

Elementi del blocco f

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf

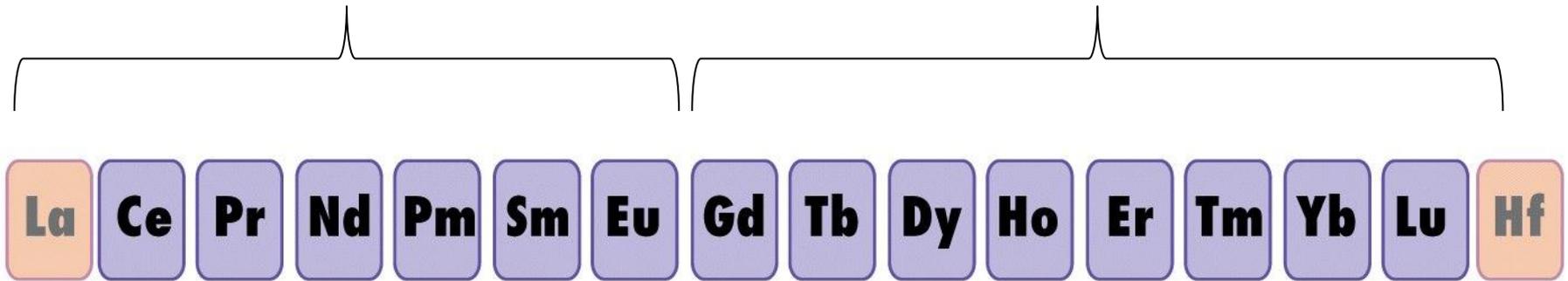
Lantanide generico = $Ln, 4f^n 5d^1 6s^2$

Attinide generico = $An, 5f^n 6d^1 7s^2$

Lantanidi

light

heavy



Terre Rare (*rare earth metals*, REM o RE) = 15
elementi La – Lu ($Z = 57-71$) + Sc ($Z = 21$) + Y ($Z = 39$)

<https://www.youtube.com/watch?v=ri7fFbrPPjw>

In the last 5 years, the average American (and likely European) has relied on **80** elements for quality of life.

General Electric uses **72** of the first **82** elements in its product line.



Pharmaceuticals

Pd, Rh, Os, Ir



Household Items

Rh, Pt



Refining

La, Pt



Hybrid/Electric Cars

Nd, Tb, Dy, Pr



Alternative Energy

Ru, Nd, Tb, Dy, Pr

...ogni auto Toyota Prius contiene 4 kg di neodimio (Nd) in supermagneti di una lega neodimio-ferro-boro ($Nd_2Fe_{14}B$). Ogni turbina eolica contiene 400 kg di neodimio.

Il 97% della richiesta mondiale di neodimio viene prodotto in una miniera a Bayan Obo, nella Cina interna al confine con la Mongolia...

<https://www.youtube.com/watch?v=lxwF93wnRQo>

Il Giappone ora è pronto a sfruttare il giacimento di "terre rare". E la Borsa vola

La scoperta nel 2012 vicino l'isola di Minami Torishima. Ma il deposito naturale finora era considerato troppo profondo per essere sfruttato. Ora la tecnica di estrazione è stata perfezionata. I materiali utili a costruire magneti per veicolo ibridi e laser



11 Aprile 2018



Minami Torishima

ROMA - Il Giappone avrebbe trovato il modo per portare in superficie, poco alla volta, un tesoro di oltre 16 milioni di tonnellate di terre rare. Sono materiali utili a costruire - ad esempio - magneti per veicoli ibridi e laser per diversi secoli. Il Giappone, dunque, sarebbe in grado di strappare alla Cina l'attuale dominio sul settore.

Le analisi fatte hanno rivelato che c'è abbastanza materia per coprire 730 anni di domanda

globale di disprosio, un elemento usato nei magneti per veicoli ibridi, e l'equivalente di 780 anni di applicazioni per l'ittrio, utilizzato nei laser. Inoltre, c'è anche un volume equivalente a 620 anni di fornitura di europio e terbio 420, utilizzati nei composti fluorescenti e nelle celle a idrogeno.

La Repubblica 22 maggio 2019

BUSINESS INSIDER
ITALIA

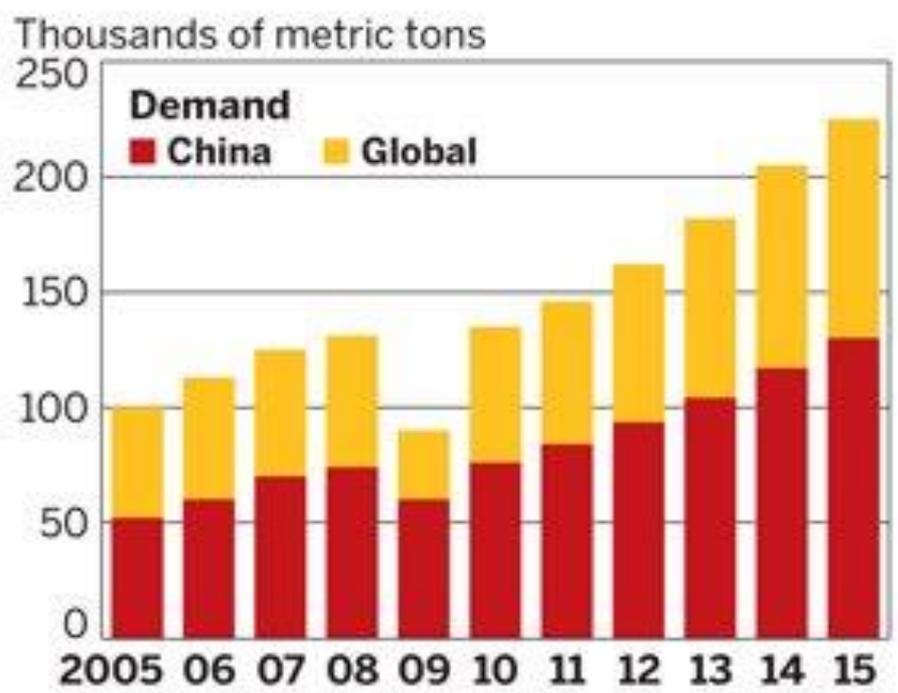
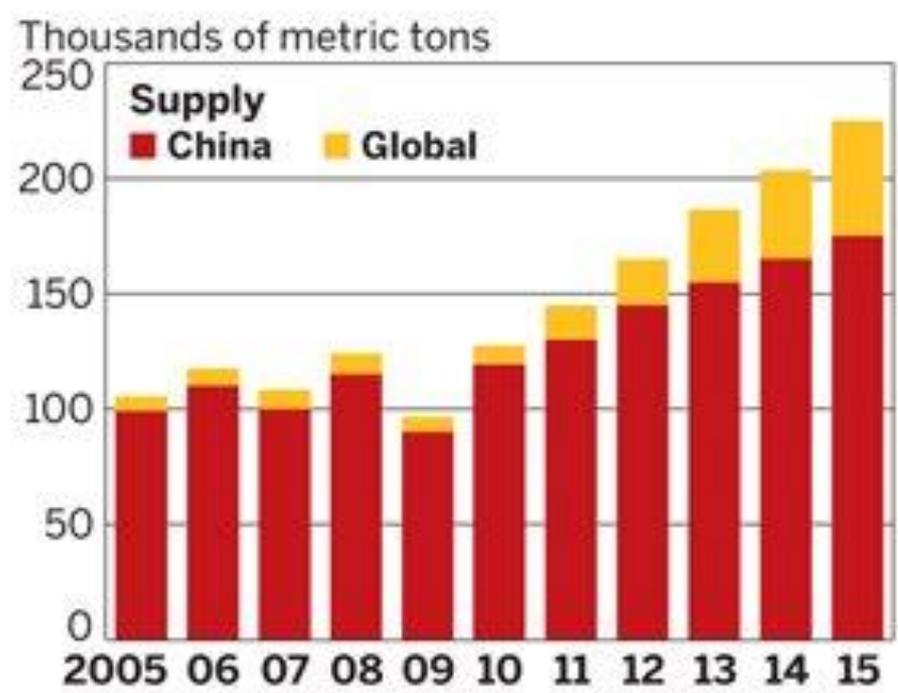
**Alla Cina sono bastate
due parole perché gli
Usa congelassero il
bando a Huawei: terre
rare**



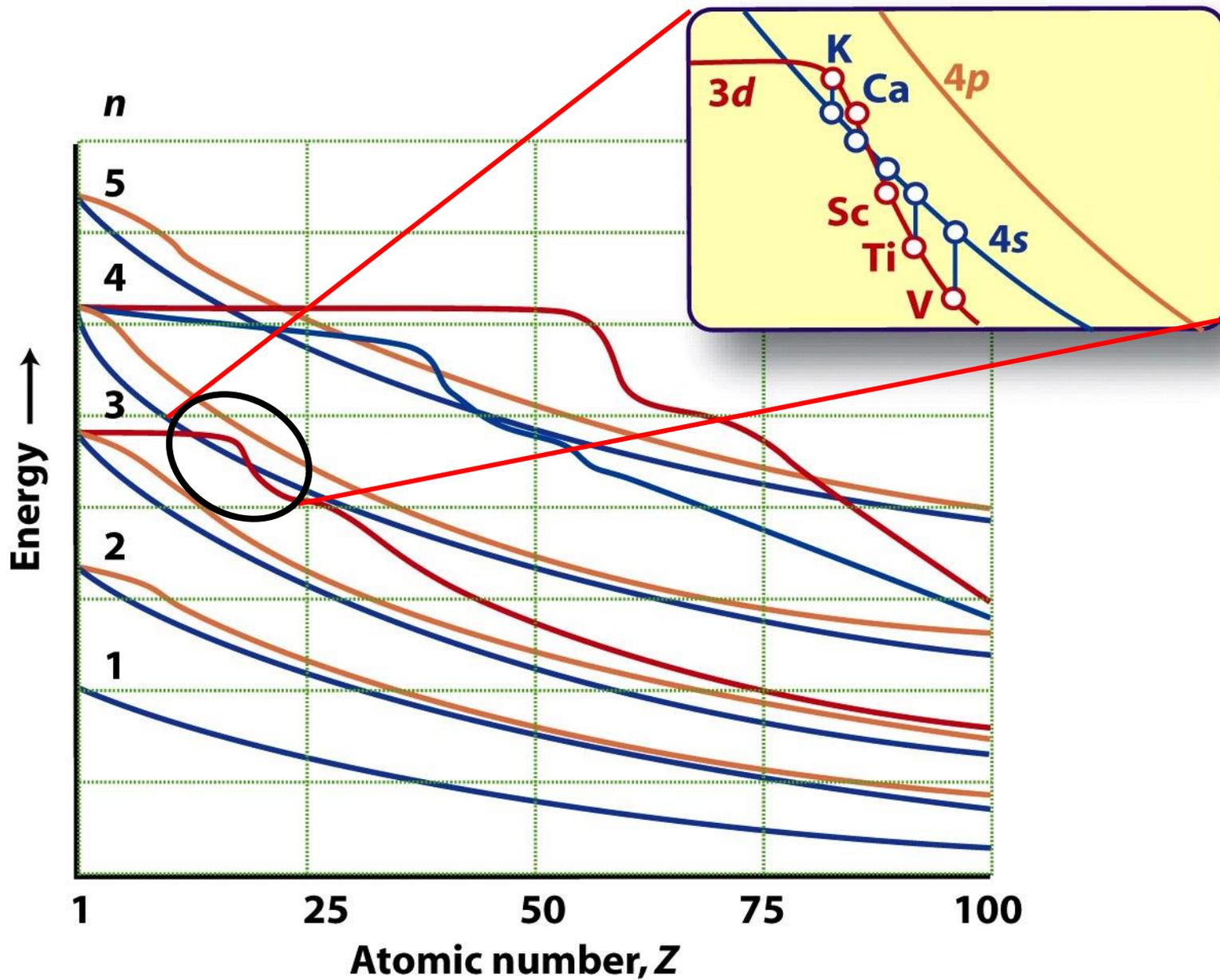
**Terre rare: ecco la
minaccia 'fine di mondo'
della Cina che ha portato
all'immediato
congelamento del bando
Usa a Huawei**

