A LANTHANIDE LANTHOLOGY

Part 1, A - L

Anthology :

> *a collection of selected written works usually with a common theme*

> hence, by extension

Lanthology :

> *a collection of notes concerning the lanthanides and related elements*

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A
LANTHANIDE
LANTHOLOGY

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PREFACE

The lanthanide elements, usually lost in an appendage to all periodic table charts, have an ever-growing variety of applications in modem technology. Along with their congener yttrium they provide many an industry with crucial materials, they provide many a customer with benefits.

The physical and chemical properties of these elements, and of their derivatives, contribute essential functions to a range of modern-day materials. Furthermore, researchers - academic and industrial - continue to uncover new possibilities through a deeper understanding of those properties. Ideas move into applications.

This lanthology :

- intends to inform but not to tell a story,

- hopes to educate but is not a text book,

- aims to be a quick-reference work but not a basic-reference tome,

- emphasizes starting materials rather than ultimate products,

- mentions briefly end-uses but does not discuss detailed applications.

This booklet is laid out as a collection of notes, alphabetically ordered, of differing lengths and detail, on a selection of topics covering the sources, production, nature and uses of lanthanide chemicals.

> Within each note, at the first mention of another topic also covered in the Lanthology, a **bold-faced entry** will cross-refer to that other entry.

In some cases those items will be found in a later booklet covering the second half of the alphabet, M to Z.

The notes emphasize the properties underlying practical technological applications of these materials. Each individual item contains its own separate footnote references that will provide deeper information; these reference listings are not comprehensive but are intended for guidance. We have attempted to select recent references whenever possible.

As a whole this brochure hopes to fit between the multi-volume basic literature reference series and the small pocket-size reference work that conveys but few facts.

This publication arises from a collection of information about the commercial production, physical and chemical properties as well as actual and potential industrial uses of the lanthanides in all their forms

ABUNDANCE

Crustal Abundance		
Z	Ln	ppm
39	Y	33
57	La	30
58	Ce	60
59	Pr	8.2
60	Nd	28
61	Pm	0
62	Sm	6
63	Eu	1.2
64	Gd	5.4
65	Tb	0.9
66	Dy	3.0
67	Ho	1.2
68	Er	2.8
69	Tm	0.5
70	Yb	3
71	Lu	0.5

Any estimate of the average concentration (or abundance) of individual elements in the earth's crust must of course be a gross approximation based on major assumptions. Several attempts have been made that are in reasonable agreement with one another. The table[l], where Z is the atomic number, reports for all the lanthanides and yttrium their estimated elemental abundance in parts per million.

One feature of the abundance pattern deserves emphasis. There is an *odd-even* relationship seen throughout the periodic table with elements with even atomic numbers being usually more abundant than their odd-numbered neighbors. This feature, the Oddo-Harkins rule, is strongly evident within the lanthanide series. **Cerium,** for example, Z = 58, the second member of the series is more abundant than **lanthanum,** Z = 57; cerium is as plentiful in the earth's crust as nickel or copper.

The least abundant lanthanides, **thulium** and **lutetium,** (with odd atomic numbers) are more abundant than silver or bismuth. The extreme case of this odd/even factor is element 61, Promethium, which does not occur in nature, i.e. zero abundance, as it has no stable isotopes.

Solar System Abundance		
w.r.t. 10^7 atoms Si		
Z	Ln	Atoms
39	Y	46
57	La	4.5
58	Ce	12
59	Pr	1.7
60	Nd	8.5
61	Pm	0
62	Sm	2.5
63	Eu	1.0
64	Gd	3.3
65	Tb	0.6
66	Dy	3.9
67	Ho	0.9
68	Er	2.5
69	Tm	0.4
70	Yb	2.4
71	Lu	0.4

[1] Abundances of Chemical Elements in the Continental Crust: a New Table; S.R.Taylor, Geochim. Cosmochim. Acta, 1964, 28, 1273

Averaged distribution within the earth's crust is but a modified reflection of inherent solar system abundance[2]. (This second table listing is on an *atom* basis whereas the first is on a *weight* ppm basis.) Geochemical processes can only improve on those inherent solar patterns. When solar system and crustal patterns are compared there is a distinction between the light and heavy groupings; here the label "light" is taken to refer to La to Gd and "heavy" to Tb to Lu.

The lighter lanthanides, when compared with their heavy analogues, have an enhanced distribution in the crust. This crustal enrichment relative to the mantle is most pronounced for Lanthanum and tails off relatively smoothly towards Lutetium, the last member of the series. The light lanthanides are thus significantly more abundant than the heavies. Furthermore, apart from anomalies occasionally found for cerium and **europium** due to the stability of *non*-trivalent ions, there has been essentially no gross modification of relative *individual* lanthanide abundances.

Yttrium behaves as the prototype heavy lanthanide, a consequence of its ionic size and chemical behavior. In terms of its chemistry it usually fits between **Dysprosium**, 66, and **Holmium,** 67. Furthermore, being inherently more abundant than individual heavy lanthanides, the minerals that supply Yttrium, e.g. Xenotime and **ion-adsorption ores**, will also be resources for the heavy Ln elements.

For potential users considering commercial availability the implication is that - if at all possible - an even numbered element, and preferably one of the earlier light lanthanides, should be chosen. In addition the most economical material could well be a mixed-light-lanthanide derivative (containing La, Ce, Pr and Nd) rather than a single element compound.

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see entries **Bastnasite; Cerium Concentrate; Concentrates, Mixed-Lanthanide Compounds; lanthanum Concentrate; Monazite** *and* **Resources** for *more information on mixed-lanthanide derivatives.*

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[2] Solar-system Abundances of the Elements, E.Anders and M.Ebihara, Geochim. Cosmochim. Acta, 1982, 46, 2363

ACETATES

The acetates of the lanthanide elements can be prepared by dissolving the appropriate **oxide,** or **carbonate,** in strong acetic acid. The carbonate will dissolve much more readily but will cause foaming. The ease with which the oxides react will depend on the reactivity of the solid phase and, as is usually the case, the oxides with the C-type structure (Y, Gd to Lu) or with tetravalent species present (Ce, Pr and Tb) are noticeably less reactive. When drying to obtain solids avoid over drying as this can produce stable basic acetates (oxyacetates), see TGA information below.

ACETATES
$Ln(CH_3COO)_3.nH_2O$

Ln	$n.H_2O$ Cryst	Form. Wt	% H_2O	Ln oxide%	% element	color
Y	4	338.1	21.3	33.4	26.3	----
La	1 ½	343.1	7.9	47.5	40.5	----
Ce	1 ½	344.3	7.8	50.0	40.7	----
Pr	3	372.1	14.5	45.8	37.9	green
Nd	3	375.4	14.4	44.8	38.4	lilac
Sm	3	381.5	14.2	45.7	39.4	cream
Eu	4	401.2	17.9	43.8	37.9	rose
Gd	4	406.4	17.7	44.6	38.7	----
Tb	4	408.1	17.6	45.8	38.9	----
Dy	4	411.7	17.5	45.3	39.5	cream
Ho	4	414.3	17.4	45.6	39.8	cream
Er	4	416.5	17.3	45.9	40.2	pink
Tm	4	418.1	17.2	46.1	40.4	pale-green
Yb	4	423.2	17.0	46.6	40.9	----
Lu	4	424.2	17.0	46.9	41.2	----

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From solution various hydrated salts can be crystallized out. In addition to those compounds listed salts with other degrees of hydration are known for many of the elements. **Neodymium**, for example, is reported to form hydrates with 4, 3, 2, 1½ or 1 waters of crystallization; anhydrous salts are also possible. Consequently, when prepared on a commercial scale where the extent of drying is determined by economic considerations, the measured degree of hydration may well not correspond to a recognized compound nor to an integral number of water molecules.

The degree of hydration varies along the Ln series and is associated with structural changes in coordination geometry around the lanthanide atom as that atom becomes smaller on moving from La to Lu[1]. There is considerable flexibility in potential structural arrangements because the acetate ion may be monodentate, bidentate, or bridging. The coordination of the central Lanthanide ion varies from ≈9, with La, down through 8 for Nd, to ≈6 at the series end.

The lighter Ln acetates are moderately soluble in water, around 100 gms/liter, and have an *inverse* temperature solubility relationship. **Cerium** acetate, for example, at 15°C will dissolve to about 115 g/l but at 25°C the solubility falls to 100 g/l. The dissolution furthermore is exothermic and the precipitation out on warming solutions may necessitate cooling during preparative chemistry using these materials. The salts of **yttrium** and the heavy lanthanides are significantly more soluble, the yttrium salt forms a concentration of ≈100 g/l at 40°C rising to more than 300 g/l at 90°C and higher.

The acetates, on heating, decompose to the oxide. The salts initially probably lose water below ≈200° C forming lower hydrates followed by the anhydrous salt though clear steps do not necessarily appear on the TGA traces. The next stage is most likely the formation of a transient oxyacetate LnO(OAc) species although again a discrete compound is not seen.

Yttrium Acetate (TGA)

The final decomposition to the oxide will start to take place, depending on the precise Ln element, below 400° C. This relatively low temperature combined with the outgassing of innocuous carbon dioxide makes the acetates attractive precursors for the controlled preparation of inorganic compounds such as super conducting ternary oxides. A typical TGA trace for Yttrium Acetate is shown in the figure. The TGA traces for this and Ln acetates may show a tail of decomposition over the range 400° to 600° C that probably corresponds to traces of carbonate formed in the samples.
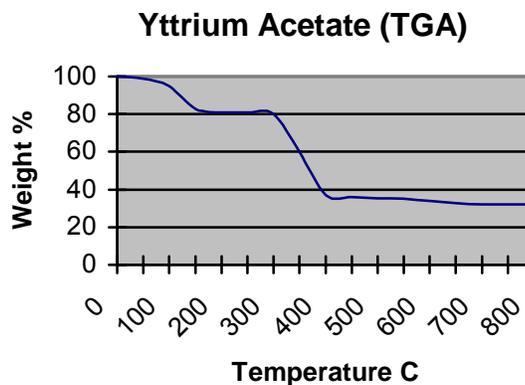
[1] Coordination of Lanthanide Acetates, D.G.Karraker, J.Inorg.NucI.Chem., 1969, 31, 2815

ALKOXIDES

The chemistry of lanthanide alkoxides has been a neglected area until recently. The steady growth, however, of research in **organo-metallic** chemistry of the Ln elements has increased interest in the alkoxides[l]. Ln alkoxides can be prepared by :

- alcohol plus Ln **metal** in the presence of an activator[2],
  the typical activator is a small amount of $HgCl_2$
- exchange between an anhydrous Ln halide and a metal alkoxide[3],
  other Ln salts, e.g. **nitrates**[4] or **carboxylates**[5], may be used

The reactions need to be carried out under anhydrous conditions and the resulting products, when isolated and characterized, rarely conform to the ideal "$Ln(OR)_3$" formula. Complex partially-substituted polymetallic alkoxides are often formed[3]. The lack of a clearly defined compound however does not prevent the subsequent use of these "alkoxides" because their reactions may well accord with the $Ln(OR)_3$ formula.

These compounds have potential, for example, :

- as reactive precursors for ultra-fine oxide powders,
- as catalysts in their own right, and
- as reagents in organic synthesis.

Metal alkoxides offer routes to oxides via the controlled hydrolysis reaction :

$$M\text{-}(O\text{-}R)_3 + H_2O \longrightarrow H\text{-}O\text{-}M\text{-}(O\text{-}R)_2 + H\text{-}O\text{-}R$$
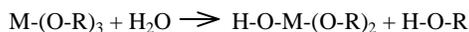
and condensation of the reactive intermediates, in a sol-gel system, to lead to the oxide.

$$H\text{-}O\text{-}M\text{-}(O\text{-}R)_2 \longrightarrow sols \longrightarrow gels \longrightarrow =M\text{-}O\text{-}M=$$
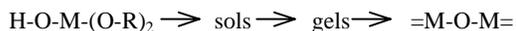
This process has potential for close control over the final product because gel microstructure determines the final oxide form be it as film, coating or ultra fine powder.

[11 Recent Advances in Alkoxo and Aryloxo Chemistry of Scandium, Yttrium and Lanthanoids, R.C.Mehrotra et al., Chem.Rev., 1991, 91, 1287
[21 Yttrium, Dysprosium and Ytterbium Alkoxides, KS.Mazdiyasni et al., U.S.Patent 3,356,703, 5-Dec-1967
[31 Synthesis and Structure of the Polyrnetallic Yttrium Alkoxide Complex […] Building Blocks in Yttrium and Lanthanide Alkoxide Chemistry, W.J.Evans, et al., J.Am.Chem.Soc., 1988, 110, 1841
[41 Process for the Preparation of Ceric Alkoxides, P.S.Gradeff and F.G.Schreiber, U.S.Patent 4,489,000 18-Dec-1984
[51 Process for the Preparation of a Rare Earth Metal Alkoxide, KKimiyoshi, S.Mitachi and Y.Ozaki, U.S.Patent 4,507,245 26-Mar-1985

ALUMINATES, ALUMINUM OXIDES

The label "aluminate" here refers to compounds and related materials in the system Ln/Al/O. This section also discusses the property modifications conferred on various aluminas, aluminum oxides, by the deliberate addition of lanthanides.

Within the Ln_2O_3/Al_2O_3 phase diagram several compounds have been identified[l], their relative stability depending on which individual lanthanide is present. (In addition to those phases listed, other less-stable compounds are known.) Some of the materials remain single-phase from ambient temperature up to their melting points.

$Ln_2O_3:Al_2O_3$ Compounds

Formula	Oxide Ratio (Abbreviation)	Structure type	Stability range
$LnAl_{11}O_{18}$	L_1A_{11}	beta-Alumina	La - Nd
$Ln_3Al_5O_{12}$	L_3A_5	Garnet	Y, Tb - Lu
$LnAlO_3$	LA	Perovskite	Y, La -≈Er
$Ln_4Al_2O_9$	L_2A	(monoclinic)	Y, Sm - Lu

$L = Ln_2O_3$ $A = Al_2O_3$

The contraction in ionic size from La down to Lu defines the stability range of a specific structure. The garnet phase, L_3A_5, for example, is only stable with the smaller (and heavier) Ln ions whereas the L_1A_{11} phase is only found for the light Ln's, La to Nd.

Published preparation techniques tend to refer to those specific materials that have commercial significance such as garnets[2]. $Ln_2O_3:Al_2O_3$ compounds can, for example, be made by:

[I] Phase Diagrams for Ceramists, publ. Am.Ceram.Soc., Vols. I to V1, 1969-1987; for Ln = La, Vol VI fig. 6438, =Ce III-4366, =Pr VI-6440, =Nd VI-6439, =Sm III-4369, =Gd III-4368, =Eu III-4367, =Er VI-6435, =Ho VI-6437, =Yb III-4371,=Y III-4370: The Al_2O_3-Nd_2O_3 Phase Diagram, J.P.Coutures, J.Am.Ceram.Soc., 1985, 68(3), 105: Coupled Thermodynamic-Phase Diagram Assessment of the Rare Earth Oxide-Aluminum Oxide Binary Systems, Ping Wu and A.D.Pelton, J.Alloys & Compounds., 1992, 179,259
[2] Controlled Nucleation for Hydrothermal Growth of Yttrium-Aluminum Garnet Powders, T.Takamori and L.D.David, Am.Ceram.Soc.Bull., 1986, 65(9), 1282 : Preparation of $Y_3Al_5O_{12}$-based Phosphor Powders, M.F.Yan et al., J.Electrochem.Soc., 1987,134(2), 493: Synthesis of Yttrium Aluminates by the Sol-gel Process, G.Gowda, J.Mat.Sc.Lett, 1986, 5, 1029

- mixing **oxides** in appropriate ratios and high temperature firing, > 1200 °C,

- mixing soluble salts, e.g. **nitrates, chlorides** or citrates, *and then*

  - co-precipitation of **hydroxides** then thermal decomposition, *or*

  - freeze-drying or spray-drying then thermal decomposition,

- salt plus **alkoxide**, sol-gel formation then low-temperature pyrolysis.

The calcination rate depends on the phase desired, e.g. $LaAlO_3$ forms relatively quickly whereas $LaAl_{11}O_{18}$ forms extremely slowly. To lower the reaction temperature, and especially if single crystals are to be grown, a low-melting flux can be added.

The **perovskites**, $LnAlO_3$, are stable high-melting materials[1][3] of possible value in refractories, catalysis and as laser hosts. The La- and Nd-aluminates are also used as substrates up on which 1,2,3-super-conducting films can be grown. The garnets, $Ln_3Al_5O_{12}$, too, are high-melting and include materials such as Y_3A_5 (YAG)[4], a laser and phosphor host and a reinforcement fiber in high temperature ceramics.

The beta-aluminas, and the related magneto-plumbite structures, can be host lattices for the newer lighting phosphors, e.g. Tb: $CeMgAl_{11}O_{19}$,[5] or for Nd lasers[6]. Retention of surface area even at > 1200 °C makes these aluminates, e.g. $LaAl_{11}O_{18}$, potential catalytically active supports for high temperature combustion.[7]

$LnAlO_3$ melting points °C	
Y	1920
La	2110
Ce	2030
Pr	2080
Nd	2090
Sm	2040
Eu	2047
Gd	2069
Tb	2040
Dy	1940
Ho	1980
Er	1963

$Ln_3Al_5O_{12}$ melting points °C	
Y	1940
Tb	1878
Dy	1916
Ho	1950
Er	1960
Tm	1980
Yb	2010
Lu	2043

[3] Stability and Thermodynamic Properties of Rare Earth Perovskites, J.-P. Coutures et al., High Temp. Sc., 1980, 13, 331

[4] The Uses and Enigmas of the Y_2O_3-Al_2O_3 Phase System, B.Cockayne, J.Less-Comm.Met., 1985, 114, 199

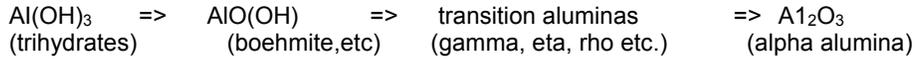[5] The Behavior of Phosphors with Aluminate Host Lattices, J.L.Sommerdijk and A.L.N.Stevels, Philips Technical Review, 1977, 37(9/10), 221

[6] Lanthanum Magnesium Aluminate (LMA) and its Derivatives ; An Example of Laser Materials Engineering, R.Collongues and D.Vivien, J.Solid State Chem., 1992, 96, 97

[7] Recent Progress in High-Temperature Combustion, H.Arai and M.Machida, Catalysis Today, 1991, 10,81

Alumina (Al_2O_3), the large volume commodity chemical, is available in many forms varying in, for example, crystalline structure, particle size and surface area. Lanthanides can modify the properties of several alumina-related materials and, in particular, the rate of transition on heating between different compounds within the Al_2O_3/H_2O system, can be changed as can the rate of sintering of alumina crystallites.

```
Al(OH)₃      =>    AlO(OH)      =>    transition aluminas        =>  A1₂O₃
(trihydrates)      (boehmite,etc)     (gamma, eta, rho etc.)         (alpha alumina)
```

Alpha-alumina, or corundum, both as a single crystal and in polycrystalline form, has exceptional mechanical properties and is used as a refractory ceramic. The addition of lanthanide derivatives have been shown to enhance the strength of high-alumina refractories. [8]

In addition this oxide forms the protective skin covering aluminum-containing structural alloys, such as MCrAlY (M = Fe,Ni,Cr)[9], when those alloys are used at elevated temperatures (up to ≈1200 °C). Trace amounts (≈0.1 wt %) of yttrium, or a lanthanide, are added to some commercial alloys to improve the adherence of the oxide scale under thermal cycling conditions. The role of the Ln or Y in the alumina skin on those FeCrAlY type alloys is believed to be to trap "tramp" sulfur, often present at ≈100 ppm levels, as a refractory **sulfide**.[10] Sulfur otherwise segregates to the metal oxide interface and destroys scale adherence.

