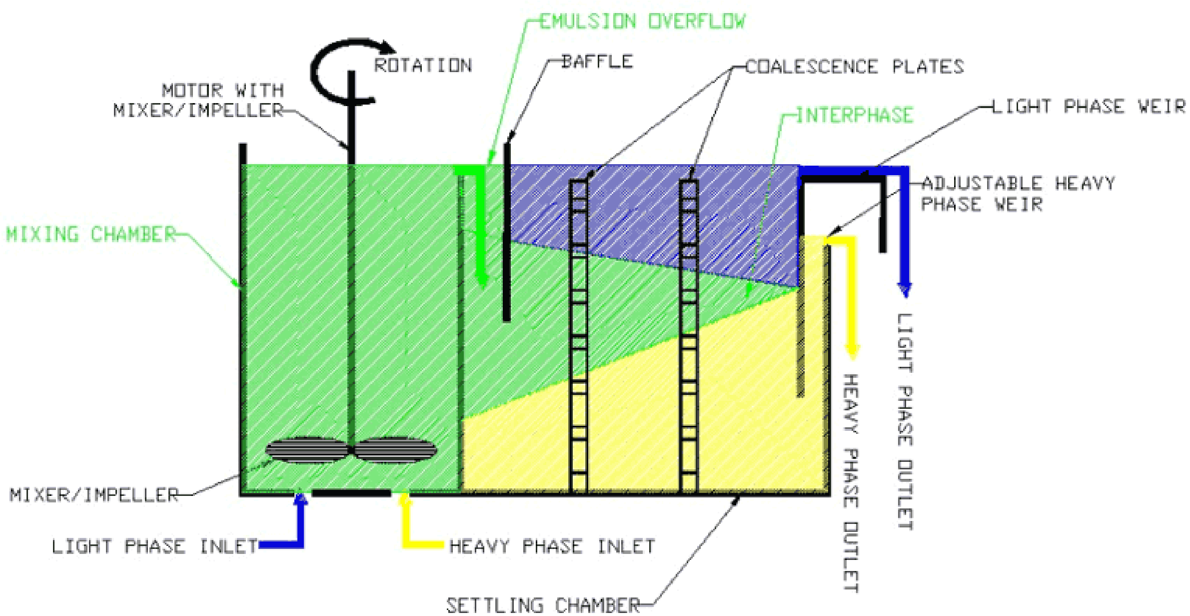
Carbonate Minerals	Bastnäsite	$(Ce,La)(CO_3)F$
Phosphate Minerals	Monazite	$(Ce,La,Nd,Th)PO_4$
	Xenotime	YPO_4
	Apatite	$Ca_5(PO_4)_3(F,Cl,OH)$
Oxidic/ Alkaline Minerals	Eudialyte	$Na_4(Ca,Ce)_2(Fe^{2+},Mn,Y)ZrSi_8O_{22}(OH,Cl)_2$
	Allanite	$(Ce,Ca,Y)_2(Al,Fe^{3+})_3(SiO_4)_3OH$
	Loparite	$(Ce,La,Na,Ca,Sr)(Ti,Nb)O_3$

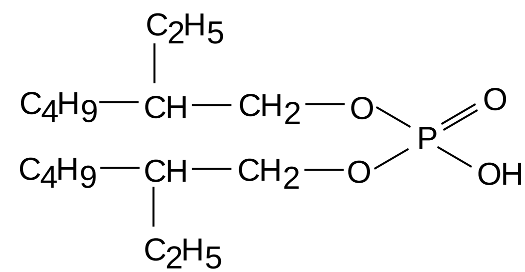
Rare-earth separation problem

- Ores contain mixtures of all rare earths (except Pm)
- Many applications require pure rare earths
- Mixtures are difficult to separate due to similarities in chemical properties of rare earths
- Separation of rare earths is one of the most difficult separations in inorganic chemistry
- Separation is done on an industrial scale by solvent extraction (SX)

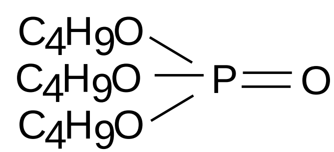
Separation of REEs by solvent extraction

LABORATORY MIXER-SETTLERS:





DEPHA

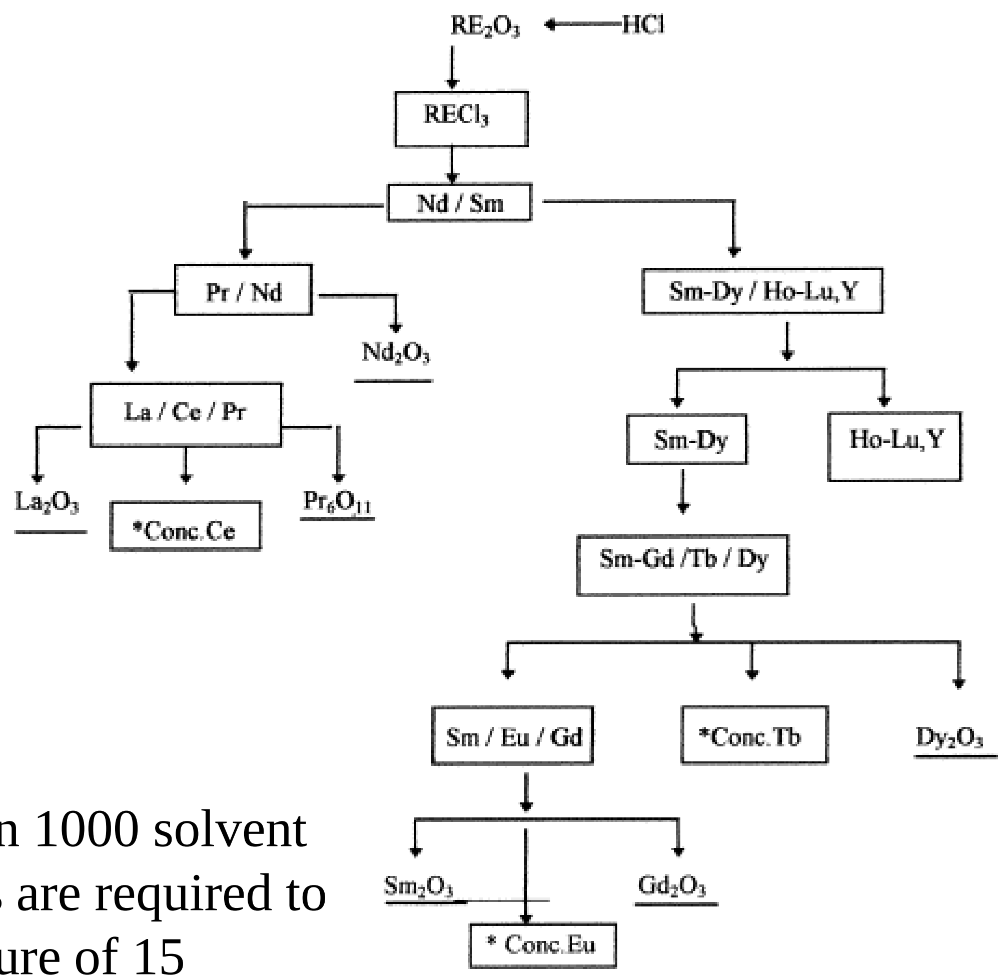


TBP

http://www.rousselet-robatel.com

REE solvent extraction plant (Solvay)

Separation scheme of REE mixtures



Often more than 1000 solvent extraction steps are required to separate a mixture of 15 elements.

Electrolytic preparation of REE metals

For REE with melting point <1050 °C (La, Ce, Pr, Nd, MM)

Traditionally from molten chlorides:

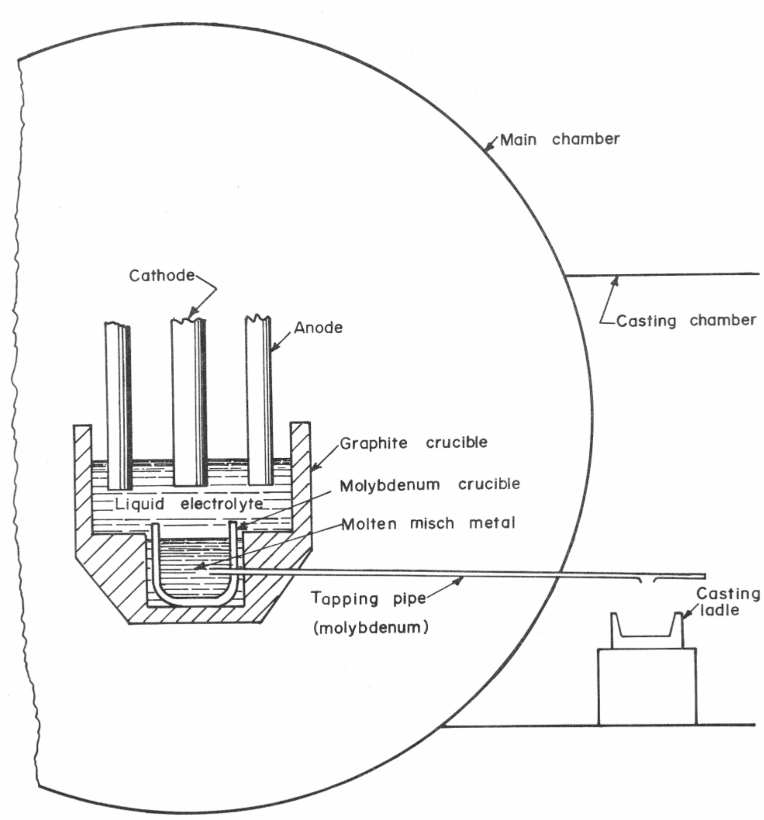
Cathode reaction: $Ln^{3+} + 3e^- \rightarrow Ln$

Anode reaction: $2\,Cl^- \rightarrow Cl_2 + 2e^-$

Iron cathode, graphite anode

More recently, from oxides dissolved in LnF_3-LiF flux at 1100 °C:

$2\,Ln_2O_3 \rightarrow 4\,Ln + 3\,O_2 + \text{some } F_2$



Calciothermic preparation of REE metals

For REEs with melting point >1050°C
(REE = Sc, Y, Gd → Er, Lu)

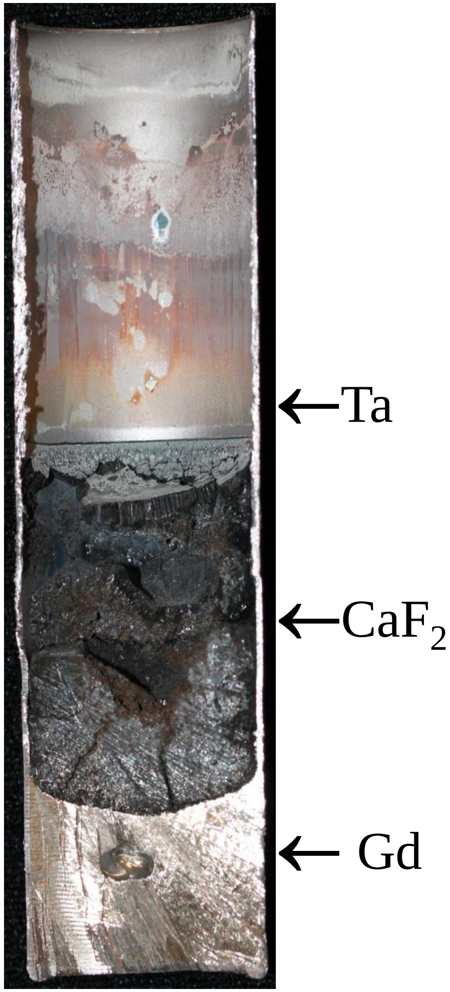
$$Ln_2O_3 + 3(NH_4F \bullet HF) \xrightarrow{700°C} 2LnF_3 + 3H_2O + 3NH_3$$

$$2LnF_3 + 3Ca \xrightarrow{1500°C} 2Ln + 3CaF_2$$

or

$$Ln_2O_3 + 6HCl \xrightarrow{\sim600°C} 2LnCl_3 + 3H_2O$$

$$2LnCl_3 + 3Ca \xrightarrow{1200°C} 2Ln + 3CaCl_2$$



Lanthanothermic preparation of Sm, Eu, Tm, Yb

$La + Ln_2O_3 \rightarrow Ln\uparrow + La_2O_3$

REE	Boiling point (°C)	Melting Point (°C)
La	3464	918
Sm	1794	1074
Eu	1527	822
Tm	1950	1545
Yb	1196	819

Configurations of rare-earth ground states

Element	Neutral Atom Configuration	
Sc		$3d4s^2$
Y		$4d5s^2$
La	$4f^0$	$5d6s^2$
Ce	$4f^1$	$5d6s^2$
Pr	$4f^3$	$6s^2$
Nd	$4f^4$	$6s^2$
Pm	$4f^5$	$6s^2$
Sm	$4f^6$	$6s^2$
Eu	$4f^7$	$6s^2$
Gd	$4f^7$	$5d6s^2$
Tb	$4f^9$	$6s^2$
Dy	$4f^{10}$	$6s^2$
Ho	$4f^{11}$	$6s^2$
Er	$4f^{12}$	$6s^2$
Tm	$4f^{13}$	$6s^2$
Yb	$4f^{14}$	$6s^2$
Lu	$4f^{14}$	$5d6s^2$

- Displayed on periodic tables and in many textbooks
- Generally not important to most scientists – who work with solids or liquids
- Important in chemical thermodynamic cycles if the $Ln_{(g)}$ gas state is involved

Electronic configurations of Ln^{3+} ions: filling of 4f orbitals

Table 9.14 Names, symbols, and properties of the lanthanides

Z	Name	Symbol	Configuration of M^{3+}	$E^{\ominus}/V$	$r(M^{3+})/Å$*	O.N.†
57	Lanthanum	La	[Xe]	−2.38	1.16	**3**
58	Cerium	Ce	[Xe]$4f^1$	−2.34	1.14	**3**, 4
59	Praseodymium	Pr	[Xe]$4f^2$	−2.35	1.13	**3**, 4
60	Neodymium	Nd	[Xe]$4f^3$	−2.32	1.11	2(n), **3**
61	Promethium	Pm	[Xe]$4f^4$	−2.29	1.09	**3**
62	Samarium	Sm	[Xe]$4f^5$	−2.30	1.08	2(n), **3**
63	Europium	Eu	[Xe]$4f^6$	−1.99	1.07	2(a), **3**
64	Gadolinium	Gd	[Xe]$4f^7$	−2.28	1.05	**3**
65	Terbium	Tb	[Xe]$4f^8$	−2.31	1.04	**3**, 4
66	Dysprosium	Dy	[Xe]$4f^9$	−2.29	1.03	2(n), **3**
67	Holmium	Ho	[Xe]$4f^{10}$	−2.33	1.02	**3**
68	Erbium	Er	[Xe]$4f^{11}$	−2.32	1.00	**3**
69	Thulium	Tm	[Xe]$4f^{12}$	−2.32	0.99	2(n), **3**
70	Ytterbium	Yb	[Xe]$4f^{13}$	−2.22	0.99	2(a), **3**
71	Lutetium	Lu	[Xe]$4f^{14}$	−2.30	0.98	**3**

*Ionic radii for C.N. = 8 from R.D. Shannon, *Acta Crystallogr.* **A32**, 751 (1976).
†Oxidation numbers in bold type indicate the most stable states; other states that can be achieved in aqueous (a) and nonaqueous (n) solution are also included.