RARE-EARTH SUPPLY AND DEMAND

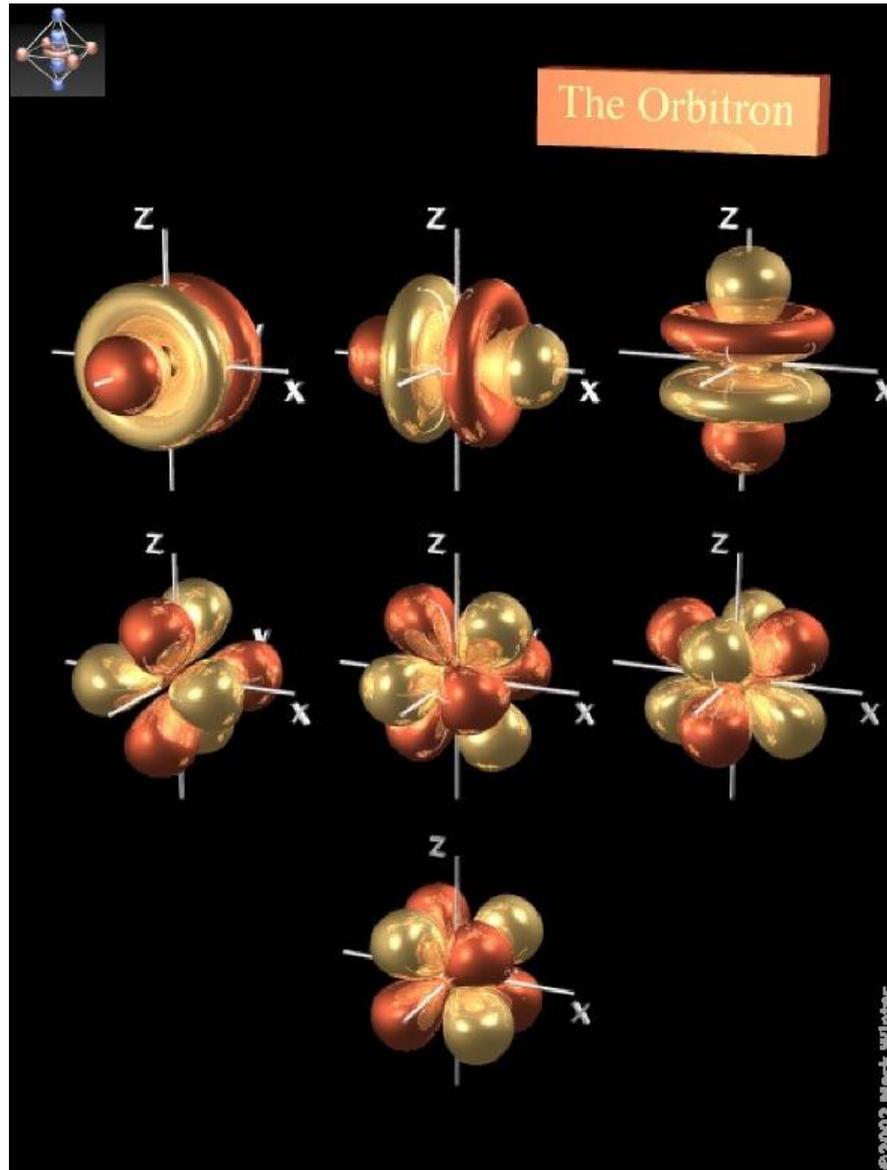
China's increasing demand for its own rare-earth materials is predicted to drive production in other countries



SOURCE: Dudley Kingsnorth/Industrial Minerals Co. of Australia



Il set cubico di orbitali f



3 piani nodali

$4f = 0$ nodi
radiali

$5f = 1$ nodo
radiale

$$f_{x^3} \quad f_{y^3} \quad f_{z^3}$$

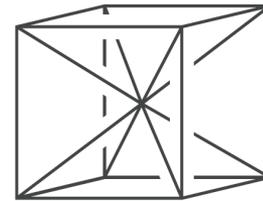
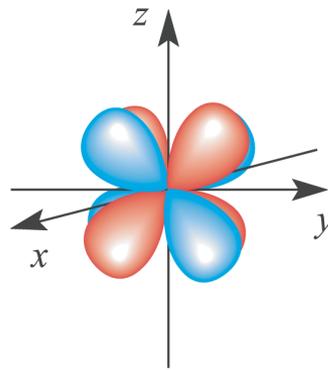
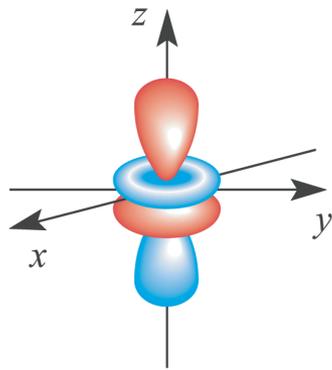
$$f_{x(z^2 - y^2)}$$

$$f_{z(x^2 - y^2)}$$

$$f_{y(z^2 - x^2)}$$

$$f_{xyz}$$

Il set cubico di orbitali f



Metal	$\Delta_a H^\circ(\text{Ln}) / \text{kJ mol}^{-1}$	$IE_1 + IE_2 + IE_3 / \text{kJ mol}^{-1}$	$\Delta_{\text{hyd}} H^\circ(\text{Ln}^{3+}, \text{g}) / \text{kJ mol}^{-1}$	$E^\circ_{\text{Ln}^{3+}/\text{Ln}} / \text{V}$	$E^\circ_{\text{Ln}^{2+}/\text{Ln}} / \text{V}$
La	431	3455	-3278	-2.38	
Ce	423	3530	-3326	-2.34	
Pr	356	3631	-3373	-2.35	-2.0
Nd	328	3698	-3403	-2.32	-2.1
Pm	348	3741	-3427	-2.30	-2.2
Sm	207	3873	-3449	-2.30	-2.68
Eu	177	4036	-3501	-1.99	-2.81
Gd	398	3750	-3517	-2.28	
Tb	389	3792	-3559	-2.28	
Dy	290	3899	-3567	-2.30	-2.2
Ho	301	3924	-3613	-2.33	-2.1
Er	317	3934	-3637	-2.33	-2.0
Tm	232	4045	-3664	-2.32	-2.4
Yb	152	4195	-3724	-2.19	-2.76
Lu	428	3886	-3722	-2.28	

† Values of $\Delta_{\text{hyd}} H^\circ(\text{M}^{3+}, \text{g})$ are taken from: L.R. Morss (1976) *Chem. Rev.*, vol. 76, p. 827.

Table 22.2 Names, symbols, and selected properties of the lanthanoids

Z	Name	Symbol	Configuration (M ³⁺)	E° /V	r(M ³⁺)/pm*	O.N.†
57	Lanthanum	La	[Xe]	-2.38	116	2(n), 3 , 4
58	Cerium	Ce	[Xe]f ¹	-2.34	114	2(n), 3 , 4
59	Praseodymium	Pr	[Xe]f ²	-2.35	113	2(n), 3 , 4
60	Neodymium	Nd	[Xe]f ³	-2.32	111	2(n), 3
61	Promethium	Pm	[Xe]f ⁴	-2.29	109	3
62	Samarium	Sm	[Xe]f ⁵	-2.30	108	2(n), 3
63	Europium	Eu	[Xe]f ⁶	-1.99	107	2, 3
64	Gadolinium	Gd	[Xe]f ⁷	-2.28	105	3
65	Terbium	Tb	[Xe]f ⁸	-2.31	104	3 , 4
66	Dysprosium	Dy	[Xe]f ⁹	-2.29	103	2(n), 3
67	Holmium	Ho	[Xe]f ¹⁰	-2.33	102	3
68	Erbium	Er	[Xe]f ¹¹	-2.32	100	3
69	Thulium	Tm	[Xe]f ¹²	-2.32	99	2(n), 3
70	Ytterbium	Yb	[Xe]f ¹³	-2.22	99	2, 3
71	Lutetium	Lu	[Xe]f ¹⁴	-2.30	98	3

Ce⁴⁺, f⁰Eu²⁺, f⁷* Ionic radii for coordination number 8 from R.D. Shannon, *Acta Cryst.*, 1976, **A32**, 751.

