

A LANTHANIDE LANTHOLOGY

Part II, M - Z

Anthology :

collection of selected written works usually with common theme

hence, by extension

Lanthology

a collection of notes concerning the lanthanides and related elements

published by

Molycorp, Inc. Mountain Pass, CA, U.S.A.

*Library of Congress Catalog Card Number. 94-75361
(Cataloging-in-Publication Data)*

A Lanthanide Lanthology; Part II, M - Z

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Molycorp, Inc.
67750 Bailey Road, Mountain Pass, CA 92366, U.S.A.

printed in the United States of America

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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 modern 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 second Lanthology booklet is again 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 are to be found in the first booklet covering the first half of the alphabet, A to L. 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.

All data and information are furnished in good faith and believed to be reliable. However, no warranty of merchantability, of fitness for any use, nor any other warranty, express or implied, is made regarding the accuracy of the data contained herein, the results to be obtained from the use of materials mentioned or the hazards connected with such use. Nothing contained herein shall be construed as a recommendation for use in violation of any patent and no responsibility is assumed by Molycorp, Inc., with respect to any claim of infringement of a patent in such use.

MANGANITES

Compounds of the **perovskite**, ABO_3 , type, with tri-valent cations, $A = Ln^{3+}$ and $B = Mn^{3+}$, are recognized within the Ln-Mn-O system for all members of the lanthanide series. Thermodynamic data have been reported[1]. These materials are ternary oxides and do *not* contain - as the labels, manganites and manganates, tend to imply - discrete manganese-containing anions.

All the perovskite $LnMnO_3$'s crystallize in the orthorhombic $[GdFeO_3]$ structure, the slightly distorted version of the ideal ABO_3 structure; in addition, with $Ln = Ho$ to Lu , a hexagonal variation can be formed. (A ternary oxide, La_2MnO_4 , of the K_2NiF_4 type with La(III) and Mn(II) valencies, can also be made.)

The ABO_3 compounds can be prepared by :

- solid state reaction between **oxide** and **carbonate** at ≈ 1200 °C,
- co-precipitation from aqueous solution followed by drying and calcination,
- mixing appropriate solutions, formation of polymeric precursors, drying and thermal decomposition.

The "liquid-mix" solution processes[2], using **nitrates** or **acetates**, rely on polyfunctional organic additives, usually hydroxy-acids[3] and frequently citrates, i.e. the Pechini technique[4], but other complexing agents[5] are possible. These additives help create an amorphous organic precursor that can then be thermally decomposed to a fine particle powder with the constituents intimately dispersed at the atomic level. Spray drying and spray pyrolysis are often an integral part of the process.

The compounds - particularly variations on the La derivative - are currently of technological interest because they are :

[1] Investigation of the La-Mn-O system, M.L.Borlera and F.Abbattista, J.Less Common-Met., 1983, **92**(1), 55 :
Chemical Potential Diagrams for Rare Earth-Transition Metal-Oxygen Systems: 1, Ln-V-O and Ln-Mn-O
Systems, H.Yokokawa et al., J.Am. Ceram. Soc., 1990, **73**(3), 649

[2] Mixed-Cation Oxide Powders via Polymeric Precursors, P.A.Lessing, Am.Ceram.Soc.Bull., 1989,**68**(5),
1002

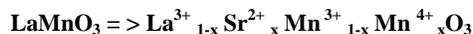
[3] Hydroxy Acid-aided Synthesis of Perovskite Oxides with Large Surface Areas, Y. Teraoka et al., J.Alloys
Comp., 1993, **193**, 70

[4] Method of Preparing Lead and Alkaline-Earth Titanates and Niobates, M.Pechini, U.S.Patent 3,330,697, 11
July 1967

[5] Synthesis of Oxide Ceramic Powders by the Glycine Nitrate-Process, L.A.Chick et al., Mater. Lett., 1990,
10(1,2),6

- thermodynamically stable up to ≈ 1200 °C,
- chemically inert to the same temperature,
- mechanically stable as well,
- electrically conductive at low and high temperatures, showing
- mixed electronic and ionic conductivity.

The LnMnO_3 's are *p*-type conductors [6] with the inherent non-stoichiometric defects being cation vacancies. The materials can show oxygen excess, stoichiometry or oxygen deficiency depending on oxygen partial pressure as well as Ln non-stoichiometry. Furthermore the electrical conductivity - due to the B cations and strong overlap of bonds with the O atoms - can be enhanced by doping with a lower valent cation. Strontium-doped LaMnO_3 is a frequently chosen material because of its high electronic conductivity in oxidizing atmospheres. This doping increases the conductivity by creating dual valency Mn ions by increasing the Mn^{4+} content by :



Ceramic fuel cells, usually termed solid oxide fuel cells (SOFC's), generate electricity directly from the reaction of a fuel with an oxidant, and operate at 1000°C . Of the electrochemically-active components compatible with those severe conditions, the preferred cathode material is Sr-doped LaMnO_3 [7]. Properties, e.g. thermal expansion, can be fine tuned by varying the Ln, the divalent dopant and the transition metal.

Variations on LnMnO_3 are also of interest for their catalytic potential[8]. (The initial claim though that they performed similarly to Pt in emission control was found to be attributable to traces of Pt in the samples.) There is of course an interplay between electrochemical and catalytic properties[9]. The newer preparation process produce catalytically-active materials with stable high surface areas[10] that have possibilities in exhaust emission control[11]. The combination of novel electrical and catalytic properties offers potential also for sensor compositions[12].

[6] Review of p-type Doped Perovskite Materials for SOFC and other Applications, H.U.Anderson, Solid State Ionics, 1992, **52**, 33

[7] Ceramic Fuel Cells, N.Q.Minh, J.Amer.Ceram.Soc., 1993, **76**(5), 563

[8] *see, for example, articles in*, Catalysis Today, 1990, **8**(2)

[9] The Electrocatalysis of Oxygen Evolution on Perovskites, J.O'M.Bockris and T.Otawaga, J.Electrochem.Soc., 1984, **131**, 290 ; Electrocatalytic Properties and Nonstoichiometry of the High Temperature Air Electrode $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, A.Hammouche et al., J.Electrochem.Soc., 1991, **138**(5), 1212

[10] Preparation of Supported $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ Catalysts by the Citrate Process, H.M.Zhang et al., Appl. Cat., 1988,**41**,137

[11] Rare Earth containing Perovskites with Catalytic properties for the Cleaning of Automobile Exhaust