Why are Ln^{3+}_{aq} ions so stable?

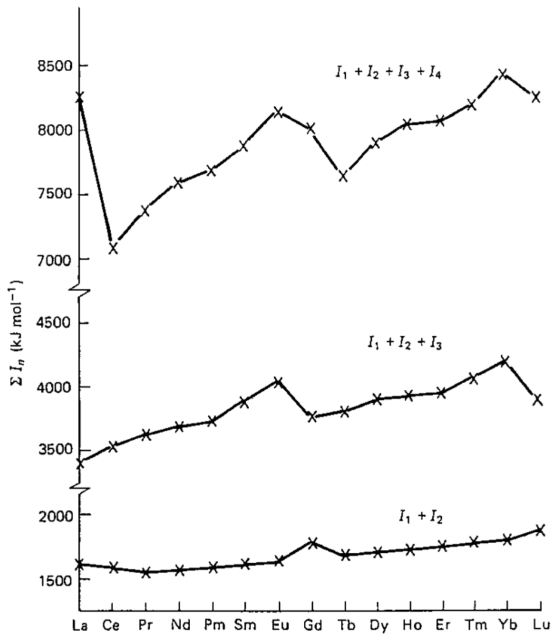
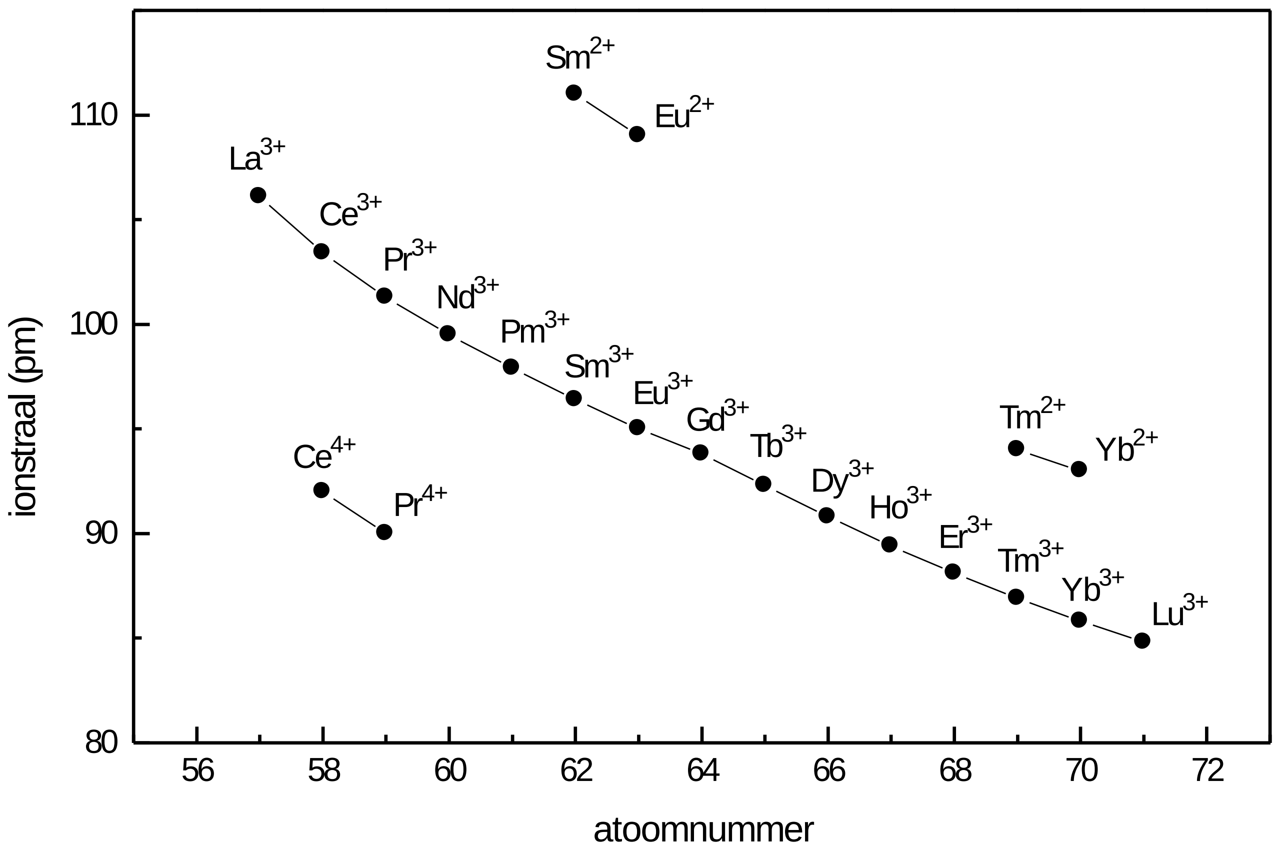


Figure 2.3
Cumulative ionization energies across the lanthanide Series (reproduced by permission of Macmillan from S.A. Cotton, *Lanthanides and Actinides*, Macmillan, 1991).

Table 2.4 Enthalpies of hydration of the lanthanide ions (values given as $-\Delta H$ hydr/kj mol^{-1}

La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}	Y^{3+}
3278	3326	3373	3403	3427	3449	3501	3517	3559	3567	3623	3637	3664	3706	3722	3583
	Ce^{4+}				Sm^{2+}	Eu^{2+}							Yb^{2+}		
	6309				1444	1458							1594		

Lanthanide contraction



Tetravalent lanthanides

- **Ce, Pr, Nd** and **Tb** may have +4 oxidation state

  E^0_{red} for $Ln^{4+}(aq) + e^- \leftrightarrows Ln^{3+}(aq)$ in acidic solutions:

  +1.72 V for Ce^{4+}, stable in water

  +3.20 V for Pr^{4+}, oxidizes water

  +3.10 V for Tb^{4+}, oxidizes water
- Many examples of Ce^{4+} compounds are known
- Ce^{4+} is used as oxidant for redox titrations and in organic synthesis
- Tb^{4+} has been reported as carbonato complexes in water
- Pr^{4+} and Nd^{4+} compounds are only known in the solid state, including in mixed-valence oxides Pr_6O_{11} and Tb_4O_7.

$(NH_4)_2[Ce(NO_3)_6]$

$(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$

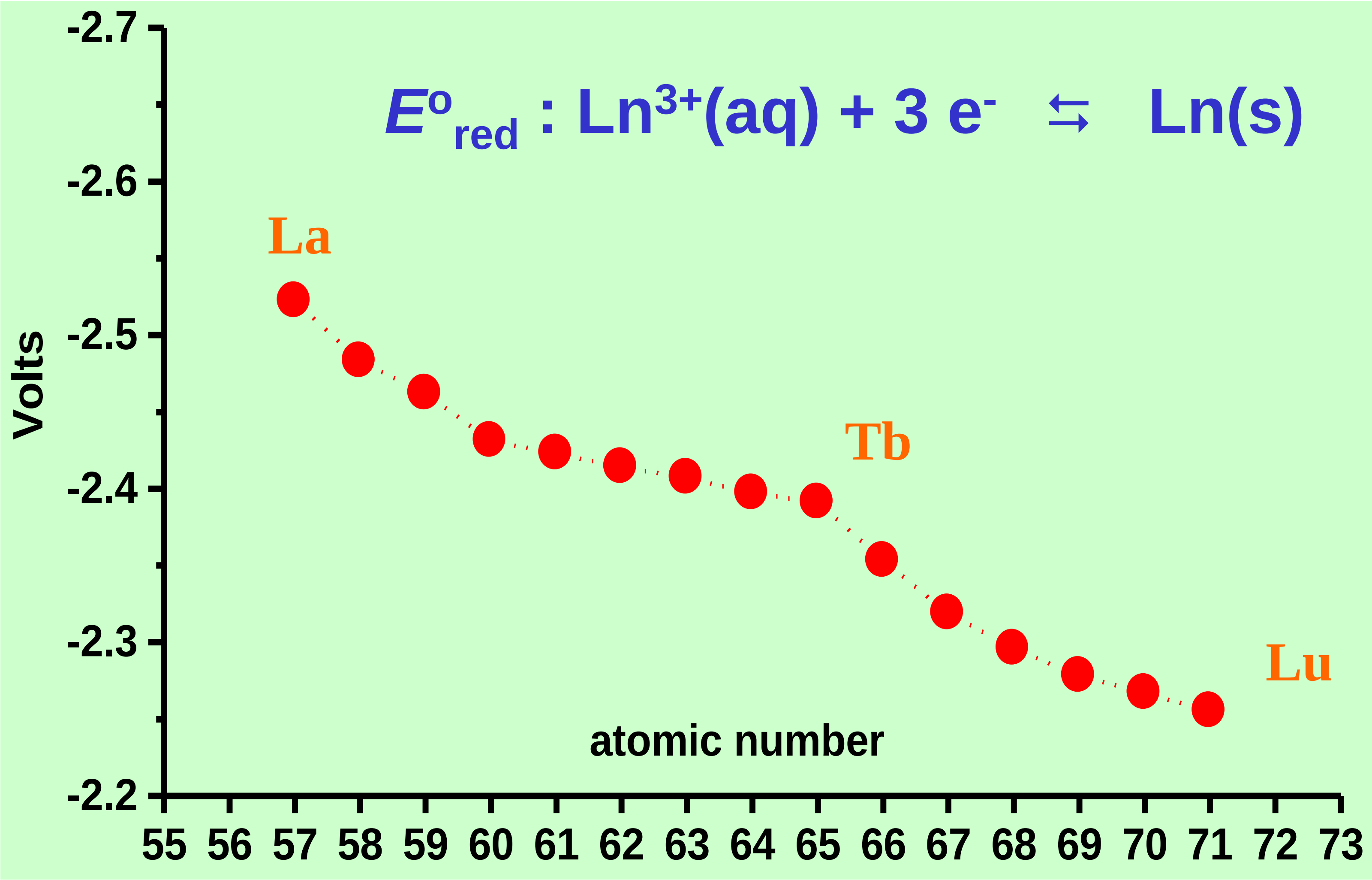
Divalent lanthanides

- **Sm**, **Eu**, and **Yb** have a relatively stable +2 state

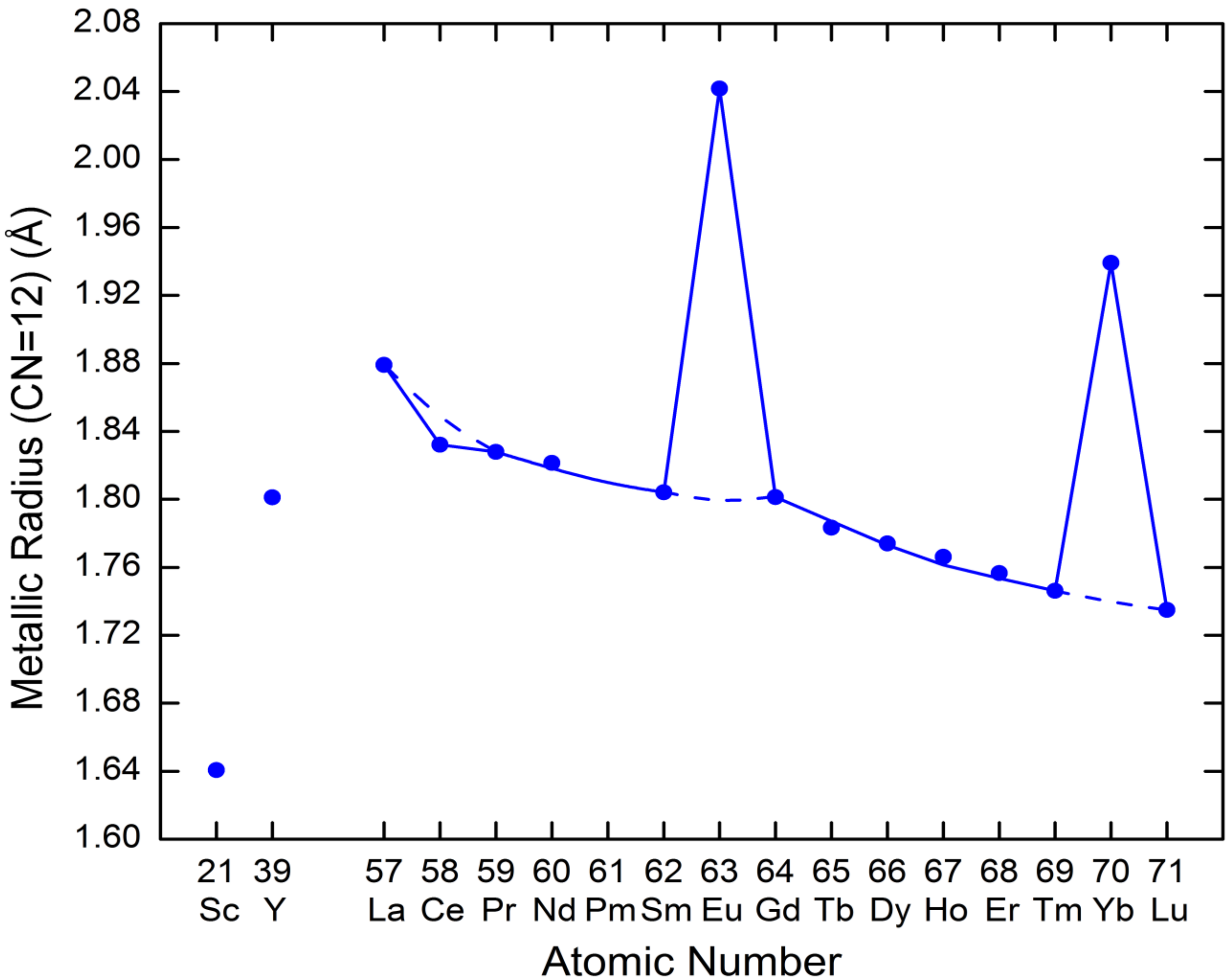
E^0_{red} for $Ln^{3+}(aq) + e^- \leftrightarrows Ln^{2+}(aq)$ in acidic solutions:

-0.35 V for Eu^{2+}, stable in water
-1.15 V for Yb^{2+}, reduces water
-1.56 V for Sm^{2+}, reduces water

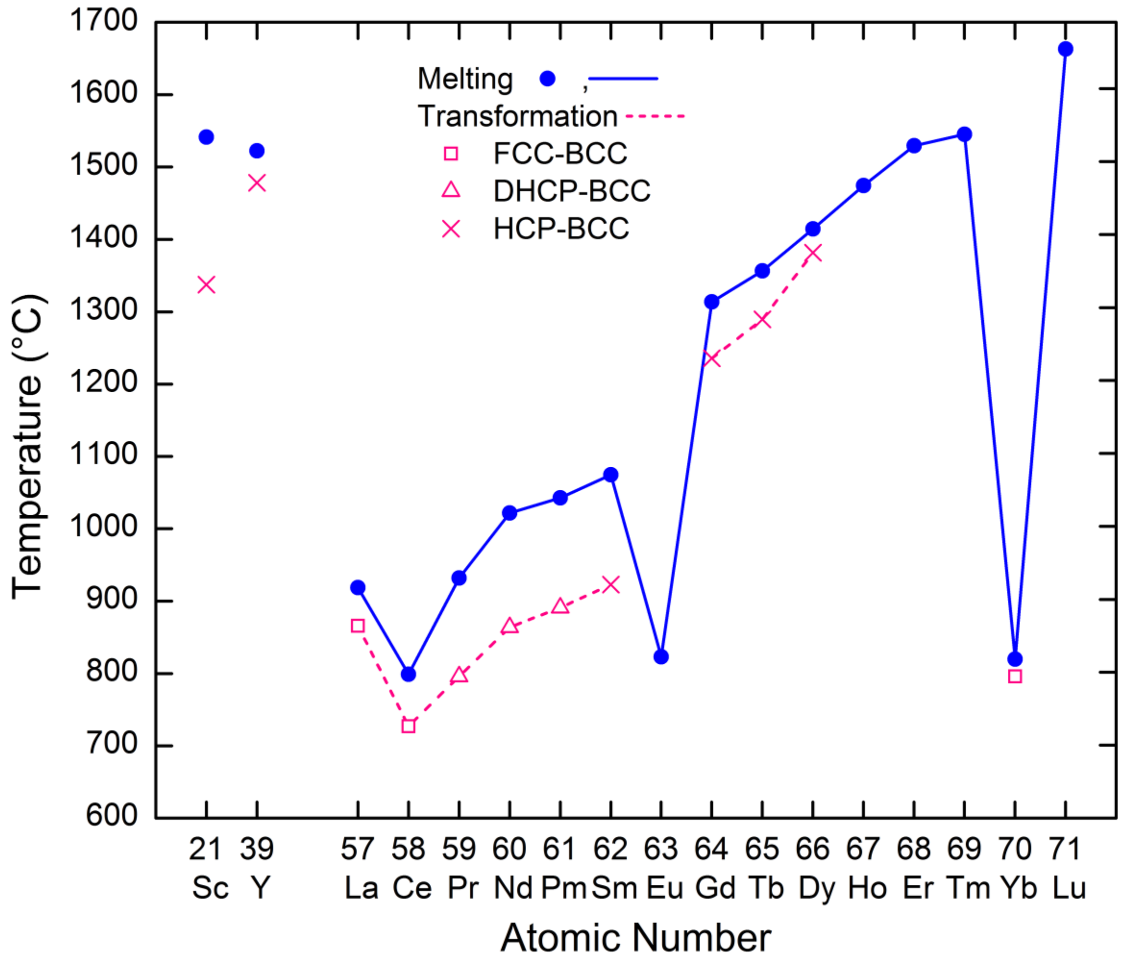
Reduction to rare-earth metals



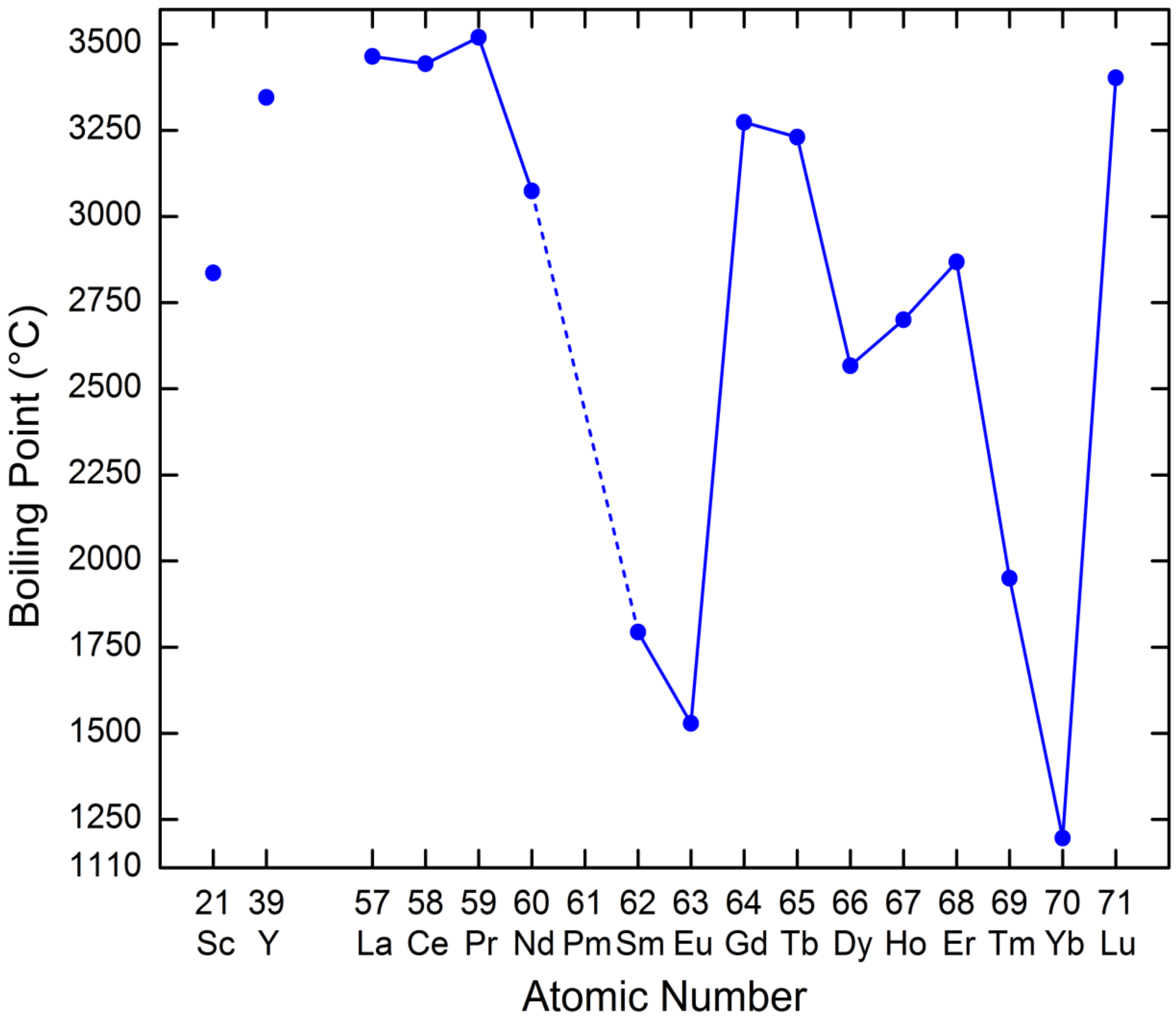
Metallic radius of rare-earth metals



Melting points and transformation temperatures of rare-earth metals



Boiling point of rare-earth metals



Rare-earth oxides

- Normal Oxides – Sesquioxide R_2O_3

  Among the most stable oxides

- Other Valence State Oxides

  Tetravalent or partially tetravalent

  CeO_2 all 4+

  Pr_6O_{11} $4PrO_2 + Pr_2O_3$

  Tb_4O_7 $2TbO_2 + Tb_2O_3$

  Divalent or partially divalent (uncommon)

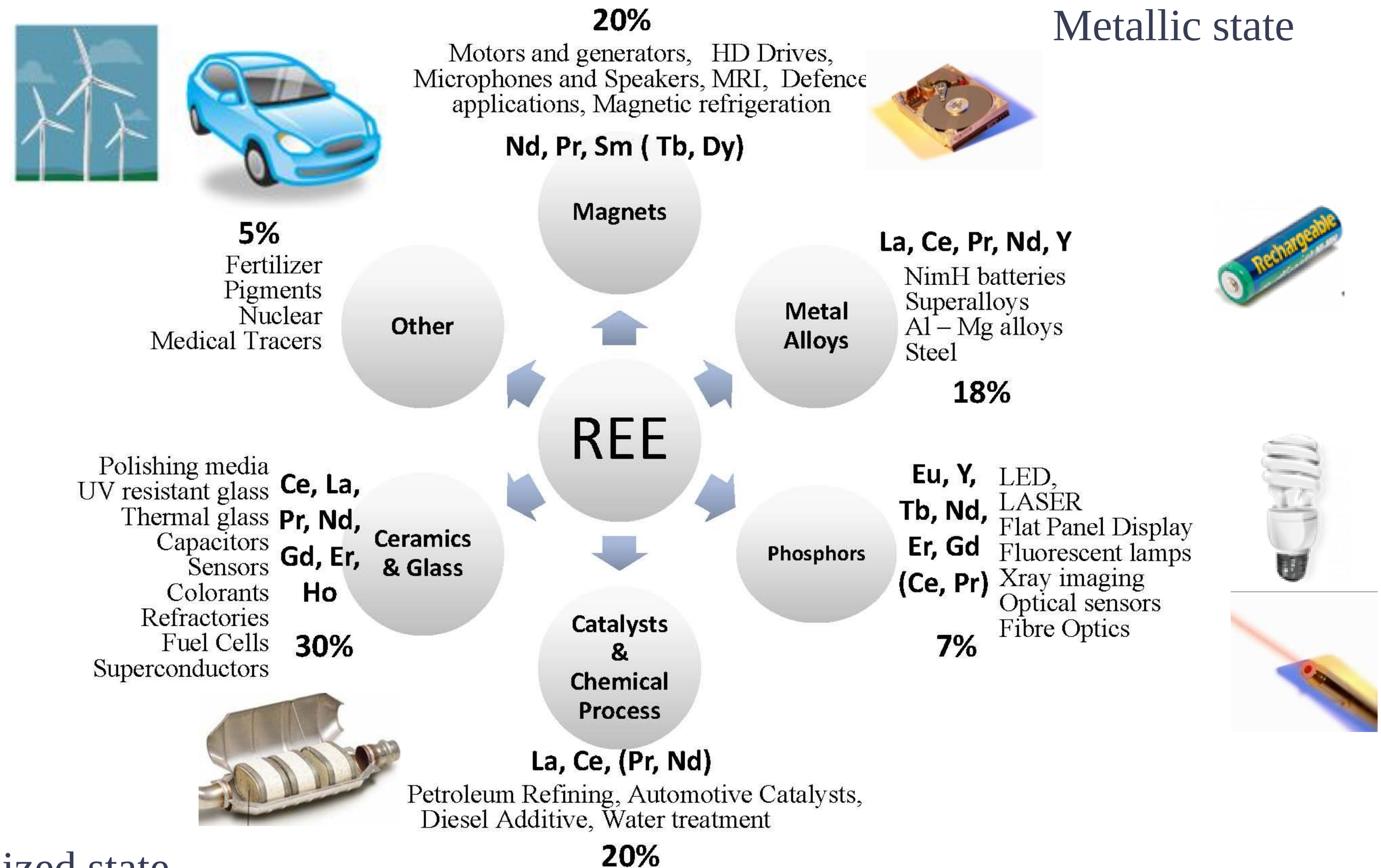
  EuO *2+*

  Eu_3O_4 $EuO + Eu_2O_3$

Pr_6O_{11}

Tb_4O_7

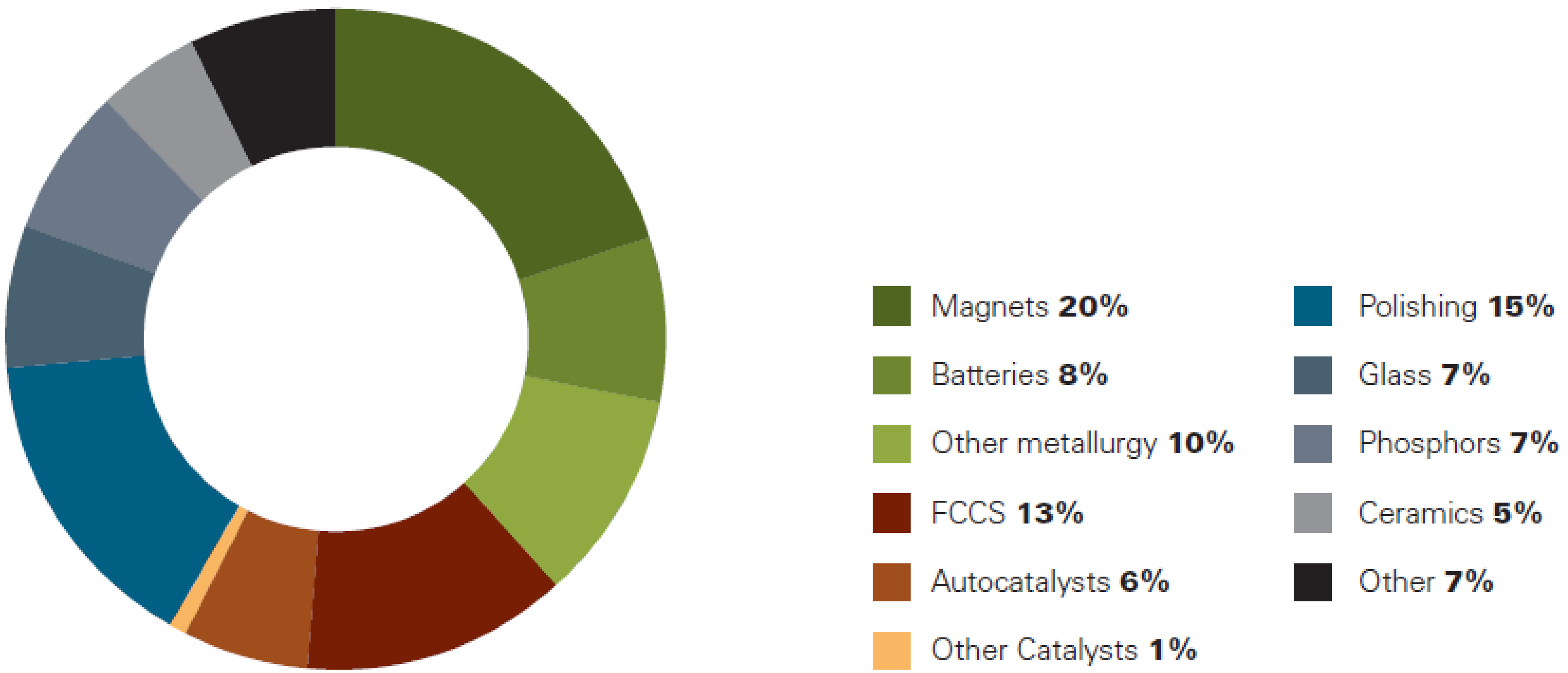
Applications of rare earths



Oxidized state

Source: www.eurare.eu

Breakdown of estimated rare-earth consumption by sector in 2012



Total REO production: 120,000 tonnes/year

Source: ERECON report (2015)

