

The Chemistry of f Block Elements

The elements in which f orbitals of the valence shell are incomplete or being filled progressively are called f-block elements or inner transition elements because the f orbitals in these elements belongs to n-2 shell.

➤ **Lanthanides or Lanthanones:** The lanthanides are characterized by the gradual filling of the 4f sub shell

Actinides: The Actinides are characterized by the gradual filling of the 5f sub shell

Lanthanide Series*	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	140.1	140.9	144.2	(147)	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0	175.0
Actinide Series~	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
	232.0	(231)	238	(237)	(242)	(243)	(247)	(247)	(249)	(254)	(253)	(256)	(254)	(257)

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Discovery of Lanthanide-Elements

S. No.	Element	Symbol	At. No.	Discoverer	Year	Derivation of name	Abundance in earth's crust g/tonne
1.	Lanthanum	La	57	Mosander	1837	Greek 'lanthano' (to conceal)	18.3
2.	Cerium	Ce	58	Berzelius	1814	Planet ceres	46.1
3.	Praseodymium	Pr	59	Welsbach	1885	Greek 'praseo' (Green) and didymos 'twin'	5.53
4.	Neodymium	Nd	60	Welsbach	1885	Greek 'neos' (new) and didymos 'twin'	23.9
5.	Promethium	Pm	61	Marinsky, Glendenin and Coryell	1947	Greek Prometheus	Traces
6.	Samarium	Sm	62	Boisbaudran	1879	Samaraki Russian army officer	16.7
7.	Europium	Eu	63	Demarcy	1896	Europe	4.06
8.	Gadolinium	Gd	64	Marignac	1886	Finnish chemist Gadolin	6.36
9.	Terbium	Tb	65	Boisbaudran	1895	Sweden Town Ytterby	0.91
10.	Dysprosium	Dy	66	Boisbaudran	1886	Greek Hard to get all	4.47
11.	Holmium	Ho	67	Cleve	1879	Latin Holmia Stockholm	1.15
12.	Erbium	Er	68	Berlin	1860	Sweden town Ytterby	2.47
13.	Thulium	Tm	69	Cleve	1879	Thule, northland	0.2
14.	Ytterbium	Yb	70	Urban and Welsbach	1908	Sweden town Ytterby	2.66
15.	Lutetium	Lu	71	Urban and Welsbach	1907	Paris ancient name Lutetia	0.75

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Lanthanides or Lanthanones

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
140.1	140.9	144.2	(147)	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0	175.0

➤ The 15 elements from Lanthanum to Lutetium in the periodic table are referred to Lanthanides.

➤ The elements in the lanthanide series resemble remarkably with each other, .e.g., +3 is the most commonest among lanthanides. These elements occur in nature in the combined form and individual elements are extremely difficult to separate

➤ Lanthanum (⁵⁷La) usually treated as IIIB Group elements is indistinguishable from lanthanides and serves as prototype of the lanthanides

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OCCURRENCE OF LANTHANIDES

➤ The lanthanides are not so scarce in the earth's crust

Classification of Rare-Earth Minerals

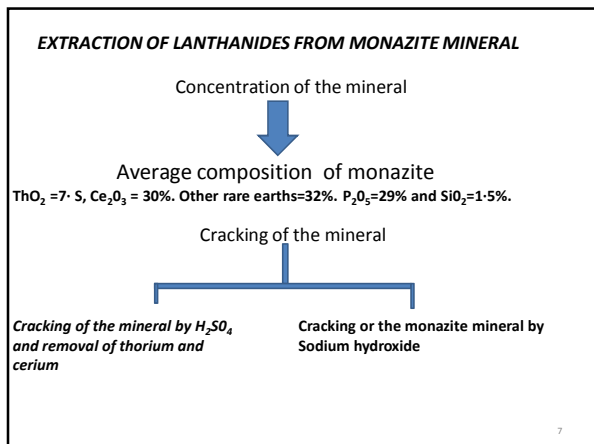
- Cerium Group Minerals.** These are also called cerite-earth minerals or simply cerium earths:
The elements with atomic numbers from 57 to 63 (i.e. La₅₇-Eu₆₃)
- Yttrium Group Minerals.** These are also called Yttrium-earth minerals or simply yttrium earths and are rich in gadolinite Earths. This group contains Yttrium and lanthanides of atomic Number from 64 to 71. (Gd₆₄-Lu₇₁)

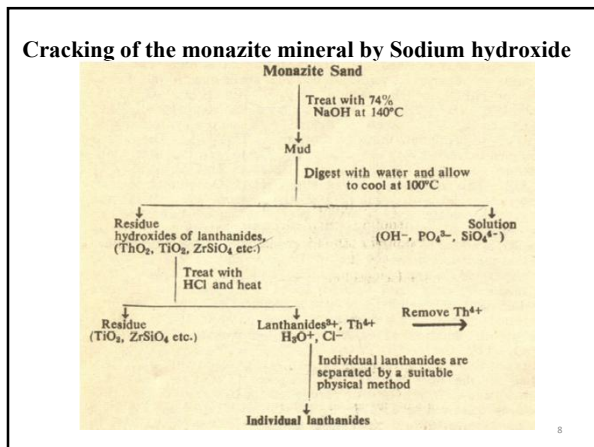
Important Minerals of Lanthanides (Cerium Group Minerals)