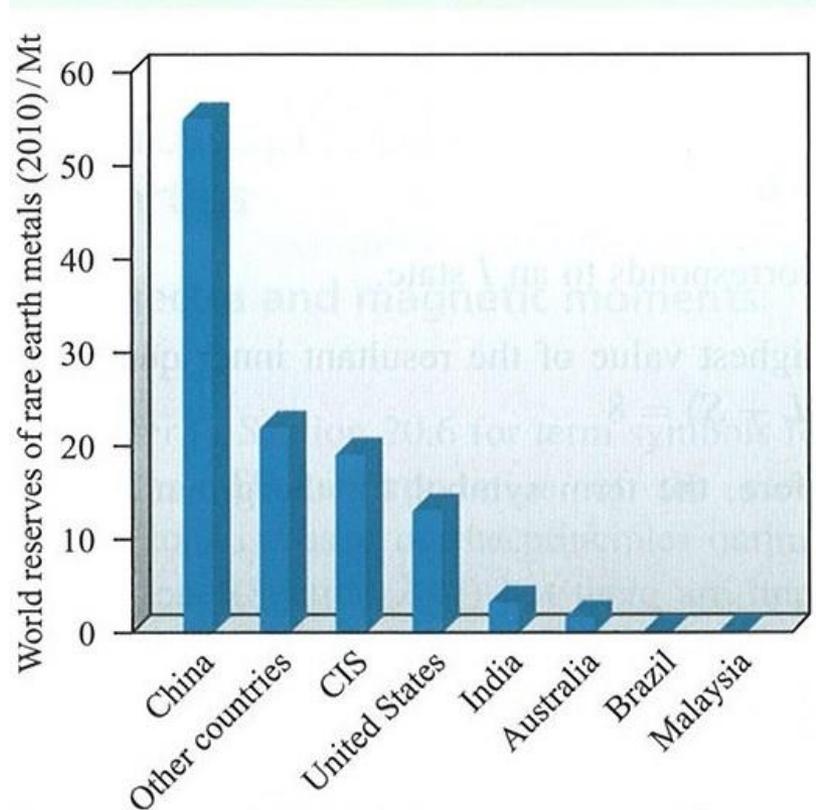
† Oxidation numbers in bold type indicate the most stable states; (n) indicates that the state is stable only in nonaqueous conditions.

Contrazione Lantanidica

Temperatura di transizione fra isolante e conduttore (T_{IM}) in Perovskiti dei lantanidi
 $LnNiO_3$

	$PrNiO_3$	$NdNiO_3$	$EuNiO_3$
$r(Ln^{3+})/pm$	113	111	107
T_{IM}/K	135	200	480

Risorse mondiali e produzione



Nel 2010: 114.000 tonnellate di REM

Ce, La, Nd, Y > 10.000 t/anno

Pr, Dy > 1000 t/anno

Gd, Sm, Eu, Tb > 100 t/anno

Miniera di Bayan Obo (4.1% di REO)

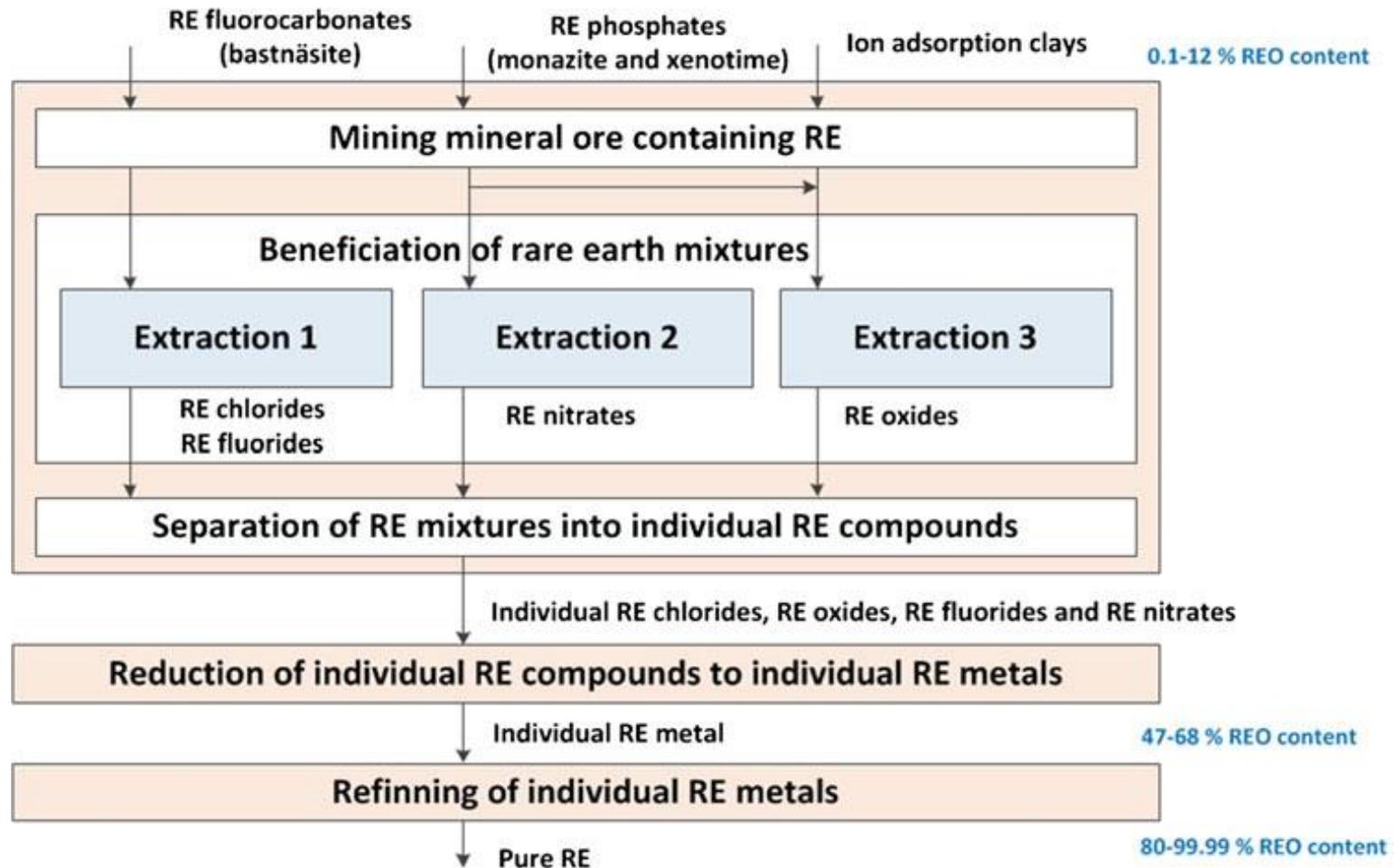


Miniera di Mountain Pass (7.7% di REO)

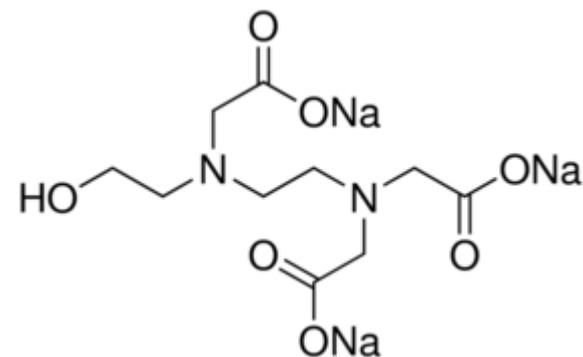
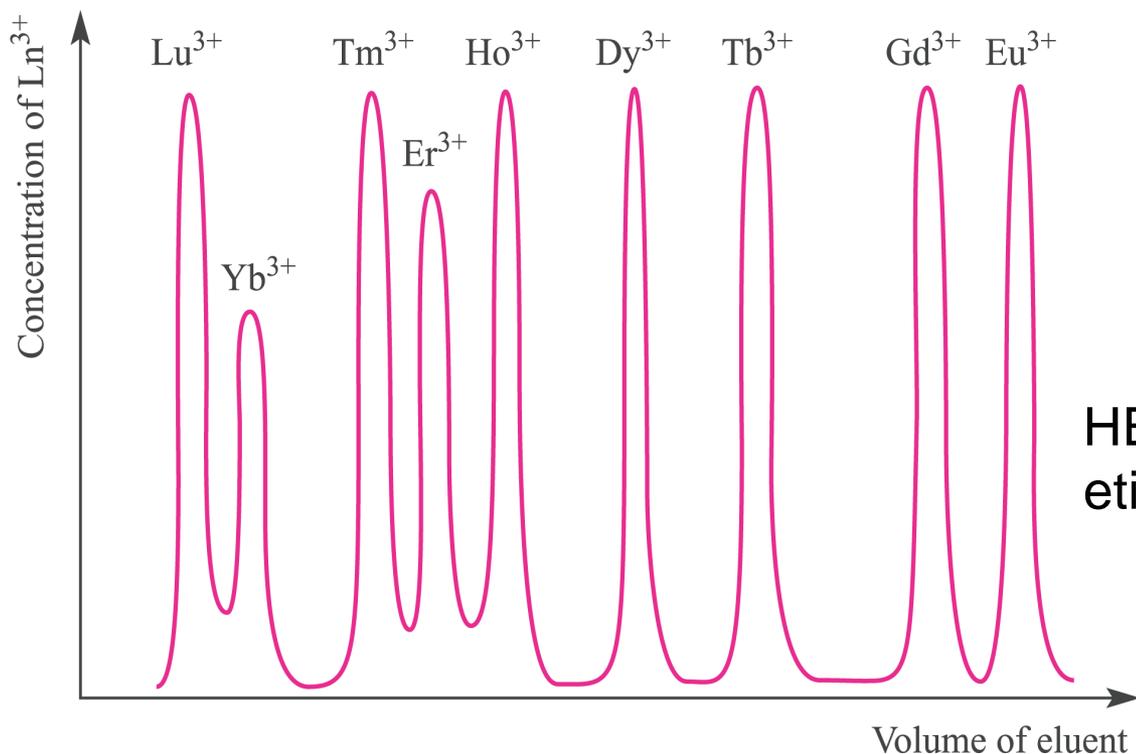




- **bastnäsite** $[\text{Ce,La,Nd}](\text{CO}_3)\text{F}$
 - **monazite** $[\text{Ce,La,Nd,Th}](\text{PO}_4)$
 - **xenotime** $[\text{Y, Ln,Th}](\text{PO}_4)$
- } Ln leggeri
Ln pesanti