Gamma-aluminas, and similar transition aluminas, are made by controlled firing of the hydroxy-alumina precursors and can have surface areas up to 400 sq.m./gm. They are important industrial catalyst supports needed, for example, in automobile exhaust catalytic converters. One problem in use is the loss of surface area when the defect-spinel structure sinters at ≥600 °C and at even higher temperatures, ≥1000 °C, the formation of *a*-alumina can cause a dramatic loss of surface area.

Small amounts of certain second cations, such as one of the lanthanides, readily introduced at a few mole per-cent by solution impregnation, have been found to greatly retard the sintering of the alumina.[11] Both **cerium** and **lanthanum** provide this function[12] (and other roles) in commercial auto-exhaust catalysts.[13]

[8] Thermal Properties of High Alumina Refractory Mortars modified with Lanthanide Chemical Admixtures, T.Novinson and H.F.Poppendiek, J.Composite Mat., 1988,22,177: Lanthanide Oxides and Phosphates for improving Properties of Heated Refractory Concrete, T.Novinson, U.S.Patent 4,961,786 9-October-1990
[9] A New,Wrought,Heat-Resistant Ni-Cr-Al-Fe-Y Alloy, R.B.Herchenroeder et al., J.Metals, 1983, 16
[10] A Relationship between Indigenous Impurity Elements and Protective Oxide Scale Adherence Characteristics, J.G.Smeggil et al., Met. Trans. 1986, 17A, 923

The thermal stabilization has been attributed to the formation of a stable surface $LnAlO_3$ layer[14], or alternatively a $Ln_2O_3.11Al_2O_3$ layer [15] (see *ß-alumina* below), hindering surface atomic diffusion and rearrangement from gamma to alpha alumina.

The *Beta-aluminas* form a family with subtle structural differences between members and are designated as *ß* or *ß*". These aluminas are non-stoichiometric materials that must contain, to create the specific structure, a second type of cation.

The lanthanide *ß*-alumina phase probably exists over a range of composition, L_1Al_{11-14}, and was listed above under **aluminates.** The Ln ions can serve as the needed second cation in *ß*"-aluminas and thereby form a family of solids with novel solid state properties including high lanthanide ion conductivity but negligible electronic conductivity.[16]

[11] The Influence of Lanthanum Oxide on the Thermal Stability of Gamma Alumina Catalyst Supports, H.Schaper et al., Appl. Cat., 1983, 7, 211 : Thermal Stabilization of High Surface Area Alumina, H.Schaper et al., Solid State Ionics, 1985, 16, 261 : Stabilization of Alumina by Addition of Lanthanum, B.Béguin et al., Appl.Cat., 1991, 119

[12] Application of Lanthanum to Pseudo-Boehmite and Gamma-Al_2O_3, I.I.M.Tijburg et al., J.Mat.Sci., 1991, 26, 6479 : Characterization of Lanthana / Alumina Composite Oxides, S.Subramanian et al., J.Molec.Catal., 1991, 69, 235

[13] Ceria-Promoted Three-Way Catalysts for Auto Exhaust Emission Control, G.Kim, Ind.Eng. Chem. Prod.Res.Dev., 1982, 21, 267 : Palladium-Lanthanum Catalysts for Automotive Emission Control, Ind. Eng. Chem.Prod.Res.Dev., 1986,25,202: The Role of Ceria in Three-Way Catalysts, A.F.Diwell et al., in "Catalysis and Auto. Poll. Control", ed. A.Crucq, publ. Elsevier, 1991, p. 139

[14] Thermal Stabilization of Transition Alumina by Structural Coherence with $LnAlO_3$ (Ln = La,Pr, and Nd), F.Oudet et al., J.Cat., 1988, 114, 112

[15] Preparation of Lanthanum *ß*-Alumina with High Surface Area by Coprecipitation, A.Kato et al., J.Am.Ceram.Soc., 1987,70(7), C-157

[16] The Lanthanide *ß*" Aluminas. A New Family of Fluorescent Solid Electrolytes, G.C.Farrington et al., Appl. Phys., 1983, 32A, 159: Investigations on Lanthanide-ion-exchanged *ß* and *ß*"-Alumina, F.Tietz and W.Urland, J.Alloys Comp., 1993, 192, 78

ANALYSIS

Production of derivatives of the lanthanides and yttrium needs to be supported by appropriate analytical services for both chemical content and physical parameters. Many techniques are available for chemical analysis for the lanthanide elements but the precise choice depends critically on the problem. For example the questions :

- How much **Cerium,** in per-cent, is in a **Cerium concentrate** ?

- How much **Terbium** is present in "pure" **Yttrium oxide** ?

- What trace elements are present in "pure" **Lanthanum** oxide ?

require different approaches. The methods suitable for intermediate products in solution may well be different from those used for final solid products. The chemical similarity of the lanthanides, caused by the minimal chemical differentiation attributable to the 4f electrons, often makes the older "wet-chemistry" methods less suitable. However the behavior of those very 4f electrons makes possible highly selective techniques for specific lanthanides, relying, for example, on luminescence.

Chemical Analysis

The analytical techniques available include :

- .. direct analysis; gravimetric, volumetric, etc.
- UV/VIS Ultra-violet and Visible Absorption Spectrometry
- SF Visible Luminescence/Spectrofluorimetry
- XOF X-ray Optical Fluorescence/Luminescence
- YRF X-ray Fluorescence Spectrometry
- AES Induction-coupled Plasma- or
         Direct Current- Atomic Emission Spectrometry
- MS Induction-coupled Plasma- or
       Glow Discharge- Mass Spectrometry
- AAS Atomic Absorption Spectrometry
- NAA Neutron Activation Analysis

Direct analysis, by the more-traditional non-instrumental methods, can be used for the determination of all the Ln elements together as one group. Gravimetric methods will usually include yttrium and thorium (that behaves similarly to cerium in precipitation) and may or may not also include Scandium. For example the total Ln (and Y) content of a sample can be found gravimetrically by oxalate precipitation followed by calcination to the oxide.

The similar behavior in aqueous solution of all the Ln elements does not readily permit - with one exception - the selective analysis for individual Ln's. The exception, Cerium, the predominant lanthanide and often present as a major component, can be measured, after oxidation to the Ce^{4+} state, directly by titration.

UV/VIS - Many of the Ln elements, when in solution, show narrow highly specific absorption bands in the visible and u.v. [1][2] that can be used for quantitative analysis. A variety of complexing agents, if needed, are known. The technique is low cost, the detection limits depend on the element and can with care go down to the ppm levels. Transition metals though can interfere.

SF - Luminescence, also termed fluorescence, is the emission of radiation above that due to thermal radiation. The energy is provided by an exciting source, usually of higher energy than the emission, such as a 254nm u.v. mercury arc. Certain Ln elements have a highly specific and sensitive luminescence, e.g. Cerium and Terbium can be measured at ppm levels when in solution with a non-luminescing lanthanide such as **Gadolinium.** (It is this luminescence that underlies the use of Ce and Tb in lamp phosphors.)

XOF - X-radiation, like u.v. radiation, can excite Ln luminescence in the visible "optical" region. This technology when used for analysis is almost solely restricted to the Ln series and provides a versatile analytical capability for these elements.[3] It is used, for example, for detecting many of the Ln's in solid high purity Y_2O_3, an inert matrix, at ppm levels. It obviously cannot measure non-emitting Ln atoms such as La or Lu, nor Y or Sc; in addition there is no suitable line emitted by Ce. Gd can both be analyzed for, e.g. in Y_2O_3, and also serve as the inert host, i.e. in Gd_2O_3 products.

XOF is a comparative method and, after calibration against known standards, can produce sub-ppm values. There can be subtle problems, though, such as self-quenching of the emission and experience is needed to ensure accurate results. (This type of luminescence also underlies a commercial use of Ln's - here in X-ray phosphors.)

[1] Analysis of Rare Earth Mixtures by a Recording Spectrophotometer, D.C.Stewart and D.Kato, Anal.Chem., 1958, 30(2), 164

[2] Molecular Spectroscopic Methods for the Determination of Lanthanides in Solutions, J.Georges, Spectrochim. Acta Rev., 1991, 14(5), 337

[3] Analytical Applications of X-Ray Excited Optical Fluorescence Spectra: The Internal Standard Principle, E.L.DeKalb, V.A.Fassel, T.Taniguchi and T.R.Saranathan, Analytical Chemistry, 1968,40(12), 2082: X-Ray Excited Optical Fluorescence Spectrometry. Scope of Application to Trace Rare Earth Determinations, E.L.DeKalb, A.P.D'Silva and V.A-Fassel, Analytical Chemistry, 1970, 42(9),1246: XRay Excited Optical Luminescence of the Rare Earths, A.P.D'Silva and V.A-Fassel, Ch 37 E, in Handbook Phys.Chem. Rare Earths, ed. K.A.Gschneidner and LEyring, North-Holland, 1979

XRF - X-ray Fluorescence Spectrometry, not to be confused with X-Ray optical fluorescence XOF, is widely used in analytical laboratories. The technique depends on measurement of the characteristic secondary X-rays emitted (fluoresced) during excitation by a primary X-ray beam and is best suited, as regards the Ln's, for fast approximate determinations of major and trace elements, in the fractions of per-cent to ten per-cent or so. It can be used for precursor mineral samples as well as for the semi-quantitative analysis of purer materials. With care it can be standardized to produce detection levels in the 100 - 500 ppm range.

AES - Atomic Emission Spectrometry is applicable to most of the Ln elements.[4] The development of inductively-coupled plasma and direct-current plasma excitation sources has increased the reliability and detection limits for this technique. The Ln atoms are excited at very high temperatures and the resulting atomic spectra are highly complex with thousands of lines. The precise lines used for quantitative measurements of an individual element must be chosen with care; the problem of spectral interference can be handled by current instruments by computation. Careful pre-separation of the Ln's and sample dilution are necessary. Here again experience is essential to produce reliable and reproducible results; the technology can be automated and can deliver numbers in the 5 - 10 ppm range up to the low percentages on 1 gram of sample.

MS - Mass Spectrometry, like atomic emission spectrometry, has benefited from the development of new excitation sources. IC-plasma, and more recently the glow-discharge, have enabled MS to be used for the analysis for the Ln's down to sub-ppm levels, approaching ppb. MS has the advantage of being applicable, with care, to all elements and is best set up, using a standard addition technique, to run on one particular material such as the regular analysis of the highest purity products.

AAS - Atomic Absorption Spectrometry, although not usually chosen for the Ln elements themselves, is routinely used in the Ln industry for the analysis of non-Ln elements in Ln matrices. Within the Ln series the heavy lanthanides, Dy onwards, can be measured down to 10 - 25 ppm, while some of the other Ln's can be detected at 100 - 500 ppm.

[4] Analysis of Rare Earth Elements in Ore Concentrate Samples using Direct Current Plasma Spectrometry, G.W.Johnson and T.E.Sisneros~ in The Rare Earths in Modern Science and Technology, Vol 3, ed. G.McCarthy et al., Plenum, 1982, p. 525: Determination of Cerium, Europium and Terbium in Rare Earth Matrices by DCP-AES, KJyrkäs and M.Leskelä, J.Less-Comm. Metals, 1986, 126, 291

NAA - Neutron Activation Analysis is a highly sensitive non-destructive technique for Ln determination [5] but has the major disadvantage of requiring a nuclear reactor. Most of the Ln elements, after being subject to a flux of neutrons, form characteristic radio-active isotopes whose activity can be measured. It can be purchased as a commercial service and will provide data down to the sub-ppm and ppb level.

Other techniques, such as polarographic analysis, are reported in the literature but are not widely used. Many of the techniques listed in detail above are highly specific to the lanthanides and have been developed either by specialized researchers or directly within the producing or consuming industries, such as phosphor makers. In consequence comparison between results from different sources can be difficult and should be done with care.

Physical Analysis

Several physical parameters help to define a lanthanide-containing material, e.g.:

• Average Particle Size
• Particle Size Distribution
• Surface Area
• Crystallite Size
• Specific Gravity or Relative Density
• Tap, or packing, Density
• Loss of Weight on Ignition, "LOI"
• Thermal Decomposition behavior
• Solubility in common solvents

Particle size analysis, particularly for the Ln **oxides,** has become increasingly essential to application technology. Several techniques[6] are available, differing in the underlying measurement principle, for example :

• Air-permeability   e.g. *Fisher*
• Electrical-zone sensing   e.g. *Coulter*
• Sedimentation rates   e.g. *Sedigraph*
• Light scattering   e.g. *Microtrac*

[5] Neutron Activation Analysis : a Powerful Tool for Assay of Rare-Earth Elements in Terrestrial Materials, M.Oddone et al., Inorg. Chim. Acta, 1984, 94, 283 : Neutron Activation Analysis, W.V.Boynton, Ch 37 F, in Handbook Phys.Chem. Rare Earths, ed. K.A.Gschneidner and L.Eyring, North-Holland, 1979, 457
[6] Direct Characterization of Fine Particles, B.H.Kaye, publ. John Wiley, 1981 : Particle Size Measurement, T.Allen, publ. Chapman Hall, 3rd ed., 1981

Particle size is reported conveniently as a single linear dimension but as such cannot fully characterize irregular objects or a range of sizes. Different techniques will give different numbers for the same samples because they measure different properties and hence derive different averages. One-point determinations, such as are usually given by the first two techniques listed above, have limitations but are suitable for monitoring oxide production for example.

The current requirement for more detailed information is usually met by using techniques relying on the scattering of monochromatic light by a suspension of fine particles. The scattering phenomenon is complex; two approaches are used to derive size data, photon correlation spectroscopy and angular intensity measurements. The inter-pretation can be fully automated to give a distribution of sizes over the range 0.1 to 800 or so microns, depending on the instrument.

By selection of production variables the particle size of, for example, oxides can be controlled to meet the various specifications needed for different application technologies. **Cerium oxide** and **Yttrium oxide,** in particular, are available in grades defined by particle properties. Standard oxide grades will have particles usually in the range from one micron to several tens of microns; smaller particle material can also be made.

Particle morphology, also strongly dependent on production conditions especially during the precipitation stages, is more difficult to define yet will be the determining factor in deciding *Tap Density,* a parameter best measured by a standard ASTM or DIN test.

Surface area and *Crystallite Size* are determined by standard BET (nitrogen adsorption) and X-ray line broadening techniques respectively. These two parameters are **not** necessarily related. Often a small crystallite size oxide will still have a low surface area because the crystallite boundaries are not accessible within the particle to a gas.

The *LOI* of oxides will be determined by the extent of calcination during the conversion from initial precipitated compound, be it hydroxide, carbonate or oxalate, to oxide. Zero LOI, although perhaps ideal, is not economically practical and usually commercial oxides may well have up to 1% or even higher LOI.

Other properties such as *Thermal Decomposition,* e.g. TGA analysis, and *Solubility* are more applicable to non-oxide materials and are discussed separately for each class of compound.

BASTNASITE

This name, derived from a location in Sweden, refers to a mixed-lanthanide fluoride carbonate, Ln F CO_3, that currently provides the bulk of the world's supply of the lanthanide elements. Bastnasite is found in *carbonatites,* igneous carbonate rocks that melt at unusually low temperatures; flowing carbonatite lavas, at ≈500 °C, are <u>not</u> incandescent. These materials are believed to be produced when mantle rocks melt in the presence of carbon dioxide.

Although it is one of the more widespread lanthanide minerals few deposits are of sufficient size to be of commercial significance. The two currently in production are

- Mountain Pass, California, U.S.A., and

- Bayan Obo, Inner Mongolia, China.

Bastnasite Mineral
Variations

(Ce,Ln)	(CO_3)	F
(La,Ce)	(CO_3)	F
(Ce,Ln)	(CO_3)	(OH,F)

and others

Related Minerals
n[$LnFCO_3$].m[$CaCO_3$]

	n	m
Bastnasite	1	0
Synchysite	1	1
Parasite	2	1
Rontgenite	3	2

and others

The open-pit mine at Mountain Pass, near Las Vegas, is the only **resource** operated *solely* for a lanthanide-containing mineral of any kind. The Ln oxide content of the ore averages ≈9%. (The northern China material occurs in a complex structure, probably created by hydrothermal mineralization of mantle rocks. There the Bastnasite is recovered as a *by-product* of iron-ore production.) Potential commercial deposits have also been found in various other countries including several in Africa.

In addition to variations in the relative proportions of individual lanthanides[1], the fluoride component of Bastnasite can be partially replaced by the similar size hydroxide ion[2]. Furthermore there are several closely-related minerals, see table, that often

occur intimately associated with the bastnasite.[3] This inherent variability, while obvious between different geographical sources of the mineral, is also seen between different portions of the *same* ore body.

[1] Relative Proportions of the Lanthanides in the Minerals of the Bastnasite group, M. Fleischer, Can. Mineral., 1978, 16, 361

[2] Lanthanum Hydroxide Fluoride Carbonate System. Preparation of Synthetic Bastnasite, J.M.Haschke, J.Solid State Chem., 1975, 12(1-2),115

[3] Synthesis and Stability of Bastnasites in a Part of the System (Ce,La)-F-H-C-O, L.C.Hsu, Mineral. Petrol., 1992,47,87

Other minerals, particularly alkaline-earth carbonates and sulphates, e.g. calcite ($CaCO_3$), barite ($BaSO_4$) and strontianite ($SrCO_3$), and other lanthanide-based compounds are also usually present in the ores.

Bastnasite - and the closely-related minerals - all adopt a crystal structure with discrete layers of [LnF], [CO_3] and, when present, [$CaCO_3$] groupings.[4] ([LnF] and[LnO] layers are seen in many lanthanide compounds.)

The ore is usually treated by conventional mineral processing technology - comminution followed by froth flotation - to produce a **concentrate.** As recovered, Bastnasite concentrate has a variable composition. For the reasons given above - the composition varies from point to point within the ore body - this concentrate will *not* have a precise invariable analysis.