REEE usage by application

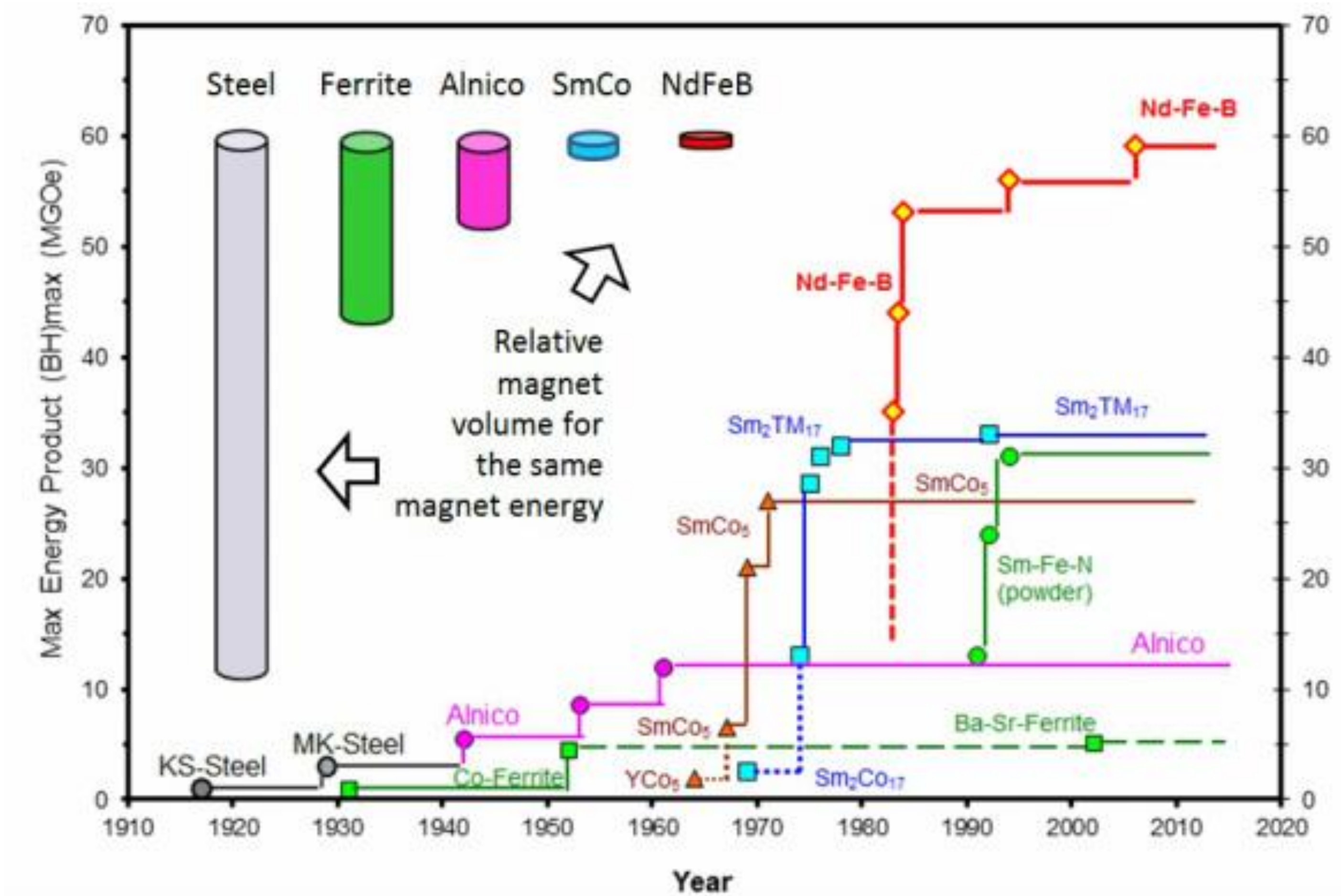
Application	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Other
Magnets			23.4	69.4			2	0.2	5		
Battery alloys	50	33.4	3.3	10	3.3						
Metallurgy	26	52	5.5	16.5							
Auto catalysts	5	90	2	3							
FCC	90	10									
Polishing powder	31.5	65	3.5								
Glass additives	24	66	1	3						2	4
Phosphors	8.5	11				4.9	1.8	4.6		69.2	
Ceramics	17	12	6	12						53	
Others	19	39	4	15	2		1			19	

(source: Lynas Corporation)[8]

Permanent magnets (Nd-Fe-B and Sm-Co)

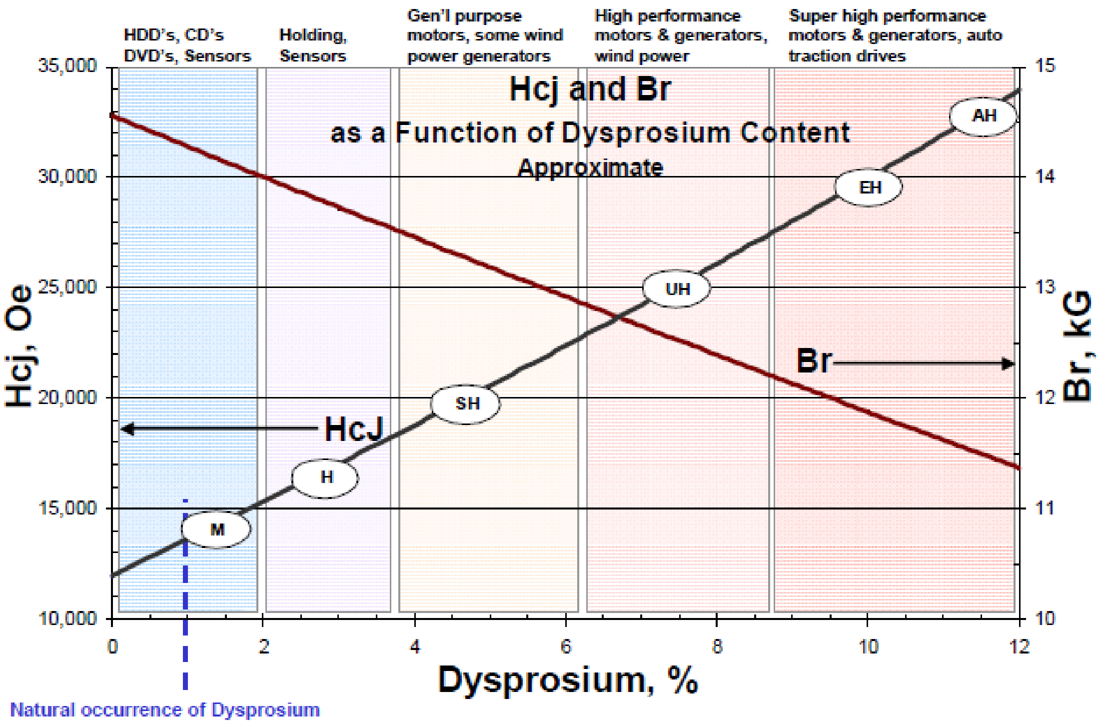
- samarium-cobalt alloys: $SmCo_5$ and Sm_2Co_{17}
  - maximum energy product $(BH)_{max}$:130 to 260 kJ/m^3
  - good corrosion resistance
  - high operating temperatures
  - relatively expensive (Co)
  - small part of REE magnet market (2-5%): niche applications, hightech
- neodymium-iron-boron alloy: $Nd_2Fe_{14}B$
  - maximum energy product $(BH)_{max}$:512 kJ/m^3
  - poor corrosion resistance (surface plating required)
  - lower operating temperatures (Dy addition)

Evolution of permanent magnets



Source: http://www.magnetnrg.com

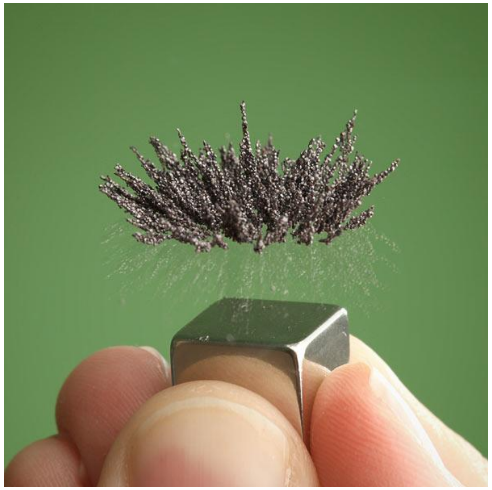
Dysprosium in NdFeB magnets



- Dysprosium is required to allow NdFeB magnets to be used at elevated temperatures (>80 ºC), especially in the presence of demagnetizing stress such as in motors and generators.
- Hcj is a measure of a magnet's resistance to demagnetization. Br is a measure of a magnet's field strength.

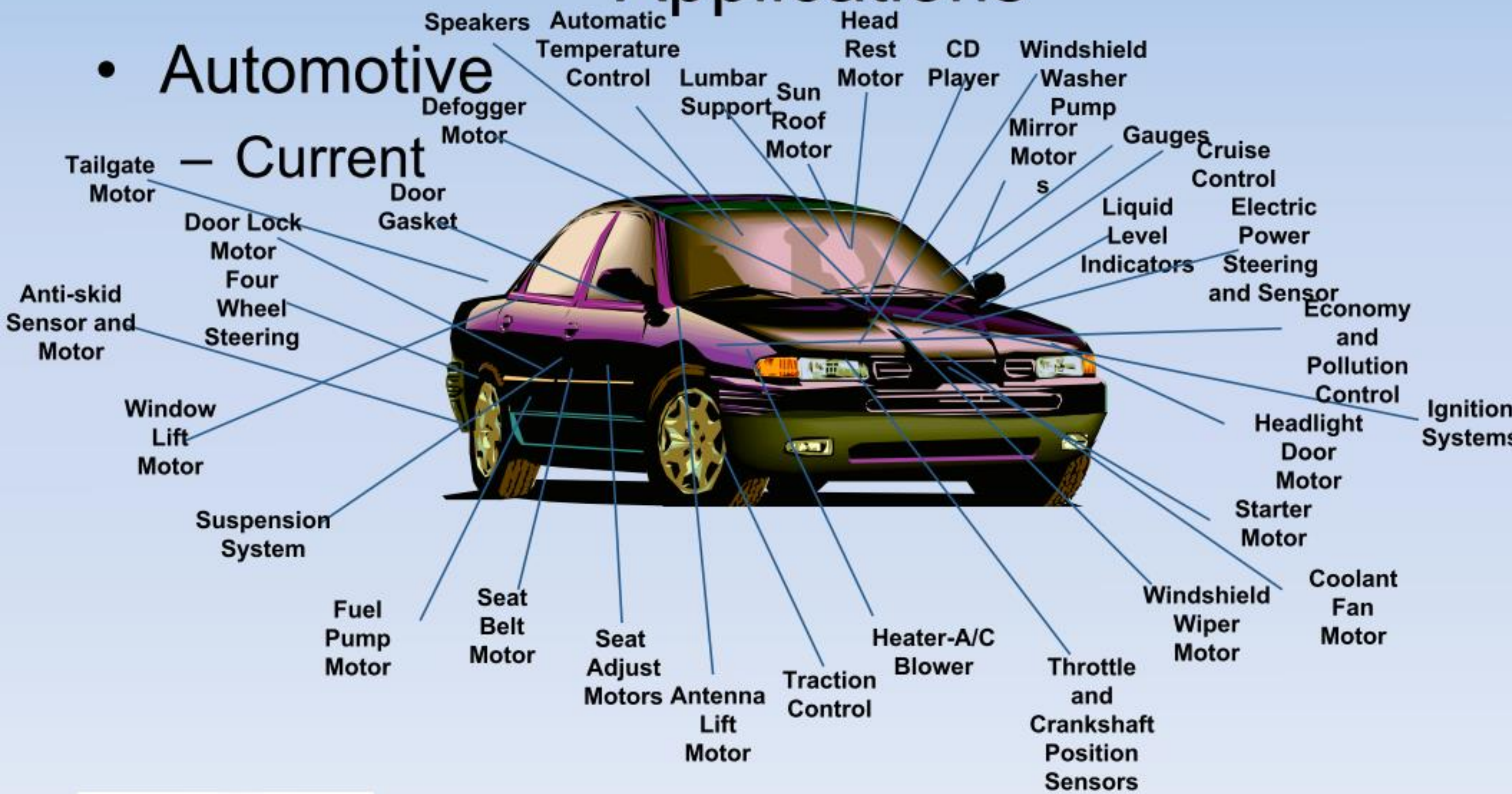
Source: Arnold Magnetics

Strong NdFeB magnets



Rare Earth Magnets
Applications

- Automotive
  - Current



Source: Magnequench

Spontaneous Materials

Electric and hybrid electric cars

- Hybrid and full electric cars are becoming increasingly more common in the US and Europe
- High dysprosium (10-12 wt%) is required due primarily to the higher temperature of the application
- Each electric car requires on average 1.25 kg of NdFeB magnets (not in Tesla)

