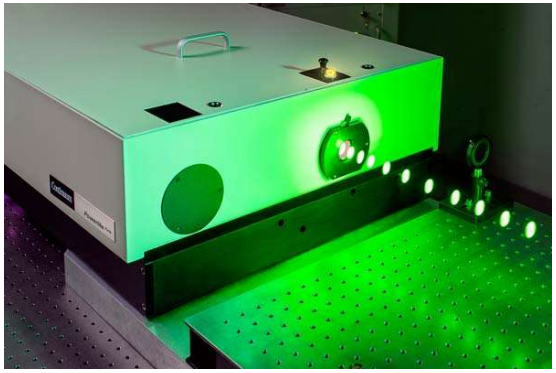
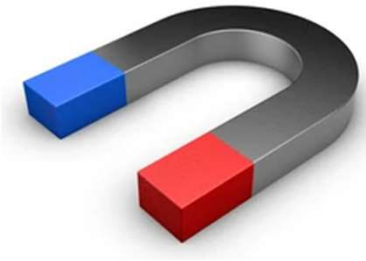
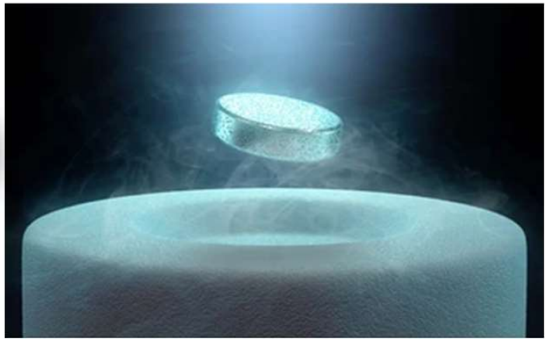
Topic: Lanthanides
Course: DSE-1A
Semester-V
Department of Chemistry
Polba Mahavidyalaya

Chemistry of Lanthanoids

Applications:

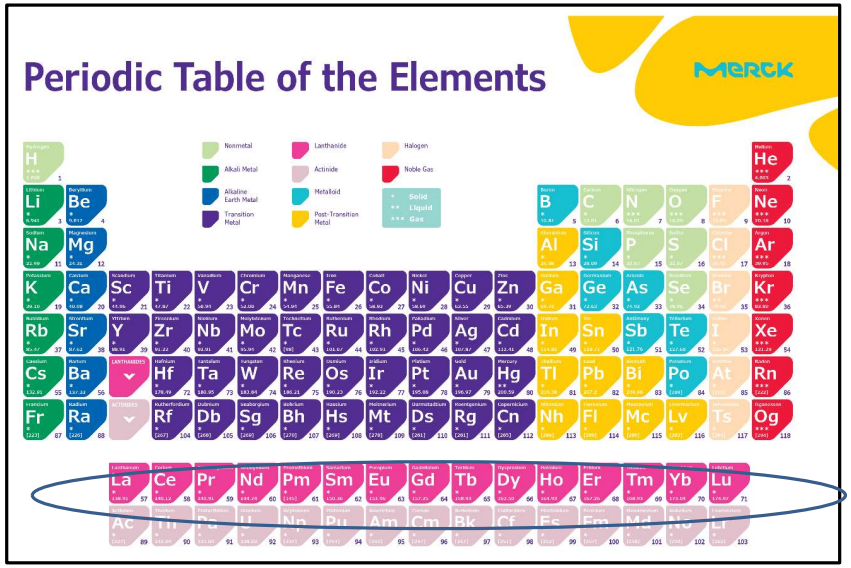





Discovery:
Ytterby, 30 km from Stockholm (1787)

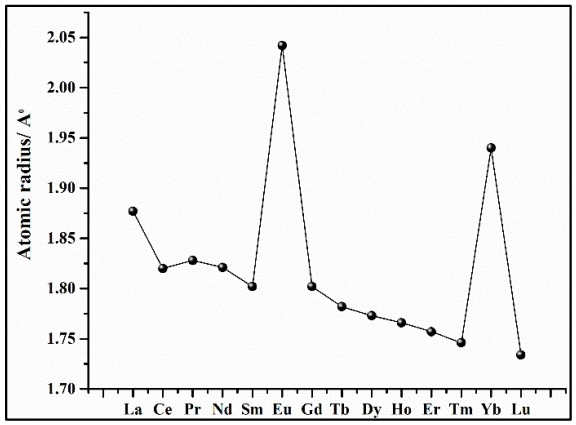
Source:
- The lanthanoid elements are not particularly rare. Apart from the unstable Pm.
- Minerals: monazite (mixed La, Th, Ln phosphates) – widely distributed, concentrated in sand & river beds.
- Bastnaesite (La, Ln fluoro-carbonate $M^{III}CO_3F$) – a vast deposit in Sierra Nevada, USA. Gadolinite ($Ln_2M_3Si_2O_{10}$), a mineral of Gadolinium.