Typical Analysis, Bastnasite Concentrate			
Ln content		**Non-Ln content**	
CeO_2	≈30 %	SrO	≈5 %
La_2O_3	≈20 %	CaO	≈4 %
Nd_2O_3	≈ 7 %	BaO	≈1.5 %
Pr_6O_{11}	≈2.4%	F	≈5.5 %
Other Ln	≈0.6 %	SiO_2	≈1.5 %
		PO_4	≈1 %
Loss on ignition		Fe_2O_3	≈0.5%
Carbonate	≈20%	SO_4,etc.	≈1 %

A typical analysis[5], with the items given as is customary in terms of "oxide equivalent", shows an ≈60 % lanthanide oxide (LnO) content. The loss on ignition, that takes place close to 600 °C, is the decomposition of the carbonate moieties to oxide.

Thermal decomposition of bastnasite tends to produce a poorly identifiable **oxyfluoride.** The concomitant oxidation of Ce^{3+} to Ce^{4+} probably means that both ions are in the calcined material.

Bastnasite is clearly a light-lanthanide resource with only trace amounts of the heavier Ln-elements; it is predominantly a source of Ce, La and Nd. The other major Ln-source, **Monazite,** has a very similar Ln distribution.

[4] The Atomic Arrangement of Bastnasite-(Ce),Ce(CO_3)F, and Structural Elements of Synchisite-Ce, Röntgenite-(Ce), and Parisite-(Ce), Y. Ni et al., Am. Mineral., 1993, 78, 415
[5] Bastnasite Data Sheet, Product Code 4000, Molycorp, 2/1987

The typical relative amounts of all the individual lanthanides, from full analysis[6] of <u>one</u> specific sample, are given in the table.

Bastnasite can be converted directly, before separation into individual Ln's to compounds such as "rare-earth **carbonate**" or

Bastnasite Ln Content (w.r.t. 100 % Ln)	
La	33.2%
Ce	49.1%
Pr	4.3%
Nd	12.0%
Pm	---
Sm	0.8%
Eu	0.12%
Gd	0.17%
Tb	160 ppm
Dy	310 ppm
Ho	50 ppm
Er	35 ppm
Tm	8 ppm
Yb	6 ppm
Lu	1 ppm

The soluble portion is not only the feedstock for further separation processes but also is the immediate precursor for **lanthanum concentrate,** one of the Ln industry's largest volume products.

The insoluble portion, **cerium concentrate,** is the starting material for the production of pure **cerium** derivatives.

(In China the bastnasite is taken into solution by sulfuric acid for further processing.)

[6] Analysis of Rare Earth Elements in Ore Concentrate Samples using Direct Current Plasma Spectrometry, G.W.Johnson and T.E.Sisneros, in "The Rare Earths in Modern Science and Technology", Vol.3, ed. G.McCarthy et al., publ. Plenum 1982, p. 525

BORATES

Ln$_2$O$_3$:B$_2$O$_3$ Compounds			
Formula	**Oxide Ratio** (Abbreviation)	**Structure type**	**Stability range**
LnBO$_3$	LB	Aragonite "vaterite" Calcite	La - Nd Sm - Yb Lu
LnB$_3$O$_6$	LB$_3$	B$_3$O$_6$-chains	La - Tb
Ln$_3$BO$_6$	L$_3$B	? [LnO][BO$_3$] --	La - Nd Sm - Yb, Lu
	L = Ln$_2$O$_3$, B = B$_2$O$_3$		

The 1:1 and 1:3 Ln borates can be prepared by dissolution of the appropriate ratios of Ln oxide and boric acid (slight excess) in nitric acid, drying, calcining and annealing at ≈900 - 1000 °C. For the 1:1 compounds various polymorphs, related to carbonates, are known[1]. The 1:1 Ln borates resist attack by water or alkali, even at high temperatures, but react readily with hydrochloric acid. The structures are stable thermally to ≈1400 °C although phase changes can occur. The 1:3 analogues react with both acid and alkali; thermal decomposition occurs at ≈900 °C. The LB system also forms glasses, around the 1:3 ratio at ≈20 - 30 mol% Ln$_2$O$_3$ composition[2].

Ternary borates, with other cations as well as Ln's, can be prepared in a similar way to the binary borates, with a flux if needed. Small trivalent cations, e.g. Al^{3+}, produce MO$_4$ units within B$_3$O$_6$ chains whereas larger ions, e.g. Mg^{2+}, replace Ln^{3+}'s.

Lanthanide borates[3] have glass, laser, and phosphor uses. Optical glass, with a high refractive index but a low dispersion, for camera lenses is made from a "lanthanum-flint" composition containing La$_2$O$_3$ and B$_2$O$_3$. A u.v.-excited green-emitting phosphor, (Ce$_{0.3}$Gd$_{0.5}$Tb$_{0.2}$)MgB$_6$O$_{l0}$, is used in energy-saving fluorescent lighting. The borate provides efficient energy transfer, along a linear Ln chain, from the Ce sensitizer, through the Gd lattice, to the Tb emitter. The borate, Nd:YAl$_3$(BO$_3$)$_4$ (NYAB), is a self-frequency-doubling laser material, with a 0.53μ green emission.

[1] Polymorphism of ABO$_3$-type Rare Earth Borates, E.M.Levin, Am. Mineral., 1961, 46,1030

[2] Structure and Properties of Lanthanum Borate Glasses, I.N.Chakraborty et al., J.Am.Ceram.Soc., 1985, 68(12), 641 : ibid, 1985, 68(7), 368; ibid, 1984, 67(12), 782

[3] Binary Rare Earth Borates *in* Inorganic Complex Compounds, M.Leskela and L.Niinisto, *in* Handbook on the Physics and Chemistry of Rare Earths, ed. K.A.Gschneidner and L.Eyring, vol.8, p.203, publ. 1986

BORIDES

Binary borides of the lanthanide elements show many unusual solid state properties associated with the boron-clusters within their crystalline structures. The electronic and magnetic behavior of the Ln borides is not only of considerable fundamental interest but has also led to applications in the electronics industries.

These boride compounds can be prepared by

- direct reaction, at above 1000 °C, of the elements, or by

- reduction of a Ln oxide/boron-carbide mixture above 1500 °C.

$$La_2O_3 + 3 B_4C \qquad LaB_6 + 3 CO$$

There are six families of binary Ln borides[1] : ⟹

- LnB_2 , Ln_2B_5 , LnB_4 , LnB_6 , LnB_{12} , $LnB_{\approx 66}$,

The structure of the borides is built up from either B_6- or B_{12}-clusters linked together in a 3-D network with the metal atoms filling lattice holes. All the boron sub-lattices are electron deficient and require electron transfer from the metal for stabilization. It is this electron transfer that gives these materials novel properties.

The only binary borides of commercial significance are the hexaborides, LnB_6 , known for lanthanides from La to Dy. (With the heavier Ln's the size of the Ln atom becomes too small to stabilize the required structure. **Yttrium** here resembles **Dysprosium** and forms a stable YB_6.) The structure is thermally very stable, melting point of ≈ 2400 °C, with a very low vapor pressure even at such high temperatures. The bonding between the boron units and lanthanide atoms involves the transfer of two electrons from Ln to B_6, leaving one electron from each Ln to provide electrons for a conduction band. The existence of this conduction band provides these materials with their metallic-like properties of good thermal and electrical conductivity.

Many analytical instruments rely on a beam of electrons created from a suitable material either by raising the temperature and causing "thermionic emission", or by the effect of an intense electrical field causing "field emission". The property essential for

[1] Critical Survey of Rare-Earth Borides : Occurrence, Crystal Chemistry and Physical Properties, J. Etourneau, J.Less-Common Metals, 1985, 110, 267 : Borides of the Rare-Earth Metals, Chapter 1, in High Temperature Compounds of Rare Earth Metals with Non-Metals, G.V.Samsonov, publ. Consultants Bureau 1965

such an emitter material, in addition to thermal stability and mechanical strength, is a low electronic work function, i.e. little energy is required to remove an electron from the material's surface. For practical device use it is the ratio of the electron emission to the material vaporization rate that will be important. As instrumental techniques have evolved, the demand for a material providing even better characteristics than the refractory metal Tungsten has been met by Lanthanum Hexaboride.[2] Electron emission efficiency is dependent on surface valence orbitals and hence, for complex structures, on precisely which crystallographic face is exposed. A further factor influencing properties is the stoichiometry of the boride, compositions near the hexa-, but not exactly hexa-, are beneficial. The technology in fabricating lanthanum hexaboride emitters is in growing and shaping crystals to meet these conditions.[3]

The resistive/conductive constituent of a resistor for electronic circuitry ideally should have a zero temperature coefficient of resistance (TCR), a feature not provided by metal particles. The hexaborides offer an alternative material, thermally stable, compatible with copper and fireable in a nitrogen atmosphere, with near zero-TCR. Formulations of glass frits and LaB_6 can be screen printed and fired to provide resistor components necessary in modern integrated circuitry.[4]

The novel neutron-absorbing properties of **Europium** along with hexaboride stability are combined in Nuclear Industry applications of EuB_6. This boride, containing both europium and boron as neutron stoppers, has been considered as the absorber in fast breeder reactors.[5]

At very high temperatures, LaB_6 shows a greater resistance to attack by aggressive fluorine atmospheres than any other material.[6] This is probably due to the formation of an adherent fluoride film on the boride.

(Among more complex Ln-B systems, $Nd_2Fe_{14}B$ is the phase responsible for the properties of the **Neodymium**-Iron permanent magnets.)

[2] Development and Use of High Brightness Lanthanum Hexaboride Electron Guns, F.J.Hohn, Scanning Electron Microscopy, Vol. 198/IV, publ. SEM Inc., 1985, 1327
[3] Single Crystals of Lanthanum Hexaboride: Preparation, Properties and Applications, M.M.Korsukova and V.N.Gurin, Current Topics Mater.Sc., ed. E.Kaldis, publ. North Holland, 1984, Vol 11, Ch. 4
[4] Resistor and/or Conductor Composition comprising a Hexaboride Conductive Material for T'hick-film Resistors, Eur. Patent 8,437, P.C.Donohue (Du Pont), 5-March-1980 : Nitrogen-Firable Resistors ; Emerging Technology for Thick-Film Hybrids, P.C.Donohue, IEEE Trans. Components, Hybrids etc., 37th Electr.Compon.Conf., Boston, MA, 1987, p 537
[5] The Compound EuB_6 as Absorber Material for Fast Reactors; Preparation and Properties, KSchwetz et al., Atomwirtsch., Atomtech., 1973, 15(11), 531 : Synthesis and Fabrication of EuB_6, A.E.Pasto et al., Trans. Am. Nucl. Soc., 1977, 26(l), 176
[6] Stable Materials for Fluorine-Rich Environments, C.E.Holcombe et al., Ind. Eng. Chem., Prod. Res. Dev., 1982, 21(4), 673

BROMIDES, IODIDES

Reaction of oxide with hydrobromic acid will produce the corresponding bromide that can be crystallized out as hydrated salts. The molecules of hydration per formula unit is high and variable, ranging from about 7 to ≈9. The crystalline salts are very hygroscopic and very soluble in water. Anhydrous bromides can be obtained by direct reaction of the metal either with the gaseous hydrogen halide or halogen. Dehydration of the hydrated bromide is possible but needs to be carried out under a flow of pure hydrogen bromide or in the presence of excess ammonium halide[1][2]. Bromide thermal decomposition is a complicated multistage process with the step-wise loss of water of hydration followed by the probable formation of both **oxybromides** and **oxides.**

The tri-iodides can, in principle, be made by methods similar to those for the bromides but closer control of reaction conditions is needed. The LnI_3's crystallize in two structure types, $PuBr_3$ (La - Nd) and BiI_3 (Sm - Lu, Y), and some are used, in the rigorously anhydrous state, in milligram amounts in metal halide high-intensity gas discharge lamps.[3] *Di*-valent **samarium** iodide, SmI_2, prepared by reduction of SmI_3, is a valued reagent in organic synthesis[4].

CARBIDES

Several lanthanide carbide phases have been identified[5], namely:

- Ln_3C, Ln_2C_3, LnC, LnC_2,   plus non-stoichiometric species

and physicochemical data reported. Not all phases are formed by all lanthanides. The LnC_2 phase appears to be the most stable and is possibly formed during the use of misch-**metal** for iron and steel making. Some oxycarbides are also known, e.g. Y_2OC and Yb_2OC.[6] The yttrium compound is stable from 930°C to 2000°C.

[1] Halides, J.M.Haschke, Chap. in "Handbook Phys.Chem. Rare Earths", Vol. 4,ed. K-Gschneidner and LEyring, publ. North Holland 1979, p. 89

[2] The Ammonium Bromide Route to Anhydrous Rare Earth Bromides MBr_3, G. Meyer et al., J.Less Comm. Met., 1987, 127, 155

[3] Color and Efficiency of Neodymium Iodide Discharges, W.A.McAllister, J.Electrochem.Soc., 1985, 132(11), 2798

[4] Divalent Samarium Compounds : Perspectives for Organic Chemistry, H.B.Kagan, New J.Chem., 1990, 14, 453

[5] Rare-Earth Carbides, G.-Y. Adachi et al., Handbook on the Physics and Chemistry of Rare Earths, ed. K.A.Gschneidner, Jr and L.Eyring, Ch. 99, Vol. 15, publ 1991, North-Holland : Thermochemistry of the Rare Earth Carbides, Nitrides, and Sulfides for Steelmaking, K.A.Gschneidner and N.Kippenhahn, IS-RIC-5, publ. 1971, Rare Earth Information Center, Ames, Iowa, U.S.A.

[6] Identification of a New Yttrium Oxycarbide, C.E.Holcombe and D.A.Carpenter, J.Am.Ceram.Soc., 1981, 64, C-82

CARBONATES

CARBONATES $Ln_2(CO_3)_3 \cdot nH_2O$					
Ln	n.H2O Cryst.	Mol. Wt.	% H2O	% Ln Oxide	% element
Y	3	411.85	13.1	54.8	43.2
La	1	475.86	3.8	68.5	58.4
Ce	3	514.31	10.5	66.9	54.5
Pr	1½	488.9	5.5	69.7	57.6
Nd	1	486.5	3.7	69.2	59.3
Sm	4	552.8	13.0	63.1	54.4
Eu	3	538.0	10.0	65.4	56.5
Gd	3	548.6	9.8	66.1	57.3
Tb	3	551.9	9.8	67.7	57.6
Dy	4	577.1	12.5	64.6	56.3
Ho	4	581.9	12.4	64.9	56.7
Er	4	586.6	12.3	65.2	57.0
Tm	4	589.9	12.2	65.4	57.3
Yb	4	598.2	12.0	65.9	57.9
Lu	4	602.0	12.0	66.1	58.1

Carbonates are of geological significance. **Bastnasite,** the main source of the light lanthanides, is a fluoride carbonate, $LnFCO_3$, that is found in several locations in *carbonatite* deposits, uncommon ores of magmatic origin. (Simple carbonate minerals, such as Lanthanite, $(La,Ce)_2 (CO_3)_3 \cdot 8H_2O$, and more complex compounds are also known[1].)

The lanthanide carbonates are readily prepared, for example, by precipitation from acid solution, e.g. of **nitrates,** by addition of sodium carbonate (soda ash) or ammonium carbonate. For highly-crystalline research-quality materials, a process such as the slow thermal hydrolysis - in situ - of salts such as trichloro-acetates or urea is preferred.

[1] Crystal Structures of Rare-Earth Minerals (in English), R. Miyawaki and I.Nakai, in "Rare Earths", publ. Rare Earth Society of Japan, 1987(11), 1

The carbonates are insoluble in water[2] (solubility $\approx 1 \times 10^{-6}$ mol dm^{-3}) and are convenient precursors for conversion to other Ln derivatives, such as Ln **oxides**. (**Oxalate** precursors though are preferred for highest-purity oxide production.)

A variety of crystalline hydrates, with n = 8 or less, have been characterized. [3] Non-forced crystallization for the larger Ln ions will produce the *lanthanite*-type octahydrate whereas those with Ln^{3+} smaller than Nd produce a *tengerite*-type, [4] $Y_2(CO_3)_3.\approx 3H_2O$, lower hydrate. (The table entries correspond, for the light Ln's, to those salts produced in commercial quantities.)

Within the Ln_2O_3-H_2O-CO_2 system many phases have been recognized [5] and - as well as the hydrated salts $(Ln_2(CO_3)_3.nH_2O)$ -hydroxy-carbonate and oxycarbonate compounds are possible. [6] The lightest Ln's tend to form only the simple $Ln(OH)CO_3$ and LnPACO3) derivatives whereas with heavy lanthanides a range of phases such as $Ln_xOH_y(CO_3)_z$ have been prepared, x,y,z > 1. The ease with which the oxy- and hydroxy- derivatives can form means that commercial hydrated light-Ln carbonates may well contain small amounts of such phases.

The carbonates crystallize in a layered structure with chains of linked carbonate ions separated by H-bonded water molecules. $Ln(OH)CO_3$'s, because hydroxide and fluoride ions are similar in size and have the same charge, tend to be isomorphous with bastnasite and both structures contain carbonate ions separating layers of $[LnOH]^{2+}$ (or $[LnF]^{2+}$) ions. A continuous solid solution, $LaF_x(OH)_{1-x}CO_3$, is possible across the entire composition range formed when F substitutes for OH in $LaOHCO_3$.[7]

Apart from normal carbonates the lanthanides will form crystalline double salts, ternary carbonates, with alkali, alkaline-earth and ammonium ions. Some of the minerals closely related to **bastnasite** are examples.