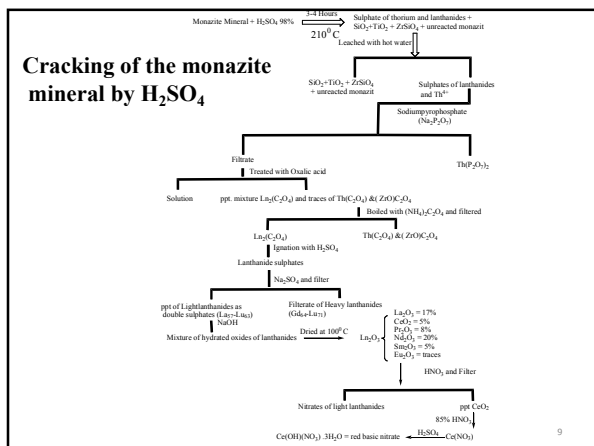
Minerals	Composition	Location of significant deposits
(i) Monazite Sand—Mixture of orthophosphates of Ce-earth, (Ce) PO ₄	(1) Cerium group minerals 90–70% Ce-earth (i.e. elements of at. no. 57 to 62 calculated as oxides) 1–4% Y-earth (i.e. elements of at. no. 63 to 71 calculated as oxides) 5–10% ThO ₂ 1–2% SiO ₂ 22–30% P ₂ O ₅ Traces of U	Occurs in the sand beaches of Travancore (India) Brazil South Africa U.S.A.
(ii) Bastnaesite-cerium earth fluoro-carbonate, (Ce) FCO ₃	65–70% Ce-earth < 1% Y-earth	Sweden, California, New Mexico
(iii) Cerite—A hydrated silicate of the composition, (Ca) ₂ M ^{II} H ₂ Si ₂ O ₁₁ (M=Ca, Fe)	Traces of Thorium 51–72% Ce-earth 7.6% Y-earth Traces of Th, U, Zr	Sweden Caucasus

Important Minerals of Lanthanides (Yttrium Group Minerals)

(i) Gadolinite or Ytterbite—A yttrium-earth, iron and beryllium silicate, (Fe, Be) ₂ (Y ₂) Si ₂ O ₁₂	(2) Yttrium group minerals 35–48% Y-earth (Calculated as oxides) 2–17% Ce-earth Upto 11.6% BeO Traces of ThO ₂	Sweden, Norway USA (Texas and Colorado)
(ii) Xenotime—An orthophosphate of Y-earth (analogous to Monazite), (Y) PO ₄	54–65% Y-earth ~ 0.1% Ce-earth	Norway Brazil
(iii) Euxenite—Mixture of titanates, niobates and tantalates of Y-earth, (Y) (Nb, Ta) TiO ₆ · x H ₂ O	Upto 3% ThO ₂ , upto 3.5% U ₂ O ₈ 2–3% ZrO ₂ 13–35% Y-earth (Calculated as Oxides) 2–8% Ce-earth (Calculated as Oxides) 20–23% TiO ₂ , 25–35% (Nb, Ta) ₂ O ₅	Australia, Idaho (U.S.A.)







Fractional Thermal Decomposition of Oxy-salts

This method is based on the fact that the rate of thermal decomposition of oxysalts such as nitrates, sulphates and acetates of lanthanide elements at a given temperature decrease from La₅₇ to Lu₇₁. This means that the oxysalts of cerium group elements decompose more readily than those of the ytterbium group. Thus if a mixture containing the nitrates of lanthanide elements is fused and then leached with water, the ytterbium group lanthanides which are less basic are rapidly concentrated and their separation from the more basic cerium lanthanides is effected. The individual members of a given sub-group can be separated from each other by repeating the whole process several times.

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Change of oxidation states by selective oxidation or reduction procedures.

Some of the lanthanides show +2 and +4 oxidation states in addition to +3 state which is the most characteristic of all the elements of lanthanide series. The properties of Ln²⁺ and Ln⁴⁺ ions are different from those of the usual Ln³⁺ ions. A change in oxidation state results in a remarkable change in properties. Selective oxidation or reduction, therefore, provides a very effective method of separating specific lanthanides.

Examples: (i) Suppose we have to separate Ce from a mixture containing Ce³⁺ and other tripositive lanthanide cations. This mixture is treated with some strong oxidizing agent such as bromate in neutral medium or chlorine or KMnO₄ in alkaline medium. By this treatment only Ce³⁺ ion is oxidized to Ce⁴⁺ ion while other lanthanide ions remain as Ln³⁺ ions. Since Ce⁴⁺ ion is smaller than Ce³⁺ ion, Ce⁴⁺ ion is less basic and less soluble. It (i.e. Ce⁴⁺ ion) can thus be precipitated as Ce(OH)₄ by the addition of a small amount of an alkali leaving all other Ln³⁺ ions in solution. By this method it has been possible to have 99% pure Ce from a mixture containing only 40% CeO

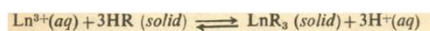
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(ii) Eu³⁺ can almost quantitatively be separated from a solution containing Eu³⁺ and other Ln³⁺ ions by reducing it to Eu²⁺ by means of Zn-amalgam and then precipitating it as EuSO₄ which is insoluble in water and hence can be separated. The sulphates of all the trivalent lanthanides, on the other hand, are soluble in water. Zn-amalgam also brings about the reduction of Yb³⁺ to Yb²⁺ but not of Sm³⁺.

(2) Modern Methods.

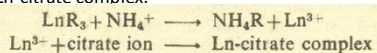
(i) Ion-exchange method.

Organic compounds containing sulphonic (-SO₃H) or carboxylic acid (-COOH) groups



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All the Ln^{3+} (aq) ions are attached with the resin as LnR_3 (solid). Since Lu^{3+} (aq) is largest in size and La^{3+} (aq) is smallest, La^{3+} (aq) is attached to the resin in the column with maximum and Lu^{3+} (aq) with minimum firmness. In order to remove Ln^{3+} ions fixed as LnR_3 (solid) on the resin, the column is eluted (i.e. leached) with a complexing agent in aqueous solution like a buffer solution of ammonium citrate-citric acid (pH = 4 to 7). Such complexing agents are called eluants or eluates or eluting agents. During elution process NH_4^+ ions of the eluting agent replace Ln^{3+} ions from LnR_3 (solid) to give Ln^{3+} ions which react with citrate ion to form the Ln-citrate complex.



La^{3+} (aq) is attached to resin with maximum and Lu^{3+} (aq) with minimum firmness, Lu-citrate complex comes out of the column first and La-citrate complex comes out last. In actual practice the process of elution is to be repeated several times by careful control of concentration of ammonium citrate-citric acid solutions.