Source: www.arnoldclark.com

Electric bikes

- Electric bikes are a fast-fast growing market, not only in Asia but also in Europe
- Small-sized performant magnets are essential
- 300-600 g of NdFeB magnets per e-bike (intermediate Dy)
- Although the amount of magnet material per unit is small, the quantities are large (> 10,000 tonnes/year)

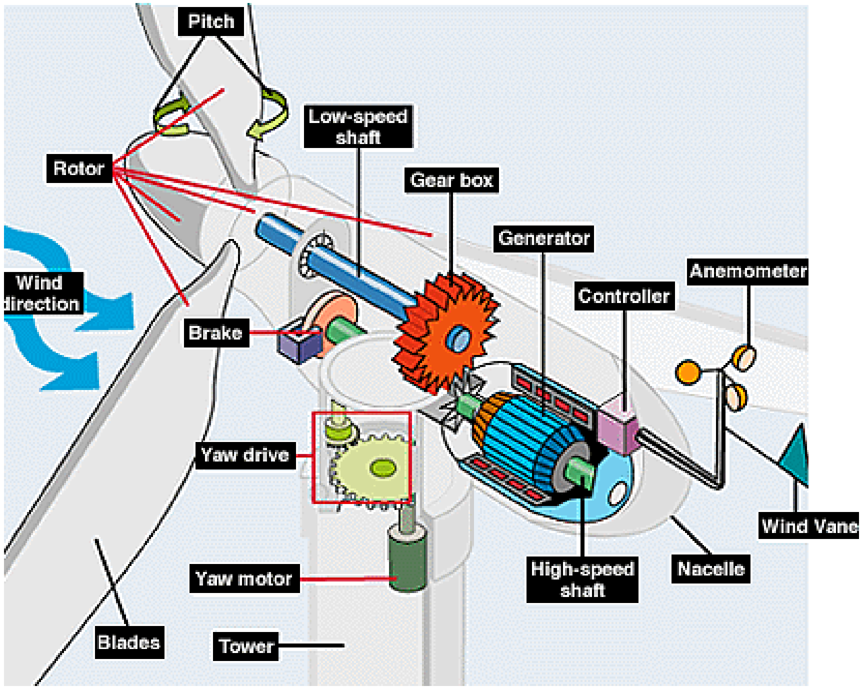
Source: www.fietsenpagina.nl

Wind power

Source: www.telegraph.co.uk

Wind turbines: induction generator

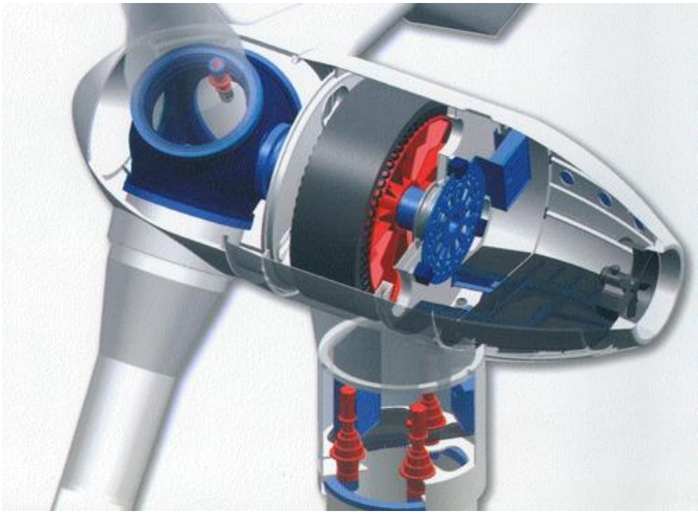
- Older types of wind turbines use **induction generators**
  - Induction generators must spin fast (> 1800 rpm)
  - Turbine rotor turn at 10-12 rpm, so that a 170:1 **gearbox** is required to increase the shaft rotational speed
  - Gearboxes are expensive, heavy, noisy, and require frequent maintenance



Source: http://www.daviddarling.info/images/wind_turbine.gif

Wind turbines: direct drive

- New generations of wind turbines use permanent magnets (**direct drive wind turbines**); no gearbox
- Low maintenance: ideal for off-shore applications or for use at difficult accessible locations
- 250 to 600 kg of NdFeB magnets per MW of output
- Replacement of 1 GW coal-fired power plant requires 400 tonnes of NdFeB magnets
- Wind power boosts NdFeB magnet usage



Source: MTorres

Nickel metal hydride batteries

Positive electrode:

$Ni(OH)_2 + OH^- \leftrightarrows Ni(OOH) + H_2O + e^-$

$\rightarrow$: charging

$\leftarrow$: discharging

Negative electrode:

$M + xH_2O + e^- \leftrightarrows MH_x + xOH^-$

$\rightarrow$: charging

$\leftarrow$: discharging

M = $LaNi_5$ or similar alloy

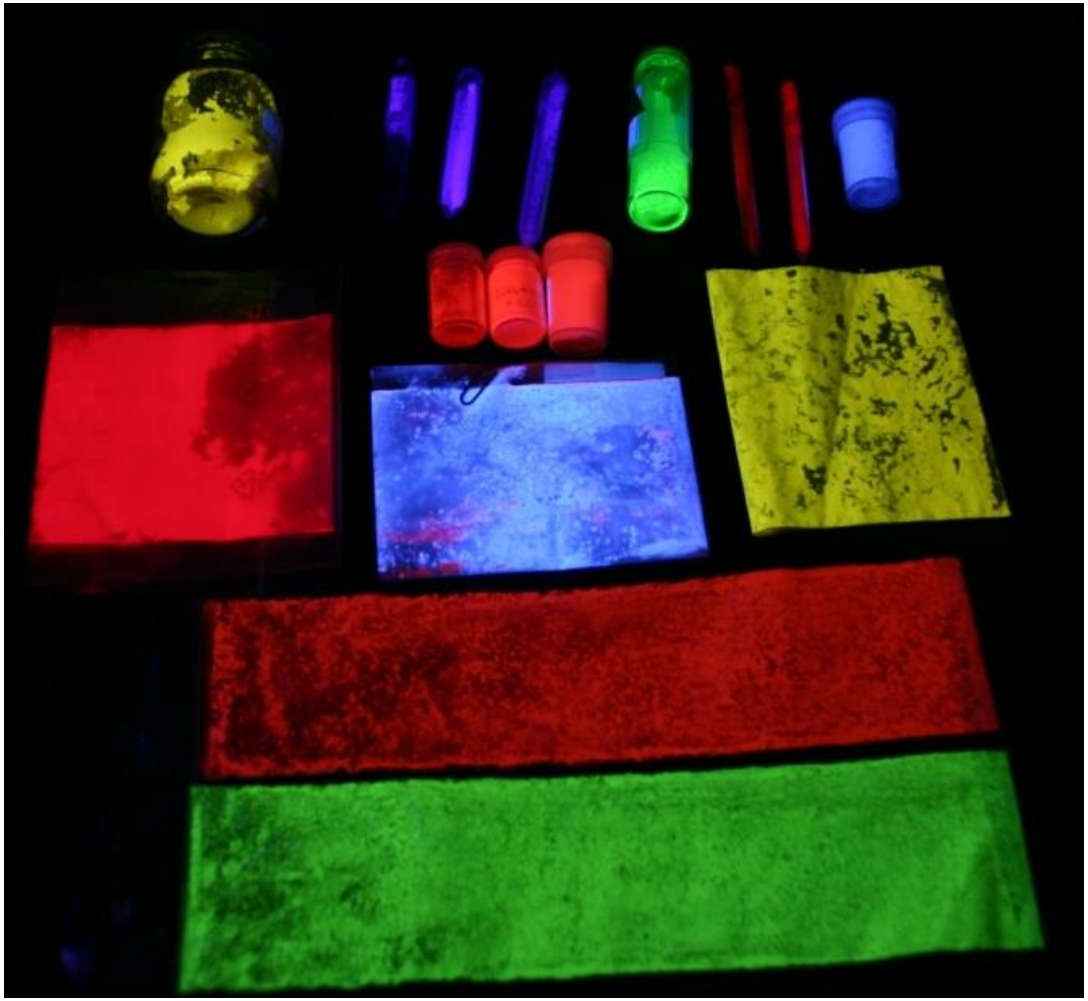
Overall reaction:

$M + xNi(OH)_2 \leftrightarrows xNiOOH + MH_x$

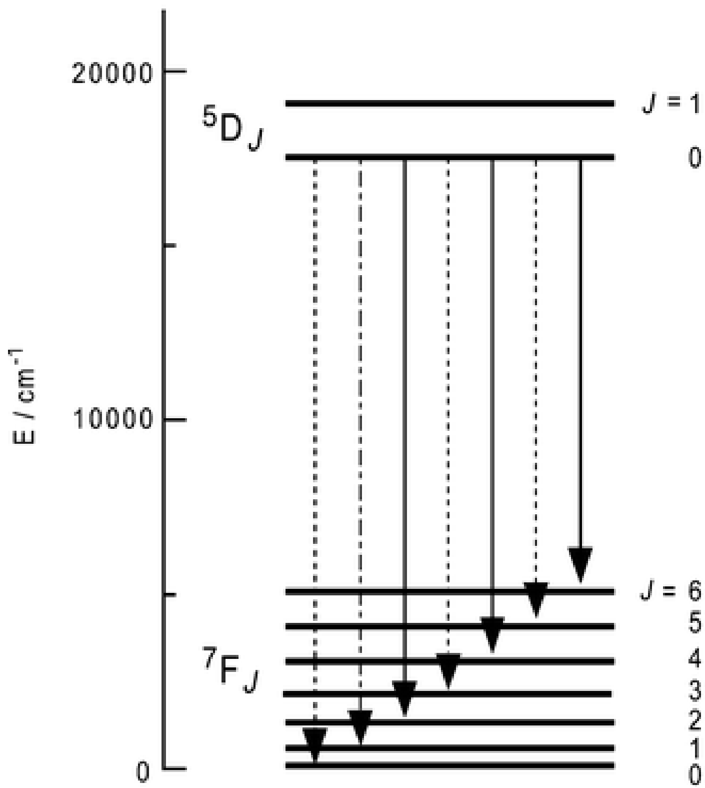
$\rightarrow$: charging

$\leftarrow$: discharging

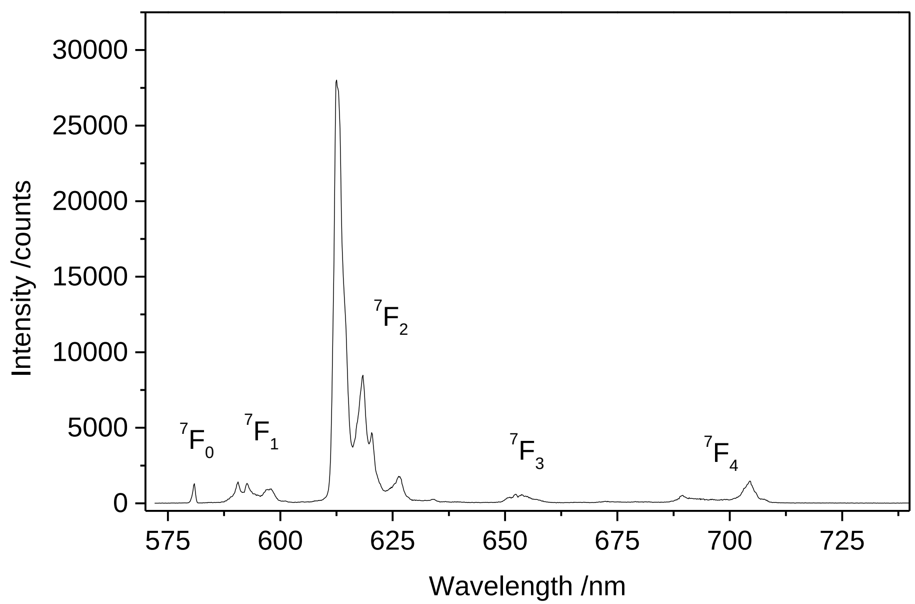
Luminescent materials

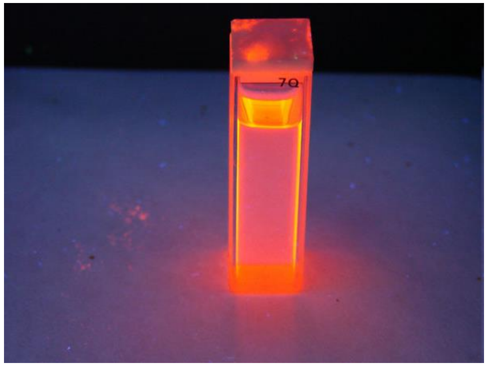


Luminescent materials

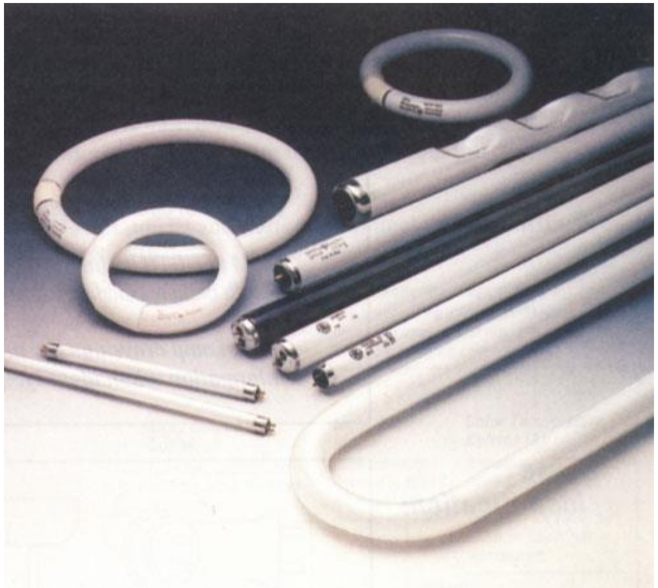


Lowest energy levels of Eu^{3+}

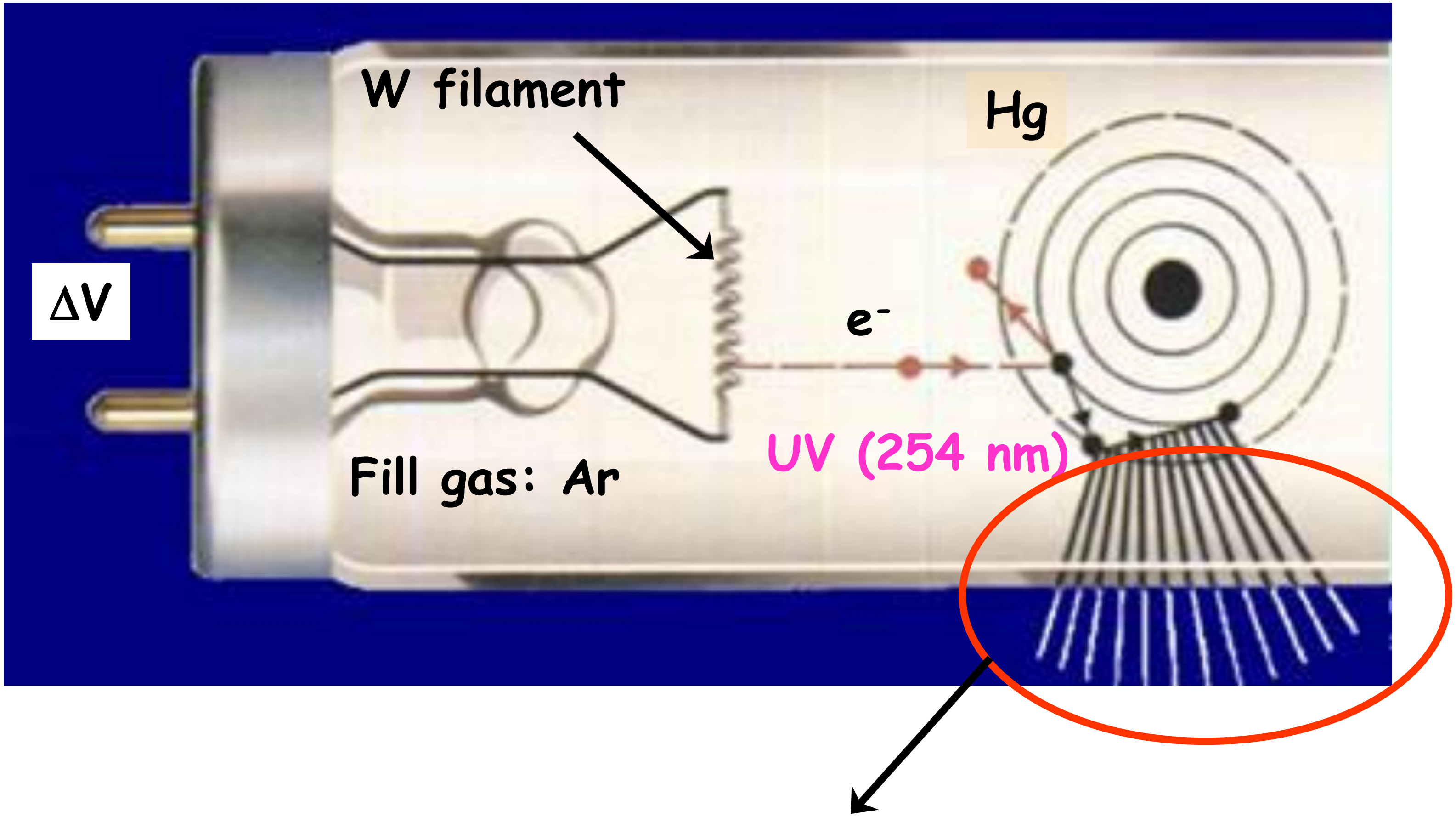




Fluorescent lamps

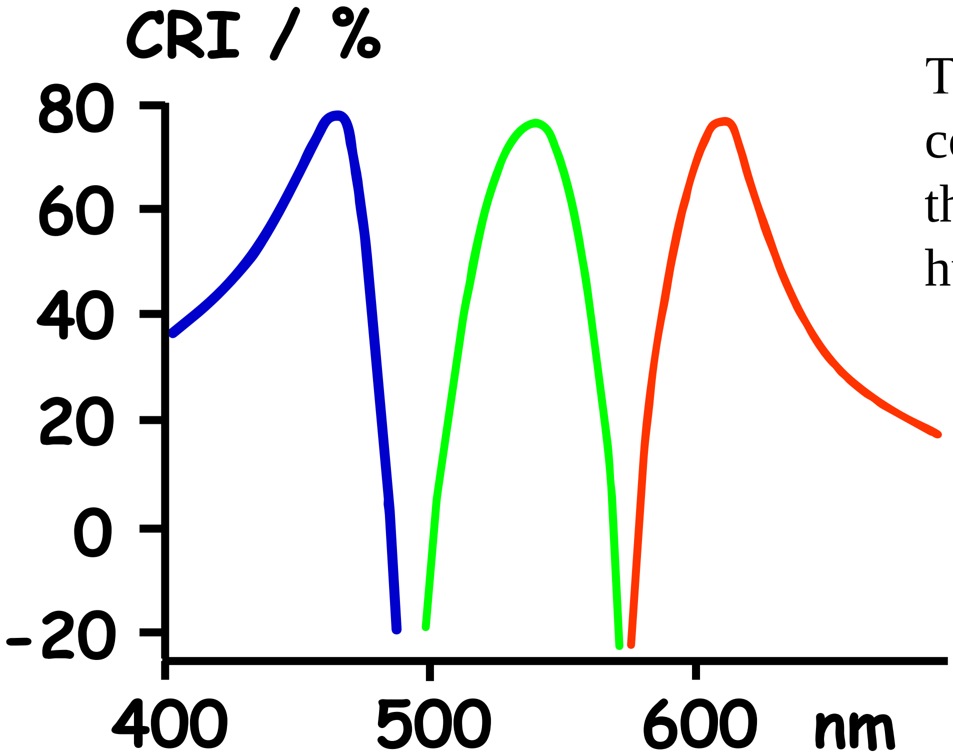


Fluorescent lamps

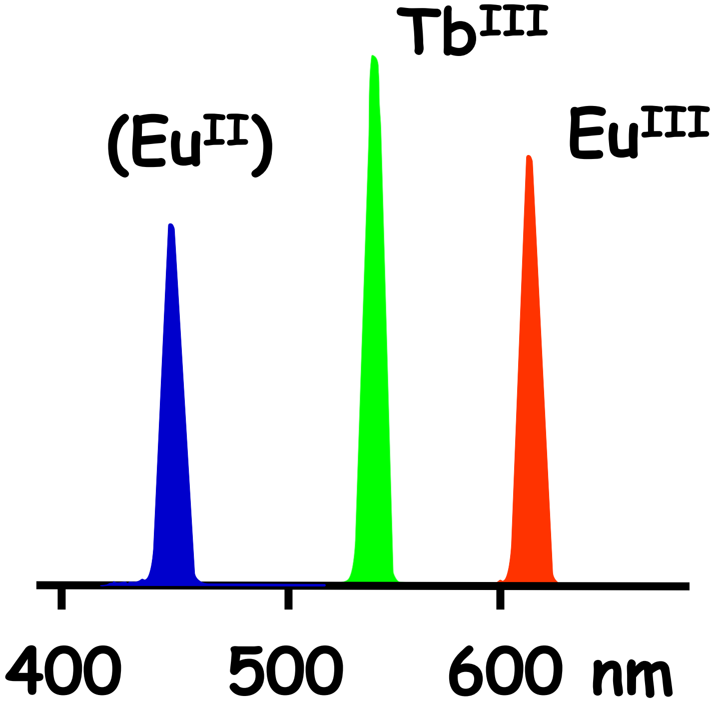


UV photons excite phosphor coating. White light is emitted.

Producing white light: trichromatic stimuli



There are three “prime” colors corresponding to the three spectral responses of human vision



Color rendering index obtained by mixing the three prime colors

Ref. : J.C.G Bünzli, Lanthanide course

Lamp phosphors

Year	Phosphors		
1960	$Ca_5(PO_4)_3Cl:Sb^{3+},Mn^{2+}$ (white)		
1974	$BaMg_2Al_{16}O_{27}:Eu^{2+}$	$CeMgAl_{10}O_{19}:Tb^{3+}$	$Y_2O_3:Eu^{3+}$
1990	$BaMgAl_{10}O_{17}:Eu^{2+}$ $(Sr,Ca)_5(PO_4)_3Cl:Eu^{2+}$	$(La,Ce)PO_4:Tb^{3+}$ $CeMgAl_{10}O_{19}:Tb^{3+}$ $(Gd,Ce)MgB_5O_{10}:Tb^{3+}$	$Y_2O_3:Eu^{3+}$
2005	$BaMgAl_{10}O_{17}:Eu^{2+}$	$(La,Ce)PO_4:Tb^{3+}$	$Y_2O_3:Eu^{3+}$

LEDs

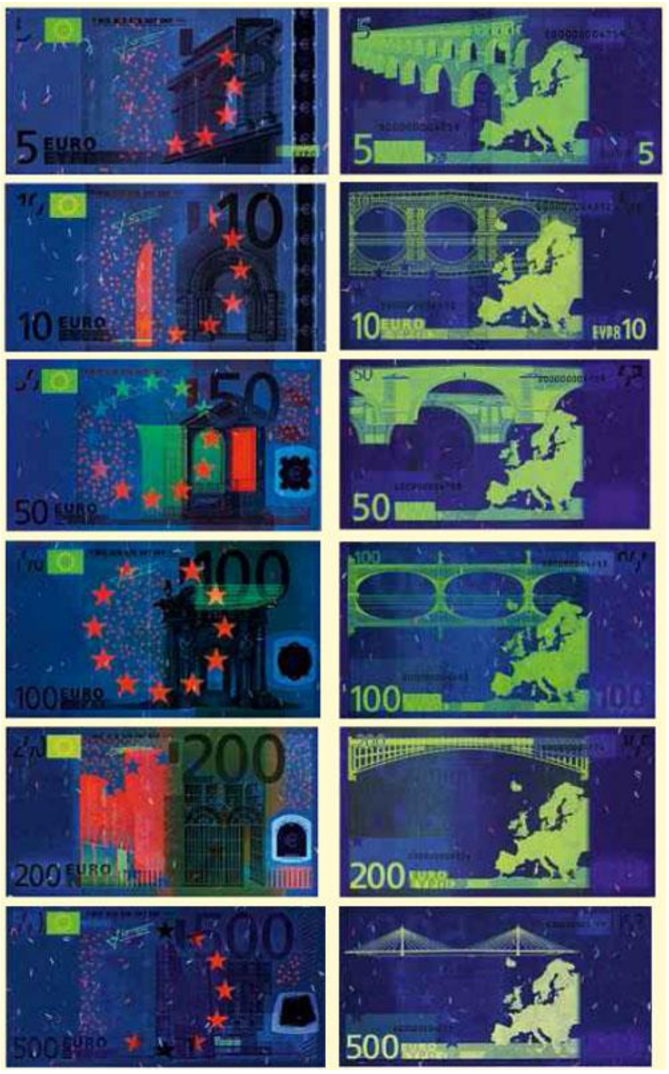
- Blue LED + yellow phosphor = white light

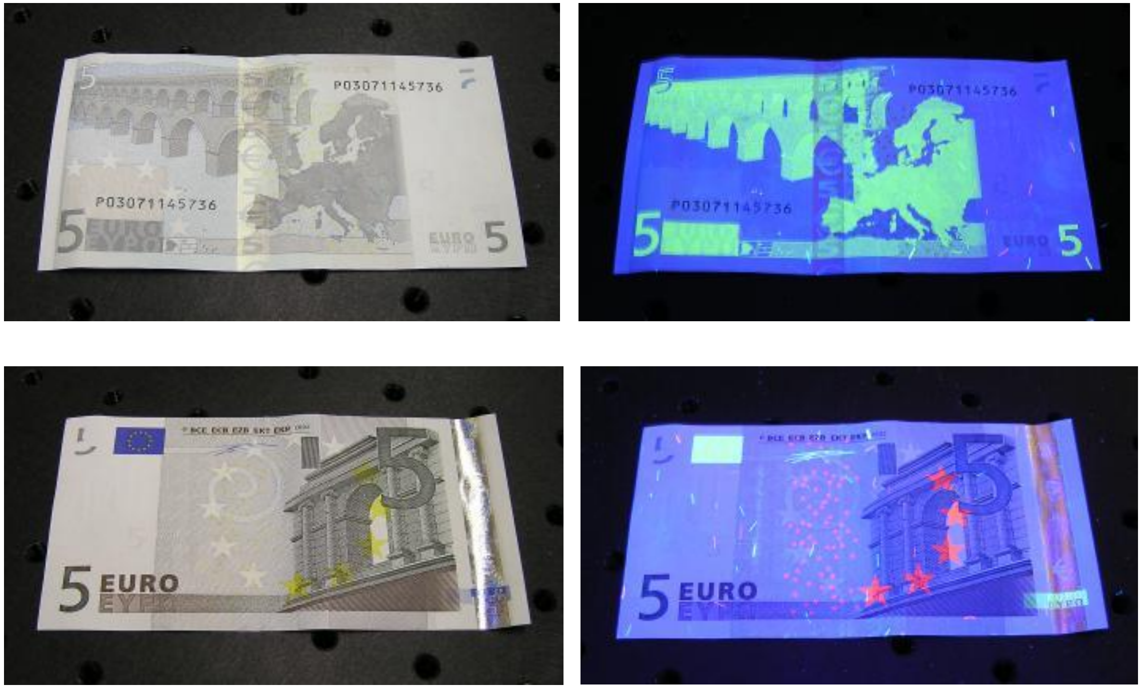
  blue LED: GaN or GaInN
  yellow phosphor: Ce-doped $Y_3Al_5O_{12}$ (Ce:YAG)

Security inks

Euro bills

Security inks





Under UV irradiation
Eu^{3+}: red luminescence
Eu^{2+}: green-yellow luminescence

X-ray phosphors

- Designed to respond to X-rays re-emitting the energy as visible light
- Incorporated into a variety of X-ray imaging devices