[2] Solubility Products of the Rare-Earth Carbonates, F.H. Firsching and J. Mohammadzadel, J.Chem. Eng. Data, 1986, 31(l), 40

[3] Inorganic Complex Compounds 1, M.Leskela and L.Niinisto, in "Handbook on the Physics and Chemistry of Rare Earths", ed. K.Gschneidner et al., publ. North-Holland 1986, Vol.8(Chap. 56), 233

[4] The Redefinition of Tengerite-(Y), $Y_2(CO_3)_3$.2-$3H_2O$, and its Crystal Structure, R. Miyawaki et al., Amer.Mineral., 1993, 78, 425

[5] Hydrothermal Phase Equilibria in Ln_2O_3-H_2O-CO_2 Systems, J.A.K Tareen and T.R.N.Kutty, J.Ctyst.Growth, 1980, 80, 527: Correlation between the Stability of Carbonates in Ternary Ln_2O_3-H_2O-CO_2 Hydrothermal Systems and Lanthanide Systematics, T.R.N.Kutty et al., J.Less-Common Metals, 1985,105, 197

[6] Formation, Structure and Decomposition of Lanthanide Basic Carbonates, M.Akinc et al., Adv. Ceram. Mat., 1988, 3(3), 211 : Preparation of Yttrium, Lanthanum, Cerium and Neodymium Basic Carbonate Particles by Homogeneous Precipitation, M.Akinc and D.Sordelet, Adv.Ceram.Mat., 1987, 2(3A), 232 : Lanthanide Oxide Carbonates, V.D.Savin et al., Russ.J.Inorg.Chem., 1987, 32(11), 1550

[7] Lanthanum Hydroxide Fluoride Carbonate System. Preparation of Synthetic Bastnasite, J.M.Haschke, J.Solid State Chem., 1975, 12(1-2), 115

The thermal decomposition of the Ln carbonates proceeds[8] initially by loss of water of hydration between ≈100 and ≈300 °C followed by the formation of intermediate oxycarbonates before the oxide is produced at ≈>650 °C. The steps in the process, the required temperatures and the intermediates formed depend on the individual lanthanide as well as on the surrounding atmosphere, e.g. CO_2 suppresses carbonate moiety decomposition.

$$Ln_2(CO_3)_3.nH_2O \quad => \quad Ln_2(CO_3)_3 \quad [=>Ln_2O(CO_3)_2 \; ??]$$

$$=> \quad Ln_2O_2CO_3 \quad => \quad Ln_2O_3$$

$$Ln_2(CO_3)_3 \quad + \quad H_2O \quad => 2Ln(OH)CO3 \quad + \quad CO_2$$

$$2Ln(OH)CO_3 \quad => \quad Ln_2O_2CO_3 \quad + \quad H_2O \quad + \quad CO_2$$
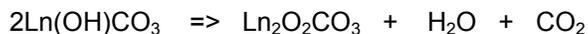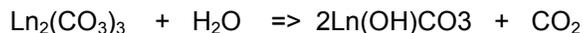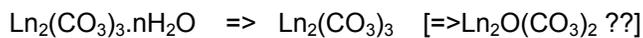
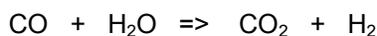When the lanthanide is cerium the concomitant oxidation of Ce(III) to Ce(IV) and the catalytic activity of CeO_2 for the *water-gas* shift reaction :

$$CO \quad + \quad H_2O \quad => \quad CO_2 \quad + \quad H_2$$

can result in the formation of some hydrogen and carbon monoxide during decomposition.[9] The controlled calcination/decomposition of cerium carbonate is a method of preparing high surface area **cerium oxide.**

The carbonates are readily converted to other compounds, e.g. to the oxides by calcination, and are easily stored and handled. The ready conversion of lanthanide carbonate to oxide is utilized in the electronic glass and ceramic industries, to introduce, for example, **cerium, neodymium** and other Ln's into compositions.

[8] The Preparation and Thermal Decomposition of some Rare Earth Carbonates, E.L.Head and C.E.Holley, Proc. 3rd. Rare Earth Research Conf., April 21-24, 1963, ed. K.S.Vorres, publ. Gordon and Breach : Thermal Decomposition of Lanthanide, Yttrium and Scandium Oxalates and Carbonates, V.A.Sharov and G.V.Bezdenezhnykh, Russ.Chem.Rev., 1981, 50(7), 630
[9] Hydrogen Evolving Reactions : The 'Thermal Decompositions of Cerous Carbonates, E.J.Peterson et al., J.Inorg.Nucl.Chem., 1978, 40, 1357

CARBOXYLATES

Metal salts of monobasic organic carboxylic acids R-COOH, where the radical R contains from ≈5 to 25 carbon atoms, are often described as metallic soaps. These water-insoluble lanthanide carboxylate salts [1] can be made by processes such as :

- Double decomposition, with precipitation, using water-soluble precursors, in, for example, hot dilute solution.

  e.g. Lanthanum   Nitrate + Potassium Caprate   **=>**
                    Lanthanum Caprate + Potassium Nitrate
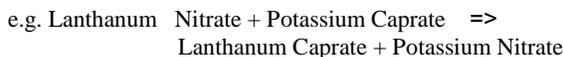
- Reaction of finely-divided Ln-containing solid with organic acid

  e.g. Cerium Hydroxide + Oleic Acid => Cerium Oleate

The Ln solid can be an aqueous slurry and the acid molten if necessary. (Several variations on this process are operated commercially.) The Ln can be an individual lanthanide or a mixture of several Ln's such as the ore-body natural ratio. Typical anions are 2-ethylhexanoate (octoate), stearate, naphthenate and neo-decanoate. Depending on the choice of organic anion or, to a lesser extent, of metal cation, these salts can be tailored to be compatible with non-aqueous environments such as organic solvents or polymer systems. (The acid portion can be considered as a carrier for the metal cation whose properties underlie many applications.)

Ln carboxylates are used as paint driers.[2] Ce carboxylate additives in alkyd resins promote the physical change from liquid to solid state of the resin coating, speeding "drying" by accelerating the cross-linking reactions within the polymer skin. They enhance the oxidation associated with air drying of alkyd paints.

Similar salts, are used as combustion additives and plastics stabilizers. Ce salts, soluble in hydrocarbons, can promote the complete oxidation of diesel fuels[2][3], where presumably Ce(IV) acts as an oxidizing agent. Heat stabilization of the halogenated polymer PVC requires limiting high temperature dehydrochlorination reactions. Cerium stearate, by controlling the labile halogens, stabilizes PVC.[2]

[1] Lanthanide and Actinide Carboxylates, KW.Bagnall, MTP Int.Rev.Sci., Inorg.Chem. Series 2, Vol 7, 41 (publ. Butterworths, 1975)

[2] Organo Rare Earths : The Newcomers in the Organo-Metallic World, P.Ducros, J.Less-Common Met., 1985, 111, 37

[3] Oil-soluble Compounds of Cerium, Preparation and Use as Drying Agents or as Combustion Additives, Gamlen Naintre SA, French Patent, 76-22426, 22-July-1976 : Diesel Fuel containing Rare Earth Metal and Oxygenated Compounds, Texaco Inc., U.S.Patent, 4,522,631, 11-June-1985

CERIUM

The second element in the lanthanide series is the most **abundant** of these elements and is characterized chemically by having two stable valence states, III and IV, readily accessible[1].

- Ce^{4+} ceric

- Ce^{3+} cerous

The ceric ion is a powerful oxidizing agent but when associated with the strongly coordinating ligand, oxygen, is completely stabilized. Indeed **cerium oxide**, CeO_2, (also known as *ceria*) with tetravalent cerium is the form of cerium most widely used and is produced when any cerium salt is calcined in air.

Ce	
element	
Atomic Number	58
Atomic Weight	140.12
Electron configuration	$[Xe]4f^1 5d^1 6s^2$
Valencies	3 and 4
Ionic radius for	(3+) 114 ppm
8-coordination	(4+) 97 ppm
Magnetic moment	$2.4\mu_B$
metal	
Crystal Structure	fcc
Melting Point	798 °C
Boiling Point	3443 °C
Density	6.77 g/cm^3
Metallic Radius	182 ppm

The ceric ion, despite a Ce(IV)/Ce(III) potential of + 1.4 to + 1.7 V (the exact value depends on the anions also present), is remarkably stable in aqueous solution, where the O_2/H_2O potential is + 1.2 V. Simple Ce(IV) salts, such as chloride, can not be prepared but more complex compounds, e.g. ammonium hexanitratocerate $(NH_4)_2 [(NO_3)_6 Ce]$, are stable. Such Ce(IV) complexes are colored orange to red and, as they are strong oxidizing agents, are used for wet chemical analyses.

The table on the next page includes useful numerical values for several salts, particularly for those prepared commercially in quantity. Most compounds contain several molecules of water of crystallization and various intermediate hydrates can also usually be made. As a consequence industrial products may well not correspond to the idealized formulas reported but contain mixtures of different crystalline, or amorphous, species. (Anhydrous compounds, particularly halides, can be obtained and some are commercially available.) More details for these salts, including physico-chemical properties can be found under the listing for the appropriate anion such as **acetate, carbonate,** etc.

[1] Cerium, A Guide to its Role in Chemical Technology, B.T.Kilbourn, booklet publ. Molycorp, 1993 (available on request)

Compound	Ideal Formula	Formula Weight	% Oxide	% Element
Oxide	CeO_2	172.12	100	81.5
Acetate	$Ce(CH_3COO)_3.1\frac{1}{2}H_2O$	344.28	50.0	40.7
Carbonate	$Ce_2(CO_3)_3.3H_2O$	514.31	66.9	54.5
Chloride	$CeCl_3.6H_2O$	354.59	48.5	39.5
Fluoride	$CeF_3.H_2O$	215.12	---	65.1
Hydroxide	$[CeO_2.2H_2O]$	208.15	82.7	67.3
Nitrate	$Ce(NO_3)_3.6H_2O$	434.23	39.6	32.3
Oxalate	$Ce_2((COO)_2)_3.9H_2O$	706.43	48.7	39.7
Sulfate	$Ce_2(SO_4)_3.8H_2O$	712.55	48.3	39.3

Apart from the **oxide** and **hydroxide** all compounds listed contain the Ce^{3+} ion that resembles the other trivalent lanthanides in properties (see **Lanthanum** for a summary). Cerous salts are only slightly hydrolyzed in solution; basic salts, e.g. $Ce(OH)CO_3$, are easily formed and may be contaminants in solid salts.

The Ce(III) salts are colorless having no absorption bands in the visible but they do however absorb strongly just outside the visible, in the u.v. Trivalent cerium, cerous, is one of the few lanthanide ions in which parity-allowed transitions between $4f$ and $5d$ configurations can take place. In consequence solids with this ion often show strong optical absorption and luminescence in the u.v., or near-u.v. Cerium, for example, is used in several CRT phosphors and also as a sensitizer, for other Ln emitters, in fluorescent lighting phosphors.

The ceric ion, is (apart from Eu^{2+}) the only non-trivalent Ln ion stable in aqueous solution. The higher cation charge and a smaller ionic size make ceric salts much more hydrolyzed in aqueous solution than those of the trivalent Ln's. Ceric salt

$$[Ce\ L_m\ (H_2O)\ ]^{n+}\ +\ H_2O\ =>\ [Ce\ L_m\ (OH)\ ]^{\{n-l\}+} + H_3O^+$$
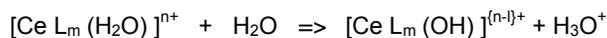
solutions are strongly acidic and there are no stable simple salts of weak acids.

CERIUM CONCENTRATE

The steps used at Mountain Pass, California, U.S.A. to crack, to "open", **Bastnasite** concentrate for further processing [1] are :

- roasting in air, whereby Ce^{3+} oxidizes to Ce^{4+}, followed by
- leaching with HCl to produce,

  - an insoluble portion, *cerium concentrate*, and
  - a soluble fraction.

The insoluble cerium-rich portion, *cerium concentrate*, although predominantly $Ce^{4+}O_2$, is of poorly defined composition; a typical analysis is given[2]. All the values reported are approximations as the content can vary with production runs.

Cerium Concentrate			
Typical Analysis			
Ln content		Non-Ln content	
CeO_2	$\approx 62\%$	CaO	$\approx 6\%$
other Ln oxides	$\approx 10\%$	other oxides	$\approx 4\%$
loss on ignition	$\approx 8\%$	F	$\approx 10\%$

The label "oxide" is used in the table but insoluble fluorides, sulfates and phosphates may be also present in the concentrate. In addition, inherent compositional variations within the ore body pass through to this concentrate, the residue of a leach process. Ceria, CeO_2, with the fluorite, CaF_2, structure, readily takes fluoride ions into the lattice with the charge difference being compensated by Ln(III) replacing Ce(IV); the "F" content is therefore probably present in an **oxyfluoride** form.

Cerium concentrate is the most economical source of cerium and is used[3] in tonnage quantities for :

- polishing of glass,

- decolorization of glass,

- providing cerium for glass that absorbs u.v. radiation, and

- production of cerium-rich mischmetal and related alloys.

[1] Cerium, A Guide to its Role in Chemical Technology, B.T.Kilbourn, booklet publ. Molycorp, 1993 (available on request)
[2] Cerium Concentrate Data Sheet, Product Code 5300, Molycorp 1/88
[3] Varied Applications for Cerium Concentrate, B.Simpson, Glass, 1987, 64(12), 469

CERIUM OXIDE

Cerium Oxide, CeO_2	
Chem. Abs. No.	1306-38-3
Formula Weight	172.1

Physical Properties

Melting Point	≈2750 K
Density	7.28 gcm^{-3}
Specific Heat	≈460 $Jkg^{-1}K^{-1}$
Thermal Conductivity	≈12 $Wm^{-1}K^{-1}$
Thermal Expansion	≈11x10^{-6} K^{-1}
Refractive Index	≈2.1 visible
	≈2.2 infra-red
Young's Modulus	≈165x10^9 Nm^{-2}
Poisson's Ratio	≈0.3
Hardness	≈5 – 6 mhos

The most stable oxide of cerium is cerium dioxide, CeO_2, also called *ceria* or *ceric oxide*[l]. When cerium salts are calcined in air, or oxygen-containing environments, this *tetra*valent Ce(IV) oxide is formed. (The sesquioxide, Ce_2O_3, with *tri*valent Ce, can be prepared under strongly reducing conditions but is unstable in air, water and the like, readily converting to the dioxide.)

Cerium (along with the other lanthanides) has one of the highest free energies of formation for an oxide. The oxide is soluble in mineral acids but is difficult to dissolve unless a trace of reducing agent, e.g. H_2O_2, is added.

Ceria has the fluorite, CaF_2, structure, space group Fm3m, with 8-coordinate cations and 4-coordinate anions.[2] It can be visualized as a cubic close-packed array of metal atoms with oxygens filling all the tetrahedral holes; the structure-determining OCe_4 coordination tetrahedra thereby share all edges in three dimensions.

CeO_2 , when pure, is a very pale yellow probably due to Ce(IV)--O(-II) charge transfer transitions. The color of the oxide is sensitive not only to stoichiometry but also to the presence of other lanthanides. A slight trace (≈0.02%) of Pr results in a buff color attributable to Ce(IV)-(PrIII) transitions. (With higher values of Pr (≈2%) the material becomes a potential red pigment.[3]) Grossly non-stoichiometric ceria samples are reported to be blue, related to Ce(IV)-Ce(III) transitions. In addition, as the oxide is usually produced by the calcination of a precursor salt, the observed color depends on the extent of that calcination.

[1] Cerium, A Guide to its Role in Chemical Technology, B.T.Kilbourn, booklet publ. Molycorp, 1993 (available on request)

[2] Binary Rare Earth Oxides, L.Eyring, in "Handbook on the Physics and Chemistry of Rare Earths", ed. K.Gschneidner and LEyring, Vol 3, p 337, Publ. North Holland 1979

[3] Optical Properties of $Ce_{1-x}Pr_xO_2$ Powders and their Applications to the Coloring of Ceramics, R.Olazcuaga et al., J.Solid State Chem., 1987. 71, 570

The oxide can exhibit large deviations from stoichiometry, CeO_{2-x}, (x can be up to 0.3) at low oxygen partial pressures, $P(O_2)$. A moderately-stable intermediate state $CeO_{1.83}$ (i.e. a Ce_6O_{11} similar to Pr_6O_{11}) can probably be formed.

In air or oxygen, though, ceria stays close to stoichiometry and its defect structure is therefore controlled by doping.[4] When doped with divalent oxides (RO) or trivalent oxides (R_2O_3) the introduction of oxygen vacancies, $V_o^{\cdot\cdot}$, provides the charge compensation. For a trivalent dopant the effective charge is -1, that is one $V_o^{\cdot\cdot}$ is produced for every two dopant ions, $2R_m + V_o^{\cdot\cdot}$. Solid solutions of ceria with, for example, trivalent ions such as Y or La, can readily be formed. The resulting oxygen vacancies are mobile and form the dominant point defect involved in transport behavior; oxygen diffusion is fast whereas cation diffusion is slow. The resulting *defectfluotites* have good oxide ion conductivity[5] and are novel solid electrolytes for temperatures above $\approx$600 °C.[6]

Ceria can be sintered (at $\approx$1400 °C) to high densities, > 97 % theoretical, by the addition of trace amounts, < 1.0 %, of oxides such as TiO_2 or Nb_2O_5[7]. These additives work either by the formation of a transient liquid-phase intermediate, e.g. $CeTi_2O_6$ m.pt. 1350 °C, or by suppressing oxygen deficiencies, e.g. high valent Nb.

The oxide is a crucial ingredient in the catalysts used to control vehicle exhaust emissions[8]; an average catalytic converter probably contains around 50 to 75 grams of $Ce0_2$. Its function is described as "an oxygen storage component" that enhances performance when the exhaust gases are fuel-rich / air-poor. The role ceria plays though is more complex as it probably also enhances the catalytic activity of the precious metals deposited onto it.

[4] Doped Ceria as a Solid Oxide Electrolyte, H.L.Tuller and A.S.Nowick, J.Electrochem.Soc., 1975, 122(2),255

[5] Point Defect Analysis and Microstructural Effects in Pure and Donor-doped Ceria, M.R.DeGuire et al., Solid State Ionics, 1992, 52, 155

[6] Oxygen Ion Conduction of the Fluorite-Type $Ce_{1-x}Ln_xO_{2-x/2}$ (Ln = Lanthanoid Element), T.Kudo and H.Obayashi, J.Electrochem.Soc., 1975,122(l),142: Oxygen Ion Conductivity of the Cera-Samarium Oxide System with Fluorite Structure, H.Yahiro et al., J.Appl.Electrochem., 1988, 18, 527

[7] Sintered Ceria : A New Dense and Fine Grained Ceramic Material, J.F.Baumard et al., J.LessCommon Met., 1987,127,125

[8] Ceria-Promoted Three-Way Catalysts for Auto Exhaust Emission Control, G.Kim, Ind. Eng.Chem.Prod.Res.Dev., 1982, 21, 267 : Ceria in Automotive Exhaust Catalysis, I Oxygen Storage, H.C.Yao et al., J.Cat., 1984, 86, 254 : The Role of Ceria in Three-Way Catalysts, A.F.Diwell et al., in "Catalysis and Auto. Poll. Control", ed. A.Crucq, publ. Elsevier, 1991, p. 139

CHLORIDES

The hydrated halides, $LnCl_3.nH_2O$, of the lanthanides are prepared by dissolving the oxide, or another compound such as the carbonate, in hydrochloric acid. (With cerium, only the Ce^{3+} species is stable; dissolution of a ceric, Ce^{4+}, salt in HCl will
evolve chlorine.) On a commercial scale **mixed-lanthanide** chlorides, derived from **concentrates**, as well as pure lanthanide analogues are made this way.

For *ideal* single-Ln salts the hydration values are :

- $LnCl_3.nH_2O$ ……….La, Ce and Pr n = 7
  ……Nd to Lu, Y n = 6

The degree of hydration however depends on the extent of drying during preparation and with the mixed-lanthanide derivatives, as well as the three lightest lanthanides, in practice *n* usually equals *6*. The crystal structures of hydrates contain highly coordinated Ln ions, $[LnCl_2(OH_2)_n]^+$, linked together by hydrogen bonds, a very flexible arrangement, and other hydrates, lower than the nominal, can easily be formed.