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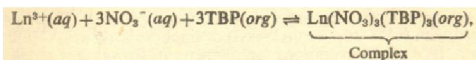
The yttrium group rare-earths have been separated by Kettle and Boyd on a column of Dowex 50 (270–325 mesh) using 5% (0.25 M) citric acid at pH 3.28. Mixtures of Eu–Sm and Y–Tb took eight hours for complete separation with 0.5 M citrate at pH 3.04 (87°C) and with 0.24 M lactate at pH 5.0. Cunningham *et al.* reduced the separation time to four hours using 1M lactate (pH=3.25) at 87°C for a mixture of Y-Pr-Nd-Pm-Sm-Eu with a Zeokarb 225.

1) Solvent (liquid-liquid) extraction method.

The separation of lanthanides by this method was first reported by Fischer.

The method is based on the differences in the solubility of lanthanide salts in water and an immiscible or partially miscible organic solvent. These organic solvents are called extracting solvents or extractants. This method has been used on both tracer and macroscales. The technique consists of passing the aqueous solution of lanthanide salts counter-current to the organic solution which extracts the lanthanides from water; The most widely used extracting solvent is tri-*n*-butyl phosphate, TBP in an inert medium like kerosene or xylene to extract the lanthanides from nitric acid solutions. TBP forms complexes with Ln^{3+} (aq) ions in presence of NO_3^- ions

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where (org) represents the organic phase. The distribution between these two phases (i.e. solvents) is described by distribution ratio (also called extraction coefficient), λ , given by

$$\lambda = \frac{\text{Total concentration of solute in one solvent}}{\text{Total concentration of solute in the other solvent}}$$

$$= \frac{C_{\text{Ln}(\text{NO}_3)_3(\text{TBP})_3(\text{org})}}{C_{\text{Ln}^{3+}(\text{aq})}} \quad \dots(9-1)$$

For two tripositive lanthanide ions, Ln^{3+} and Ln^{2+} , the separation factor, α , is given as,

$$\alpha = \frac{\lambda'}{\lambda} = \frac{C_{\text{Ln}(\text{NO}_3)_3(\text{TBP})_3(\text{org})} \cdot C_{\text{Ln}^{3+}(\text{aq})}}{C_{\text{Ln}(\text{NO}_3)_3(\text{TBP})_3(\text{org})} \cdot C_{\text{Ln}^{2+}(\text{aq})}} \quad \dots(9-2)$$

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Peppard has reported that an average separation factor for adjacent lanthanides for 15.8 M nitric acid–100% TBP system is about 1.5.

Equilibrium constant, K , is given by :

$$K = \frac{C_{\text{Ln}(\text{NO}_3)_3(\text{TBP})_3(\text{org})}}{C_{\text{Ln}^{3+}(\text{aq})} \cdot C_{\text{NO}_3^-}^3(\text{aq}) \cdot C_{\text{TBP}(\text{org})}^3} \quad \dots(9-3)$$

Combination of equation (9-3) with equation (9-1) gives equation (9-4), viz.

$$K = \frac{\lambda}{C_{\text{NO}_3^-}^3(\text{aq}) \cdot C_{\text{TBP}(\text{org})}^3} \quad \dots(9-4)$$

or $\lambda = K \cdot C_{\text{NO}_3^-}^3(\text{aq}) \cdot C_{\text{TBP}(\text{org})}^3 \quad \dots(9-4)$

Kilogram quantities of 95% pure lanthanides have been prepared by solvent extraction technique. Another organic solvent which is a better extractant than TBP is *Di (2-ethyl hexyl) phosphoric acid*. For this extractant the average separation factor of 2.5 for adjacent lanthanides has been reported. Other extractants used in the separation process are : monoalkylphosphoric acids : $\text{RP}(\text{O})(\text{OH})_2$ or RH_2PO_3 , pyrophosphate esters : $(\text{RO})_2\text{P}(\text{O})-\text{O}-\text{P}(\text{O})(\text{OR})_2$, phosphonates : $(\text{RO})_2(\text{R})\text{PO}$ and $(\text{RO})(\text{R})\text{P}(\text{O})(\text{OH})$ and 1, 3-diketones or 8-quinolins.

Paper chromatography.

Cerrai and Testa separated some rare-earths by ascending paper chromatography, using CRL/I papers treated with 0.1M dil. (2-ethylhexyl)orthophosphoric acid (HDEHP).

Under the same conditions an increase in R_f value is noted with decreasing atomic number, Z , of the rare-earths. For a given element the R_f value increases with the molarity of eluting acid (HCl) and with temperature, but decreases with the concentration of HDEHP.

The following R_f values for 1 M HCl eluant have been reported:

Ln^{3+}	La	Ce	Pr	Sm	Eu	Gd	Dy	Er	Yb	Y	Sc
R_f	0.92	0.91	0.90	0.76	0.64	0.51	0.12	0.06	0.03	0.07	0.0

Later, Cerrai and Triulzi used a mixture of 3M HNO_3 and 80% CH_3OH as solvent on Whatman cellulose paper DE-20 to separate La, Ce, Pr, Nd, Sm and Gd. Whatman DE-20 is a cellulose anion exchanger, containing amine groups bonded to the cellulose matrix. It has been found that a mixture of HCl and various aliphatic alcohols can successfully be used as eluant for the separation of rare-earths by paper chromatography (Whatman No.1).

Gas Chromatography:

The 2, 2, 6, 6-tetra ethyl-3, 5-heptanedione complexes of Ln^{3+} ions, $\text{Ln}(\text{THD})_3$ are quite stable, volatile and monomeric in C_6H_6 . These complexes have appreciable and significant differences in the volatilities. Eisentraut and Sievers have recently separated these complexes by gas chromatographic technique. It has been found that these complexes are eluted without decomposition.

The variation of the retention times (in minutes) of the rare earth tris-complexes with ionic radii (in Å) shown in Fig. exhibits the effect of lanthanide contraction.