Gas, A.Maijanen et al., Eur.J.Solid State Inorg. Chem., 1991, **28**, 437

[12] Gas Sensors, T.Kudo, Catalysis Today, 1990, **8**(2), 263

METALS

The lanthanides, when prepared in the elemental form, are metallic; their basic physico-chemical data[1] are summarized below. The route chosen to prepare any lanthanide depends on a blend of economic factors and physical properties such as Ln melting point and ultimate desired purity. They can be made[1], in principle, by either

- metallothermic reduction, $\text{Ln}^{\text{III}} + \text{M}^0 \Rightarrow \text{Ln}^0 + \text{M}^{\text{III}}$

or

- electrolytic reduction, $\text{Ln}^{\text{III}} + 3\text{e} \Rightarrow \text{Ln}^0$

METALS, Ln ⁰								
Z	Ln	Atomic Wt.	density g/cm ³	m.pt. °C	vapor Pressure at m. pt. (torr)	b.pt. °C	12-coord radius pm	crystal structure
39	Y	88.906	4.469	1522	2.1×10^{-3}	3338	180.1	hcp
57	La	138.905	6.146	918	2.6×10^{-10}	3464	187.9	dhcp
58	Ce	140.12	6.770	798	8.5×10^{-13}	3433	182.5	fcc
59	Pr	140.907	6.773	931	1.1×10^{-7}	3520	182.8	dhcp
60	Nd	144.24	7.008	1021	3.4×10^{-5}	3074	182.1	dhcp
61	Pm	[145]						
62	Sm	150.4	7.520	1074	5.8	1794	180.4	rhom
63	Eu	151.96	5.244	822	0.91	1527	204.2	bcc
64	Gd	157.25	7.901	1313	1.4×10^{-4}	3273	180.1	hcp
65	Tb	158.925	8.230	1356	8.6×10^{-4}	3230	178.3	hcp
66	Dy	162.50	8.551	1412	0.71	2567	177.4	hcp
67	Ho	164.930	8.795	1474	0.54	2700	178.3	hcp
68	Er	167.26	9.066	1529	0.37	2868	175.7	hcp
69	Tm	168.934	9.321	1545	185	1950	174.6	hcp
70	Yb	173.04	6.966	819	19	1196	193.9	fcc
71	Lu	174.967	9.841	1663	9.7×10^{-3}	3402	173.5	hcp

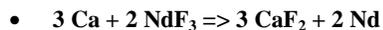
[1] Preparation and Basic Properties of the Rare Earth Metals, B.J.Beaudry and K.A.Gschneidner, in Handbook on the Physics and Chemistry of Rare Earths, ed. K.A.Gschneidner and L.Eyring, Vol. 1, 173, publ. 1979, North Holland

Metallothermic Processes

The metallothermic approach, widely used for pure element production, is suitable for most of the Ln series (including mixed-Ln's) and uses as the precursor :

- **fluoride, chloride**, or, for certain elements, **oxide**.

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



The charge is then held at a high temperature, above the Ln m.pt., to ensure a good separation of the lighter immiscible calcium fluoride slag from the heavier Ln metal.

Metallothermic reduction of anhydrous chloride precursors has limited applicability. It has been explored as a route to some of the heavy non-volatile Ln's, using Lithium metal vapor as the reductant. The resulting Lithium chloride is distilled off.



Oxide reduction is used for the metals, Sm, Eu, Tm and Yb, that have high vapor pressures around their melting points, with La metal (essentially non-volatile at reaction temperatures) as the reductant. The volatile lanthanide is distilled off and collected on a cooled surface, e.g. an inverted Ta crucible.



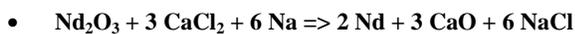
A extension of oxide-reduction is used for the commercial production [2] of the permanent-magnet intermetallic compound SmCo_5 , a process that avoids the intermediate step of Sm metal production and goes directly to a powder form of the desired metal.



[2] C.Herget and H.-G.Domazer, Methods for the Production of Rare Earth-3d Metal Alloys with Particular Emphasis on the Cobalt Alloys, Goldschmidt Informiert, 1975, **35**, 3 (publ. Th.Goldschmidt AG)

METALS

Metallo-thermic oxide-reduction routes to neodymium metal and commercial important Nd-Fe-B alloys, have been proposed, e.g. in a molten salt [3] :



Electrolytic Processes

The electrolytic production of Lanthanide metals[4] is, for practical reasons limited to the four lightest Ln's (La, Ce, Nd and Pr - all with low melting points) either for their production as the individual pure elements or, on a larger commercial scale as their mutually-mixed form, **Mischmetal** and its variations. (The four lightest lanthanides are however most usually prepared industrially by the metallothermic route.)

The Ln salt precursor can again be either **fluoride, chloride, or oxide**, dissolve in a molten alkali or alkaline earth salt. Chloride systems offer lower operating temperatures and a wider choice of electrode and containment materials but tend to be hygroscopic creating **oxychloride** contaminants. Fluorides, in contrast, are not hygroscopic, can dissolve Ln oxides directly but have the severe practical limitations of higher melting points and greater corrosivity. The electrolytic cell needs to be operated above the melting point of the product metal in order to facilitate recovery of the molten element.

Although used industrially for many years there is very little published about the technology for producing mischmetal from **mixed-lanthanide** chlorides. The dehydrated Ln chloride, mixed with CaCl_2 and other salts, is electrolysed in a cell at temperatures of $\approx 850^\circ\text{C}$ using a graphite-anode and, for ferro-alloy production, a consumable iron cathode. The molten mixed-Ln metal, formed at the cathode, can be tapped off.

Purification

Commercial metals tend to contain oxygen, calcium and other elements although careful attention to the purity of intermediates, e.g. complete dehydration of precursor salts, and operation in inert atmospheres reduces the impurity content. The Ln metals can be purified[5] by :

[3] Neodymium Production Process, R.A-Sharma, J.Metals, 1987, **39**(2), 33

[4] Fused-Salt Electrowinning and Electrorefining of Rare-Earth and Yttrium Metals, E.Morrice and M.M.Wong, Miner.Sci.Eng., 1979,**11**(3),125

[5] Preparation and Purification of Rare Earth Metals and Effect of Impurities in their Properties, K.A.Gschneidner, Jr., in "Science and Technology of Rare Earth Materials", ed. E.C.Subbarao and W.E.Wallace, publ. Academic Press, 1980,25

- vacuum remelting, *to remove volatiles such as CaF₂*
- sublimation / distillation, *to treat the more volatile Ln metals,*
- zone melting and *for research quantities and*
- electrotransport[6], *for high "research purities".*

On an industrial scale vacuum remelting is often adequate to produce material of acceptable purity.

The elements are available commercially in a range of purities, from "**Mischmetals**" through 96 % to 99.99 % and higher, and in a variety of forms, although the heavier Ln's tend to be small-volume research items. The growing interest in their practical applications [7] will continue; the production of **Neodymium** metal, for example for permanent magnets, dominates the pure-Ln metal industry.