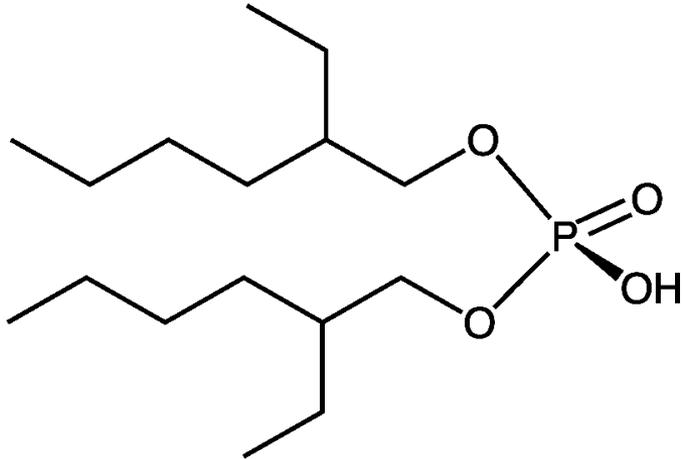
Sequenza di eluizione da una colonna a scambio cationico (fase stazionaria non selettiva, e.g. Dowex) dei complessi dei lantanidi più pesanti eluendo con una soluzione di EDTA⁴⁻



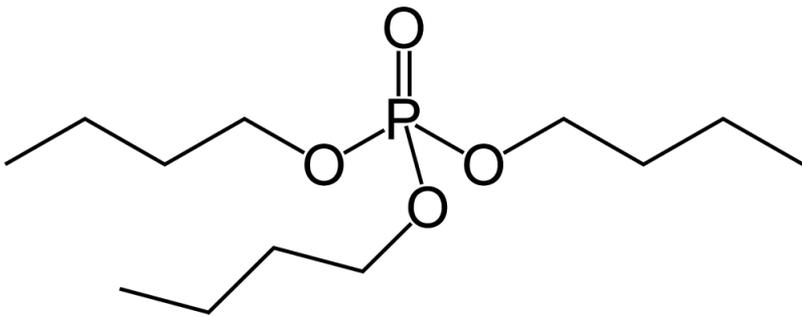
HEDTA = acido N-idrossietil-etilendiaminotriacetico

SX, Solvent eXtraction

fattore di separazione $\alpha_B^A = \frac{D_A}{D_B}$



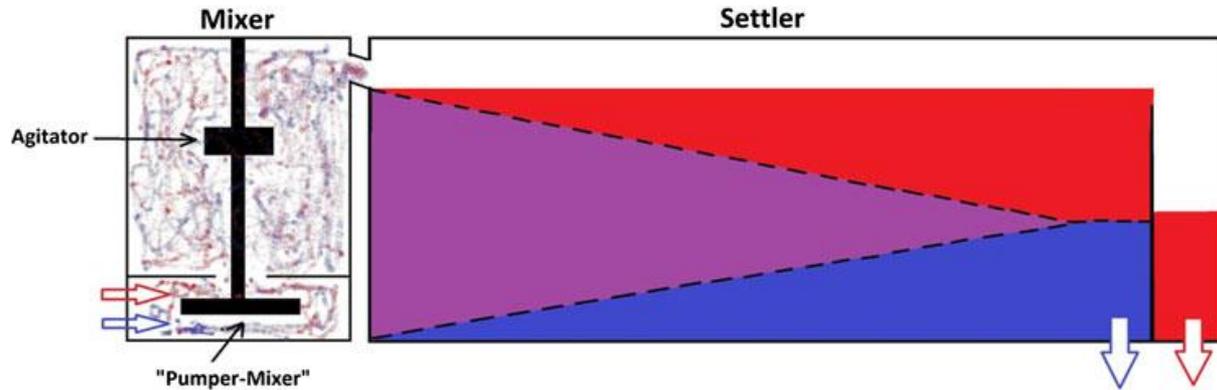
acido di-2-etil-esilfosforico
(**HDEHP** o DEHPA) per RE
come cloruri o solfati



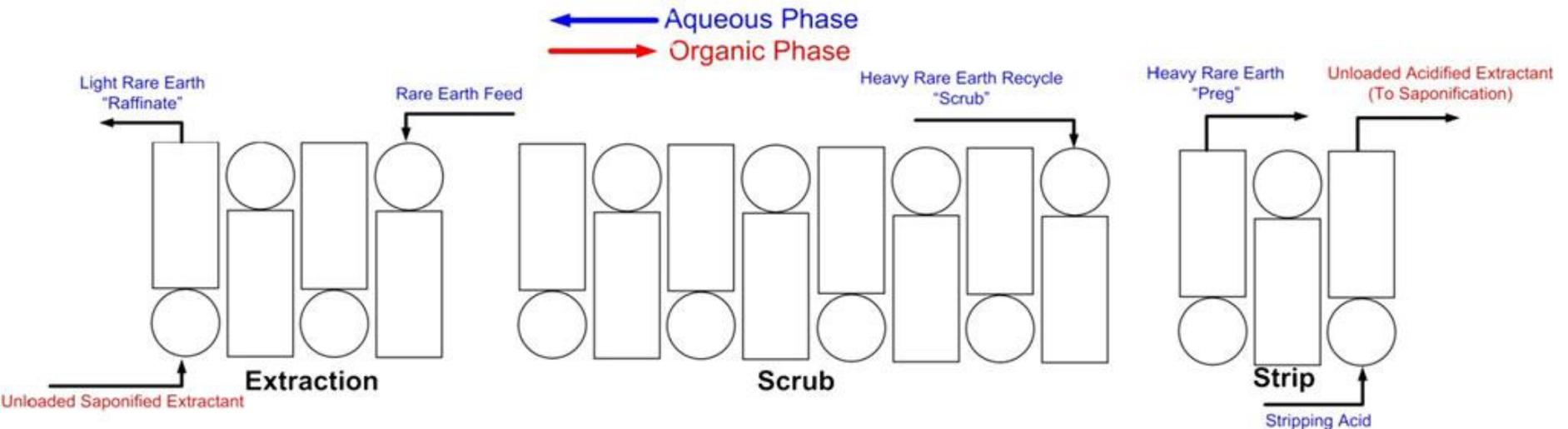
tri-*n*-butil fosfato (**TBP**) per RE
come nitrati