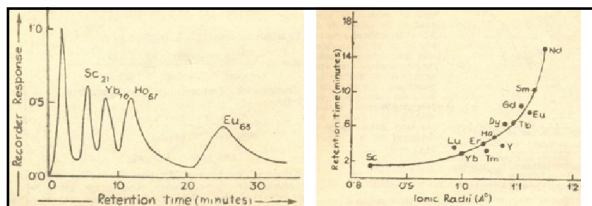


Fig. shows a gas chromatographic Separation of a mixture of Ln (THDh complexes in C_6H_6 solution).

Variation of the retention time, (minutes) of the rare-earth tris-complexes with ionic radii (Å) showing the effect of lanthanide contraction.

Thin layer chromatography. Daneels has separated Sm, Eu, Gd and Tb by this technique using Silica gel II- Radioactive traces were used to detect the rare-earths. The R_f values for Sm, Eu, Gd and Tb are 0.54, 0.29, 0.73 and 1.00 respectively.

Complex formation: oxalate precipitation in presence of EDTA. In the presence of complexing reagent namely ethylene diamine tetra-acetic acid (EDTA), J.K. Marsh (1950-51) has been able to effect an efficient separation of rare-earths by precipitation as oxalates. Lanthanide oxalates are insoluble in water, but they can be dissolved by complexing with EDTA.

Properties of lanthanides

1. Position in the Periodic Table

➤ Properties of the elements depend on the electronic configuration of the outer most shell (5d and 6s in case of lanthanides). In lanthanides electrons are added in 4f orbital which is embedded in the interior of the atom while outer most orbitals are same in lanthanides. That is why these elements have similar properties.

➤ Atomic number of these elements lie between those of Ba (56) and Hf (72). Therefore these elements should be placed between Ba and Hf.

➤ Moreover these elements exhibit similar properties and should be placed in the same group. In doing so different elements will fall below one another which will jeopardize the main purpose of the periodic table.

➤ That is why Lanthanides have been placed below the main body of the periodic table in the form of a series.

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PREPARATION OF THE METALS

Because of the ease of oxidation of these metals it is not a simple task to obtain the elements in the metallic state. The following methods may be used for the preparation of metals:

(i) Thermal decomposition of lanthanide-mercury amalgam.

Using a mercury cathode an amalgam of the lanthanides may be prepared by the electrolysis of aqueous solutions. The amalgam thus formed is thermally decomposed to get the metals in a finely divided state, but complete elimination of mercury is difficult.

(ii) Electrolysis of fused chlorides. The anhydrous lanthanide

(+3) chlorides are fused with sodium, potassium or calcium chloride by external heating and the molten mass is electrolysed in an iron pot or in a refractory lined pot which serves as the anode. Graphite cathodes are used. The molten metal collects as a pool at the bottom of the pot from where it is withdrawn and cast into 'ingots.

This method does not give the metals in high degree of purity required in modern technology

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(iii) Metallothermic reduction of the salts.

In this method the anhydrous fluorides and chlorides of lanthanides are reduced with calcium in a tantalum container at about 1000°C. Calcium is volatilised from the lanthanide-calcium alloy. This method is successful for all the lanthanides except Sm, Eu and Yb because these metals form stable divalent fluorides. However these metals can be prepared by reducing their oxides with lanthanum metal at 1400°C in vacuum and distilling out Sm, Eu and Yb. These metals are more volatile than lanthanum. The metals can be purified by vacuum distillation (pressure 10^{-6} mm Hg) in tantalum apparatus.

GENERAL PROPERTIES OF LANTHANIDES

Some of the important properties of lanthanides are discussed here.

(1) Electronic Configuration

In Ba_{56} 6s-orbital is completely filled ($Ba_{56} [Xe] 6s^2$) and at La_{57} 5d-orbital is singly occupied ($La_{57} [Xe] 5d^1 6s^2$). But after La_{57} , further filling of 5d-orbitals is discontinued. As the nuclear charge increases by one unit from La_{57} to Ce_{58} , 4f-orbitals which were higher in energy up to La_{57} fall slightly below the 5d level. 4f-orbitals, therefore, begin to fill and are completely filled up to Lu_{71} before the filling of 5d-orbitals is resumed.

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Electronic Configuration of Lanthanides

	Atomic Number	Symbol	Element	Electronic Configuration	Probable Electronic Configuration
Stable	57	La	Lanthanum	$[Xe]4f^0 5d^1 6s^2$	
Empty	58	Ce	Cerium	$[Xe]4f^1, 5d^1 6s^2$	$[Xe]4f^2, 5d^0 6s^2$
	59	Pr	Praseodymium	$[Xe]4f^2, 5d^1 6s^2$	$[Xe]4f^3, 5d^0 6s^2$
	60	Nd	Neodymium	$[Xe]4f^3, 5d^1 6s^2$	$[Xe]4f^4, 5d^0 6s^2$
	61	Pm	Promethium	$[Xe]4f^4, 5d^1 6s^2$	$[Xe]4f^5, 5d^0 6s^2$
	62	Sm	Samarium	$[Xe]4f^5, 5d^1 6s^2$	$[Xe]4f^6, 5d^0 6s^2$
	63	Eu	Europium	$[Xe]4f^6, 5d^1, 6s^2$	$[Xe]4f^7, 5d^0 6s^2$
Stable	64	Gd	Gadolinium	$[Xe]4f^7, 5d^1, 6s^2$	$[Xe]4f^7, 5d^1 6s^2$
Half filled	65	Tb	Terbium	$[Xe]4f^7, 5d^1, 6s^2$	$[Xe]4f^9, 5d^0 6s^2$
	66	Dy	Dyspromium	$[Xe]4f^9, 5d^1, 6s^2$	$[Xe]4f^{10}, 5d^0 6s^2$
	67	Ho	Holmium	$[Xe]4f^{10}, 5d^1, 6s^2$	$[Xe]4f^{11}, 5d^0 6s^2$
	68	Er	Erbium	$[Xe]4f^{11}, 5d^1, 6s^2$	$[Xe]4f^{12}, 5d^0 6s^2$
	69	Tm	Thulium	$[Xe]4f^{12}, 5d^1, 6s^2$	$[Xe]4f^{13}, 5d^0 6s^2$
Stable	70	Yb	Ytterium	$[Xe]4f^{13}, 5d^1, 6s^2$	$[Xe]4f^{14}, 5d^0 6s^2$
Filled	71	Lu	Lutetium	$[Xe]4f^{14}, 5d^1, 6s^2$	$[Xe]4f^{14}, 5d^1 6s^2$