Properties

The Lanthanide elements have a very high affinity for oxygen; they have the highest free energy for oxide formation of all elements in the Periodic table. In consequence the metals will react with air, the rate depending on temperature, humidity and lanthanide atomic number. The heavy Ln's, and **yttrium**, are much more stable to oxidation, a consequence of the different structure of the **oxide** product being formed. The C-type oxide produced on the surface of the heavy Ln's forms a coherent coating resistant to spalling, analogous to the behavior of Al₂O₃ on Aluminum. In contrast the A- (and B-) type oxides, produced on the lighter Ln metals, are "open" structures readily allowing atom diffusion whereby oxidation can continue.

The metals react exothermically with sulfur to form **sulfides**, or if oxygen is also present, **oxysulfides**. **Hydrides** can be formed at moderate temperatures, a process that decrepitates the bulk metal to produce a fine powder. The metals will also react directly with other elements such as nitrogen, phosphorus, etc. The reactivity of the metals provides a route to moisture-sensitive Ln compounds such as **alkoxides**, alkyls and other **organo-metallics**.

The solid-state properties of the metals [1], in particular structure, magnetic and electronic behavior, are of considerable research interest. **Gadolinium**, as an example, is a ferromagnetic metal at room temperature and several of the elements show complex magnetic behavior at low temperatures.

[6] The Purification and Crystal Growth of Rare Earth Metals using Solid State Electrotransport, D.Fort, J.Less.Comm.Met., 1987, **134**, 45

[7] Metallurgical Applications of Yttrium and the Lanthanides, B.T.Kilbourn, J.Metals, 1988, **40**(5), 22

MISCHMETAL

When a lanthanide mineral is processed – without separation into the individual lanthanides - to yield a **metal**, the product, termed *Mischmetal*, will still contain the Ln's in the "natural-ratio" as they occur in the ore body. The close similarity in Ln content between **bastnasite** and **monazite** means that mischmetals from those two sources will also be similar. In addition it often usual to remove, before metal production, the small amount of heavy lanthanides, of high value, from the precursor. Consequently mischmetal contains predominantly the first four lanthanides, the light Ln's.

Mischmetal	
Typical Composition	
La	≈ 25 %
Ce	≈ 50 %
Pr	≈ 6 %
Nd	≈ 15 %
heavies, etc.	≈ 1 %
Fe	≈ 3 %

It is prepared by electrolysis at ≈850 °C of molten rare earth **chloride**, as anhydrous as is practical, preferably under an inert atmosphere, see **metals**. The few percent of iron is present in order to lower the melting point towards the eutectic point and to make the casting of shapes easier. The material does not have a definite melting point but melts over a range near 800 °C, close to that of Ce. It is a strong reductant, comparable to magnesium, and will react with hot water plus also forming surface oxides on exposure to air.

The start of the lanthanide metals industry was the production of lighter flints (a 1903 patent), based on a mischmetal- iron (≈65 % : ≈35 %) alloy, Auer metal. Due to the high content of pyrophoric **cerium** this alloy, when struck to create small fragments, produces glowing particles, sparks, and is used to ignite flammable gases.

The major use of mischmetal is as an additive for steel treatment[1], an application that is no longer as dominant for Ln usage in most countries as it once was. The prime purpose of mischmetal addition during steel alloy production is to tie up sulfur impurities, through the high affinity of Ln's for O and S, as stable lanthanide **oxysulfides**. A trend towards "cleaner" starting materials and more efficient use of competitive additives has reduced mischmetal consumption. In China though, with its abundant **resources**, mischmetal accounts for the major portion of internal lanthanide demand.

Mischmetal-based alloys are promising electrode materials in nickel-metal-**hydride** rechargeable batteries that offer high capacity and long-life[2].

[1] The Rare Earth Metals in Steel, L.A. Luyckx, in Industrial Applications of Rare Earth Elements ed.

K.A.Gschneidner, Am.Chem.Soc. Symposium 164, publ. 1981, p. 43

[2] Rare-Earth-Based Hydrogen Storage Alloys for Rechargeable Nickel-Metal-Hydride Batteries, T.Sakai et al., J. Alloys Comp., 1993, **192**, 155

MONAZITE

Monazite, a light-lanthanide thorium **phosphate**, (Ln,Th)PO₄ is found in many countries. It is an accessory mineral in granites and the weathering, by wave action over time, of those primary rocks causes the monazite to segregate out - because of its high specific gravity - in placer deposits. Monazite-bearing placers, in association with other heavy minerals such as ilmenite, zircon and rutile, have been identified in many beach and dune sand deposits throughout the world. Those other minerals are usually the economic driving force for exploiting the deposits and hence monazite is almost always derived as a by-product.

Several countries supply monazite (or monazite derivatives such as rare-earth chloride) onto the world market.[1] Extensive deposits along the Indian Ocean coast of Western Australia near Perth are worked for ilmenite and are the major source of world monazite. Other regions of Australia, along with the southern region of India[2], China and Brazil also supply the mineral.

In terms of lanthanide and **yttrium** content monazite closely resembles **bastnasite**, both containing predominantly La, Ce and Nd. (The values in the table are approximate as they do vary considerably from deposit to deposit.) The phosphate mineral, in comparison with bastnasite however, tends to contain less La, more Nd and more heavy Ln's from Sm onwards. In addition, monazite contains ~10 % of Thorium, a radio-active element. The environmental constraints that this imposes on handling the mineral have become much more significant in recent years. Many countries have severely restricted the processing of monazite and the importance of the mineral as a major source of Ln's has significantly declined.

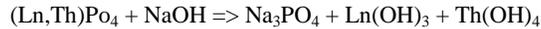
The processing of monazite ores begins with gravity, electrostatic and magnetic separation to produce a monazite concentrate with a Ln oxide content of ≈ 60 %. Monazite can be cracked by reaction with sulfuric acid, like bastnasite, to yield

Monazite Ln, Y & Th Typical %	
La	20
Ce	43
Pr	4.5
Nd	16
Sm	2.5
Eu	0.1
Gd	1.5
Tb	0.05
Dy	0.6
Ho	0.05
Er	0.2
Tm	0.02
Yb	0.1
Lu	0.02
Y	2.5
Th	9

[1] Availability of Rare-Earth, Yttrium, and Related Thorium Oxides-Market Economy Countries: A Minerals Availability Appraisal, T.F.Anstett, U.S.Dept of Interior, Bureau of Mines Information Circular/1986, IC9111

[2] Monazite, The Basic Raw Material for Rare Earths: Beneficiation from Beach Sands, V.S.Bashir, Materials Sc.Forum, 1988, **30**, 33

a mixture of sulfates but the usual process is with alkali [3]. The concentrate is finely ground and digested with an excess of caustic soda at $\approx 150^\circ\text{C}$ for several hours.