Unità *mixer-settler*

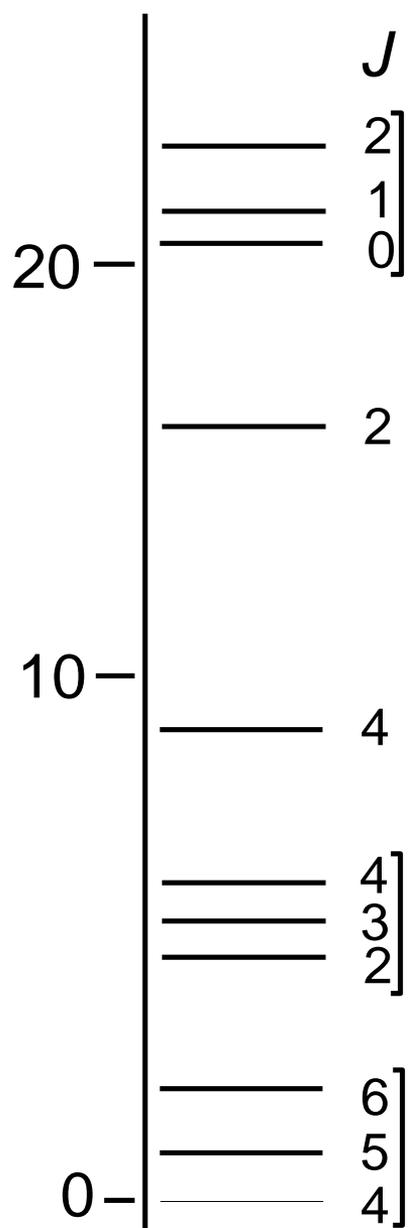


Schema di impianto SX



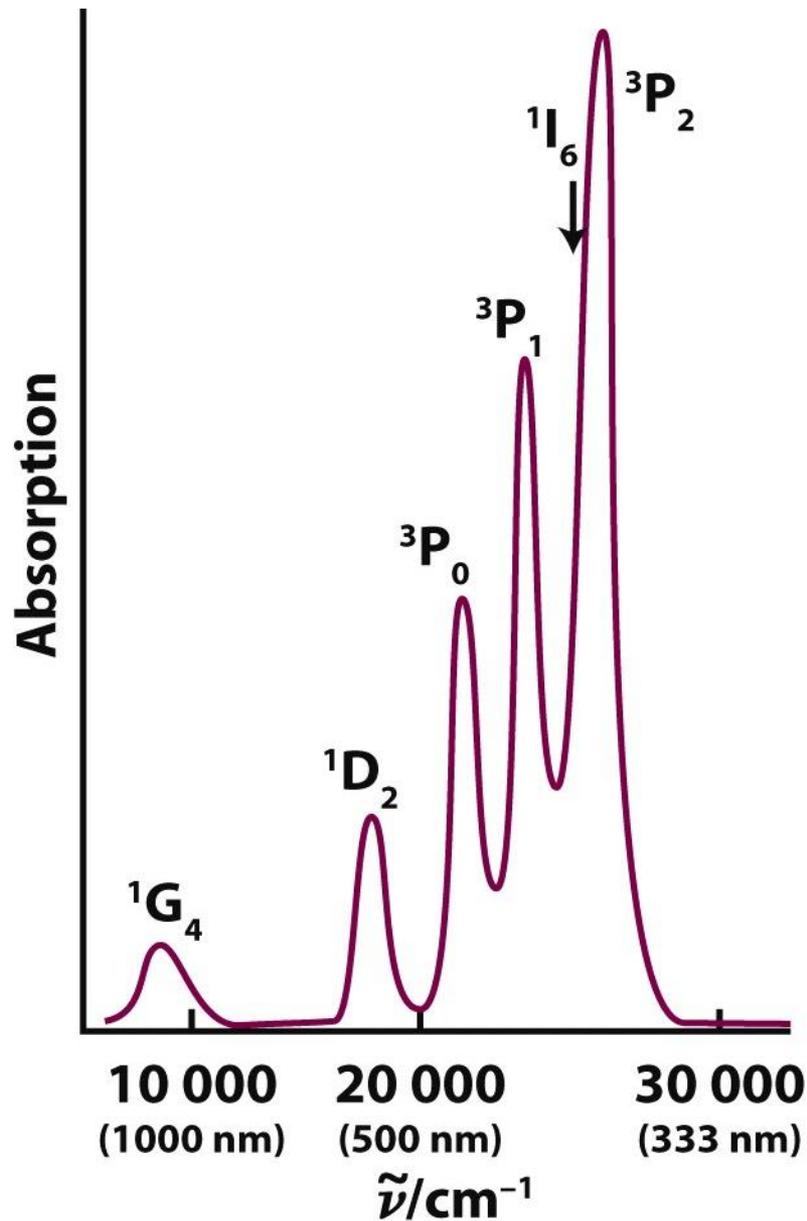
Metal ion	Colour	Ground state electronic configuration	Ground state term symbol	Magnetic moment, μ (298 K) / μ_B	
				Calculated from equation 25.1	Observed
La ³⁺	Colourless	[Xe]4f ⁰	¹ S ₀	0	0
Ce ³⁺	Colourless	[Xe]4f ¹	² F _{5/2}	2.54	2.3–2.5
Pr ³⁺	Green	[Xe]4f ²	³ H ₄	3.58	3.4–3.6
Nd ³⁺	Lilac	[Xe]4f ³	⁴ I _{9/2}	3.62	3.5–3.6
Pm ³⁺	Pink	[Xe]4f ⁴	⁵ I ₄	2.68	2.7
Sm ³⁺	Yellow	[Xe]4f ⁵	⁶ H _{5/2}	0.84	1.5–1.6
Eu ³⁺	Pale pink	[Xe]4f ⁶	⁷ F ₀	0	3.4–3.6
Gd ³⁺	Colourless	[Xe]4f ⁷	⁸ S _{7/2}	7.94	7.8–8.0
Tb ³⁺	Pale pink	[Xe]4f ⁸	⁷ F ₆	9.72	9.4–9.6
Dy ³⁺	Yellow	[Xe]4f ⁹	⁶ H _{15/2}	10.63	10.4–10.5
Ho ³⁺	Yellow	[Xe]4f ¹⁰	⁵ I ₈	10.60	10.3–10.5
Er ³⁺	Rose pink	[Xe]4f ¹¹	⁴ I _{15/2}	9.58	9.4–9.6
Tm ³⁺	Pale green	[Xe]4f ¹²	³ H ₆	7.56	7.1–7.4
Yb ³⁺	Colourless	[Xe]4f ¹³	² F _{7/2}	4.54	4.4–4.9
Lu ³⁺	Colourless	[Xe]4f ¹⁴	¹ S ₀	0	0

91 microstati



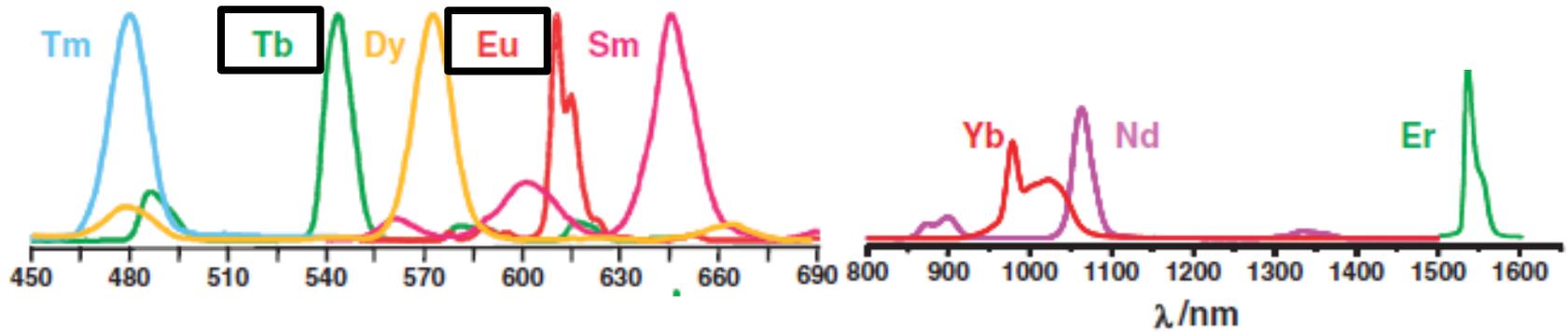
Pr^{3+}, f^2

$$\frac{[2(2l + 1)]!}{x! \times [2(2l + 1) - x]!}$$

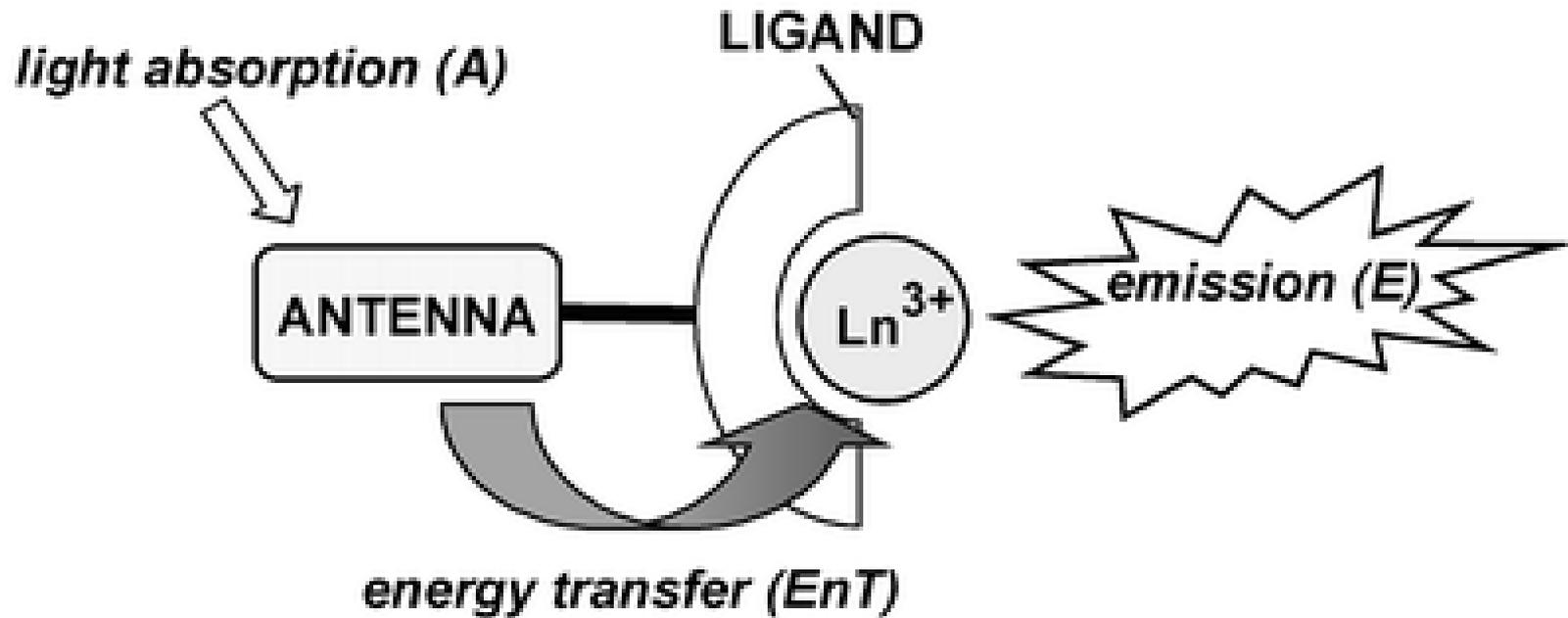


- Numero elevato di assorbimenti a causa del gran numero di microstati.
- Assorbimenti deboli a causa della mancanza di mescolamento fra gli orbitali (transizioni proibite). I coefficienti di assorbanza molare (ϵ) valgono tipicamente $1 - 10 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; in confronto, quelli dei metalli d sono prossimi a $100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.
- Bande affilate a causa delle deboli interazioni degli orbitali f con le vibrazioni dei leganti.
- Spettri in larga parte indipendenti dalla natura dei leganti e dal numero di coordinazione.

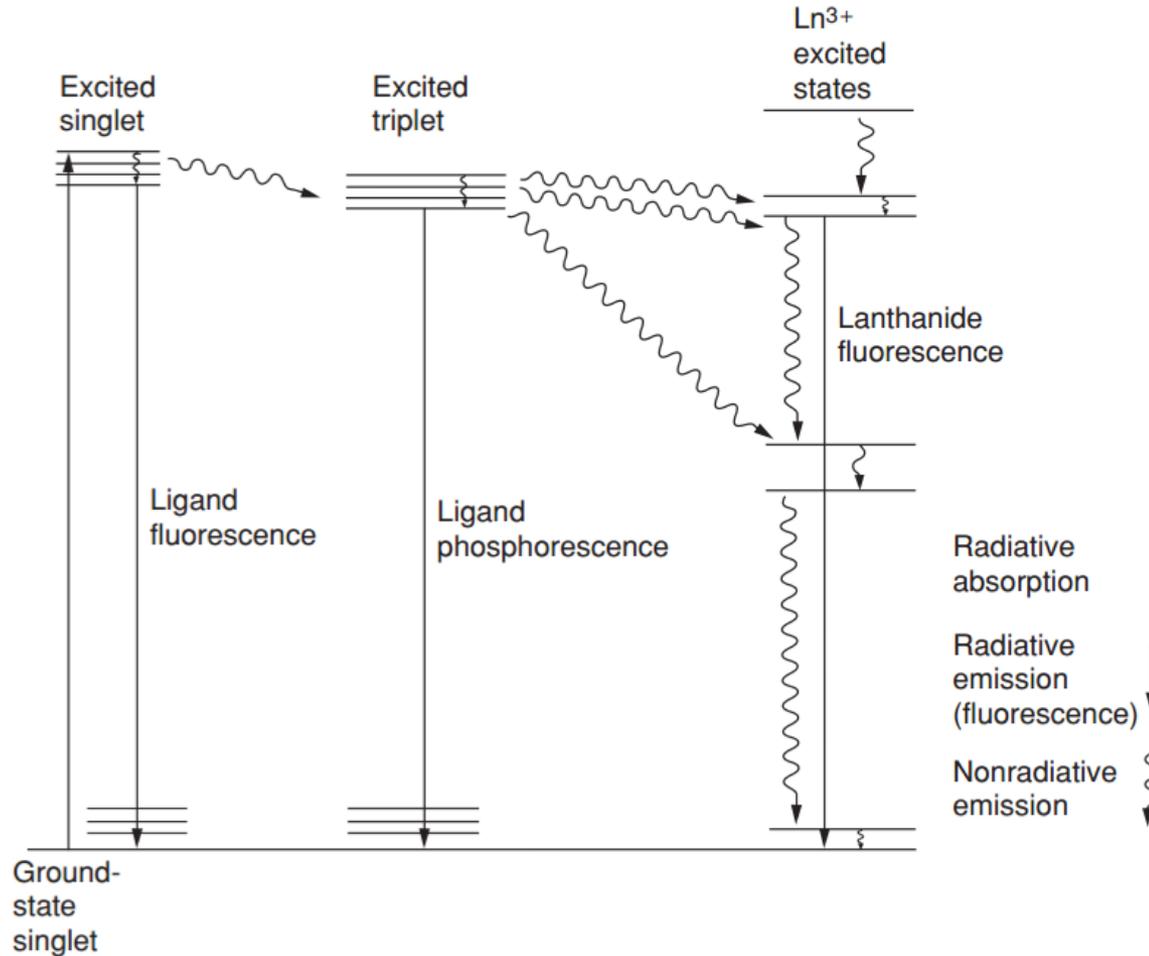
Spettri di emissione di alcuni cationi dei lantanidi