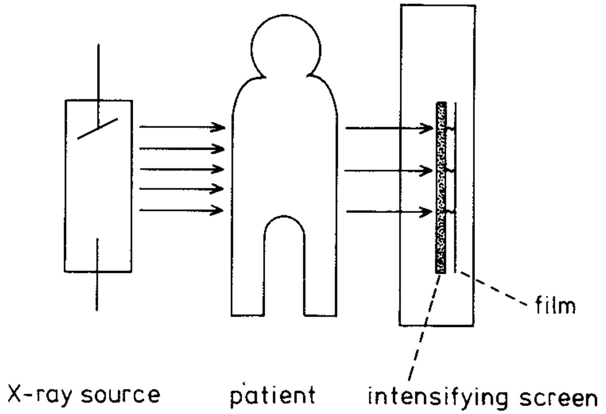
  Medical and security applications
- Most used phosphors:

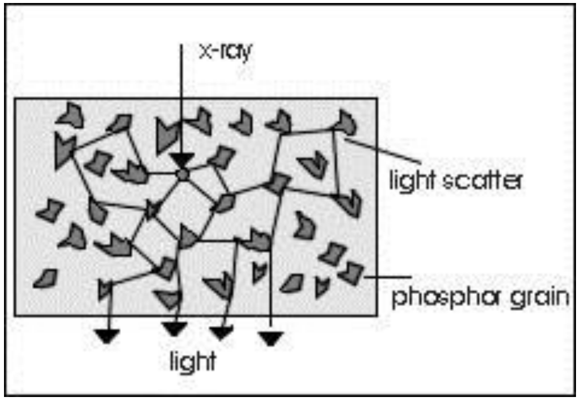
  $Gd_2O_2S:Tb^{3+}$ green

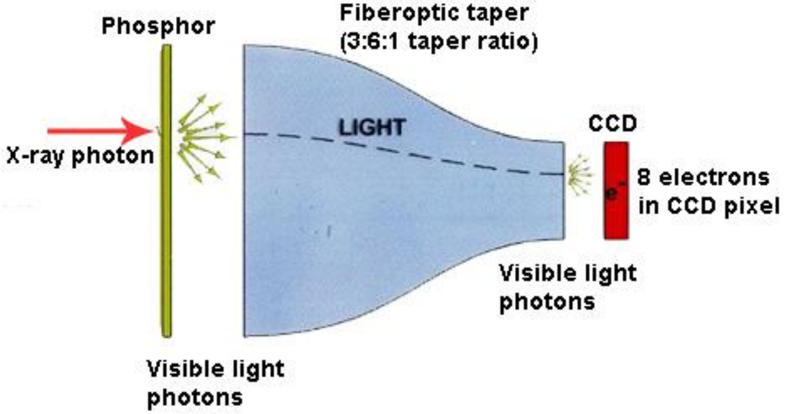
  $La_2O_2S:Tb^{3+}$ green

  $Gd_2O_2S:Pr^{3+}$ green

  $Gd_2O_2S:Eu^{3+}$ red





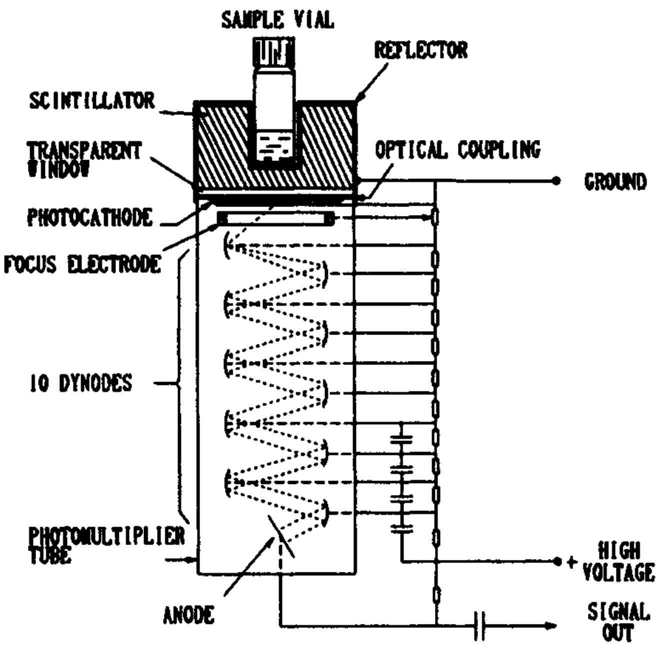


Scintillation phosphors

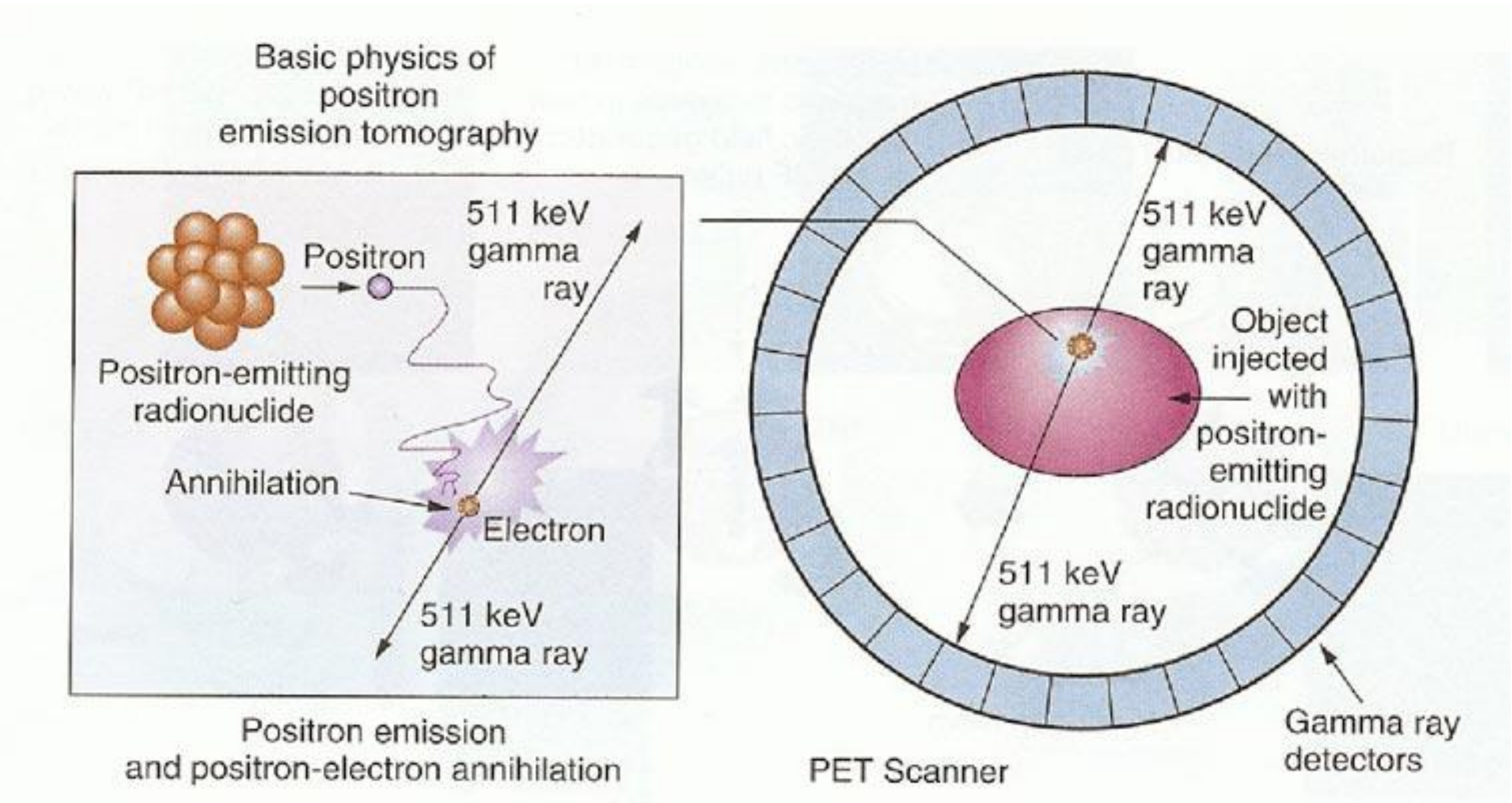
- Used in the detection of alpha, beta and gamma radiation
- Need to have fast decay times (40-65 ns) and high densities
- Most used phosphors:

$Lu_2SiO_5:Ce^{3+}$	peak: 400 nm
$YAlO_3:Ce^{3+}$	peak: 365 nm
$Y_3Al_5O_{12}:Ce^{3+}$	peak: 550 nm

- Use of $Lu_2SiO_5:Ce^{3+}$ in PET scanners is most important application of lutetium

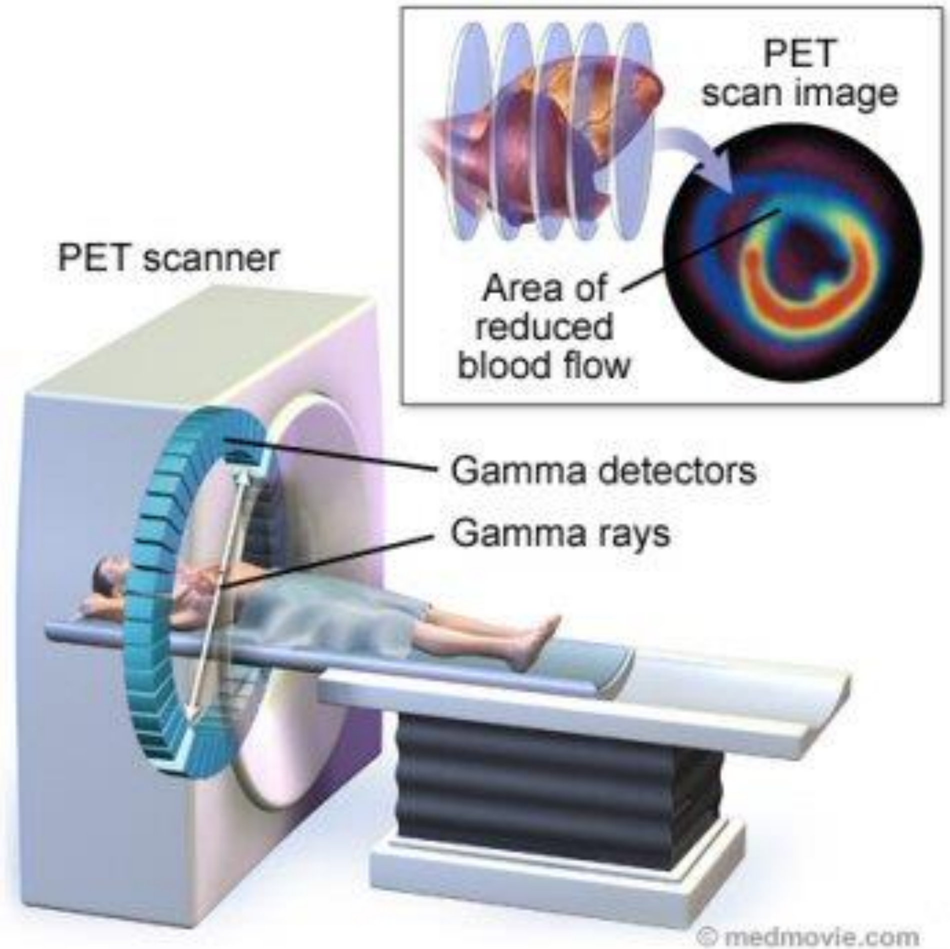


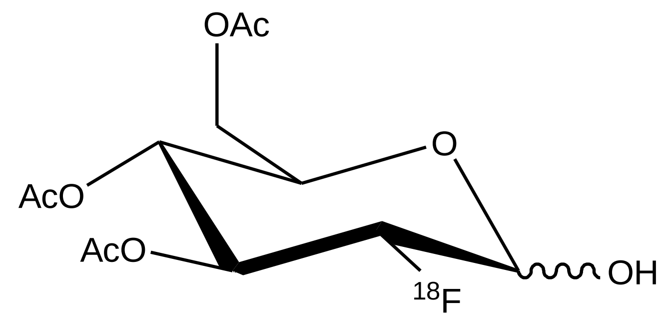
PET scanner



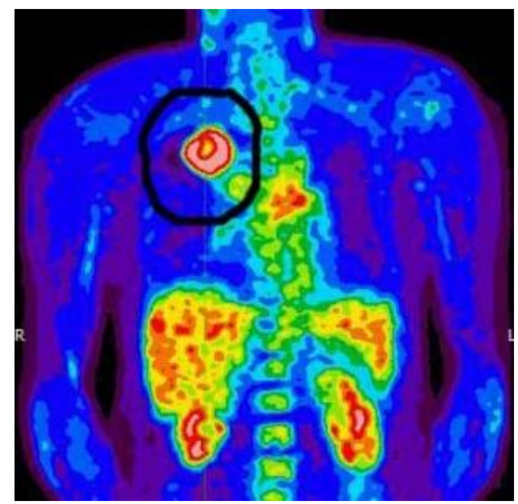
Source: http://www.cellsighttech.com

PET scanner



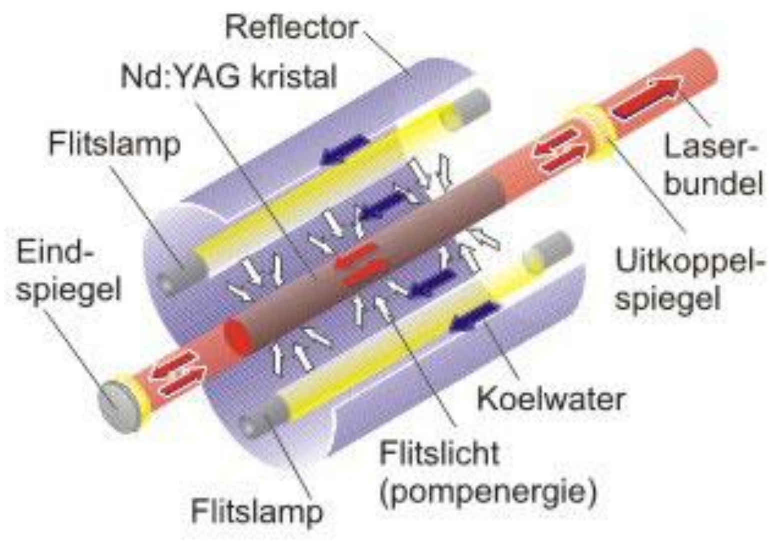


Positron emitter (^{18}F)