The phosphate portion produces a soluble sodium triphosphate while the lanthanides, along with thorium, form insoluble **hydroxides** (hydrated **oxides**) that can be recovered.

The next step is hydrochloric acid attack, at $\approx 70^\circ\text{C}$ and pH 3-4, on the solids portion. The thorium remains insoluble and a crude thorium hydroxide can be filtered off. (The small amounts of trace contaminants that do carry through into solution, such as uranium and lead as well as some thorium, are removed by coprecipitation with barium sulphate in a deactivation step.) The chloride solution containing the rare earths, lanthanides, is concentrated by steam heat and can be cast into solid form.

The rare-earth-**chloride** (RECl_3), like monazite concentrate, is a material traded commercially not only for further separation processes but also for the production of ferro-alloys such as **mischmetal**. Treatment of the RECl_3 solution with sodium carbonate will precipitate a RE **carbonate** that can be converted to other mixed-lanthanide derivatives, e.g. **fluorides**, **nitrates** and, by calcination, a rare-earth oxide. (Rare earth chlorides, whether derived from Bastnasite or from Monazite, have very similar compositions and can most times be used interchangeably in later processes.)

The thermally stable (m.pt. $>2000^\circ\text{C}$) monazite **phosphate** structure[4] accommodates the light Ln's, La to $\approx\text{Gd}$, with an irregular nine-coordinate Ln atom. Within the structure, the Ln(III) and P(V) can be substituted by Th(IV) and Si(IV) somewhat by analogy with Xenotime, YPO_4 , and zircon, ZrSiO_4 , that are isostructural.

Rare Earth Chloride a.k.a. Lanthanide Chloride $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ Typical Analysis	
total as Ln Oxides	$\approx 46\%$
CeO ₂	$\approx 22-25\%$
La ₂ O ₃	$\approx 11-16\%$
Nd ₂ O ₃	$\approx 5-9\%$
Pr ₆ O ₁₁	$\approx 2-3\%$
Chloride	$\approx 31\%$

[3] Processing of Monazite at the Rare Earths Division, Udyogamandal, N.S.Narayanan et al., Mater.Sci.Forum, 1988, **30**, 45

[4] The Structure of Cerium Orthophosphate, a Synthetic Analogue of Monazite, G.W.Beall et al., J.Inorg.Nucl. Chem., 1981, **43**, 101

NEODYMIUM

Neodymium is the third most abundant lanthanide and is recovered from the minerals **bastnasite** and **monazite**. This element is of current commercial interest because of the development of the Nd-Fe-B alloys as permanent magnet materials.[1] In addition Nd-based lasers are becoming more widely used.

In all readily prepared compounds Neodymium is trivalent and the Nd^{3+} ion shows typical Ln^{3+} chemical properties, see **Lanthanum** for a summary. The table on the next page lists data for some of the commonly encountered salts and more details can be found under the appropriate anion heading, e.g. nitrate, oxide, etc.

Neodymium salts usually appear pale purple, a consequence of the spectral absorption of the Nd^{3+} ion. (The **oxide**-in contrast to the salts-is sky-blue, with the subtle shift from the normal Nd-salt color being caused by the stronger ligand field influences in the oxide.) Nd has a strong absorption band centred at 580 nm, others at ≈ 740 and ≈ 800 nm and several more bands of lesser strength.[2]

The 580 nm band is in the yellow and very close to the position of the eyes' maximum sensitivity. In consequence, the perceived color of Nd-containing glass - being here caused by both reflection and subtraction phenomena - depends on the spectrum of the illuminating light; this creates so-called "dichroism". The Nd-ion colors artistic glassware and is added, for example, to the glass used in protective goggles worn during welding in order to block light of the 580 nm wavelength. Nd-doped glass can be used as a contrast-enhancing filter, clarifying the eye's discrimination between reds and greens, on CRT displays.

Nd	
element	
Atomic Number	60
Atomic Weight	144.24
Electron configuration	$[\text{Xe}]4f^6 6s^2$
Valency	3
Ionic radius for 8-coordination	111 pm
Magnetic moment	3.62 μB
metal	
Crystal Structure	dhcp
Melting Point	1021 °C
Boiling Point	3074 °C
Density	7.01 g/cm ³
Metallic Radius	182 pm

[1] New Permanent Magnet Materials, K.H.J.Buschow, Materials Sc. Rep., 1986, 1, 1: Neodymium-Iron-Boron Permanent Magnets prepared by Rapid Solidification, J.J.Croat, J.Mater.Eng., 1988, 10, 7 : Permanent Magnets, J.F.Herbst, Am.Sci., 1993, 81(3), 252

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

Compound	Ideal Formula	Formula Weight	% Oxide	% Element
Oxide	Nd ₂ O ₃	336.48	100	88.5
Acetate	Nd(CH ₃ COO) ₃ .1½H ₂ O	348.44	48.3	41.4
Carbonate	Nd ₂ (CO ₃) ₃ .3H ₂ O	486.52	69.2	59.3
Chloride	NdCl ₃ .6H ₂ O	358.69	46.9	40.2
Fluoride	NdF ₃ .H ₂ O	219.25	---	65.8
Hydroxide	Nd(OH) ₃ .3H ₂ O	249.31	67.5	57.9
Nitrate	Nd(NO ₃) ₃ .6H ₂ O	438.34	38.4	32.9
Oxalate	Nd ₂ ((COO) ₂) ₃ .10H ₂ O	732.69	45.9	39.4
Sulfate	Nd ₂ (SO ₄) ₃ .8H ₂ O	720.78	46.7	40.9

The most common solid state laser is Neodymium-based[3], usually in a glass or a **Yttrium**-aluminum-garnet (YAG) host. Neodymium, at ≈1 - 5 wt.% in the host, is exposed to intense broad-spectrum light that, through absorption, "pumps" those Nd- atoms to an excited energy state. The lasing transition to a lower energy level that then follows produces a line emission at, or very close to, 1060nm (the exact value varies with host). Neodymium has an optimal selection of absorption and emitting wavelengths. Nd-lasers are used in material processing, particularly drilling, spot welding and marking, and also in medicine.

The dielectrics used in multi-layer capacitors essential to electronic equipment often require a high dielectric constant and a capacitance invariable over a wide temperature range, -50 — +120°C. Neodymium barium **titanate** formulations are widely used for this so-called "NPO" dielectric material. Several components are probably present including a BaO : Nd₂O₃ : nTiO₂, (n≈3 - ≈5) material[4].