Electronic configurations of lanthanides are shown in Table. From this table the following points may be noted:

- The complete electronic configuration of lanthanides can be represented by a general configuration viz., $2, 8, 18, 4s^2 p^6 d^{10} f^{0,2, \dots, 14} 5s^2 p^6 d^0 \text{ or } 1, 6s^2$ (including La) which shows that the valence-shell configuration can be represented a $4f^{0,2, \dots, 14}, 5d^0 \text{ or } 1 6s^2$. The valence-shell configuration indicates that the additional electron enters the 4f-orbital without altering the electrons in the outermost 6s-orbital.
- The filling of 4f-orbitals is not regular, e.g., the additional electron in Gd_{64} does not enter 4f-level but, instead, it goes to 5d level. This is because the 4f and 5d orbitals in Gd are at about the same energy level and Gd atom has a tendency to retain the configuration with half-filled 4f-orbitals which are relatively more stable.

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Oxidation States

+3 Oxidation state: The chemistry of Lanthanides is virtually the chemistry of +3 oxidation state. The hydroxides are precipitated from aqueous solution by NH_4OH as gelatinous $\text{M}(\text{OH})_3$. These are basic in nature and the basicity decreases with the decrease in ionic radii from Ce to Lu. The anhydrous halides MX_3 and oxides M_2O_3 are also known.

+4 and +2 oxidation states: These oxidation states are shown by those elements which by doing so attain f^0 , f^7 and f^{14} configurations. The +4 state is known only for cerium which acquires the $[\text{Xe}] 4f^0$ configuration and the common compounds are CeO_2 , CeF_4 , and $\text{Ce}(\text{SO}_4)_2$ and Ceric ammonium nitrate $(\text{NH}_4)_2 [\text{Ce}(\text{NO}_3)_6]$. Similarly the most stable divalent state is shown by Europium and ytterbium which acquire the $[\text{Xe}]4f^7$ and $[\text{Xe}]4f^{14}$ configuration and are known in the form of sulphates (MSO_4) and Carbonates MCO_3 .

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Oxidation states

The sum of the first three ionization energies corresponding to the loss of both 6s and the solitary 5d electrons are comparatively low ranging from 5.9 for La to 5.0 for Lu and hence the elements are distinctly electro positive and ionic. The +3 state is the characteristic for all Lanthanides in the solid as well as solution state while for some as cerium the +4 state is also recognized. The M^{2+} ion also occurs but is less stable than +3. The most stable M^{2+} and M^{4+} ions are those with configuration f^0 , f^7 and f^{14} corresponding to empty, half filled and filled f shells. The configuration of La^{3+} is the same as that of xenon and hence a higher oxidation state for Lanthanum is not possible.

+3 Oxidation state: +3 is the most common oxidation state in the lanthanides. The hydroxides are precipitated from aqueous solution by NH_4OH as gelatinous $\text{M}(\text{OH})_3$. These are basic in nature and the basicity decreases with the decrease in ionic radii from Ce to Lu. The anhydrous halides MX_3 and oxides M_2O_3 are also known.

+4 and +2 oxidation states: These oxidation states are exhibited by those elements which by doing so attain f^0 , f^7 and f^{14} configuration. The +4 state is known only for cerium which acquires the $[\text{Xe}] 4f^0$ configuration and the common compounds are CeO_2 , CeF_4 and $\text{Ce}(\text{SO}_4)_2$ and Ceric ammonium nitrate $(\text{NH}_4)_2 [\text{Ce}(\text{NO}_3)_6]$. Similarly the most stable divalent state is shown by Europium and ytterbium which acquire the $[\text{Xe}]4f^7$ and $[\text{Xe}]4f^{14}$ configuration and are known in the form of sulphates (MSO_4) and carbonates MCO_3 .

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Oxidation Potential

The values for the standard oxidation potential of some Lanthanides are given in the following table and it is indicated that each element is a strong reducing agent in acidic medium and gives M^{3+} ion. The ions with empty and half filled shells show more stability. These values indicate that in acidic solution each of the Lanthanides is a powerful reducing agent and yields tripositive ion readily.

Oxidation Potentials			
Element	E^0 at 25°C	Element	E^0 at 25°C
Y	+ 2.40	Eu	+ 2.43
La	+ 2.39	Gd	+ 2.40
Ce	+ 2.48	Tb	+ 2.39
Pr	+ 2.47	Dy	+ 2.32
Nd	+ 2.44	Ho	+ 2.32
Pm	+ 2.42	Er	+ 2.30
Sm	+ 2.41	Yb	+ 2.27
		Lu	+ 2.25

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Magnetic Properties

Lanthanides differ appreciably from transition elements in their magnetic properties, and this is because the 4f electron is well shielded from external fields by the 5s² and 5p⁶ orbitals. Magnetic moment can be calculate by using formula $\mu_{IS} = \sqrt{n(n+2)}$

In Lanthanides the magnetic behaviour is different. The ions La³⁺, Lu³⁺ are diamagnetic due to their closed shell Configurations and absence of unpaired electrons. The other ions contain unpaired 4f electrons and exhibit paramagnetism and the values are given in Table.

Magnetic Moments of M³⁺ Ions

M ³⁺ ion	μ_B Experimental	μ_B Theoretical	M ³⁺ ion	μ_B experimental	μ_B Theoretical
La	0.00	0.00	Gd	7.00-8.00	7.94
Ce	2.54	2.54	Tb	9.50-9.80	9.72
Pr	3.40-3.60	3.58	Dy	10.40-10.60	10.65
Nd	3.50-3.60	3.62	Ho	10.40-10.60	10.60
Pm	—	2.68	Er	9.40-9.10	9.56
Sm	1.40-1.70	1.60	Yb	4.30-4.90	7.56
Eu	3.30-3.50	3.60	Lu	0.00	0.00 ³¹

Bonding

The ground state electronic configuration of given Ln^{x+} compounds shows the bonding to be primarily ionic with very little covalent character. The binary halides show properties characteristic of ionic compounds like high melting and boiling points and dissolving in polar solvents to give conducting solutions, while with an increase in anionic charge, the electrostatic interactions decrease and hence these properties are not characteristic of oxides, phosphates or chromates. The covalency is exhibited in those complexes which are derived from strong chelating ligands and those ligands which can participate in back bending through π -interactions.