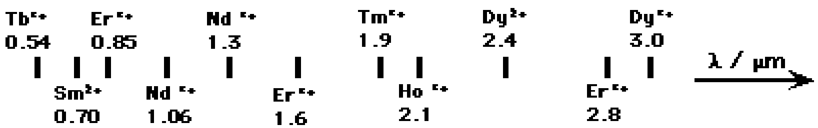


Detects increased metabolic activity

Laser crystals



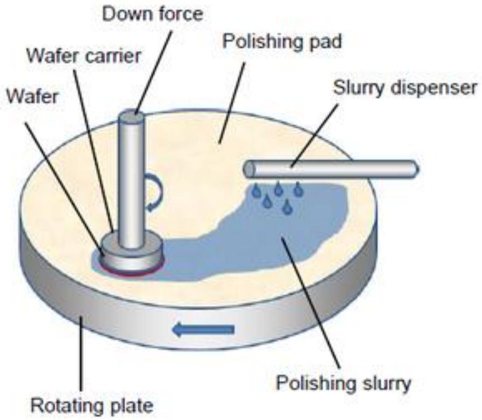
$YAG = Y_3Al_5O_{12}$

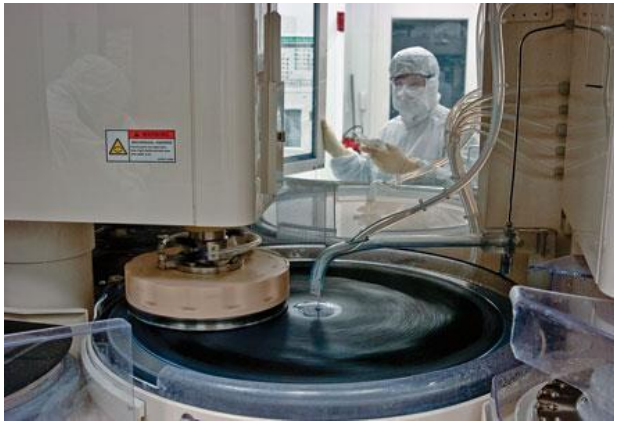


Spectral Range of Rare Earth Lasers

Glass polishing powder (CeO_2)

- **CeO_2** used from medium to high purity level
- Applied as powder in range 0.5 – 2.0 μm
- To achieve clean glass surfaces free from any scratches
- Applications: optical lenses, optical components, LCD parts, flat glass like TV screens and mirrors
- CMP (Chemical Mechanical Polishing) process: Polishing of Si-Wafers with **n-sized CeO_2 slurries** (< 100 nm)





Optical glass

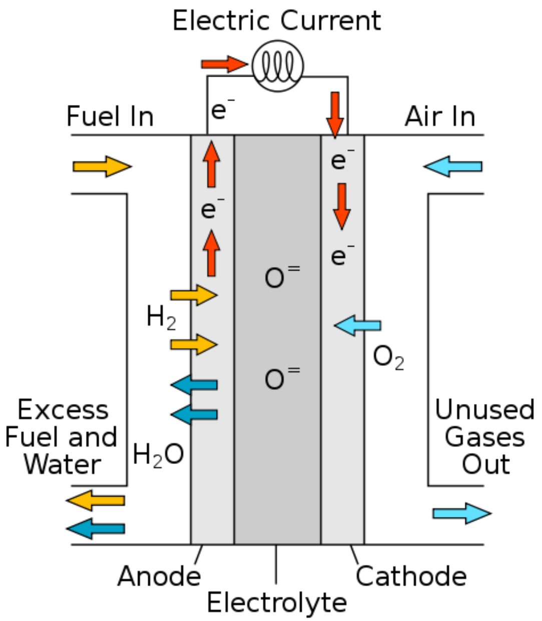
Optical glass for lenses contains up to 40% La_2O_3

(high refractive index and low dispersion)

Advanced ceramics

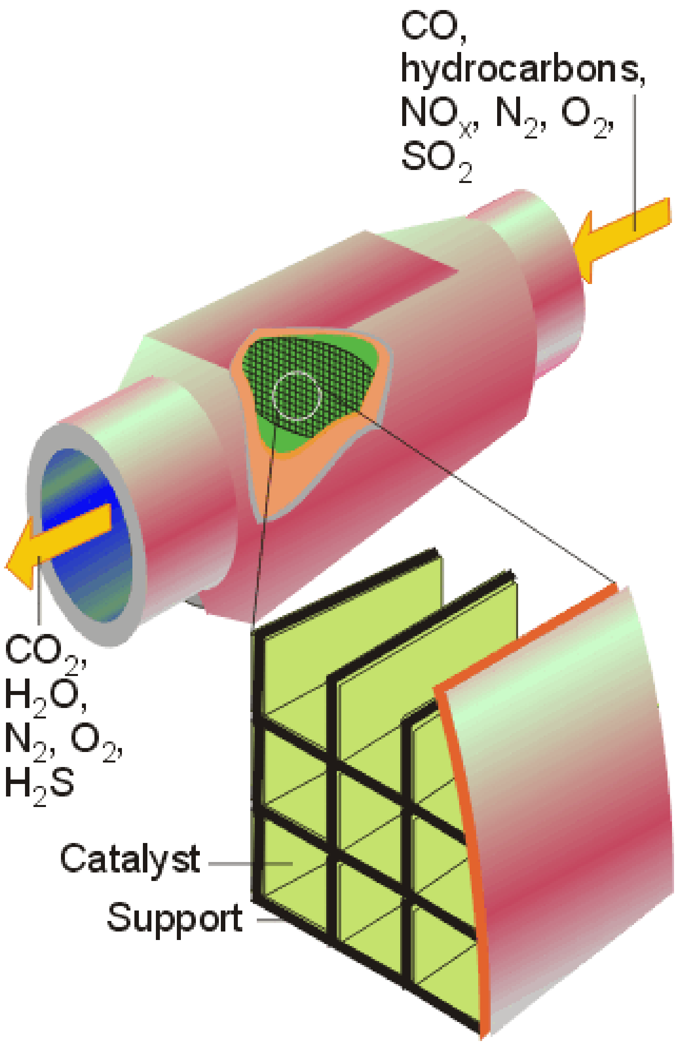
- Y_2O_3 is one of the most thermodynamically stable oxides
  Can be used up to 2200 °C (m.p.: 2425 °C)
- High purity Y_2O_3 used in casting of industrial and aerospace gasturbine blades, structural and automotive parts
- Compounds of Y, Yb Gd used in thermal spray applications in aerospace and industrial gas turbine applications (thermal barriers)
- Stabilization of ZrO_2 in cubic phase:
  yttria-stabilized zirconia (YSZ)
  oxide conductor

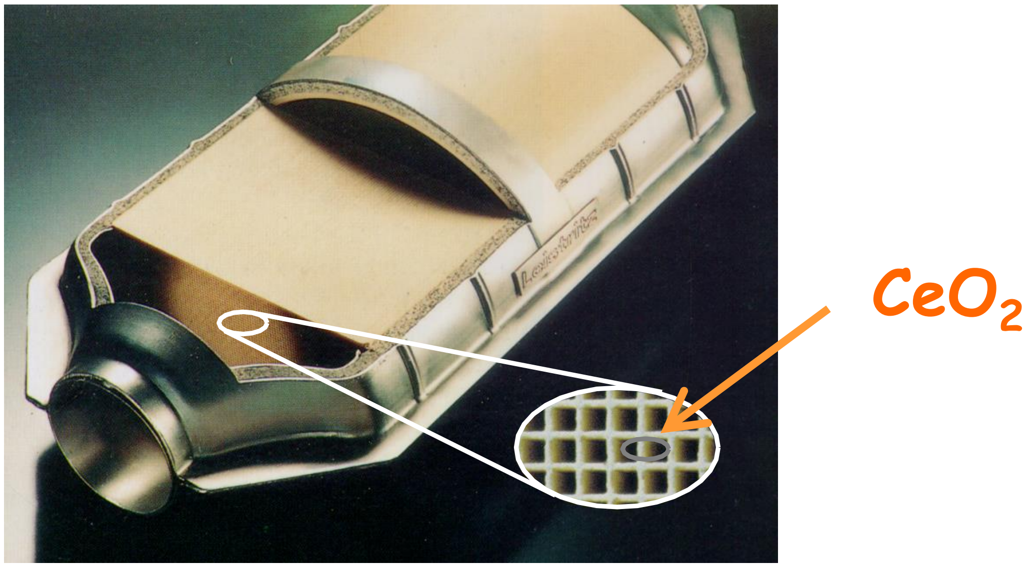
  solid oxide fuel cells (SOFCs)
  used to generate electricity from natural gas or from renewable fuels



Source: wikipedia

Automobile exhaust catalysts

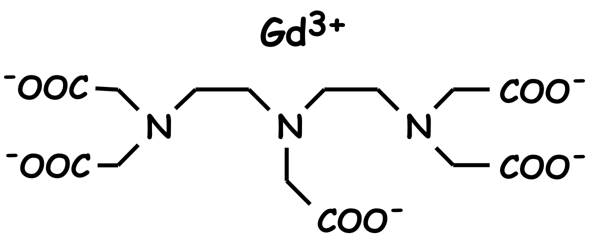




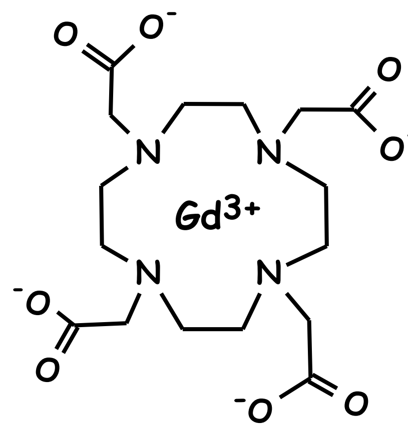
Fluid Cracking Catalyst (FCC)

- Catalytic cracking plays key role in crude oil refining
- FCC split oil into light oil fractions (gasoline and diesel)
- Additionally gases like H_2 and C1 – C4 hydrocarbons are formed
- FCC units utilize large amounts of catalyst (50,000 barrel feedstock/day utilize 200–500 t of catalyst)
- REE chloride solutions (mainly $LaCl_3$ are used in the process, impregnated onto aluminosilicate (zeolite) carrier materials with additional additives (e.g. Pt, Sb,…)

MRI contrast agents



$[Gd(dtpa)]^{2-}$ Magnevist®



$[Gd(dota)]^{-}$

Dotarem®

Military applications

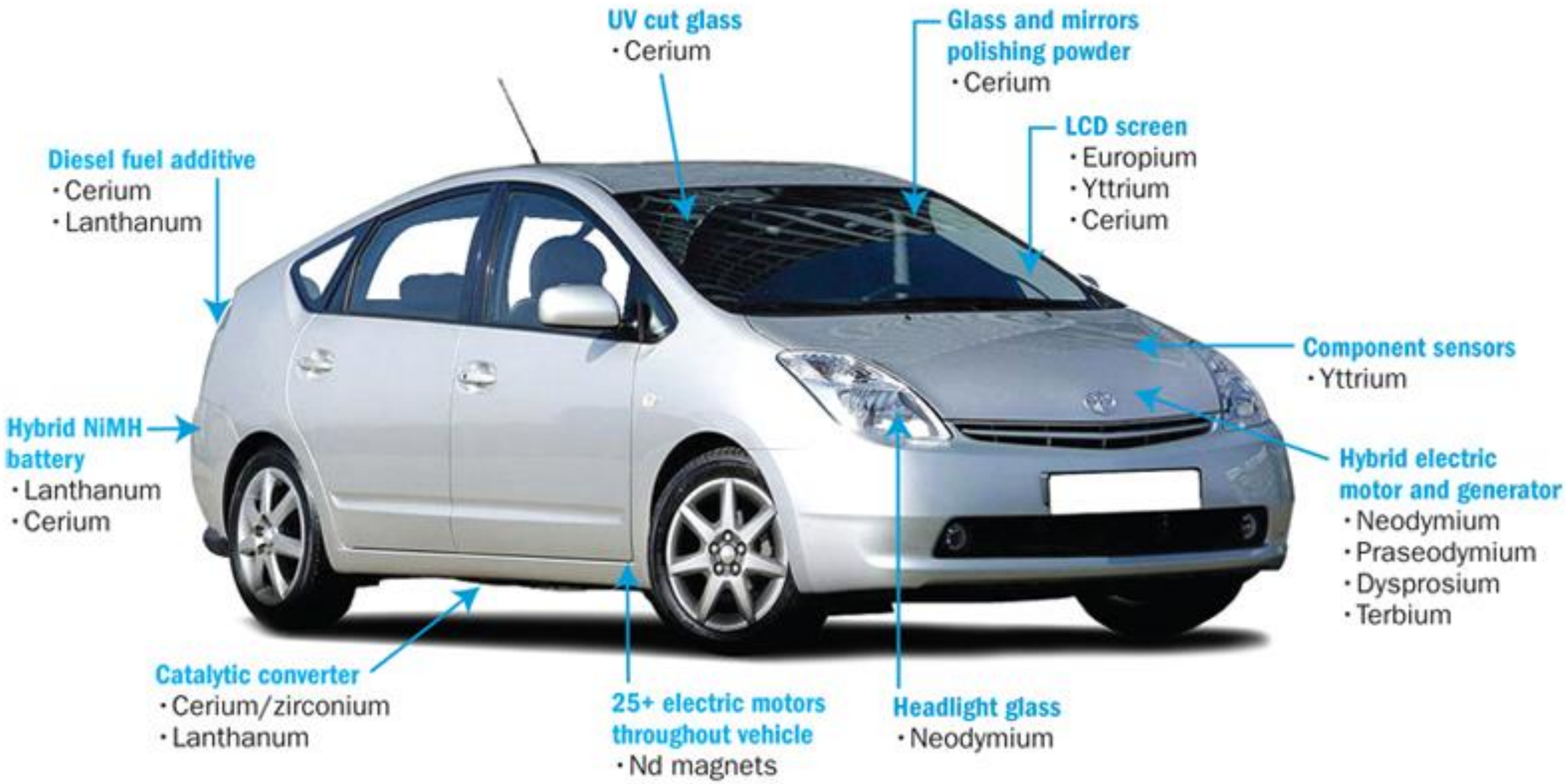
F-16 Avionics with REE phosphors

BGM-109 Tomahawk Cruise missile

Nd:YAG designator-rangefinder laser

F-15 with yttria-stabilized zirconia

Rare earths for the car industry



Source: Molycorp

Useful links

rare3

Research Platform for the
Advanced Recycling and Reuse of Rare Earths

KU LEUVEN

http://www.kuleuven.rare3.eu/links/