Sensibilizzazione (*antenna excitation*)



Sensibilizzazione (*antenna excitation*)



Lanthanide-doped LED

White-emitting LED = core LED blu (GaN, $\lambda_{em} = 450 - 470$ nm) ricoperto da uno strato di resina epossidica contenente un *Ln phosphor* che emette nel giallo (e.g. *yttrium aluminium garnet*, YAG, drogato con cerio (YAG:Ce)).

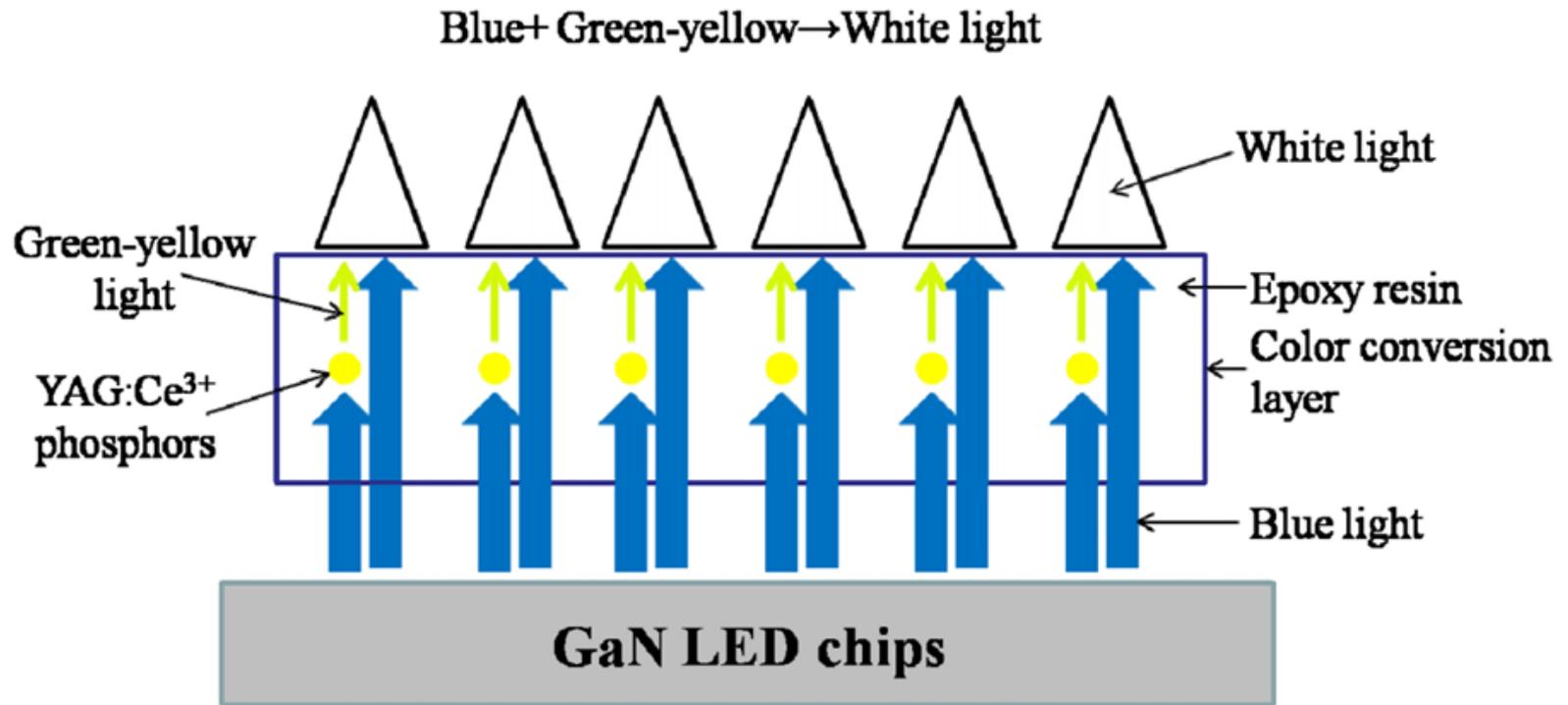
Blu + giallo = bianco

Granato (*garnet*) = $M_3M'_2(XO_4)_3$, (M/M' = 2⁺/3⁺, X = Si, Al, Ga, Ge)

Granato di ittrio e alluminio (YAG) = $Y_3Al_5O_{12}$

La struttura del granato definisce dei siti ottacoordinati che possono venire occupati da ioni dei lantanidi (e.g. al posto di Y³⁺)

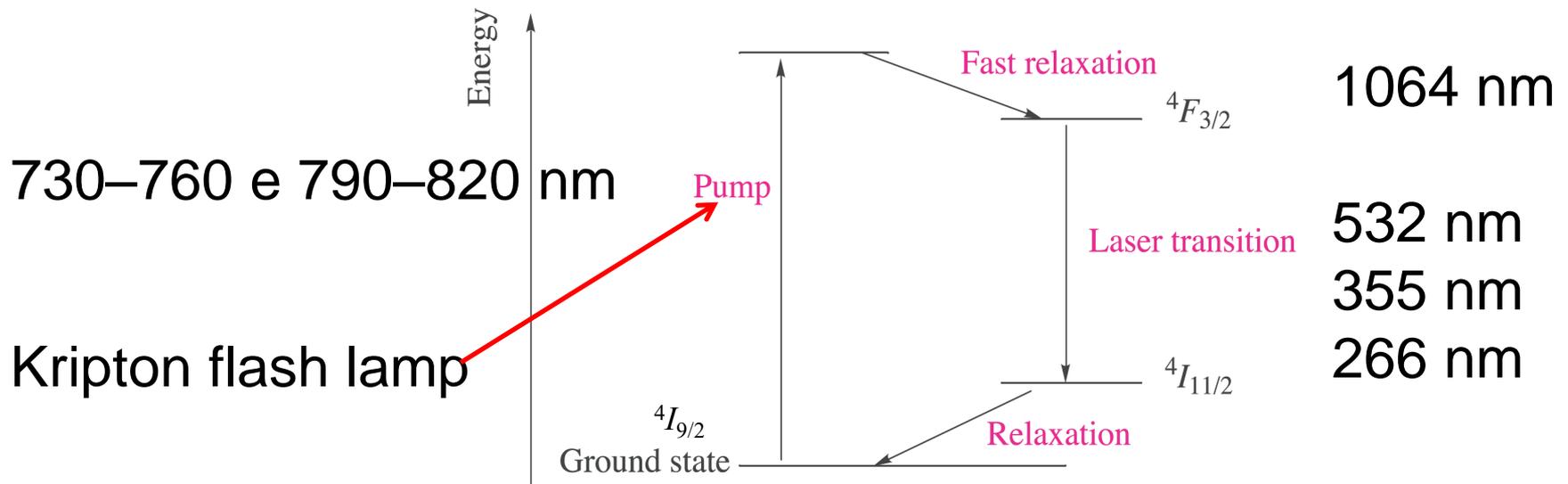
Lanthanide-doped LED



Laser Nd:YAG (*yttrium aluminum garnet*, $Y_3Al_5O_{12}$)

granati: $M_3M'_2(XO_4)_3$ X = Si, Al, Ga, Ge

inversione di popolazione

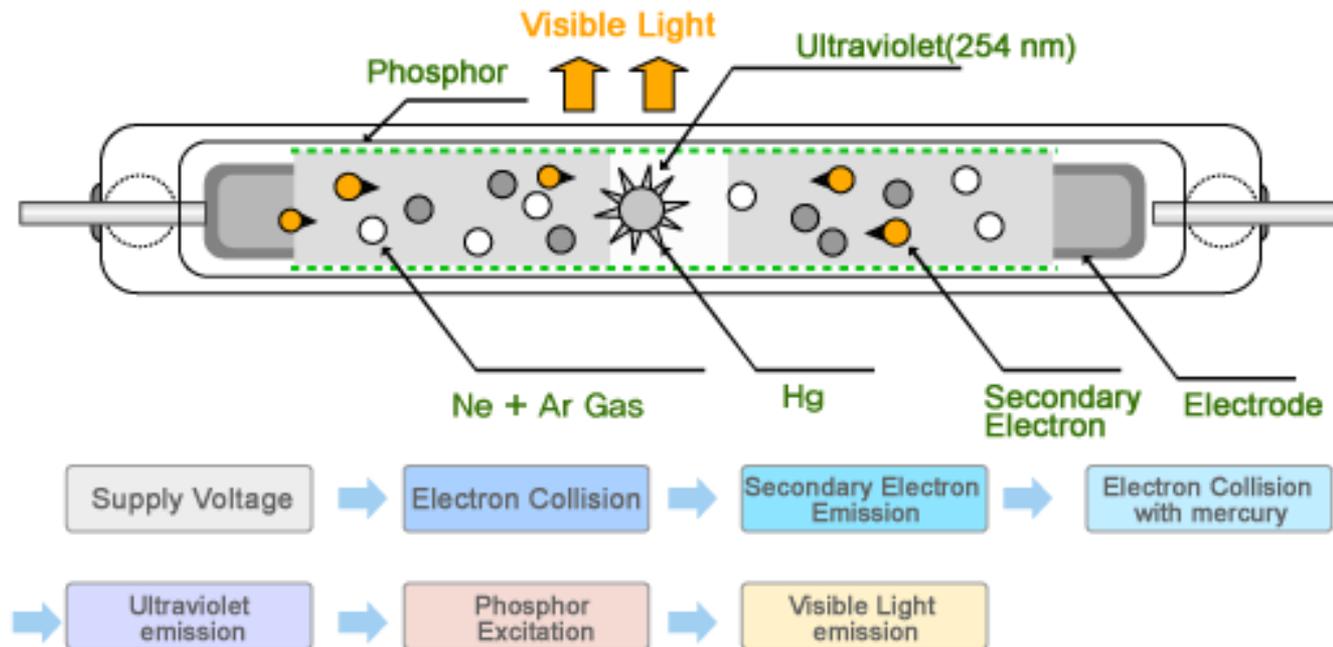


LASER a 4 livelli

Phosphors a base di lantanidi per lampade fluorescenti (Cold Cathode Fluorescent Lamp, CCFL)