[3] Rare Earth Lasers, M.J.Weber, in "Handbook on the Physics and Chemistry of Rare Earths", ed. KA.Gschneidner and L.Eyring, publ. North- Holland, 1979, vol.4, 275 (Ch. 35) : Neodymium Lasers Prove Versatile over Three Decades, J.Hecht, Laser Focus World, 1992, **28**(4), 77

[4] Ceramic and Dielectric Properties of Selected Composition in the BaO-TiO₂-Nd₂O₃ System, D.Kolar et al., Ber.Deutsch.Keram.Ges., 1978, **55**(7), 346

NITRATES

The nitrates of the trivalent lanthanides are readily prepared by dissolving the appropriate **oxide**, or other salt such as **carbonate**, in nitric acid. A variety of hydrated crystalline salts, $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, can be obtained from the solution with probably the most stable being $n = 6$, the hexahydrate. The nitrates are very soluble in water[1], $\approx 5 \text{ mol kg}^{-1}$ at ambient rising to ≈ 16 near 100°C , i.e. at ambient $\approx 70\%$ solution strength for the hexahydrate. The solutions should be kept acidic, $\text{pH} \approx 2$, to avoid hydrolysis.

A wide variety of double salts, e.g. $(\text{NH}_4)_2\text{Ln}(\text{NO}_3)_5 \cdot n\text{H}_2\text{O}$, are known that tend to be of lower solubility than simple nitrates. Anhydrous nitrates can be prepared by reaction of N_2O_5 on the hydrated nitrates. **Cerium(IV)** forms a moderately stable $\text{Ce}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ but is usually met as the analytical oxidizing agent, ammonium hexa-nitrato-cerium, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, that contains a 12-fold nitrato-coordinated cerium *anion*. The crystal structure of the solid, simple-nitrate, hexahydrate for the largest Ln's, La and Ce, contains a polycoordinated Ln ion with 3 bidentate nitrate groups and 5 water molecules. For the remainder of the Ln series, Pr to Lu, the structure changes to 3 nitrate groups and 4 water molecules bound to the central ion.

Much of the older literature describes the solution chemistry of the nitrate materials that were used in early separation operations. Nitrate solutions, today, are the basis of many of the **solvent extraction** procedures used to separate and purify the individual lanthanides on a commercial scale.

On heating the nitrates will undergo dehydration through a series of ill-defined lesser hydrates and then to an oxy-nitrate species, $[\text{LnOJ} \text{NO}_3]$, stable near 400°C , before forming the stable oxide at $\approx 600^\circ\text{C}$. (No clear intermediate occurs with the cerium salt because Ce(IV) is formed concurrently.)

Hydroxy-nitrates, $\text{Ln}(\text{OH})_2(\text{NO}_3)$, have been characterized[2] for La to Dy as well as Y. These materials are similar to the $\text{Ln}(\text{OH})_2\text{Cl}$ complexes, see **lanthanum concentrate**, and also contain anion layers separating the $[\text{Ln}(\text{OH})_2]^{+}$ polymeric cations. A variety of other hydroxy derivatives can probably exist and account for the difficulty of precipitating clearly defined **hydroxide** species out of solution.

[1] Solubility Data Series, Volume 13, Scandium, Yttrium, Lanthanum and Lanthanide Nitrates, ed, S.Sierkierski et al., publ. Pergamon for IUPAC, 1983

[2] Preparation, Phase Equilibria, Crystal Chemistry and Some Properties of Lanthanide Hydroxide Nitrates, J.M.Haschke, Inorg.Chem., 1974, **13**(8), 1812

NOMENCLATURE

The International Union of Pure and Applied Chemistry (IUPAC) is accepted world-wide as the arbiter in chemical nomenclature and produces rules for naming chemical compounds. The rules for inorganic compounds[1] discuss the terminology recommended for element 39, Yttrium, and elements 57 to 71, Lanthanum to Lutetium.

The relevant paragraph, 1.3.8.2 .. Collective Names of Groups of Atoms, states:

- *the following collective names for groups of atoms are IUPAC approved :*
 - *lanthanoids or lanthanides (La, Ce Yb, Lu) (Note 3h)*
 - *rare earth metals (Sc, Y, and the lanthanoids)*

The "note 3h" adds a comment, using "actinium" to illustrate the example but explicitly defining "lanthanum" to be handled in a similar manner.

Although [lanthanoid] means "like [lanthanum]" and so should not include [lanthanum], [lanthanum] has been included by common usage. The ending -ide normally indicates a negative ion, and therefore "lanthanoid" [is] preferred to "lanthanide". However, owing to wide current use, lanthanide [is] still allowed.

(The 1960 IUPAC rules differentiated between lanthanide and the term "lanthanon". *Lanthan-ide* meant elements 58 to 71 whereas *lanthan-on* meant lanthan-ides plus lanthan-um, i.e. elements 57 to 71. This subtle distinction is now rarely used).

There is of course a body of usage dating back even further than the rules. The full collective term, and pedantically correct, "rare earth metals", is often replaced by the shortened term "rare earths". This is frequently taken to mean - erroneously - just the fifteen elements 57 to 71; that is scandium and yttrium are not considered "rare earths". This is implicit in, for example, article titles and abstract entries that read:

- Rare Earth Elements and Yttrium
- Rare Earths (Lanthanides)
- Lanthanides, see Rare Earths ...

There is now wide acceptance - acknowledged in the latest IUPAC rules - that, when any collective term is used, the label refers to elements 57 - 71 and not just to

[1] Nomenclature of Inorganic Chemistry, Recommendations 1990, International Union of Pure and Applied Chemistry, ed. G.J.Leigh, p. 43, publ. Blackwell 1990

NOMENCLATURE

58 - 71; the term is *inclusive* of the naming element, lanthanum, and not *exclusive*. This custom, implicit in the indexing used by most abstracting journals, agrees with the practice accepted for the "actinides". Chemical Abstracts, for example, states : "Actinides, Studies of the class of elements with atomic numbers 89 - 103", i.e. it includes Ac, element 89.

Those earlier (1960) rules included in their explanatory phrases the following comment :

- *the inclusion of Sc with the rare earths is questioned by some.*

In practice, Scandium is almost never included under "Rare Earth" index entries. Chemically it is sufficiently different and does not occur naturally with the other elements under discussion.

In actual use both the terms:

- *Lanthan-ide*
- *Lanthan-oid*

are used to cover elements 57 to 71. The first probably receives the majority verdict despite the IUPAC comment mentioned above. There is perhaps a case of geographical "allotropism" here with British and German publications, e.g. J.Chem. Soc. and Angew. Chem., using *-oid* but with *-ide* preferred in the U.S.