Image source: Wikipedia

Chemistry of Lanthanoids



- The lanthanoids are part of group 3, and are the elements with atomic numbers 57−71 in period 6.
- Electronic configuration: [Xe] $4f^{1-14}5d^{n}6s^{m}$



Ce: [Xe] $4f^{1}5d^{1}6s^{2}$
Eu: [Xe] $4f^{7}\ 6s^{2}$
Yb: [Xe] $4f^{14}\ 6s^{2}$

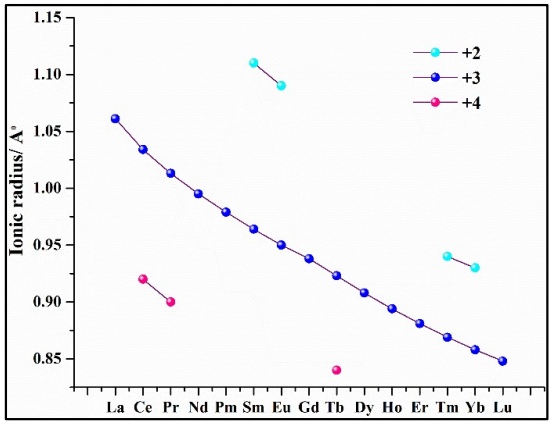


Image source: MERCK website

Chemistry of Lanthanoids

Symbol	Configuration		
	+2	+3	+4
La		$[Xe]4f^0(La^{3+})$	
Ce	$[Xe]4f^2(CeCl_2)$	$[Xe]4f^1(Ce^{3+})$	$[Xe]4f^0(Ce^{4+})$
Pr		$[Xe]4f^2(Pr^{3+})$	$[Xe]4f^1(PrO_2, Na_2PrF_6)$
Nd	$[Xe]4f^4(NdI_2)$	$[Xe]4f^3(Nd^{3+})$	$[Xe]4f^2(Cs_3NdF_7)$
Pm		$[Xe]4f^4(Pm^{3+})$	
Sm	$[Xe]4f^6(Sm^{2+})$	$[Xe]4f^5(Sm^{3+})$	
Eu	$[Xe]4f^7(Eu^{2+})$	$[Xe]4f^6(Eu^{3+})$	
Gd		$[Xe]4f^7(Gd^{3+})$	
Tb		$[Xe]4f^8(Tb^{3+})$	$[Xe]4f^7(TbO_2, TbF_4)$
Dy		$[Xe]4f^9(Dy^{3+})$	$[Xe]4f^8(Cs_3DyF_7)$
Ho		$[Xe]4f^{10}(Ho^{3+})$	
Er		$[Xe]4f^{11}(Er^{3+})$	
Tm	$[Xe]4f^{13}(TmI_2)$	$[Xe]4f^{12}(Tm^{3+})$	
Yb	$[Xe]4f^{14}(Yb^{2+})$	$[Xe]4f^{13}(Yb^{3+})$	
Lu		$[Xe]4f^{14}(Lu^{3+})$	

- It is possible to correlate the stability of various oxidation states of lanthanoids with the electronic configuration**.**

Lanthanide contraction:

- We move along the lanthanoid series, there is a decrease in atomic as well as ionic radii, called Lanthanide Contraction.
- The shielding effect of the electrons decreases in the order s > p > d > f.
- Relativistic effect has a 10% contribution to lanthanide contraction.

Chemistry of Lanthanoids

Consequences of Lanthanoide Contraction:

- The basicity of the hydroxides decreases from La to Lu.
- Occurrence of yttrium with heavy lanthanoids.
- For the various Ln^{3+} ions, since the charge remains the same and the decrease in size is just marginal, making their separation difficult.
- The hardness, melting, and boiling points of the elements increase from Ce to Lu.

Lanthanoide coordination complex:

- High coordination number
- Oxophilic center
- Chelate formation

- Lanthanoid carbonyl complexes are very unstable.[1]
- Is there any possibility of backbonding?

$$Ln + xCO = Ln(CO)_x$$

1. a) R. K. Sheline, J. L. Slater, *Angew. Chem., Int. Ed. Engl*. **1975**, *14*, 309; b) W. H. Xu, X. Jin, M. H. Chen, P. Pyykko, M. F. Zhou, J. Li, *Chem. Sci*. **2012**, *3*, 1548; J. Jin, S. Pan, X. Jin, S. Lei, L. Zhao, G. Frenking, M. Zhou, *Chem. Eur. J.* **2019**, *25*, 3229