The salts as solids are strongly hygroscopic and readily soluble in water, approaching a concentration, as hexahydrate, of 55-60 %. Heavy-Ln chlorides, and Y, are somewhat less soluble. Thermo-dynamic and physico-chemical data for solutions of pure-Ln chlorides can be found in the primary literature.

The hydrated salts on heating pass through the poorly-defined stepwise loss of water before decomposing to form hydroxychlorides, $Ln(OH)_2Cl$, more stable oxychlorides, LnOCl and ultimately the oxide.[1]

$$LnCl_3.6H_2O \Rightarrow LnOCl + 2HCl + 5H_2O \Rightarrow Ln_2O_3$$

The anhydrous chloride can nevertheless be made from the hydrated salt by suppressing oxychloride formation by carrying out the dehydration

- under a stream of hydrogen halide[2], or
- with excess ammonium chloride present.

[1] Thermographic and Thermogravimetric Investigation of the Crystal Hydrates of the Chlorides of the Rare Earth Elements and Yttrium, L.G.Sokolova et al., Zh.Neorg.Khim., 1981, 26(7), 1736 : Characterization of Neodymium Trichloride Hydrates and Neodymium Hydroxychloride, G.J.Kipouros and R.A.Sharma, J.Less.Common Metals, 1990, 160(1), 85
[2] Preparation of High Purity Anhydrous Neodymium Chloride, G.J.Kipouros and R.A.Sharma, in "Rare Earths; Resources, Technology and Applications" ed. R.G.Bautista and N.Jackson, publ. TMS 1991, p. 43

This step occurs more readily with the light Ln's than with the heavies. Other procedures[3] for the anhydrous salts include

- metal plus chlorine or hydrogen chloride,

- oxide plus ammonium chloride, and,

- metal plus mercury(II) chloride in THF, for solvated salts.[4]

    e.g. $2Er + 3HgCl_2 \implies 2ErCl_3.(THF)_{\approx3} + 3Hg$
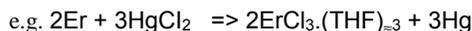
LnCl3 anhydrous melting points °C	
Y	721
La	860
Ce	817
Pr	786
Nd	758
Sm	682
Eu	dec.
Gd	602
Tb	582
Dy	647
Ho	720
Er	776
Tm	824
Yb	865
Lu	925

Anhydrous chlorides can be used to prepare lanthanide **metals.** Electrowinning by electrolysis of a fused salt bath (700 - 1000 °C) containing $LnCl_3$ and other compounds is a commercial route to the various **Mischmetals** that are important ferrous metallurgy additives. The necessary precursors are the **mixed lanthanide** chlorides. "Rare-earth" chloride, derived from **monazite,** and containing the natural-ratio of lanthanides is traded internationally for this application.

The electrolytic process, also a potential route to each of the four individual elements La, Ce, Pr and Nd, is possible because those four all have low melting points. The Ln **metals** can also be made from the chloride by metallothermic reduction, with calcium for example. (The **fluoride,** however, is the usual choice for this alternative route to metal.)

The melting points of the anhydrous chlorides decline from La to Tb and then a rise to Lu. This correlates with a structural change from the nine-coordinate $Y(OH)_3$ (or UCl_3) model to a six coordinate $AlCl_3$ type. The UCl_3 structure can be described as alternate layers of $[MX_2]_n^{n+}$ and $[X]_n^{n-}$.[5] (YCl_3 resembles $DyCl_3$ / $HoCl_3$ in properties; $EuCl_3$ decomposes to the divalent halide.)

[3] Lanthanide, Yttrium and Scandium Trihalides. : Preparation of Anhydrous Materials and Solution Thermochemistry, J.Burgess and J.Kijowski, Adv.lnorg.Radiochem., 1981,24,57: Halides, J.M.Haschke, Chap. in "Handbook Phys.Chem Rare earths", Vol. 4, ed. KGschneidner and L.Eyring, publ. North Holland 1979, p. 89 : Halides of the Lanthanides and Actinides, D.Brown, publ. J.Wiley, 1968 : M.D.Taylor, Chem. Rev. 1962, 62, 503
[4] Lanthanide Trichlorides by Reaction of Lanthanide Metals with Mercury(II) Chloride in Tetrahydrofuran, G.B.Deacon et al., in Inorganic Syntheses, Vol. 28, Reagents for Transition Metal Complex and Organometallic Syntheses, ed. R.J.Angelici, publ. J.Wiley, 1991, 28, 286

The anhydrous chlorides are moisture sensitive and are soluble in many organic solvents, e.g. alcohols[6], ethers and amides; the solutions are useful intermediates for the preparation of **organometallic** compounds.[7] Because of their appreciable vapor pressure at high temperatures[8], about 1 torr at 1000 °C, $LnCl_3$ compounds are used for chemical vapor deposition reactions, for example in preparing doped optical fibers.

The Ln chlorides form, at elevated temperatures, gas phase complexes with $AlCl_3$; in some instances the discrete complex has been separated and characterized.[9] Similar complexes are formed with other halides such as the alkali chlorides:

$$LnCl_3 (s_1l) + MCl(s_1l) => ALnCl_4(g)$$
$$M = \text{alkali metal element}$$
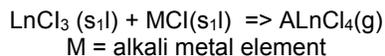
The complexation conditions differ slightly between adjacent lanthanides and a mutual separation is possible by a vapor transport process.[10]

Reduced chlorides, made by reduction of the trichloride with alkali metal, are known that contain Ln's in valence states apparently less than three. These derivatives can have structures with clusters of, for example, $[M_6Cl_8]$, groupings while others have a metallic properties.[11]

[5] Structural Relations Crystal Chemistry and Anion Substitution Processes for $M(III)X_3$ Systems of Lanthanides and Actinides J.M.Haschke,
J. Solid State Chem., 1975, 14(3), 238
[6] Addition Compounds of Rare Earth Chlorides with Methanol, Ethanol and 2-Propanol, Preparation, Solubility and Transsolvation, A-Merbach   et al., HeIv.Chim.Acta, 1972, 55, 44
[7] Organolanthanoid Compounds, H.Schumann, Angew-Chem.Int.Ed., 1984, 23, 474
[8] The Vapor Pressures of Yttrium and Rare Earth Chlorides above their Melting Points, J.L.Moriarty, J.Chem.Eng.Data, 1963, 8, 422
[9] $HoAl_3AlCl_{12}$ in Crystalline Form, D. Hake and W. Urland, Angew.Chem-lnt.Ed.(Engl.), 1992,28(10), 1365
[10] Mutual Separation Characteristics for Lanthanoid Elements via Gas Phase Complexes with Alkaline Chlorides, G-Y. Adachi et al., Chem. Lett., 1992, 511
[11] Reduced Halides of the Rare-Earth Elements, G.Meyer, Chem.Rev., 1988, 88, 93 : Metallic halides of the Lanthanides, G. Meyer, Eur.J.Solid State Inorg.Chem., 1991, 28, 473

CHROMITES

Within Ln/Cr/O systems several compounds have been characterized, the most important being the LnCrO$_3$ materials in Cr$_2$O$_3$-Ln$_2$O$_3$ systems, Ln = *trivalent* lanthanide, Cr = *trivalent* chromium. These Ln chromites, with the perovskite structure, are very refractory materials with melting points above 2300 °C, the most refractory being LaCrO$_3$ melting at 2510 °C.[1] They can be made by the solid-state direct co-firing of oxides or, preferably to provide better control of dopant ion distribution and of powder physical parameters - by the liquid-mix Pechini-type processes[2]. The compounds are of interest to technology because they both conduct electricity and resist degradation at high temperatures.

Lanthanide Chromites LnCrO3 m.pt. °C	
La	2510
Nd	2415
Sm	2380
Gd	2370
Dy	2340
Er	2330
Yb	2330

The electrical conductivity of LaCrO$_3$ is reasonably constant - around 0.1 (ohm cm)$^{-1}$ - for the whole range 500 °C to 1900 °C. The electrical conduction processes in this material are almost all electronic, associated with the overlap of the electron energy levels on the chromium atoms. Although already significant the conductivity can be markedly increased, particularly at low temperatures, by doping the material with divalent ions[3], with the charge balance kept by the formation of Cr^{4+} ions and small holes that act as charge carriers.

Calcium and strontium, at levels up to 20 mole %, give (LaM)CrO$_3$ a greater conductivity than for the pure LaCrO$_3$ alone. The conductivity, for example, of La$_{0.84}$Sr$_{0.16}$CrO$_3$, already >2 (ohm cm)$^{-1}$ at ambient, rises (above 300 °C) to >10 (ohm cm)$^{-1}$ and remains close to this value up to 2000 °C. The good low temperature conductivity of the Sr doped perovskite means that it can be used as a conductor over a wide temperature range.

Potential uses for these materials, in particular (La,M)CrO$_3$, include furnace heating elements, stable at 1800 °C in oxidizing environments. The most significant use will probably be as the crucial intercell connecting material in solid oxide fuel cells (SOFC's) for efficient power generation.[4]

[1] Contributions to the Study of Interactions between Oxygen, Lanthanum Oxide, Chromium(III) Oxide or Lanthanum, Chromite, R.Berjoan, Rev. Int. Hautes Temp. Refract., 1976, 13(2), 119

[2] Method of Preparing ... Alkaline-Earth Titanates..., M.P.Pechini, U.S.Patent 3,330,697, 1 1-July- 1967

[3] Fabrication and Property Control of LaCrO$_3$ based Oxides, H.U.Anderson, Mater.Sci.Res., 1978, 11, 469: Synthesis, Properties, Applications of High Conductive LaCrO$_3$-based Ceramic Materials, S.T.Song et al., Ceram.Int. 1984, 10(4), 143 : Electrical and Thermal Transport properties of the Y$_{1-x}$M$_x$CrO$_3$ System, W.J.Weber et al., J.Mater.Res., 1986,1(5),675; Effects of Cation Substitution on Electrical and Thermal Transport Properties of YCrO$_3$ and LaCrO$_3$, *ibid,* J.Am.Ceram.Soc., 1987, 70(4), 265

[4] Ceramic Fuel Cells, N.Q.Minh, J.Amer.Ceram.Soc., 1993, 76(3), 563

COBALTATES

Within the Ln-Co-O system, the simple ABO_3 **perovskite** is formed by most lanthanide elements[1] whereas the other structure types probably only exist with the lighter Ln's[2]. The lanthanum perovskite adopts a rhombohedral ABO_3 structure while the other $LnCoO_3$'s take up the more common orthorhombic symmetry. The low-spin / high-spin Co possibilities, a potential variable valency for the Cobalt and non-stoichiometry, of either the oxygen or the Ln content or both, all add to the structural complexity of Ln-Co-O phases.[3].

Ln:Co:O Compounds Formula	Structure Type
$LnCoO_3$	"Perovskite"
Ln_2CoO_4	"K2NiF4"
$Ln_4Co_3O_{10}$	---

$LnCoO_3$ melting points °C	
La	1740
Nd	1420
Sm	1340
Gd	1380
Dy	1270
Er	1220
Yb	1180

The perovskites can be prepared by firing intimate **oxide** mixtures or, preferably, by firing co-precipitated precursors such as **hydroxides** or **carbonates**[4] or by spray pyrolysis of **nitrate** solutions.[5] "Sol-gel" routes, e.g. based on citrates, using controlled hydrolysis followed by polymerization, are also possible.

$LnCoO_3$ compounds - especially variations on $LaCoO_3$ -are of considerable technical interest because of novel electrical, magnetic[6] and catalytic properties[1][7]. The good electrical conductivity, due to delocalization of electrons among the Co-O-Co lattice, can be further enhanced by doping with a divalent alkaline earth, e.g. Sr. Such $(La,M)CoO_3$ compounds are possible catalytically active electrodes, stable in high-temperature aggressive environments for fuel cells and sensors. They have even been considered as catalysts for the automobile emission control.

[1] Solid State and Catalytic Properties of Rare Earth Cobaltites - New Generation Catalysts, B.Viswanathan, J.Sci.Ind.Res., 1984, 43(3), 151
[2] Ternary Compounds in the System La-Co-O, J.J.Janacek and G.P.Wirtz, J.Am.Ceram.Soc., 1978,61, 242
[3] Non-stoichiometric K_2NiF_4 Phases in the Lanthanum-Cobalt-Oxygen System. J.T.Lewandowski et al., J.Am.Ceram.Soc., 1986, 69(9), 699
[4] Characterization of Lanthanum Cobalt Magnesium Oxide prepared by a Co-precipitation Method, O.Parkash et al., J.Phys.D: Appl.Phys, 1988, 21, 1512 : Preparation of $La_{1-x}Sr_xCoO_3$ (x=0,0.3) by two Solution Routes, H.Kido and S.Komarneni, SPIE, Electro-optical Materials, 1990, 1307, 129
[5] Preparation of $CoLaO_3$ Catalyst Fine Particles by Mist Decomposition Method, H.Imai et al., Mat.Res. Bull., 1984, 19, 1293
[6] Perovskites and Garnets, C.P.Khattak and F.F.Y.Wang, Ch. 29, in "Handbook on the Physics and Chemistry of Rare Earths, ed. K.AGschneidner and LEyring, publ. North-Holland, 1979
[7] Catalytic Properties of Perovskite-Type Mixed Oxides consisting of Rare Earth and 3d Transition Metals. The Roles of the A- and B-site Ions, T.Nitadori et al., Bull.Chem.Soc.Jpn., 1988, 61, 621

CONCENTRATES, MIXED-LANTHANIDE COMPOUNDS

The term concentrates is usually applied to materials derived directly from processes operating on the starting mineral before any separation into individual lanthanides has taken place. One unrecognized feature of the lanthanide industry is that by far the greatest consumption of the lanthanides is *not* as separated compounds *but* in the form of these concentrates, i.e. derivatives of mixed-lanthanides. After all, in the real economic world, why go through the costly separation processes if such steps are not needed ?

The initial mineral beneficiation steps will produce the appropriate mineral concentrate, e.g. for the light lanthanides :

- **Bastnasite** concentrate, and

- **Monazite** concentrate.

These two mineral concentrates contain essentially the same *natural-ratio* of lanthanides but differ in anion content. They can, *without* any Ln separation steps, be converted to discrete chemical compounds such as **chlorides** or **nitrates.** Once converted to such salts the difference between bastnasite and monazite origins has practically disappeared. The resulting mixed-lanthanide salts behave almost as "pure" compounds although they contain a mixture of Ln-cations. Lanthanide chloride (or rare-earth chloride) is a commercially available material produced in quantity.

One preferred method of "opening" bastnasite concentrate, i.e. rendering it acceptable to later Ln-separation processes, is to split roasted concentrate, by a hydrochloric acid leach, into two fractions :

- **Cerium Concentrate** and

- **Lanthanum Concentrate**

the one cerium-rich and the other lanthanum-rich (see figure).[1] The lanthanum rich portion not only provides the feed for the **solvent extraction** routines to produce individual Ln's but also is the lanthanide industry's product with the largest single market, catalysts. The cerium-rich fraction, nominally an impure cerium oxide, also has major commercial uses.

I1] Lanthanides and Yttrium (Raw Materials for Advanced and Engineering Ceramics), B.T.Kilbourn, Cer.Eng.Sc.Proc., 1985, 6(9-10), 1331
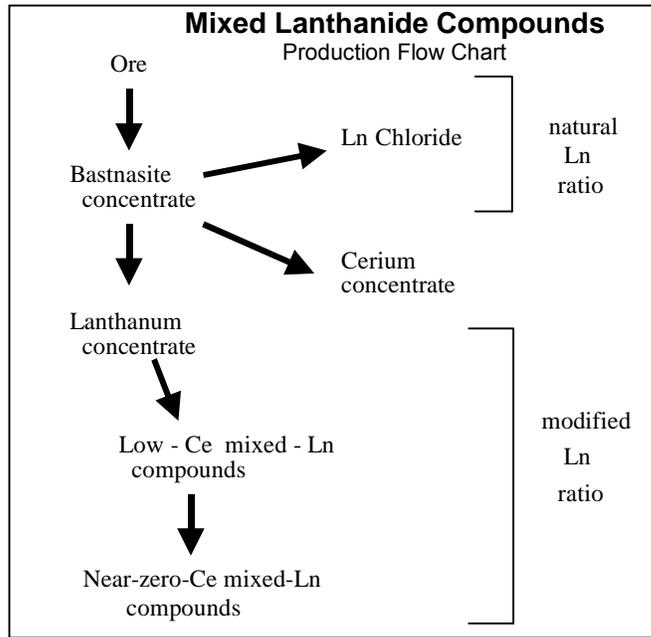
Lanthanum concentrate contains only a small percentage of Cerium; it is a low-Ce mixed-Ln compound. However there is a commercial demand for mixed Ln compounds with even lower fractions of Ce. Hence the entry "zero-Ce mixed-Ln" compounds on the flow chart in the figure. The "low-Ce" and the "zero-Ce" groups of compounds will have a modified natural ratio; the second figure compares the Ln contents of the examples of various categories.

The mineral resources from which **yttrium** and the heavy lanthanides are derived also give rise to concentrates. However, the underlying demand here is for separated pure single-Ln materials and not for mixed species. As a consequence these Y-concentrates are almost exclusively used just as precursors to those individual elements and not as materials in their own right.
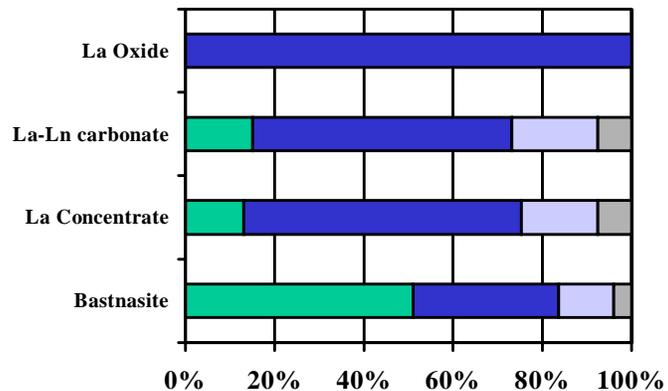
Mixed lanthanide compounds, are less expensive than pure compounds and acceptable for many applications if :

- all the Ln's present behave similarly in the potential use, *or*

- one Ln dominates, is the required Ln, and other Ln's present have no detrimental effect.