The symbol "Ln" is now widely used in formulas to stand for any of the elements 57 to 71. The symbols RE or Re can lead to errors as well as being monolingual in their implications. Why not SE (Seltene Erde) or TR (Terre Rare) ?

In conclusion the term "rare earths" means different groupings of elements to different writers. It leads to ambiguities in indexing and in retrieval of information. It is also inappropriate; these elements are not rare. There is widespread acceptance of a collective noun .. with the root *lanthan-* .. to define all the elements lanthanum to lutetium, atomic numbers 57 to 71 inclusive. Universal agreement is needed on the ending of this noun. The most widely accepted term of the two possibilities, lanthanide and lanthanoid, is :

- lanthanide

Molycorp for this reason has chosen to use this particular term, *Lanthanide*, in describing its products and throughout these booklets. It is actively encouraging all its customers and contacts to do likewise.

ORGANO-METALLIC COMPOUNDS

The term "organo-metallic" here defines compounds in which the lanthanide atom is bound to carbon through single sigma-bonds or through multiple pi-bonding. The term excludes materials containing Ln's bonded to oxygens that are constituent parts of organic groupings such as the anions found in, for example, **carboxylates** or acetylacetonates.

Only in the last two decades have a wide range of such derivatives been isolated and characterized[1]. For example, many cyclopentadienyl compounds such as $\text{Ln}(\text{C}_5\text{H}_5)_3$ and more complex species[2], have been made. In some the bonding is considered to involve Ln(0) atoms and π -bonded arene ligands[3]. These materials, all very sensitive to oxygen and water, have become a fruitful field for research.

The absence of a rigid stereo-chemical arrangement around the Ln atom coupled with an inherent high reactivity creates potential applications in catalysis and as organic synthesis reagents. Organo-lanthanide compounds are particularly effective in activating C-H bonds and some are known to activate methane, to break the C-H bond. Many react readily with, and promote polymerization of, olefines. The freedom of access to the Ln atom means that the stereochemistry around the Ln is determined by the ligands themselves bound to the Ln. In turn the polymerization can be highly stereospecific with different specificity to that seen with other catalytic systems[4].

The active lanthanide organo-metallic in catalysts can be generated *in situ*, e.g. from an anhydrous Ln halide plus an aluminum alkyl, rather than introduced as a previously isolated compound. In this way Ln analogues of the well recognized Ziegler Natta (metal-halide aluminum-alkyl) polymerization catalysts can be obtained [5]. As an alternative the lanthanide, initially present as an organo-metallic, can be activated by the Al alkyl[6].

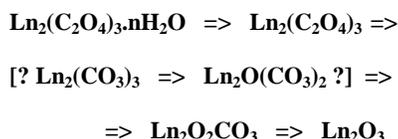
- [1] Organo-Lanthanoid Compounds, H.Schumann, Angew.Chem.Int.Ed., 1984,**23**,474; Organometallic Compounds of the Rare Earths, H.Schumann and W.Genthe, *in* Handbook Phys. Chem. Rare Earths, ed. K.A.Gschneidner and L.Eyring, 1984, Vol. 6, 445
- [2] Achieving new Lanthanide Chemistry within the Tetracyclopentadienyl Cavity formed by two (C_5Me_5) Moieties, W.H.Evans, J.Allcys Comp., 1993, **192**, 205
- [3] Zero Oxidation State Compounds of Scandium, Yttrium and the Lanthanides, F.G.N.Cloke, Chem.Soc.Rev., 1993,17
- [4] Polymerization of Dienes on Lanthanide containing Catalytic Systems. Review, N.G.Marina et al., Polymer Sci., 1984, **26**(6), 1251 ; Lanthanide Compounds - Catalysts of Stereospecific Polymerization of Diene Monomers. Review, *ibid*, 1991, **33**(3), 387
- [5] Titanium and Rare Earth Chloride Catalysts for Ethylene Polymerization, J.L.Martin, J.Polym.Sci., Polym.Chem., 1984, **22**, 3843 ; Mechanism of Rare-Earth Catalysis in Coordination Polymerization, H.L.Hsieh and G.H.C.Yeh, Ind.Eng.Chem.Prod.Res.Dev., 1986, **25**, 456
- [6] Polymerization of Styrene by Rare Earth Coordination Catalysts, M.Yang et al., Polym.J., 1990, **22**(10),919

OXALATES

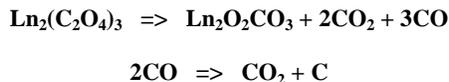
Addition of oxalic acid, or an alkali oxalate or ammonium oxalate, to a neutral or slightly acidic solution of a trivalent lanthanide will precipitate a hydrated oxalate. The deca-hydrate is obtained with La - Ho (and Y), an isomorphous series, whereas another series, the hexa-hydrate, tends to form for Er - Lu, the heavier lanthanides. In strongly acidic solutions the other anion present may be included in the solid brought down, chloro-oxalate from HCl for example, or an insoluble acid salt be produced.

The high insolubility of the hydrated oxalate in near-neutral solutions is used in the commercial-scale preparation of high-purity derivatives of the lanthanides and **yttrium**. Calcination of the precipitate produces a pure **oxide**. This process is also used for the gravimetric analysis of lanthanides. The oxalate is preferred to the **carbonate** because transition metals ions tend to be rejected and remain in solution. Physical occlusion of contaminant ions though can be a problem.

Thermal decomposition[1] of the light-Ln oxalates involves initially the steady loss of water of hydration, from ambient up to $\approx 250^\circ\text{C}$, but intermediate hydrates are not seen. With the heavy lanthanides an intermediate dihydrate can be formed. The anhydrous oxalates are not stable and the first clearly identifiable species is the dioxomonocarbonate, $\text{Ln}_2\text{O}_2\text{CO}_3$, containing the stable $(\text{LnO})_n$ grouping seen in many Ln compounds.



The temperatures corresponding to the various transitions depend on the surroundings, the presence of CO_2 delays decomposition. In addition localized reducing conditions can cause spot formation of carbon. This can give a gray cast to the resulting oxide product if the C is not burnt off during the final stages of the decomposition.



With cerium, oxidation of Ce(III) to Ce(IV) starts at low temperatures, $\approx 300^\circ\text{C}$, and, because of the formation of the oxide, CeO_2 , no intermediate stages are seen.