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Complex Formation

Lanthanide ions have comparatively little tendency to form complexes. The most obvious differences as compared to d block elements are:

- (i) Unavailability of f orbitals for forming hybrid orbitals which is due to high shielding of inner 4f orbitals by other orbitals as a consequence of which f-orbitals can not make contact with ligand orbitals. Any involvement of metal ion orbitals is thus restricted to higher energy orbitals and thus the ligand field stabilization is small (1k cal/mole)
- (ii) The lanthanide ions are larger as compared to transition metal ions and thus covalent interaction with ligands is minimized and electrostatic forces of attraction are lowered.

The net result is that in comparison to d-block elements Lanthanides form fewer complexes with different properties.

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Most of the solid and solution complexes are derived from oxygen donors while other atoms are found to act as very weak donors. Thus ammine complexes are easily decomposed by adding water, while weakly basic amines do not react. Ethylene diamine reacts readily forming complexes of type- $[\text{Ln}(\text{en})_3]^{3+}$ in which Ln – N bond is of moderate strength. The chelates of o-phenanthroline (phen) and 2, 2'-bipyridyl of type $[\text{Ln}(\text{L})_3]$ are known. The other donor atoms like S, Se, P, As can bind to Lanthanides under zero minimal competition but definite data are not available. Many of complexes have coordinated anions and species such as $\text{Ln}(\text{NO}_3)_2^{2+}$ and $\text{Ln}(\text{SO}_4)_2^{2+}$ are known. A variety of nitro and carbonate complexes have been isolated. Halo complexes are also known.

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Coordination Chemistry and Stereochemistry

The geometrical shapes of complexes both in crystalline state as well as in solution are of importance in understanding the detailed Chemistry of Lanthanides. The stereo chemistry of Ln^{3+} complexes can be established with the help of diffraction methods. There is no major difference between simple salts and Coordination complexes in terms of the number of close neighbours i.e., coordination number for the given Ln^{3+} ion and geometry. The aqueous Chemistry is more complex due to unknown degree of coordination of water. The coordination number of Ln^{3+} ion is rarely 6 and larger coordination numbers are a rule rather than exception, due to increased space available around these larger cations. The main coordination numbers and geometries encountered are summarized below:

(a) **Coordination number 6:** Six coordination with octahedral geometry is encountered for $[\text{Ln} \text{X}_6]^{3-}$ (X = Cl, Br); triphenyl phosphonium salts and anions $[\text{Ln}(\text{NCS})_6]^{3-}$

(b) **Coordination number 7:** Known among these are LnO_7 with a mono capped octahedral geometry, and $[\text{TbF}_7]^{3-}$ with pentagonal bipyramidal geometry. Other $[\text{LnF}_7]^{3-}$ ions are known but their structures have not been established.

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(c) **Coordination number 8:** This is a characteristic of the large Lanthanide ions. The species $[\text{Ln}(\text{H}_2\text{O})_8]^{3+}$ and $[(\text{NH}_4)_2\text{CeF}_8]$ possess square antiprismatic arrangement. The other examples are $\text{LnI}_3 \cdot 8\text{DMF}$ (DMF = N,N-dimethyl formamide); $\text{Ln}(\text{ClO}_4)_3 \cdot 8\text{DMA}$ (DMA = N,N-dimethylacetamide and $[(\text{Lnlen})_4] \text{X}_4$ (en = ethylenediamine).

(d) **Coordination number 9:** This is most common for higher Lanthanide ions and is known for $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$ with a symmetrical tricapped trigonal prism structure. The other examples are $[\text{Ln}(\text{EDTA})(\text{H}_2\text{O})_3]$ (EDTA : Ethylene Diamine, N,N,N,N-Tetracetate) with a quasi dodecahedral geometry.

(e) **Coordination number 10:** This is restricted only to 3+ ions. The structural data are available for only two compounds $[\text{La}(\text{EDTA})(\text{H}_2\text{O})_4]$ and $[\text{La}(\text{bip})_2(\text{NO}_3)_2]$ which possess dodecahedral geometry.

(f) **Coordination number 12:** The compound $\text{Ln}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ and the double salt $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ have a slightly distorted icosahedral arrangement of 12 oxygen atoms. The same type of structure is found in compound $[\text{Co}(\text{NO}_3)_6]^{4-}$.

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Colours

The colours which are observed for compounds of lanthanides are due to the absorption and emission of light of visible wave length. A remarkable periodicity in the colour of trivalent Lanthanides has been given by Smith and is called Smith colour scheme. If the ions are arranged in the order of atomic numbers the colour of elements containing xf electrons is about the same as those with $(14-x)f$ electrons and this shows that $4f$ orbitals are the main cause of colour. The absorptions bands in Lanthanides or colours arise from the transition of electrons from a lower $4f$ orbital to higher $4f$ orbital and are called f-f transition. As clear from Table , colour depends upon number of f electrons. The ion having n electrons in $4f$ orbital has the same colour as an ion having $14-n$ electrons in $4f$ orbital. For e.g., La^{3+} which has zero electrons in the $4f$ orbital is colourless and similarly Lu^{3+} which has $(14 - 0) = 14$ electrons in $4f$ orbital is also colourless. Similarly Pr^{3+} has two $4f$ electrons while Tm^{3+} has $14 - 2 =$ twelve $4f$ electrons and the two exhibit almost the same colour which is green. But this scheme is not always rigidly followed as Ce^{4+} has orange colour.