Cold Cathode Fluorescent Lamp (CCFL)



phosphors a base di Y, La, Ce, Eu, Gd, Tb

$$\mu = g_J \{J(J + 1)\}^{1/2} \mu_B$$

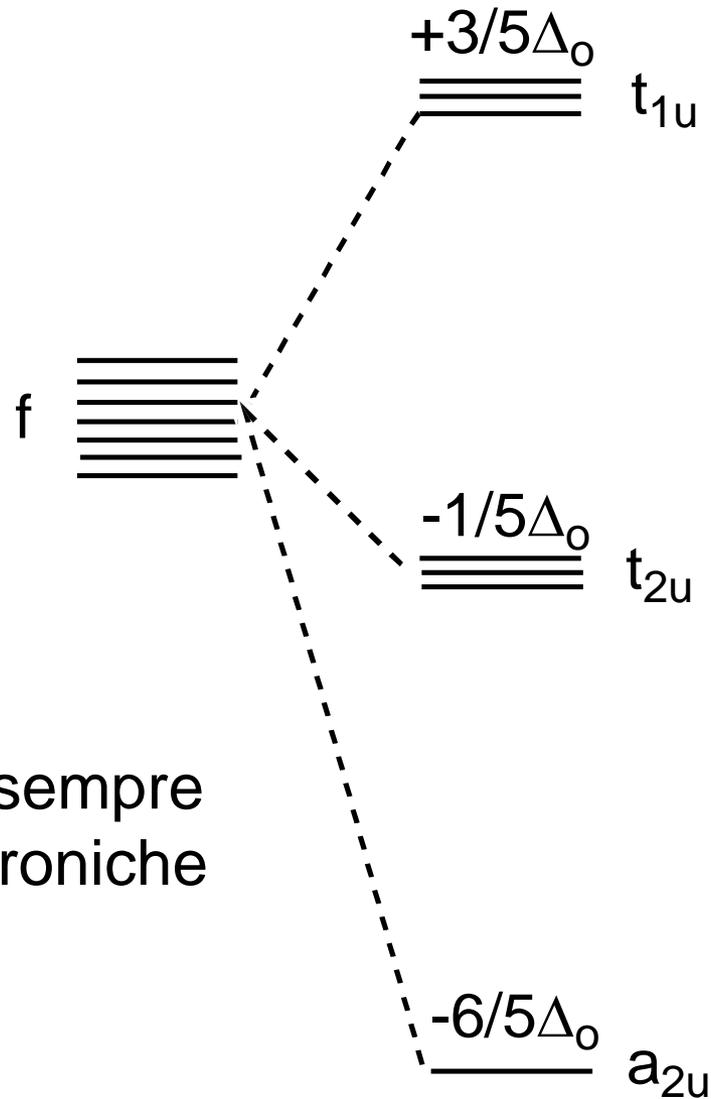
$$g_J = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)}$$

Metal ion	Colour	Ground state electronic configuration	Ground state term symbol	Magnetic moment, μ (298 K) / μ_B	
				Calculated from equation 25.1	Observed
La ³⁺	Colourless	[Xe]4f ⁰	¹ S ₀	0	0
Ce ³⁺	Colourless	[Xe]4f ¹	² F _{5/2}	2.54	2.3–2.5
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Eu ³⁺	Pale pink	[Xe]4f ⁶	⁷ F ₀	0	3.4–3.6
Gd ³⁺	Colourless	[Xe]4f ⁷	⁸ S _{7/2}	7.94	7.8–8.0
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Er ³⁺	Rose pink	[Xe]4f ¹¹	⁴ I _{15/2}	9.58	9.4–9.6
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Yb ³⁺	Colourless	[Xe]4f ¹³	² F _{7/2}	4.54	4.4–4.9
Lu ³⁺	Colourless	[Xe]4f ¹⁴	¹ S ₀	0	0