[1] Thermal Analysis of the Oxalate Hexahydrates and Decahydrates of Yttrium and the Lanthanide Elements, M.J. Fuller and J. Pinkstone, J. Less-Common Metals, 1980, **70**, 127

OXIDES

The Ln₂O₃ sesqui-oxides are the stable well-defined solids usually obtained as the final product of the calcination in air of most Ln metals and Ln salts such as **oxalates, carbonates and nitrates**. (The three elements, **cerium, praseodymium and terbium**, however, have stable oxides of different compositions, see comments below.) This is a consequence of the high thermodynamic affinity of the lanthanide elements for oxygen and the stability of the Ln(III) valence state. The lanthanide oxides have the greatest, most negative, standard free energies of formation for any oxides[1] accounting for their exceptional thermodynamic stability. (**Yttrium oxide** resembles oxides of the heavy lanthanides such as **dysprosium oxide**). The basic physico-chemical data for the oxides are summarized in the table.

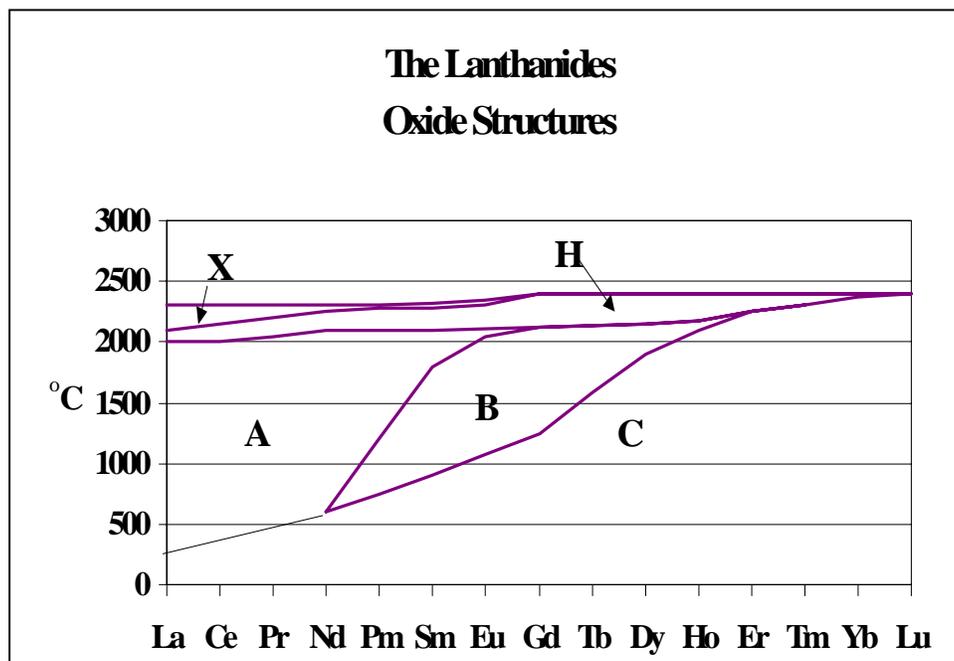
OXIDES							
Ln _m O _n							
Ln	stable oxide	formula wt.	element %	color	structure type [†]	density gcm ⁻³	m.pt. °C
Y	Y ₂ O ₃	225.8	78.7	white	C	5.0	2430
La	La ₂ O ₃	325.8	85.3	white	A	6.6	2305
Ce	CeO ₂	172.1	81.4	off-white	fluorite	7.3	≈2600
Pr	Pr ₆ O ₁₁	1021.5	82.8	black	[fluorite]	6.9	≈2200
Nd	Nd ₂ O ₃	336.5	85.7	pale blue	A	7.3	2320
Sm	Sm ₂ O ₃	348.8	86.2	cream	B/C	7.1	2335
Eu	Eu ₂ O ₃	351.9	86.4	white	B/C	7.3	2350
Gd	Gd ₂ O ₃	362.5	86.8	white	B/C	7.6	2420
Tb	Tb ₄ O ₇	747.7	85.0	dark-brown	[fluorite]	7.7	≈2410
Dy	Dy ₂ O ₃	373.0	87.1	white	C	8.2	2408
Ho	Ho ₂ O ₃	377.9	87.3	white	C	8.4	2415
Er	Er ₂ O ₃	382.5	87.5	pink	C	8.6	2418
Tm	Tm ₂ O ₃	385.9	87.6	pale green	C	8.9	2425
Yb	Yb ₂ O ₃	394.1	87.8	white	C	9.2	2435
Lu	Lu ₂ O ₃	397.9	87.9	white	C	9.4	2490

[†]see text

[1] Thermochemistry of The Rare Earths, Part 1. Rare Earth Oxides,...., K.A.Gschneidner et al., Report IS-RIC-6, publ. 1973, Rare-Earth Information Center, Iowa State University, Ames, IA, available from Molycorp

Calcination in air for the three exceptions to sesquioxide formation, cerium, praseodymium and terbium, produces oxides containing Ln^{IV} ions. With cerium, $\text{Ce}^{\text{IV}}\text{O}_2$, **cerium oxide** (also known as ceria) contains only *tetravalent* Ce, and is the stable form produced when most cerium salts, Ce^{III} or Ce^{IV} , are calcined in air. For both the elements praseodymium and terbium the tetravalent state has a limited but sufficient stability and causes stable oxides with mixed III/IV compositions, Pr_6O_{11} and Tb_4O_7 respectively, to be produced. The co-existence of two valence states in the solid makes charge-transfer absorption bands possible and these two oxides are strongly colored. The formulae are given with integer values but the actual composition does depend on preparation prehistory.

The true sesquioxides, Ce_2O_3 , Pr_2O_3 and Tb_2O_3 , can be made under strongly reducing conditions but are unstable in air and readily oxidize. A divalent oxide, EuO , is also known, a dark red solid with unusual magnetic properties.



Structures

Several structural types are known[2] for the sesquioxides, see figure. The A-type (hexagonal) and the closely related B-type (monoclinic) are adopted by the lighter Ln's whereas the C-type (cubic) is found for the heavy (smaller) Ln's and similarly sized **Yttrium**. (The H and X structures found only at very high temperatures.)

The oxides of the three elements in the middle of the Ln series, Sm, Eu and Gd, can be made in B or C forms depending on precursor calcination temperature. At, and near ambient temperatures, the conversion from A- (or B-) to C-type is so slow that the A and B forms are stable once prepared. The B (and A) to C conversion on cooling is unusual in that it is accompanied by a volume *increase* of $\approx 10\%$.

The Ln^{III} ion's size, ranging for 8-coordination from 116 pm for La to 98 pm for Lu, is not so different from that of the O^{2-} anion. This, along with the imposed Ln_2O_3 formula, means that the crystal structures of the Ln_2O_3 's are not easy to visualize ... unlike oxides of smaller elements where the cations fit into holes within arrays of close-packed O^{2-} ions. The A- and B-type Ln_2O_3 structures can be described[3] as based on layers of polymeric $[\text{LnO}]_n^{\text{nt}}$ cations separated by discrete layers of O^{2-} anions. (Similar $[\text{LnO}]_n^{\text{nt}}$ layers are seen in many Ln oxo-compounds.) The arrangement around the Ln ion is 7-coordinate with several differing Ln-O distances.