Mixed Lanthanide Compounds
Production Flow Chart

Ore
↓
Bastnasite concentrate → Ln Chloride
↓ ↘
  Cerium concentrate

} natural Ln ratio

Lanthanum concentrate
↓
Low - Ce mixed - Ln compounds
↓
Near-zero-Ce mixed-Ln compounds

} modified Ln ratio

Lanthanide Content
Comparison of various products

La Oxide					
La-Ln carbonate					
La Concentrate					
Bastnasite					

0%   20%   40%   60%   80%   100%

37

CUPRATES

Simple compounds in the Ln-Cu-O system had been studied, e.g.[1], well before the explosion of interest in this family of materials due to the discovery of high temperature superconductivity. In addition to that feature members of this family show unusual magnetic properties, catalytic behavior and other types of conductivity. [2] La_2CuO_4 has semi-metallic character with a nearly constant electrical conductivity up to 1000 K.

La_2CuO_4 crystallizes in a distorted form of the K_2NiF_4 structure. There is, however, for other members of the Ln_2CuO_4 series containing nominally Cu(II), a change in structural type, from the 9-coordinate La ion to 8-coordination with the smaller Pr and later light-Ln ions. (Other structural changes, in the Cu-O unit, also occur.) The difference between La_2CuO_4 and the Nd analogue in structural terms[3] is of considerable interest due to the apparent differing super-conductivity mechanisms that can be induced, p-type versus n-type.

Ln-Cu-O	
Formula	**Stability range**
$LnCuO_2$	
Ln_2CuO_4	La
Ln_2CuO_4	Pr - Gd
$Ln_2Cu_2O_5$	Y, Tb - Lu

With the smallest, heavy-Ln's, as well as yttrium, an alternative composition, $Ln_2Cu_2O_5$ is the preferred composition. Materials with a Cu(I) ion, the $LaCuO_2$ type, can also be made whereas the limited stability of a Cu(III) state tends to make
perovskite-type compounds, ABO_3, unstable.

[1] The High Temperature Stabilities of $LaCuO_2$ and La_2CuO_4, M.S.Chandrasekhariah et al., High Temperature Science, 1979, 11, 65 : Preparation and Properties of the Compounds Ln_2CuO_4 and some of their Solid Solutions, I.S.Schaplygin et al., Russ. J. Inorg. Chem., 1979, 24(6), 820.
[2] Superconductivity and Magnetism in the La_2CuO_4-Based Compounds, Z.Fisk et al., MRS Bull., 1989, 14(l), 33: Non-stoichiometry and Electrical Properties of La_2CuO_4 and $La_2(Cu,Ni)O_4$, N.Kieda et al., Solid State Ionics, 1991, 49, 85
[3] The Crystal Chemistry of High-Temperature Oxide Superconductors and Materials with Related Structures, H. Müller-Buschbaurn, Angew.Chem.Int.Ed.Engl., 1989, 28, 1472

DYSPROSIUM

In chemical properties Dysprosium closely resembles **Yttrium,** both elements having trivalent ions of very similar size. Data for several Dy compounds are given under the appropriate anion listing.

The 4f electrons, shielded from their surroundings, give Dy, through a strong spin-orbit coupling, a very high magnetic moment of ≈10.6 Bohr magnetons. Dy, and its neighbor, **Holmium**, have the highest values of any element.

Dysprosium's name is derived from a Greek term meaning "difficult to

Dy	
element	
Atomic Number	66
Atomic Weight	162.50
Electron configuration	$[Xe]4f^{10}6s^2$
Valency	3
Ionic radius, 8-coord	103 pm
Magnetic moment	10.6 μ_B
metal	
Crystal Structure	hcp
Melting Point	1412 °C
Boiling Point	2567 °C
Density	8.55 g/cm^3
Metallic Radius	177 pm

prepare". It is found in Yttrium ores such as Xenotime and the **ion-absorption** minerals. Dy is separated from adjacent Ln's by the standard **solvent extraction** routines and is commercially available as **oxide**, **metal** and other salts.

The oxide is used as a dopant in special ceramic $BaTiO_3$-based compositions for producing high-capacitance small-size capacitors for electronic applications. It also a possible additive, a burnable poison, to uranium oxide fuels used in nuclear power generation. The ability of Dy's isotopes to absorb strongly neutrons makes possible an extended life for the fuel rods.

The 4f electrons provide Dy with specific spectral energy levels that lead to some specialized luminescent uses. Dy's emission spectra consists of several lines across the spectrum, particularly in the regions 470 - 500 nm and 570 - 600 nm and, in some host lattices, this emission can appear white.[1]

Dosimeters, for monitoring exposure to ionizing radiation, such as gamma-rays or neutrons, can be based on Dy-doped crystals[2], particularly $CaSO_4$ or CaF_2.

[1] Efficiency of Dy^{3+}- Activated Phosphors, J.L.Sommerdijk and A.Bril, J.Electrochem.Soc., 1975, 122(7), 952
[2] Thermoluminescent Dosimetry and its Applications, A.S.Pradhan, Radiation Protection Dosimetry, 1981,1(3), 153: Role of Dy in the Thermoluminescence of $CaSO_4$; Dy, M.D.Morgan and T.G.Stroebe, *ibid,* 1990, 33, 31 : Mechanism of "Thermoluminescence in $CaSO_4$: Dy, S.M.Dhopte et al., Rad. Effects Defects in Solids, 1991, 117, 337

Exposure of such a crystal to energetic radiation creates - in situ and quantitatively - excited Dy atoms. On heating that crystal these atoms luminesce, i.e. a glow peak is produced, the magnitude of which determines the radiation damage and hence the radiation dose.

Dysprosium's high magnetic moment *per se* does not directly confer high performance in practical magnetic materials. Nevertheless Dy is now an essential additive, for enhancing coercivity, to Nd-Fe-B high-strength permanent magnets.[3] It is probable that the Dysprosium substitutes into the magnetic phase, that is it creates $Nd_{2-x}Dy_xFe_{l4}B$ with a higher anisotropy (a needed property for coercivity) than the non-substituted material.

Another use depending on magnetic properties is in the material, $Tb_xDy_{1-x}Fe_2$, "Terfenol" ™, that changes dimensions in a magnetic field. This essentially instantaneous effect is at the heart of advanced sonar transducers and micropositioners.

The atomic emission spectra of Dysprosium at high temperatures contains, like most of the other lanthanides, many lines in the visible spectrum. Metal halide discharge lamps, relying on this property, efficiently produce high intensity illumination. [4] Added as anhydrous halides, e.g. DyI_3, the salts dissociate in the lamp's hot center, there absorb energy and emit radiation ; the ions later recombine at the cooler wall surfaces.

[3] Reactivity of DY_2O_3 and Tb_4O_7 with $Nd_{l5}Fe_{77}B_8$ Powder and the Coercivity of the Sintered Magnets, M.H.Ghandehari, Appl.Phys.Lett., 1986, 48(8), 548: Magnetizability of Nd-Fe-B-type Magnets with Dy Additions, M.Tokunaga et al., J.Appl.Phys., 1988, 63(8), 3510
[4] Metal-Halide Discharge Lamps, P.C.Drop et al., Philips Tech. Rev., 1975, 35(11/12), 347 :
Tbermodynamic Properties of the Melt of the NaI - DyI_3 System, K. Hilpert et al., Ber.Bunsenges. Phys.Chem., 1990, 94(1), 35

ERBIUM

The chemical behavior of trivalent Er^{3+} closely resembles that of **Yttrium** and the heavy lanthanides. Consequently it is recovered from **resources** such as the **ion adsorption ores, monazite** and xenotime followed by purification by **solvent extraction (SX)** techniques. *See individual anion listings, e.g. oxide, chloride for further data.*

The ion has a narrow absorption band, in the green, at ≈530 nm coloring Er salts pink. Other prominent Er-absorption bands are at ≈650 nm, 800 nm and 980 nm. (The converse of absorption is emission and an incandescent Er-impregnated gas mantle will glow emerald green !)

Er	
Element	
Atomic Number	68
Atomic Weight	167.26
Electron configuration	$[Xe]4f^{12}6s^2$
Valency	3
Ionic radius, 8-coord	100 pm
Magnetic moment	9.6 μ_B
metal	
Crystal Structure	hcp
Melting Point	1529 °C
Boiling Point	2868 °C
Density	9.07 g/cm^3
Metallic Radius	176 pm

The ion's stability means that glass formulations with Er will be colored pink. It is the only pink truly stable in glass melts and is used in some opthalmic materials such as sun-glasses as well as in decorative crystal glassware. The Er-absorption can "neutralize", complement, discoloration due to impurities, particularly ferric ions, in the glass and hence produce a neutral gray, "colorless", shade. The purity required for this application is not high and, as this is the dominant use for erbium, the most readily available forms of erbium are an "erbium concentrate" and an oxide of ≈96% purity.

The current major high-technology interest in Er is its potential in amplifiers for fiber-optic data transmission. Optical telecommunication relies on signals, transmitted down silica fibers, that need regular amplification because of a loss of signal strength as transmission distance increases. The signals use a wavelength of 1.55 microns, a low loss wavelength "window" in the fiber. Erbium fortuitously lases efficiently at this wavelength and can be "pumped" by light of other wavelengths, e.g. in the visible or near i.r., thereby providing a very efficient optical method of amplification.

The basis of an Erbium-doped fiber amplifier (EDFA)[1] is a length of fiber, doped with Erbium (at ppm levels), spliced into the optical fiber at regular intervals. The pumping energy is transmitted *down* the fiber along with signal energy. The Er in the EDFA lases, amplifying those lower energy, longer wavelength, light signals also propagating down the complete fiber.

Lasers based on erbium, e.g. Er:YAG lasing at ≈2.9 microns, have been introduced for medical and dental uses. This wavelength, strongly absorbed by water, is ideally suited to energy delivery without thermal build-up in tissue.

Erbium has one neutron absorbing isotope, ^{167}Er, with properties that can provide an extremely long lifetime for nuclear fuels for specialized reactors and, for example, it has been used in a U-Zr-H fuel in research submersibles. In a current application the oxide erbia, Er_2O_3, being compatible with the UO_2 fuel, is homogeneously mixed into that fuel and enables pressurized water reactors to operate with a 2-year reload cycle[2].

Phosphors for the conversion of infra-red radiation into visible light, up-conversion, can be based on Erbium[3]. In a matrix such as a fluoride and in combination with a sensitizer, Yb^{3+}, that absorbs strongly in the infra-red, two long wavelength photons are successively absorbed and converted to a visible emission in the green. Cards, for example, using these phosphors are used to check for the presence of infra-red laser emission.

The magnetic behavior of Erbium underlies a specialist use in refrigeration at the very low temperatures of liquid Helium. Certain alloys containing Erbium have large heat capacities at temperatures below ≈20K due to their magnetic properties[4]. This large heat capacity, for an alloy such as Er_3Ni, by "mopping-up" thermal energy fluctuations, enables the He in magnetic resonance imaging (MRI) scanners to be kept economically at 2 K.

[1] Review of Rare Earth Doped Fibre Lasers and Amplifiers, P.Urquhart, IEEE Proc., 1988(December), 133(J6), 385 : A Review of the Fabrication and Properties of Erbium-doped Fibers for Optical Amplifiers, B.J.Ainslic, J.Lightwave Technol., 1991, 9(2), 220: Lightwave Communications; The Fifth Generation, E.Desurvire, Scientific American, 1992(January), 114
[2] Analysis of Critical Experiments with Erbia-Urania Fuel, A.Jonsson et al., Trans. Am. Nucl. Soc., 1992, 65, 415
[3] Phosphors for the Conversion of Infrared Radiation into Visible Light, J.L.Sommerdijk and A.Bril, Philips Tech. Rev., 1974, 34, 24: On the Efficiency of Yb^{3+}-Er^{3+} Activated Up-Conversion Phosphors, A.Bril et al., J.Electrochem.Soc., 1975, 122(5), 660
[4] Magnetic Intermetallic Compounds for Cryogenic Regenerator, R.Li et al., Cryogenics, 1990,30, 521

EUROPIUM

This element is characterized by having two stable valencies :

- Eu(II)   (europous)

- Eu(III)   (europic)

The Eu(ll)/Eu(III) redox potential is such that divalent compounds can be made in aqueous solution; water only oxidizes Eu(II) very slowly. In solid salts the Eu^{2+} ion can be completely stable, e.g. in lighting phosphors. (Europium(II) salts can be used in a purification step in europium production. The insoluble $EuSO_4$ salt is precipitated out without bringing down other, trivalent, lanthanides.)

Eu	
Element	
Atomic Number	63
Atomic Weight	151.96
Electron configuration	$[Xe]4f^76s^2$
Valency	2 and 3
Ionic radius, 8-coord	(2+) 125 pm
	(3+) 107 pm
Magnetic moment	3.4 μ_B
metal	
Crystal Structure	Bcc
Melting Point	826 °C
Boiling Point	1439 °C
Density	5.26 g/cm^3
Metallic Radius	208 pm

The greater stability, relative to other Ln(II) species, of the Eu(II) state is evident in the properties of the element as a metal. Eu is divalent in the metallic state and has a lower melting point, an enhanced volatility and a larger atomic (metallic) radius compared to other lanthanide metals. Eu metal is also more reactive than other Ln's.

The chemistry of trivalent europium [1] resembles other Ln(III) systems (see **Lanthanum** for a summary) with aqueous-insoluble **carbonates** and **oxalates** but soluble **nitrates** and **chlorides**. The usual commercial form is the oxide, Eu_2O_3, available in 99.99 % or higher purities. This sesqui-oxide can adopt either the b.c.c. C-type Ln_2O_3 structure, the usual form, or the monoclinic B-type; a high-temperature structure is also possible, see **Oxides**. A brown-red monoxide, EuO, with a NaCl structure, is known.

Elements in the lanthanide series derive most of their special properties from the 4f electrons and this is typified by Europium's luminescent behavior. Excitation of the Eu atom, for example by absorption of energetic electrons or ultra-violet radiation, can result in specific energy level transitions within the atom creating an emission of visible radiation. Almost all practical uses of Europium utilize such a luminescence.

[1] Chemistry and Thermodynamics of Europium and some of its simpler Inorganic Compounds and Aqueous Species, J.A-Rard, Chem.Rev., 1985, 85, 555

Eu^{3+} produces, upon excitation, a line emission at about 610 nm and, as the doped **oxysulflde,** Eu^{3+} :Y$_2$O$_2$S, provides the perfect red found in almost all color televisions.[2] It was this red that ushered in the age of color television.

In three-prime energy-efficient fluorescent lighting Europium provides not only the necessary red, this time as
Eu^{3+} :Y$_2$O$_3$, but also the broad emission of Eu^{2+}, at just the right spectral position, for the blue.[3] Commercial blue phosphors are :

- Eu : Sr$_5$(PO$_4$)$_3$Cl
- Eu : BaMg$_2$Al$_{16}$O$_{27}$, and
- Eu : Sr$_4$Al$_{14}$O$_{25}$.

For the automation of X-ray detection systems Europium-based photostimulable phosphors are now in use. Eu-doped BaFBr, or variations on this material, will absorb X-radiation and, in a separate *later* processing step, upon stimulation by a discrete small-spot laser beam, emit visible radiation proportional to the absorbed dose. [4]

Eu luminescence is also used as a probe in biochemistry[5] and for highly sensitive analytical techniques in biomedical applications. [6]

Europium has several naturally occurring isotopes most of which have high neutron absorption properties. In addition this absorption value is maintained over time because of the formation of a succession of high neutron-capture cross-section daughter isotopes. The element, in the form of the oxide, has been used in some specialized nuclear reactors.[7]

[2] Recent Developments on Phosphors for Fluorescent Lamps and Cathode-Ray Tubes, T.Welker, J.Lumin., 1991, 48 & 49, 49

[3] Phosphors based on Rare Earths, a new Era in Fluorescent Lighting, B.M.J.Smets, Mat.Chem.Phys., 1987, 16, 283

[4] Photostimulable Phosphors for X-Ray Imaging ; Applications and Mechanism, M.K.Crawford and LH.Brixner, J.Lumin., 1991,48 & 49,37: Mechanism of Charge Storage and Luminescence Stimulation in BaFBr : RE Phosphors, A.Harrison et al., Nucl.Inst.Meth. Phys.Res., 1991, A310, 220

[5] Terbium(III) and Europium(III) Ions as Luminescent Probes and Stains for Bimolecular Systems, F.S.Richardson, Chem.Rev., 1982, 82, 541 : The Europium(III) Ion as a Spectroscopic Probe in Bioinorganic Chemistry, J-C.G.Bunzli, Inorg.Chim.Acta, 1987, 139, 219

[6] Multiple Fluorescence Labeling with Europium Chelators. Application to Time-Resolved Fluoroimmunoassays, E.P.Diamandis et al., Anal.Chem., 1989, 61, 48 : Europium Chelate Labels in Time-resolved Fluorescence Immunoassays and DNA Hybridization Assays, E.P.Diamandis et al., Anal.Chem., 1990, 22, 1149A

[7] Europia Ceramics for use as Fast Reactor Neutron Absorbers, J.B.Ainscough et al., Ceramurg. Intern., 1977, 3(l), 18 : Physical Properties of Europium Sesquioxide, K.E.Gilchrist, R.G.Brown and S.D.Preston, J.Nucl.Mat., 1977, 68, 39: Europia as a Nuclear Control Material, P.C.S.Wu, Nucl.Tech., 1978,39,84

FLUORIDES

The trifluorides, LnF_3, are well characterized stable compounds recognized for all elements in the lanthanide series.[1] (Unstable difluorides, LnF_2, are known for Sm, Eu and Yb while tetrafluorides, LnF_4, can be made for Ce, Pr and Tb.)

The LnF_3 compounds can be prepared[2] by reaction of fluorinating agents, such as hydrofluoric acid, with the oxide or other salts. However the rate of reaction with an oxide depends on the particular oxide and, in practice, it is easier to start with an oxide precursor such as **carbonate** or **oxalate.**

$$Ln_2(CO_3)_3 + 6\ HF\ \Rightarrow\ 2\ LnF_3 + 3\ CO_2 + 3\ H_2O$$
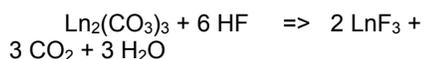
**Lanthanide Fluorides**			
Ln	**melting Point °C**	**density g/cm³**	**color**
YF_3	1155	5.07	white
LaF_3	1493	5.94	white
CeF_3	1432	5.99	white
PrF_3	1399	6.18	green
NdF_3	1377	6.50	violet
SmF_3	1300	6.64	white
EuF_3	(1262)	6.79	white
GdF_3	1232	7.05	white
TbF_3	1177	7.24	white
DyF_3	1157	7.47	off-white
HoF_3	1143	7.64	pink
ErF_3	1146	7.81	pink
TmF_3	1158	7.97	white
YbF_3	1162	8.17	white
LuF_3	1184	8.33	white

With aqueous HF the resulting fluoride is partially hydrated; typically the products correspond to $LnF_3 \cdot \tfrac{1}{2}H_2O$ (Complete dehydration in a later step is difficult and, prior to the subsequent conversion of the fluoride to the **metal,** the presence of crystalline water can lead to the undesirable formation of stable **oxyfluorides**, LnOF.)

An alternative fluorinating agent is ammonium bifluoride.