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Colours of Lanthanide ions

Trivalent ion	No. of $4f$ electrons	Colour	Trivalent ion	No. of $4f$ electrons	Colour
La^{3+}	0	Colourless	Lu^{3+}	14	Colourless
Ce^{3+}	1	Colourless	Yb^{3+}	13	Colourless
Pr^{3+}	2	Green	Tm^{3+}	12	Pale green
Nd^{3+}	3	Bright pink	Er^{3+}	11	Pink
Pm^{3+}	4	Pink	Ho^{3+}	10	Pink
Sm^{3+}	5	Yellow	Ho^{3+}	10	Pink
Eu^{3+}	6	Pale pink	Dy^{3+}	9	Yellow
Gd^{3+}	7	Colourless	Tb^{3+}	8	Pale pink

The colours are a consequence of absorption of light and the corresponding transitions among the f orbitals called f-f transition. Because the f orbitals are very well shielded from the surrounding $5s$ and $5p$ orbitals the broadening effect due to ligand vibrations is kept to a minimum and the bands are pencil sharp. It is also noted that in contrast to transition metals where colours depend upon ligands in lanthanides there is no major effect of ligands on colours, since the f orbitals are so well deep inside the ion that the environmental factors are unable to affect the transition. However the intensities of the bands are found to depend upon the nature of coordinated ligand.

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Chemistry of +3 state

In general, the lanthanides behave as active metals. Their electrode potential values are comparable to those of alkaline earths. All the metals act as strong reducing agents. They are all attacked by acids with the liberation of hydrogen. The metals dissolve slowly in cold but more rapidly in warm water and liberate hydrogen. They absorb hydrogen to form interstitial hydrides. Nearly all known anions form the compounds with Ln^{3+} cation. These compounds are stable in solid as well as in solution state. Compounds of Ln^{3+} cation with the anions such as OH^- , CO_3^{2-} , SO_4^{2-} , $C_2O_4^{2-}$, NO_3^- etc, decompose on heating, give first basic salts and finally oxides. Hydrated salts that Cl^- , F^- , normally stable anions such as P^- , Cl^- , Br^- , IO_3^- etc. also give similar products on heating because of hydrolysis.

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Atomic (covalent) Radii (in Å) of the elements preceding and following lanthanides.

Transition series	III B	IV B	V B	VI B	VII B	VIII	IX	X	IB	II B	
First	Sc ₂₁ 1.44	Ti 1.32	V 1.22	Cr 1.18	Mn 1.17	Fe 1.17	Co 1.16	Ni 1.15	Cu 1.17	Zn ₃₀ 1.25	
Second	Y ₃₉ 1.62	Zr ₄₀ 1.45	Nb 1.34	Mo 1.30	Tc 1.27	Ru 1.25	Rh 1.25	Pd 1.28	Ag 1.34	Cd ₄₈ 1.48	
Third	La ₅₇ 1.69	Ce ₅₈ –Lu ₇₁ 1.65 1.45 14 Lanthanides	Hf ₇₂ 1.44	Ta 1.34	W 1.30	Re 1.28	Os 1.26	Ir 1.27	Pt 1.30	Au 1.34	Hg ₈₀ 1.49

If we compare the covalent radii values of the elements of the second transition series with those of the third series, we find that the normal increase in the covalent radii values from Sc₂₁ to Y₃₉ at La₅₇ disappears after lanthanides and the pairs of elements: Zr–Hf, Nb–Ta, , Ag–Au, Cd–Hg possess almost same values. If the fourteen lanthanides had not been intervened between La₅₇ and Hf₇₂, the value of covalent radius, for example, of Hf₇₂ should have been greater than that of Zr₄₀ since Zr and Hf both are in the same subgroup IV.B and Zr lies immediately above Hf. The occurrence of lanthanide contraction cancels the expected increase in the covalent radius value from Zr to Hf. This situation is also with other pairs of elements in the second and third series of transitional elements.

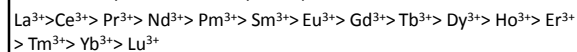
Since the pairs of elements of second and third transition series, occurring after lanthanides, (e.g. Zr–Hf, Nb–Ta etc. pairs) have almost similar size (which is due to lanthanide contraction), they are much more close to one another in properties than do the pairs of elements of first and second transition series, e.g., solubilities of their salts are very much similar to one another.

(b) High density of post-lanthanide elements.

Because of lanthanide contraction the atomic sizes of the post-lanthanide elements become very small. Consequently the packing of atoms in their metallic crystals become so much compact that their densities are very high. Thus, while the densities of the elements of second transition series are only slightly higher than those of the elements of first series, the densities of the elements of third transition series are almost double to those of the elements of second transition series.

(ii) Basic character of oxides, Ln₂O₃ and hydroxides, Ln(OH)₃

The chemical properties of an element or an ion depend on the size of the atom or ion. The greater the atomic or ionic radius, greater is the ease with which the species (i.e. atom or ion) will lose electrons. Thus the ease with which a species loses electrons is the measure of the basicity of the species. Basicity decreases as the ionic radius decreases. Thus, basicity of Ln³⁺ ions may be expected to decrease in the order:



These differences in basicity are reflected in:

- thermal decomposition of oxy-salts, e.g., more basic oxy-salt decompose with difficulty
- hydrolysis of ions: More basic ions hydrolyze less readily
- solubilities of salts
- formation of complexes
- metals with increasing atomic number are difficult to oxidize - oxidation potential for the couple Ln → Ln³⁺ + 3e⁻ regularly goes on decreasing.

Due to lanthanide contraction the decrease in size of Ln^{3+} ions from La^{3+} to Lu^{3+} increases the covalent character (*i.e.* decreases the ionic character) between Ln^{3+} and OH^- ions in $\text{Ln}(\text{OH})_3$ hydroxides (*Fajans rules*). Thus $\text{La}(\text{OH})_3$ is the most basic while $\text{Lu}(\text{OH})_3$ is the least basic. Similarly there is a decrease in the basic strength of the oxides, Ln_2O_3 with the increase of atomic number of Ln atom.

(iii) *Small variation in the properties on account of lanthanide contraction* allows the separation of lanthanides by the methods based on fractional crystallization and basicity differences.