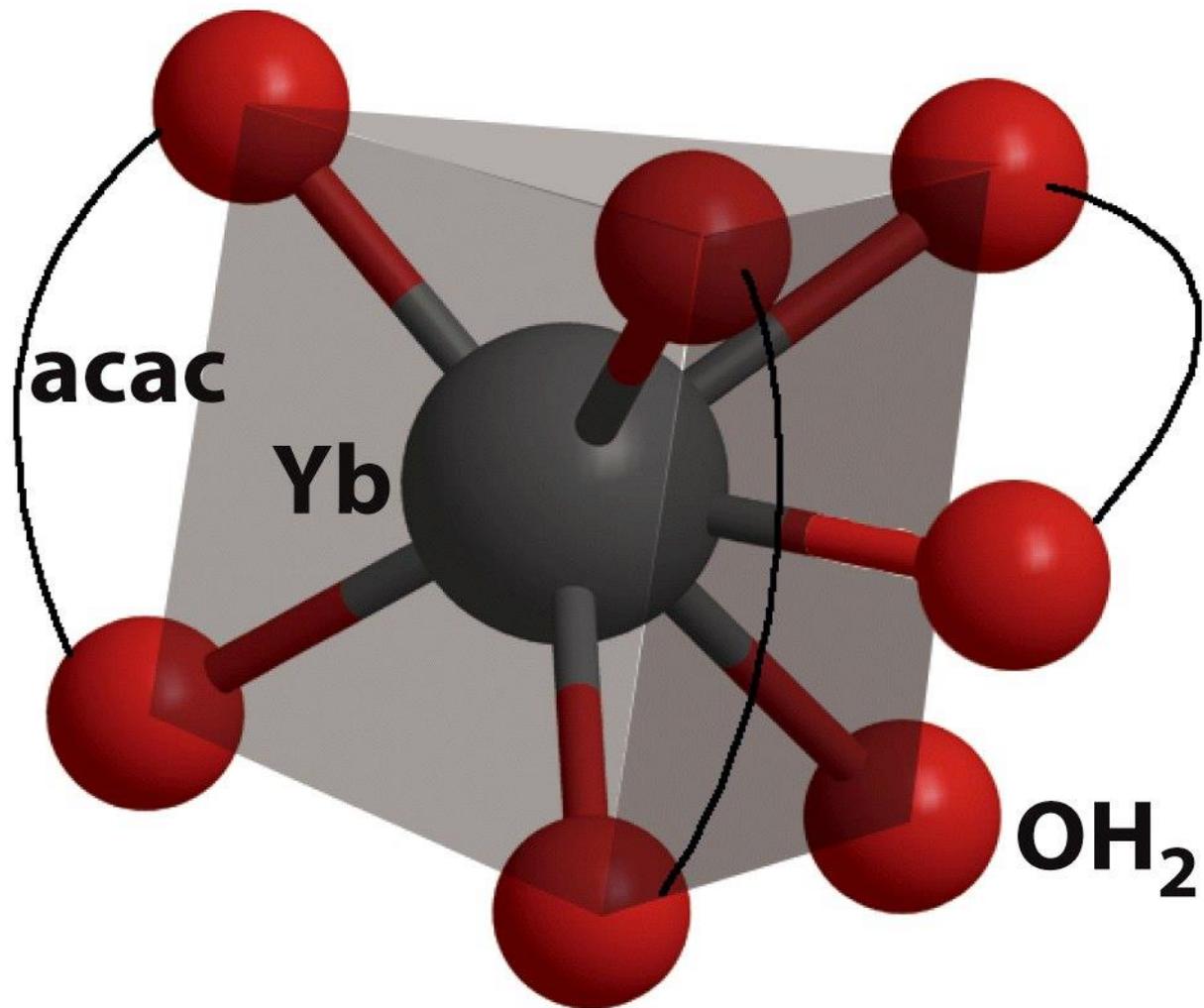
Supermagneti



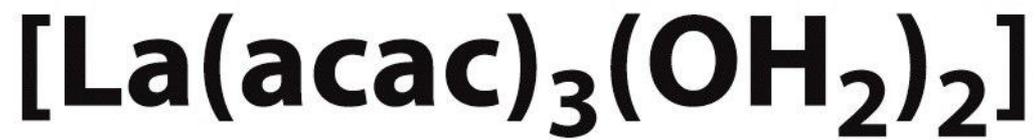
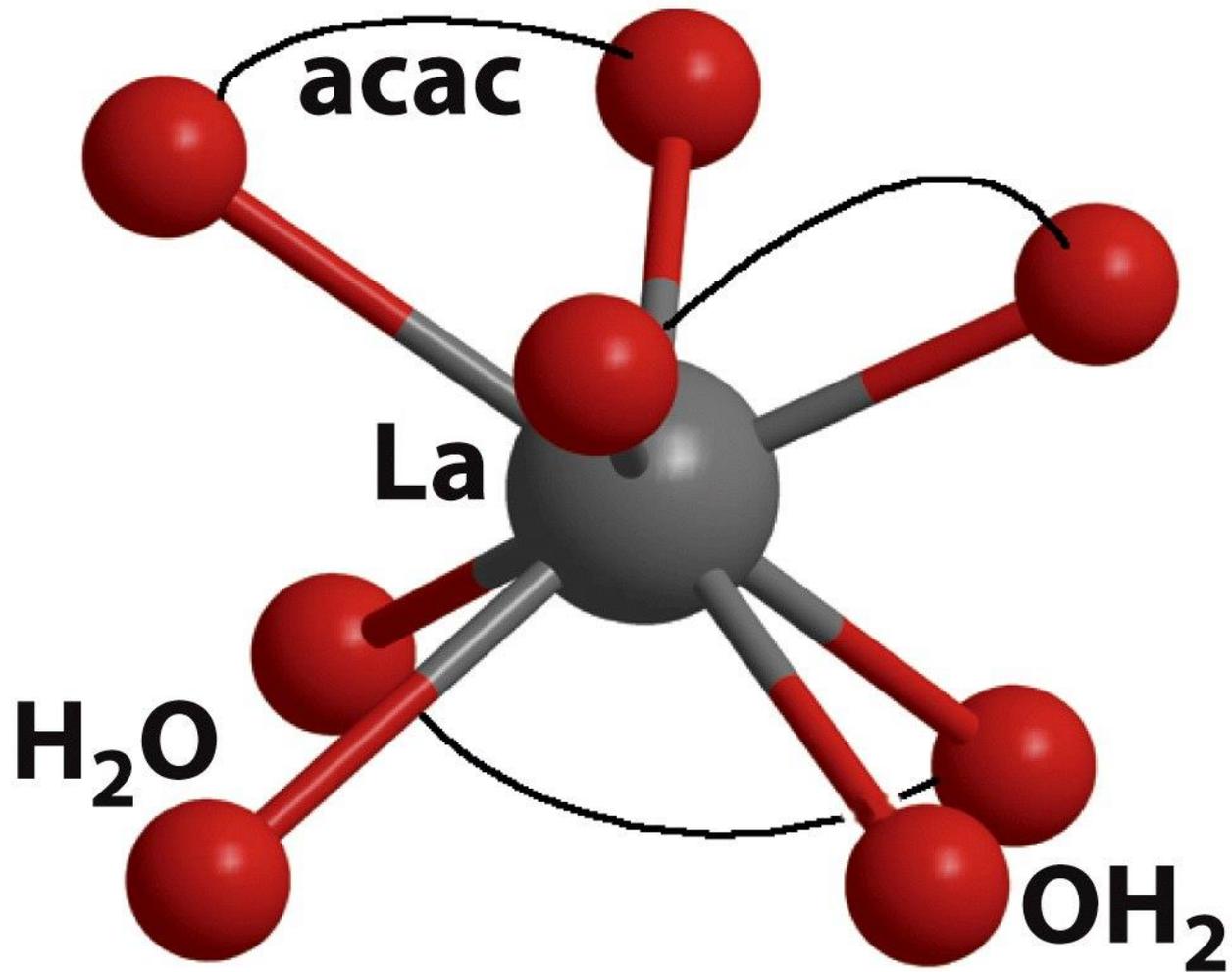
Splitting in campo ottaedrico



Splitting modesto, sempre configurazioni elettroniche ad alto spin

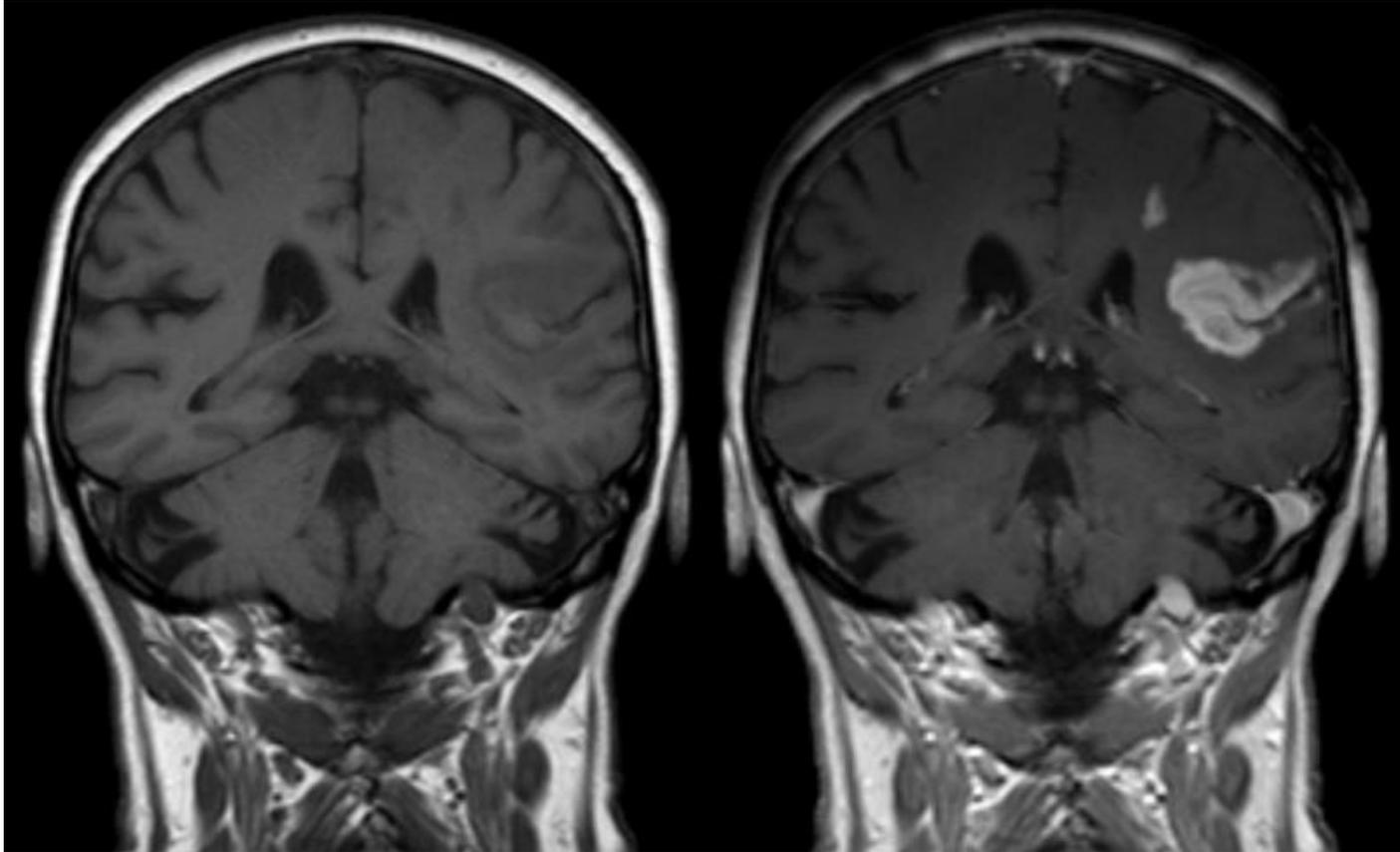


Prisma trigonale cappato



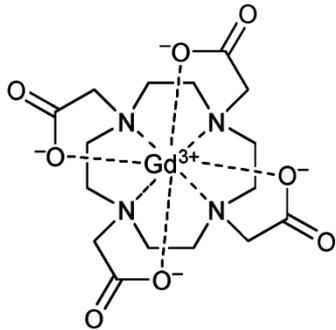
Antiprisma quadrato

Magnetic Resonance Imaging (MRI)

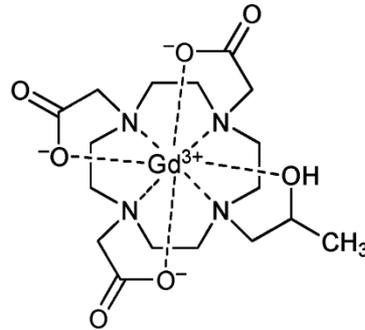


Defect of the blood-brain barrier after stroke shown in MRI. T1-weighted images: left image = without; right image = with contrast medium administration

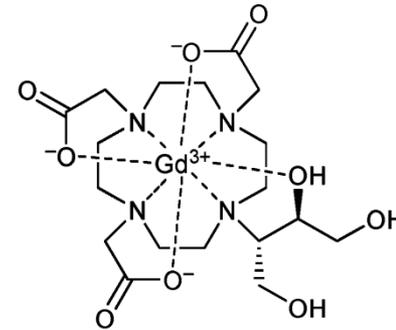
Some commercial T₁ contrast agents (extracellular fluid CAs)



Gd-DOTA
Dotarem®
(Guerbet)

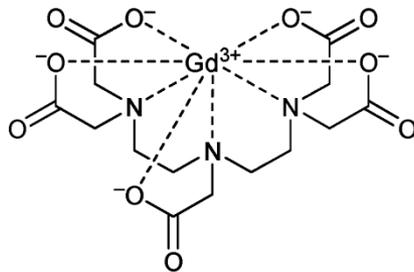


Gd-HP-DO3A
ProHance®
(Bracco)

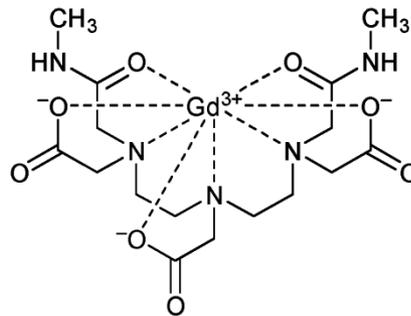


Gd-BT-DO3A
Gadovist®
(Schering)

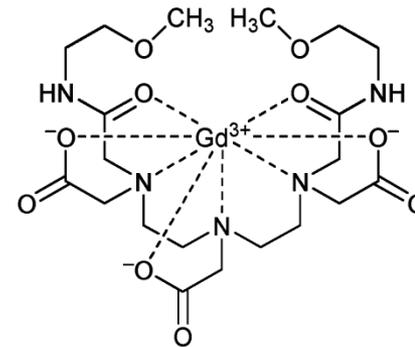
Typical dose =
0.1 – 0.3 mmoles/kg



Gd-DTPA
Magnevist®
(Schering)



Gd-DTPA-BMA
Omniscan®
(Amersham)



Gd-DTPA-BMEA
OptiMARK®
(Mallinckrodt)