- $Ln_2(CO_3)_3 + 6\ NH_4HF_2\ \Rightarrow\ 2\ LnF_3 + 6\ NH_4F + 3\ H_2O$
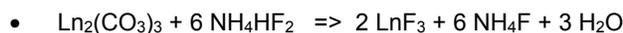
The excess of fluorinating agent can be sublimed off at 250 °C or so. This process leads to anhydrous fluorides that show less contamination by oxyfluorides in later conversion steps to the metals.

[1] Rare Earth Fluorides, O.Greis and J.M.Haschke, in "Handbook on the Physics and Chemistry of Rare Earths", ed. K.A.Gschneidner and L.Eyring, publ. North-Holland, 1982, Vol.5, p.387 : Halides of the Lanthanides and Actinides, D.Brown, publ. J.Wiley, 1968
[2] Halides, J.M.Haschke, in "Handbook on the Physics and Chemistry of Rare Earths", ed. K.A.Gschneidner and L.Eyring, publ. North-Holland, 1979, Vol.4, p.89 : Lanthanide, Yttrium and Scandium Trihalides : Preparation of Anhydrous Materials and Solution Thermochemistry, J.Burgess and J.Kijowski, Adv. Inorg. Radiochem., 1981, 24, 57

The fluoride is the preferred salt-precursor for metal production because it can be prepared relatively oxygen-free, it is not hygroscopic and a stable end-product slag results. *Calcium* metal is the reductant most usually employed in industry. **Neodymium,** as an example, is produced commercially by mixing a slight excess of Calcium particles with the fluoride and heating to initiate the exothermic reaction:

- $3 \, Ca + 2 \, NdF_3 \; => \; 3 \, CaF_2 + 2 \, Nd$
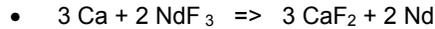
The trifluoride salts are insoluble in water and, at ambient temperatures, are stable in air and moisture but on heating ($\approx >800$ °C) oxide-fluorides and then oxides are produced. The trifluorides adopt (apart from high-temperature modifications) two crystalline structures; the heavy Ln's (and Y) occur in the YF_3 modification whereas the lighter Ln's (La to $\approx$Eu) take up the *tysonite* structure.

The precise details of the tysonite structure have been much discussed and the coordination arrangement around the Ln atom can be described in several ways. The Ln atom, nominally nine coordinate, can be considered to be part of a [LnF] layer separated by F ions. The structural subtleties no doubt underlie the unusual physical properties of these *tysonite*-fluorides, namely very high fluoride ion mobility and hence ionic conductivity[3] as well as high pressure shear-type lubricating behavior[4].

Applications

The fluorides have a range of technological uses including

- precursors for the calciothermic winning of the lanthanide metals,
- thin-film coating of optical elements[5],
- as LaF_3, as fluoride-ion sensitive electrodes,
- as "core" material in welding electrodes,
- as "core" material in carbon-arc electrodes,
- in heavy metal fluoride glasses for optical fibers for telecommunications,
- as high-pressure anti-wear lubricants[4],
- as host lattices for phosphors and scintillators.

[3] Ionic Conductivity in Tysonite-type Solid Solutions $La_{1-x}Ba_xF_{3-x}$. A.Roos et al., Solid State Ionics, 1984, 13, 191

[4] Lubricant Grade Cerium Fluoride - A new Solid Lubricant Additive for Greases, Pastes and Suspensions, J.M.Dumdum et al., NLGI Spokesman, publ. National Lubrication and Grease Institute, July 1984, 111

[5] Fluoride Compounds for IR Coatings, S.F.Pellicori and E.Colton, Thin Solid Films, 1992, 209, 109
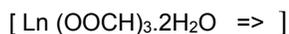
FORMATES

Lanthanide formates can be prepared[1] by the direct reaction of excess formic acid with the oxide, or more readily with an aqueous suspension of the carbonate. From dilute solution a dihydrate crystallizes out for the heavy Ln's (Ho to Lu including Y) otherwise the unhydrated $Ln(OOCH)_3$ salt precipitates.

Several structural types have been recognized

- $Ln (OOCH)_3$, for Y, and La to Tm inclusive,
- $Ln (OOCH)_3.2H_2O$, for Y, Ho and Er,
- $Ln (OOCH)_3.2H_2O$, for Yb and Lu.

Thermo gravimetric analysis (TGA) shows that for both the dihydrate and the anhydrous salts the general decomposition pathway is

$[Ln (OOCH)_3.2H_2O \Rightarrow]$

$\qquad Ln (OOCH)_3 \Rightarrow$

$\qquad$ possibly $\quad Ln_2O(OOCH)_4 \Rightarrow$

$\qquad\qquad LnO(OOCH) \Rightarrow$

$\qquad\qquad\qquad Ln_2O_2(CO_3) \Rightarrow$

$\qquad\qquad\qquad\qquad Ln_2O_3$

The intermediate species are more clearly defined for the lighter ln's, the tetraformate was only resolved with La for example. The monooxoformate, $LnO(OOCH)$, is formed by about 400 °C for most of the Lanthanides and is followed by slow conversion to an oxocarbonate by 650 °C or so and ultimately to the oxide. With the heaviest Ln's no clear intermediates can be seen on the TGA traces.

[1] A Structural and Thermo gravimetric Investigation of the Rare Earth Formates, R.P.Turcotte et al., J.Sol.St.Chem., 1970, 2, 593 : Rare Earth Formates, Decomposition, Infrared and Single Crystal Data, F.L.Carter et al., Proc. 9th. Rare Earth Res.Conf. (Blacksburg, VA, U.S.A.) 1971, 752

GADOLINIUM

Gadolinium is recovered from both the light-lanthanide ores, **bastnasite** and **monazite**, and is available as the pure oxide from which other compounds are derived.

This middle member of the Ln series has properties, as a stable trivalent ion, typical of all Ln^{3+} derivatives, see **lanthanum** and **yttrium.** There are no absorption bands in the visible and simple Gd compounds will be colorless (unless the anion causes color); see entry under the appropriate anion for more details.

The metal is unusual in being ferromagnetic up to ≈ambient temperatures but,

Gd	
Element	
Atomic Number	64
Atomic Weight	157.25
Electron configuration	$[Xe]4f^{7}5d^{1}6s^{2}$
Valency	3
Ionic radius, 8-coord	105 pm
Magnetic moment	7.94 μ_B
metal	
Crystal Structure	Hcp
Melting Point	1313 °C
Boiling Point	3273 °C
Density	7.90 g/cm^3
Metallic Radius	180 pm

because of a 20°C T_c (Curie temperature), loses this behavior in, for example, hot water.

Gd^{3+} has the stable $4f^7$ configuration and, with seven unpaired electrons, a high magnetic moment; many uses depend on Gd's magnetic properties. The extra-stable half-full 4f shell, with no low lying energy levels, also creates applications as an inert phosphor host.

Magnetic resonance imaging, now widely used medically, depends on the nmr signal from water to create a proton density map. Paramagnetic ions, such as Gd^{3+} with its high magnetic moment μ_B, can reduce relaxation times and thereby enhance signal intensity. For this reason Gadolinium, complexed with EDTA-type ligands, is used as an injectable contrast agent in MRI(magnetic resonance imaging).[1]

Gadolinium, as the metal or in Gd-alloys, has been proposed as the working substance in magnetic refrigeration cycles[2] that could operate around room temperature. Paramagnetic salts of Gd, such as $Gd_3Ga_5O_{l2}$, are used in ultra-low

[1] Lanthanide Chelates as Magnetic Resonance Imaging Contrast Agents, A.D.Sherry, J.Less-Comm. Metals, 1989, 149, 133
[2] Magnetic Heat Pumping, G.V.Brown, U.S.Patent 4,392,356,12-July-1983 : Magnetic Refrigeration in the Temperature Range 10K to Room Temperature ; the Ferromagnetic Refrigerants, T.Hashimoto et al., Cryogenics, 1981(11), 647

temperature refrigeration, $\leq 1K$. These refrigerative methods rely on the fact that, at a fixed temperature, the entropy, and hence temperature, of a system of magnetic moments is lowered by the presence of a magnetic field.

The element is also used, because of its magnetic behavior, in the rare-earth transition-metal alloys that form the thin film at the heart of magneto-optic recording technology[3] used for handling computer data. The alloys, e.g. GdTbFe, need to show magnetic anisotropy and have an accessible Curie temperature. Another type of data storage device, this time non-volatile, is based on the garnet, $Gd_3Ga_5O_{12}$ (GGG), as a substrate crystal for ferrimagnetic films. These films permit the creation of "magnetic bubbles", or bubble memories. Another garnet type, Gd-Iron garnets - GIG's - helps control microwave communications.

Bulk materials that luminesce in the visible upon impact of high-energy X-ray photons are potential X-ray phosphors. Certain Ln ions other than Gd can provide the emission but the host material needs to be inert and to "dilute" the active emitter (to avoid quenching). Gadolinium compounds can act as hosts; a common phosphor used in X-ray cassettes is $Tb:Gd_2O_2S$[4] and scintillator materials for computed tomography can be $Eu:(Y,Gd)_2O_3$ or $Pr,Ce:Gd_2O_2S$[5].

Gadolinium is unique in having a high neutron absorption cross section coupled with a burn-up rate that can match that of the ^{235}U isotope used as nuclear fuel.[6] (Two natural Gd isotopes, ^{155}Gd - 15 % abundance and 61,000 barns cross-section -and ^{157}Gd - 16 % abundance and 255,000 barns - create this behavior, cf. B with 760 barns.) In addition the oxide, Gd_2O_3, has physical and chemical properties very similar to UO_2, Consequently gadolinia is used as a "burnable poison", intimately mixed at $\approx 5\%$ with UO_2 in a pellet form, in various nuclear reactors to make more efficient use of the fissionable Uranium.

[3] Magneto-Optical Recording Technology and Data Storage Materials, F.J.A.M.Greidanus and S.Klahn, Angew.Chem.Int.Ed.Eng., 1989, 28(2), 235

[4] New X-Ray Phosphors, L.H.Brixner, Mat.Chem.Phys., 1987, 16, 253

[5] Ceramic Scintillators for Advanced, Medical X-Ray Detectors, C.D.Greskovich et al., Ceram.Bull., 1992, 71, 1120 : A Scintillator Gd_2O_2S:Pr,Ce for X-Ray Computed Tomography, H.Yamada et al., J.Electrochem. Soc., 1989, 136(9), 2713

[6] A Comparison of Gadolinia and Boron for Burnable Poison Applications in Pressurized Water Reactors, L.Goldstein and A.F. Strasser, Nucl.Tech., 1983, 60, 352

HOLMIUM

Holmium is recovered from ores processed for their yttrium content such as **Xenotime** and the **Ion-adsorption ores.** It is commercially available as the oxide and other compounds. Salts containing the Ho^{3+} ion resemble those of other tri-valent lanthanides in their properties. It is one of the least **abundant** lanthanides and has few commercial uses.

Ho	
Element	
Atomic Number	67
Atomic Weight	164.93
Electron configuration	$[Xe]4f^{11}6s^2$
Valency	3
Ionic radius, 8-coord	102 pm
Magnetic moment	10.6 μ_B
metal	
Crystal Structure	Hcp
Melting Point	1474 °C
Boiling Point	2700 °C

Holmium has the highest magnetic moment of any element, 10.6 Bohr magnetons, and at low temperatures the element in bulk form is ferromagnetic. This property is utilized in"magnetic flux concentrators", pole pieces placed at the heart of super-strength magnets to create the highest known magnetic fields. The record dc magnetic field of 33.6 Tesla was achieved with a "concentrator" relying on pole pieces made from Ho[1]. Because of its magnetic moment there is a small demand for the Ho3+ ion as an additive to YIG (Yttrium Iron Garnet) crystals, used in microwave technology.

The Holmium ion shows several strong and very sharp spectral absorption bands in the blue particularly at and near 450 nm. As these arise from 4f transitions they are independent of host lattice and are used as spectrophotometric standards.

The Ho^{3+} ion lases at ≈2.08 microns, an eye-safe wavelength, and has been tested, for example, in YLF (Yttrium Lanthanum Fluoride) and YAG (Yttrium Aluminum Garnet) crystals. This wavelength offers certain advantages for medical uses; it can be delivered through the silica fibers designed for shorter wavelengths but also provides the tissue cutting ability, due to absorption by water content of tissue, associated with longer wavelengths. The Ho laser, in systems such as Cr,Tm,Ho: YAG, is FDA approved, for example, for various surgeries[2].

[1]33.6 T DC magnetic Field produced in a Hybrid Magnet with Holmium Pole Pieces, L.G.Rubin et al., Appl.Phys.Lett., 1986, 49(l), 49
[2] Holmiurn Laser cuts into Medical Applications, P.Moulton et al., Laser Focus World, 1992(3), 65

HYDRIDES

All lanthanides, plus yttrium, form binary hydrides, LnH_x, that, except for Eu and Yb, have the fluorite structure[1]. Wide variations in composition makes a continuous range $LnH_{=2}$ to $LnH_{=3}$ possible. The light-Ln hydrides show a metal, LnH_2, to a semiconductor, LnH_3, transition; a color change can also occur e.g. from a dark metallic green, CeH_2, to a bronze, CeH_3.[2]

Many lanthanide-transition metal intermetallic compounds, AB_n, form ternary hydrides, AB_nH_m, (where m can be non-integral) that have interesting physical properties. With some compounds, e.g. $LaNi_5$, the reaction :

$$Metal + Hydrogen <====> Metal\ Hydride + Heat$$
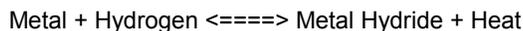
is readily reversible at convenient (i.e. near ambient) pressures and temperatures. [3] The exact equilibrium position depends on the compound involved, and on the external conditions, e.g. hydrogen pressure and temperature.

Of the two reaction paths :

$$Ln\text{-}M + Hydrogen ====> Ln\text{-}M\text{-}Hydride$$

$$Ln\text{-}M + Hydrogen ====> Ln\text{-}Hydride + M$$
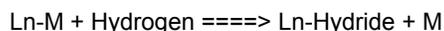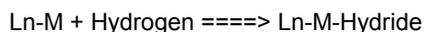
the first, despite being thermodynamically less favored, occurs because of kinetic constraints. A higher activation energy for the second, the disproportionation reaction, suppresses this step. $LaNi_5$, for example, absorbs hydrogen very easily, much more readily than do the component elements/metals separately.

As an alternative to direct reaction of metal with dihydrogen gas, aqueous BH_4^- is a general and effective method[4] for hydriding those intermetallics comparable in stability to the $LaNi_5$ systems.

$$M + BH_4^- => M\text{-}H + H_2BO_3 + 3.5\ H_2$$
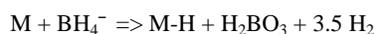
[1] Hydrides, G.G.Libowitz and A.J.Maeland, in "Handbook on the Physics and Chemistry of Rare Earths", ed. K.A-Gschneidncr and L.Eyring, Vol.3, Chap. 26, publ. North-Holland 1979, p.299.
[2] P-T-x Phase Diagrams of the Light Lanthanide-Hydrogen Systems (Ln ≡ La - Nd), R.Bischof et al., J.Less-Common Met., 1985, 110, 99: The Phase Diagram of the $Ce\text{-}H_2$ System and the $CeH_2\text{-}CeH_3$ Solid Solutions, M.Tellefsen et al., J.Less-Common Met., 1985, 110, 107
[3] Physicochemistry and Crystallochernistry of Intermetallic Hydrides containing Rare Earths and Transition Metals, K.N.Semenenko et al., J.Less-Common Met., 1985, 105, 1
[4] A new Route to Metal Hydrides, D.W.Murphy et al., Chem.Mater., 1993, 5, 767

The active hydrogen-absorbing intermetallics all contain atoms of disparate sizes and the crystalline structures offer a wide variety of inter-stitial sites all of which can accommodate the small H atom. This inherent variety, along with a range of metal atom metal-atom contacts, allows for an inherent flexibility within the lattice and a low activation energy for hydrogen absorption.

The potential lattice locations for the incoming hydrogens are easily deformable and no major structural changes are needed to create the intermetallic hydride. There is a gradual transition from the intermetallic structure to the hydride structure with a concomitant gradual increase in bulk volume. This accounts for the variable and often non-integral number of H's per formula unit in the resulting intermetallic hydride.

The absorption/desorption behavior of these materials is best described with pressure composition (P-C) isotherms. At a specific pressure the hydriding reaction begins, the material starts absorbing large quantities of hydrogen while the pressure remains essentially constant. This plateau region corresponds to a two phase mixture of metal and metal hydride. The pressure corresponding to the plateau region is strongly dependent on temperature. The higher the temperature, the higher the plateau pressure, a consequence of the exothermic hydriding reaction. The desorption step can be achieved by supplying heat at a temperature above the dissociation (plateau) pressure.

Compositions of hydridable Ln-intermetallics can be tailored to provide specific properties and, in particular, a less-expensive misch**metal**-type of material, with the modified natural-ratio of Ln's rather than the more expensive pure La, can often be used.[5]

The ready interconversion between heat energy and hydrogen pressure offered by these intermetallics provides new approaches for many technologies.[6][7] Current development topics include hydrogen compression, purification and storage as well as energy conversion through heat pumps and refrigeration.

[5] RNi$_5$, Hydrogen Storage Compounds (R=Rare Earth), J.Liu and E.L.Huston, J.Less-Comm. Metals, 1983,90,11

[6] Rare Earths and Rechargeables, The Role of REE's in Reversible Metal Hydrides, G.D.Sandrock and E.L.Huston, in Rare Earths, ed. R.G.Bautista and N./Jackson, publ. TMS, 1991, 423

[7] Hydrogen Storage in Metal Hydrides, J.J.Reilly and G.D.Sandrock, Scientific American, 1980, 242, 98: How Metals Store Hydrogen, G.D.Sandrock and E.LHuston, Chemtech, 1981, 11, 754: Rechargeable Metallic Hydrides for Hydrogen Storage, H.C.Angus, Phys. Technol., 1981, 12, 245: Properties and Applications of Metal Hydrides in Energy Conversion Systems, H.Wenzl, Int.Metals Rev., 1982, 27(3), 140

In addition the dissociation of hydrogen molecules to potentially reactive hydrogen atoms through the intermediacy of these materials has implications for catalysis and electrochemistry. [8]

The major application though is in

- rechargeable batteries [5] [9],

where the metal hydride system (Ni/MH) is an alternative to NiCd cells. An intermetallic, usually based on $LaNi_5$, essentially replaces the $Cd(OH)_2$ in the Ni-Cd system. During charging, hydrogen is generated at the negative electrode where it enters the lattice of that electrode metal, a lanthanide intermetallic.