(iv) **Occurrence of Y with heavy lanthanides.** The crystal radii of Y^{3+} and Er^{3+} are equal ($\text{Y}^{3+} = 0.93 \text{ \AA}$ and $\text{Er}^{3+} = 0.96 \text{ \AA}$). This similarity in ionic size of these two cations coupled with the equality in ionic charge (= +3 in both the ions) accounts for the invariable occurrence of Y with heavier lanthanides. The marked similarities in the crystal structure, chemical properties and solubility between yttrium compounds and the corresponding ones of the heavier lanthanides make it difficult to separate yttrium from the heavier lanthanides. It is because of these similarities that yttrium is regarded for all practical purposes as a member of lanthanide series.

Uses of lanthanides

The following are some of the important uses of the lanthanides:

- (i) Due to their extremely reducing nature these are used in metallo-thermic reactions. Lanthanide-thermic processes can yield sufficiently pure Nb, Zr, Fe, Co, Ni, Mn, Y, W, U, and Si. These are used also as deoxidizing agents in the manufacture of copper and its alloys.
- (ii) These are used as Catalysts in hydrogenation and dehydrogenation reactions, in Ceramics for polishing glass.
- (iii) Cerium sulphide (CeS) is used for making special kind of crucibles meant for melting metals at a temperature of 1800°C .
- (iv) Ceric salts are used in Volumetric analysis for the estimation of hydrogen peroxide, nitrites and iodides.
- (v) Lanthanides and their compounds are also used as nuclear fuel control, shielding and fixing devices. Pr^{147} is used in the production of battery.
- (vi) Uses of mish-metals. Alloys of lanthanides are known as *mish-metals*. The major constituents of mish-metals are Ce (45- 50%), La (25%), Nd (5%) and small quantities of other lanthanide metals and Fe and Ca impurities. Mish-metals are used for the production of different brands of steel like heat resistant, stainless and instrumental steels. The addition of 0.75% of mish-metal to steel raises its yield point and its workability in heated state and improves its resistance to oxidation. Misch metal is an excellent scavenger for adsorbed oxygen and sulphur in metallurgy. Mg-alloys containing about 30% misch metal and 1% Zr are useful in making parts of jet engine. When alloyed with 30% iron, it is sufficiently pyrophoric to be useful in lighter flints.

(B) Uses of the Lanthanide Compounds

(a) Non-nuclear applications. The following uses are important.

- (i) Ceramic applications. CeO_2 , La_2O_3 , Nd_2O_3 and Pr_2O_3 are widely used for decolorizing glass. Approximately 1% CeO_2 is used in the manufacture of protective transparent glass blocks to be used in nuclear technology because these blocks are not affected by prolonged exposure to radiations. Because lanthanide oxides can absorb ultra-violet rays, these are used as additives in glasses for special purposes, e.g. for making (i) sun-glasses (by adding, Nd_2O_3)
- (ii) goggles for glass blowing and welding work ($\text{Nd}_2\text{O}_3 + \text{Pr}_2\text{O}_3$)
- (iii) glasses protecting eyes from neutron radiation ($\text{Gd}_2\text{O}_3 + \text{Sm}_2\text{O}_3$) etc. The addition of more than 1% CeO to a glass gives it a brown colour. Nd_2O_3 and Pr_2O_3 give respectively red and green colours. ($\text{Nd}_2\text{O}_3 + \text{Pr}_2\text{O}_3$) gives a blue colour.
- (iv) Refractories. CeS (*m.p.* 2000°C) is used in the manufacture of a special type of crucibles which are used for melting metals in a reducing atmosphere at temperatures up to 1800°C . Borides, carbides and nitrides of lanthanides are also used as refractories.
- (v) Abrasives. Lanthanide oxides are used as abrasives for polishing glasses, e.g. the mixture of oxides, CeO_2 (47% $\text{La}_2\text{O}_3 + \text{Nd}_2\text{O}_3 + \text{Pr}_2\text{O}_3$ (51%)+ SiO_2 , CaF_2), Fe_2O_3 etc. (2%) which is called polfrit has been used for polishing glasses.
- (vi) Paints. Lanthanide compounds are used in the manufacture of lakes, dyes and paints for porcelain, e.g. cerium molybdate gives light yellow colour, cerium tungstate gives greenish blue colour and salts of Nd give red colour.

(v) **In textiles and leather industries.** Ceric salts are used for dyeing in textile industries and as tanning agents in leather industries. $\text{Ce}(\text{NO}_3)_4$ is used as a mordant for alizarin dyes. Chlorides and acetates of lanthanides make the fabrics water-proof and acid resistant.

(vi) **In medicine and agriculture.** Dimals which are salicylates of Pr and Nd are used as germicides. Cerium salts are used for the treatment of vomiting and sea-sickness. Salts of Er and Ce increase the red-blood corpuscles and haemoglobin content of blood. In agriculture lanthanide compounds are used as insecto-fungicides and as trace elements in fertilizers.

(vii) **In lamps.** Salts of La, Ce, Eu and Sm are used as activators of luminophores. They are used in the manufacture of gas mantles, in the coatings of luminescent lamps and for painting the screens of cathode-ray tubes.

(viii) **In analytical chemistry.** $\text{Ce}(\text{SO}_4)_2$ is used as an oxidizing agent in volumetric titrations. Radio-isotopes of lanthanides (e.g. La_{140} , Ce_{142} , Tb_{160} etc.) are used in the study of co-precipitation, chromatographic separations etc.

(ix) **Catalytic applications.** Certain compounds of lanthanides are employed for the hydrogenation, dehydrogenation and oxidation of various organic compounds. Cerium phosphate finds use as a catalyst in petroleum cracking.

(x) **Electronic applications.** Ferrimagnetic garnets of the type $3\text{Ln}_2\text{O}_3 \cdot 5\text{Fe}_2\text{O}_3$ are employed in microwave devices.

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(b) Nuclear applications

Lanthanide elements and their compounds find many important nuclear uses, e.g., in nuclear fuel control, shielding and fluxing devices. Pr^{147} is used in the production of atomic battery.

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