The overall reaction, fully reversible, in such hydride batteries is :

$$\begin{array}{c} charge > \\ 1/6\ LaNi_5 + Ni(OH)_2 <==> 1/6\ LaNi_5H_6 + NiOOH \\ < discharge \end{array}$$
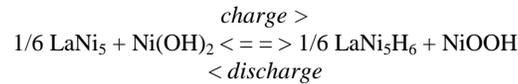
Corrosion resistance, storage capacity, discharge rate and other properties of the simple $LaNi_5$ system can be noticeably improved by partial replacement of the Ni and/or La by other elements and by addition of other components. One standard commercial alloy in use as the negative electrode is $La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Si_{0.1}$[10], other compositions are also in use[11].

These batteries provide power for notebook computers for example. In comparison to Nickel-Cadmium, the metal hydride batteries offer higher energy densities, higher charge rates, few environmental problems and could eventually replace the Ni-Cd systems.

[8] Electrochemical Utilization of Metal Hydrides, H.F.Bittner and C.C.Badcock, J.Electrochem.Soc., 1983, 130(5), 193C

[9] Investigation of a new type of Rechargeable Battery, the Nickel-Hydride Cell, J.J.G.Willems, Philips Tech.Rev., 1986, 43(1/2), 22 :

[10] Metal Hydride Electrodes, Stability of LaNi$_5$-related Compounds, J.J.G.Willems, Philips J.Res.Suppl., 1984, 39(l), 1

[11] Metal Hydride Anodes for Nickel-Hydrogen Secondary Battery, T.Sakai et al., J.Electrochem.Soc., 1990,1137(3), 795

HYDROXIDES, HYDRATES

Within the Ln_2O_3-H_2O system the hydroxides, $Ln(OH)_3$, and oxyhydroxides, $LnO(OH)$, have been recognized and characterized for all the Ln elements. The hydroxides are insoluble in water hence, although the Ln_2O_3 oxides are basic, concentrations of $[OH]^-$ do not arise.

The pH at which precipitation of $Ln(OH)_3$ begins, upon the addition of base to solutions of Ln compounds, depends on concentration and on anion present, failing from ≈ 8 for **Lanthanum** to ≈ 6 at **Lutetium**[1]. The initial precipitates tend to be amorphous and only after sufficient aging do these become crystalline.

Yttrium behaves ideally like **Holmium** but, because its hydrolytic behavior is more dependent on concentration (due to stable oligomers ?), its apparent placement in the Ln series can vary.

Addition of base to solution tends to produce gelatinous, hard-to-filter, precipitates and, for material preparation, the addition of a Ln solution to a base is preferred. The crystallinity of the solid increases with "aging" particularly for the lighter Ln's. Upon thermal decomposition the hydroxides pass through the poorly defined oxy/hydroxy species to produce, at ≈ 650 °C, the appropriate oxide.

Cerium(III) hydroxide initially comes down as a white $Ce(OH)_3$ that, on standing, readily oxidizes and passes through intermediate violet-tinged mixed-valence species to from the stable $Ce(OH)_4$, "ceric hydrate". The amorphous ceric compound, after drying, is best regarded as $CeO_2 \cdot 2H_2O$, a reactive hydrated oxide.

The solubility of the hydroxides increases slightly in strong base, especially for the heavier-Ln derivatives.

$$Ln(OH)_3(s) + OH^-(aq.) \Rightarrow Ln(OH)_4^-(aq.)$$
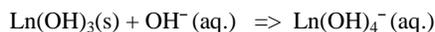
The ready formation of basic salts means it may be possible to precipitate out an Ln compound with less than stoichiometric base. Many hydroxy salts have been identified in compounds of simple anions, e.g. $Ln(OH)(CO_3)$ and $Ln(OH)_2Cl$, see below.

[1] Precipitation Incidence of the Lanthanoid(III) Hydroxides, Y. Suzuki et al., J.Less-Common. Met., 1986, 126, 351; 1989, 149, 179

The trihydroxides adopt the UCl_3 crystal structure[2], with a nine coordinated metal atom and non-equal M-0 bond lengths, that can be considered as built up from alternating $Ln(OH)_2^+$ and $(OH)^-$ layers. (Nine-coordination is found for many salts due to the common packing requirements of ligand-oxygen bonding atoms around the larger Ln atom. The interactions are essentially completely ionic and there are no preferred geometries.) The smallest Ln atom, **Lutetium,** does from a six-coordinate octahedral $Lu(OH)_3$ structure.

The systems [Ln,OH,X], where $X = F^-$, Cl^-, NO_3, etc., show the existence of several discrete species within series such as $Ln(OH)_{3-x}Cl_x$, some with apparently noninteger atom counts.[3] This is due to the formation of structures based on alternating $Ln(OH)_2^+$ and X^- layers, related to the UCl_3 type, with ready structural interchange between certain X and OH ions.

Lanthanum Concentrate, nominally $Ln(OH)_2Cl$ is produced commercially on a large scale for incorporation into cracking catalysts for gasoline production from crude oil. It has a composition approximated by the formula, $Ln(OH)_{2.5}Cl_{0.5}$ and probably belongs to this [Ln,OH,X] class of materials.

[2] Structural Trends in the Lanthanide Trihydroxides, G.W.Beall et al., J.Inorg.Nucl.Chem., 1977, 39, 65
[3] Preparation, Phase Equilibria, Crystal Chemistry and some Properties of Lanthanide HydroxideNitrates, J.M.Haschke, Inorg. Chem., 1974, 13(8), 1812 : Preparation, Phase Equilibria and Crystal Chemistry of Lanthanum, Praseodymium and Neodyntium Hydroxide Chlorides, E.T.Lance and
J.M.Haschke, J.Solid State Chem., 1976, 17, 55

ION ADSORPTION ORES

During the 1980's China emerged as a major supplier of rare earth compounds not only by processing its major **bastnasite** deposit but also by processing the so-called "ion adsorption" ores found in southern part of the country.[1] This type of ore is apparently unique to China and results from the controlled in-situ weathering over long periods of time - in geological terms - of lanthanide-containing igneous rocks.

Surface layers of granite, under warm moist sub-tropical conditions suffer strong chemical weathering and, if no erosion occurs, the rare earth cations are mobilized into the aqueous phase and migrate downwards. Concurrent with the weathering various alumino-silicate minerals, such as kaolinite clays, are formed and these, in turn, adsorb the Ln_3+ cations.

As the weathering proceeds there is what could be termed "geological chromatography" and the relative proportions of the various elements can change. Furthermore, chemical weathering, by the oxidation of Ce^{3+} to Ce^{4+} in the topmost part of the weathering zone, can significantly reduce the cerium content of the later adsorbed species. (The Ce^{4+} cation is much more readily hydrolysed and is retained as hydroxide species in the upper humic layer.) Ion adsorption ores are normally low in **cerium** but high in **lanthanum** content and tend to be dominated by the middle elements of the Ln series. In particular as **yttrium** is inherently appreciably more **abundant** than those middle Ln's this one element often dominates; the composition of three such ores shows their wide variability.

The deposits are of substantially lower grade (≈0.1% REO) than other rare earth deposits but this is offset by the easier mining and processing. The ion-adsorption ores are mined by open pit methods and a simple leach produces a Ln/RE containing solution from which a concentrate can be precipitated. (Separation into individual Ln's is by the usual **solvent extraction** (SX) technology.)

Ion Adsorption Ores typical Ln & Y content (w.r.t 100% Ln + Y)		
Ore A	Ore B	Ore C
La	2.2	29.8	23.2
Ce	1.1	7.2	2
Pr	1.1	7.4	5.1
Nd	3.5	30.2	19.5
Sm	2.3	6.3	4.4
Eu	0.4	0.5	0.8
Gd	5.7	4.2	4.9
Tb	1.1	0.5	0.7
Dy	7.5	1.8	4.7
Ho	1.6	0.3	0.5
Er	4.3	0.9	2.4
Tm	0.6	0.1	0.3
Yb	3.3	0.6	1.6
Lu	0.5	0.1	0.3
Y	64.9	10.1	29.5

Il] China's Rare Earth Potential, Industry and Policy, AL. Clark and S.Zheng, paper presented at "International Conference on Rare Earth Mineral and Minerals for Electronic Uses", Hat Yai, T'hailand, January 1991, publ. Prince of Songkla University, Thailand

LANTHANUM CONCENTRATE

The splitting of **bastnasite** into two portions by an HCl leach results in a soluble fraction still containing all the Ln's but with much of the Ce removed; the cut though is not perfect and some cerium does pass into solution. A simple **solvent extraction (SX)** process on this soluble fraction can then remove the heavy-Ln portion, i.e. the elements Sm and onwards, for later SX processes to produce the separated heavier lanthanides. The soluble portion remaining contains La, Nd, and Pr and also some Ce.

Addition of base to this soluble portion produces a crystalline precipitate of a composition approximating the formula $Ln(OH)_{2.5}Cl_{0.5}$. This material, in the past, has been given several names :

- Rare Earth Hydrate
- Lanthanum Hydrate
- Lanthanum Concentrate

The last is the one now preferred.

Although the *relative* proportion of cerium can be changed - it depends on the earlier processing steps - this lanthanum concentrate essentially has a reproducible composition. It is a "clean" product with none of the variability and practically none of the impurities associated with **cerium concentrate.** It is readily soluble in acids and provides an economical source of the hydrated Ln^{3+} ions.

Lanthanum Concentrate Typical Analysis		
total Ln Oxides		≈80%
La_2O_3	≈49 %	
CeO_2	≈11 %	
Nd_2O_3	≈14 %	
Pr_6O_{11}	≈6 %	
Cl		≈10 %
loss on Ignition		balance

For the lanthanide industry this is a major product because of the lanthanides role as crucial components of catalysts used in the FCC (fluid catalytic cracking) process for gasoline production. Demand for the concentrate peaked in the mid 1980's and has recently declined because of gasoline formulation changes and new catalyst technologies. Nevertheless lanthanum concentrate remains a large-volume product.

The systems [Ln,OH,X], where X = F⁻, Cl⁻, NO3⁻, etc., show the existence of several discrete species within series such as $Ln(OH)_{3-x}Cl_x$, some with apparently non-integer atom counts.[1] This arises from the formation of structures based on alternating $Ln(OH)_2^+$ and X⁻ layers, derived from the UCl$_3$ type, with ready structural interchange between certain X and OH ions.

[1] Preparation, Phase Equilibria and Crystal Chemistry of Lanthanum, Praseodymium and Neodymium Hydroxide Chlorides, E.T.Lance and J.M.Haschke, J.Solid State Chem., 1976, 17, 55

LANTHANUM; LANTHANIDES

The first member of the lanthanide series, Lanthanum, is recovered from the minerals **Bastnasite** and **Monazite;** the processing is described under those entries and also under the heading **Solvent Extraction.** La is the second most **abundant** Lanthanide after **Cerium.**

In broad terms the chemical properties of the lanthanides fall between those of the alkaline-earths and of iron/aluminum. La(III) is the only easily accessible valence state for lanthanum and the chemistry of La(III) species is the prototype for the behavior of all the trivalent, Ln^{3+} lanthanides.[1] In terms of basicity La is the most basic.

La	
Element	
Atomic Number	57
Atomic Weight	138.91
Electron configuration	$[Xe]4f^{0}5d^{1}6s^{2}$
Valency	3
Ionic radius, 8-coord	116 pm
Magnetic moment	0 μ_B
metal	
Crystal Structure	Dhcp
Melting Point	918 °C
Boiling Point	3464 °C
Density	6.15 g/cm^3
Metallic Radius	188 pm

*See the individual lanthanide for data specific to that element, e.g. for magnetic properties, spectral behavior and oxidation states other than Ln^{3+}; see **yttrium** for a summary of the behavior of the heavy Ln's.*

There is often a gradual, nearly-linear, change in properties along the Ln series from La to Lu, attributable to a reduction in ionic size from the largest, La, to the smallest, Lu - the so-called "lanthanide contraction" - as the 4f shell fills. This size contraction arises because of poor shielding of the atomic nucleus by the highly directional 4f electrons. The 4f electrons themselves are shielded from interaction with external forces and have little influence on chemical reactions. Consequently when there is no change in 4f electron count the chemistry of all the Ln's is very similar.

La^{3+}, and all of the trivalent Ln^{3+}, ions form compounds based on :

* *ionic* bonding between cation and ligand atom,

* preference for bonding with negatively charged "hard" atoms, and in the order 0 > N > S, and
*
* lack of stereochemical definition in the arrangement around the cation.

[1] Handbook on the Physics and Chemistry of Rare Earths, ed. KA.Gschneidner and L.Eyring, publ. North-Holland, many volumes: T'hermochemical Properties of Yttrium, Lanthanum and the Lanthanide Elements and Ions, LR.Morss, Chem Rev., 1976, 76(6), 827: Chemistry of the Lanthanides, T.Moeller, publ. Reinhold, 1963 : Chemistry of the Lanthanons, Vickery, Butterworths, publ. 1953

One consequence is that water molecules, and hydroxide ions, are particularly strong ligands and in aqueous solutions only negatively charged oxygens, e.g. in oxalates, carbonates, can also bind strongly.

At pH's on the acidic side of ≈6 the Ln ions will exist as unhydrolyzed aquo ions. If the pH decreases, goes basic, hydrolysis of the hydrated cation occurs :

> • $Ln(H_2O)_n^{3+} + OH^- \Rightarrow Ln(OH)(H_2O)_n^{2+} \bullet\bullet\bullet \Rightarrow Ln(OH)_3$
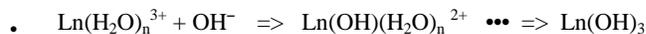
and the **hydroxide** precipitates out at a pH ranging from 7.5, La, to 5.8, Lu.

For the simple compounds aqueous solubility can be summarized :

- readily soluble   **nitrate, chloride, bromide,** and iodide, (≈ 400 gms oxide-equivalent/liter)

- partially soluble   **acetate, sulfate,** ($< ≈$ 100 gms oxide-equivalent/liter and occasionally with an inverse temperature/solubility relationship)

- insoluble in water   **oxide, carbonate, oxalate, fluoride, hydroxide, and phosphate.**

Double salts can be sometimes less soluble than the simple soluble salts, e.g. La/Mg nitrates and sulfates.

In the solid state the precise coordination arrangement around the cation is very variable being determined by ligand flexibility, chelating effects, overall packing, etc. The coordination number however around the central Ln atom is often decided by the packing of oxygen atoms from the anions and in consequence similar coordination numbers for any individual Ln are found, somewhat independent of the actual anion. For the lighter Ln's a coordination number of 9 is common whereas for the heavier smaller cations 8 is the choice. The switch over from 9 to 8 often leads to a structural change within the Ln series, e.g. oxides, nitrates, phosphates.

The table below includes useful numerical values for several Lanthanum salts, particularly for those prepared commercially in quantity. As can be seen most compounds contain many molecules of water of crystallization and various intermediate hydrates can also usually be made. As a consequence industrial (and specialty suppliers') products may well not correspond to the idealized formulas reported but contain mixtures of different crystalline, *or not so crystalline*, species. (Anhydrous compounds, particularly halides, can be obtained and some are commercially available.)

Compound	Ideal Formula	Formula Weight	% Oxide	% Element
Oxide	La_2O3	325.82	100	85.3
Acetate	$La(CH_3COO)_3.1\frac{1}{2}H_2O$	343.07	47.5	40.5
Carbonate	$La_2(CO_3)_3.H_2O$	475.86	68.5	58.4
Chloride	$LaCl_3.6H_2O$	353.36	46.1	39.3
Fluoride	$LaF_3.H_2O$	213.92	---	64.9
Hydroxide	$La(OH)_3.3H_2O$	243.98	66.8	56.9
Nitrate	$La(NO_3)_3.6H_2O$	433.01	37.6	32.1
Oxalate	$La_2((COO)_2)_3.9H_2O$	704.01	46.3	39.5
Sulfate	$La_2(SO_4)_3.8H_2O$	710.12	45.9	39.1

More details, including physico-chemical properties can be found under the listing for the appropriate anion such as **acetate, carbonate, etc.** See the individual light lanthanide entries for data on their salts.

Lanthanum, and all the lanthanides, form very stable complexes with chelating oxygen-bonding ligands such as EDTA. Lanthanum, however, is very electro-positive (as are all the Ln's) and does not readily form complexes with pi-bonding ligands nor form covalent Ln-C bonds, i.e. true organic compounds. In inert environments, though, a wide range of Ln-C compounds can be prepared; most are not stable with respect to air and moisture. The **organo-metallic** chemistry of the lanthanides is now a rapidly growing discipline [2]. These organic derivatives have potential as catalytically active species for certain polymerization and other reactions.

Lanthanum, and the lanthanides, are considered relatively inert in biochemical terms[3].

[2] Organo-lanthanoid compounds, H.Schumann, Angew. Chem. Int. Ed. Eng., 1984, 23, 474
[3] Biochemistry of the Lanthanides, C.H.Evans, book publ. Plenum, 1990 : Effects of Lanthanum in Cellular Systems, T.Das et al., Biol.Trace EI.Res., 1988, 18, 201

LUTETIUM

The last member of the Lanthanide series is, along with **thulium,** the least abundant. It is recovered, by ion-exchange routines, in small quantities from yttrium-concentrates and is available as a high-purity oxide.

Lutetium has a full 4f electron shell and, in many respects, *it* rather than lanthanum should be considered the prototype element in Group 3B of the Periodic table.[1] (In consequence the correct collective name for the 4f elements should be *lutetiides*.) The properties of its derivatives will resemble comparable compounds of **yttrium** and the other heavy lanthanide elements.

Lu	
Element	
Atomic Number	71
Atomic Weight	174.97
Electron configuration	$[Xe]4f^{14}5d^{1}6s^{2}$
Valency	3
Ionic radius, 8-coord	98 pm
Magnetic moment	0 μ_B
metal	
Crystal Structure	hcp
Melting Point	1663 °C
Boiling Point	3402 °C
Density	9.84 g/cm^3

The full 4f shell means that the Lu atom will be spectrally inert, analogous to yttrium, and its compounds are therefore potential phosphor hosts. The densest white material known is lutetium tantalate, $LuTaO_4$, (9.75 g/cm^3) and this, along with other properties, make it an ideal host matrix for an X-Ray phosphor.[2]; cost nevertheless precludes any such use.

The reduction of ionic radius from La (116 pm) to Lu (98 pm) causes Lu to have the smallest radius of the Ln series. This feature, along with the absence of a magnetic moment, accounts for a very small demand for Lu as a necessary dopant in matching lattice parameters of substrate garnet ($A_3B_5O_{12}$) crystals to those of the active crystalline overlayers. The magnetic bubble memories using modified-garnets, $Gd_3Ga_5O_{12}$ - GGG's, as a host are an example.

[1] The Positions of Lanthanum (Actinium) and Lutetium (Lawrencium) in the Periodic Table, W.B.Jensen, J.Chem.Educ., 1982, 59(8), 634
[2] New X-Ray Phosphors, L.H.Brixner, Materials Chem. & Phys., 1987, 16(3-4), 253