The C-type Ln_2O_3 structure is related to the fluorite, CaF_2 , system by the ordered removal of one-quarter of the anions. (The Ln atom is coordinated to 6 oxygens but there are two vacant sites at cube corners.) Ceria, CeO_2 , crystallizes as a fluorite and, as a consequence of the close similarity of the C-type Ln_2O_3 and fluorite structures, a range of stable intermediate non-stoichiometric compositions, $\text{Ce}_{1-x}\text{Ln}_x\text{O}_{2-x/2}$, is possible. Praseodymium and Terbium oxides have complex fluorite-derived structures.

The oxides are among the most thermally stable materials known, melting in the range 2200 - 2500 °C. In general the metal cation structure is rigid up to the melting point whereas there is high mobility in the oxide anion lattice, starting above $\approx 300^\circ\text{C}$.

Properties

The oxides will dissolve in aqueous acids to produce the corresponding salt, e.g. **nitrates**, **chlorides**. To avoid hydrolysis of the hydrated lanthanide ion the solutions should be kept acidic, $\text{pH} < 4$. The reactivity with acid is noticeably slower for C-type structures, i.e. the heavy-Ln oxides, than for the A- and B-types, the light Ln-oxides.

[2] Binary Rare Earth Oxides, L.Eyring, in "Handbook on the Physics and Chemistry of Rare Earths", ed. KGschneidner and L.Eyring, Vol 3, p 337, Publ. North Holland 1979: A Study of the Polymorphism of Rare Earth Sesquioxides at High Temperatures, M.Foex and J.P.Traverse, Bull.Soc.Fr.Mineral Cristallog., 1966, **89**, 184

[3] OM_4 Tetrahedra Linkages and the Cationic Group $(\text{MO})_n^{\text{nt}}$ in Rare Earth Oxides and Oxysalts, P.E.Caro, J.Less- Common Metals, 1968, **16**, 367

Furthermore oxides with Ln^{IV} ions are even less reactive and a trace of reducing agent, e.g. H_2O_2 , may be required to take the oxide into solution. All the oxides will absorb water and/or carbon dioxide onto their surface forming a layer of hydrate, carbonate or hydroxy-carbonate[4]. The A- and B- types do this more readily with **lanthanum** oxide the most hygroscopic of the series.[5]

Production

After separation by **solvent extraction** into individual pure-Ln containing solutions, a precursor, usually **oxalate** but possibly **carbonate**, is precipitated out. Calcination at $\approx 1000^\circ\text{C}$ then produces the desired oxide. Commercially the oxides are available in high purities, from $\approx 95\%$ to 99.99% and higher, and are frequently the most readily available pure compound for any individual lanthanide.

Control of the precursor precipitation stage determines the particle morphology of that precursor *and* also of the derived oxide. As usually produced the oxide particle sizes range from a micron or so to a few tens of microns in size. Finer particle material can be made by controlled nucleation, either in dilute solutions or by hydrolysis in situ of an additive, e.g. urea, that creates the precipitating anion[6].

Another physical variable is surface area. In applications such as catalysis, a high surface area ($\approx 100 - >200\text{ m}^2/\text{gm}$) is often needed and some oxides can be prepared with such a parameter by control of the precipitation and calcination conditions.

A dopant can be deliberately introduced at the precipitation step into the bulk phase. The very similar ionic size means that a luminescing Ln-ion is easily incorporated, at the desired few per cent, into a stable non-luminescent host, for example, to prepare (after calcination) the **Europium-doped Yttrium** oxide essential for energy-efficient fluorescent lighting. This potential control over composition is also used to produce oxygen ion conductors, e.g. Sm-doped: CeO_2 , suitable for use as solid electrolytes.

[4] Lanthanide Oxides: Thermochemical Approach to Hydration, R.Alvero et al., J.Mat.Sci., 1987, **22**(4), 1517 : Behavior of Rare Earth Sesqui-Oxides Exposed to Atmospheric CO_2 and H_2O . A Review and New Experiments, S.Bernal et al., Reactivity of Solids, 1987, **4**(1-2), 23

[5] Study of some Aspects of the Reactivity of La_2O_3 with CO_2 and H_2O , S.Bernal et al., J.Mat.Sci., 1985, **20**, 537

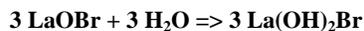
[6] Preparation of Yttrium, Lanthanum, Cerium and Neodymium Carbonate Particles by Homogeneous Precipitation, M.Akinc and D.Sordelet, Adv.Ceram.Mat., 1987, **2**(3A), 232 : Preparation and Properties of Monodispersed Colloidal Particles of Lanthanide Compounds, E. Matijevic and W.P.Hsu, J.Colloid Interf.Sci., 1987, **118**(2), 506

OXYBROMIDES

One oxy-bromide, or oxide bromide, is used commercially; LaOBr, doped with the blue-emitter **thulium**, is an important X-ray phosphor[1]. The compound has a high intrinsic absorption of X-rays and a high efficiency for the conversion of X-radiation to visible radiation.

The **lanthanum** compound (and the Ln analogues) can be made by reacting the **oxide** with ammonium bromide initially at 500°C followed by recrystallization at 800 - 1000 °C in a flux containing bromides. The **oxalates** can also be used as the Ln source as they are more reactive than the corresponding oxides.

Like the oxychlorides, the heavier Ln oxybromide compounds are thermally less stable than the light-Ln analogues; LaOBr, for example, is stable to above 1000°C. The oxybromides are susceptible to attack by moisture and have to be protected in use. The hydrolysis seems to be initiated by traces of unreacted bromide ions at the surface of particles.



The heavier-Ln compounds will decompose further:

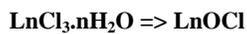


The oxybromides, like the oxychlorides, contain the $[\text{LnO}]_n^{n+}$ layers and also adopt the BiOCl structure.

[1] New X-Ray Phosphors, L.H.Brixner, Materials Chem. Phys., 1987, **16**(3-4), 253

OXYCHLORIDES

Thermal decomposition of hydrated Lanthanide **chlorides**, at temperatures near 400 °C, tends to produce Lanthanide oxide chlorides, commonly called oxychlorides :



The products are insoluble in water and traces of unreacted chloride can be removed by washing. A more controlled preparative method is the reaction of the appropriate **oxide** with an excess of ammonium chloride, or gaseous hydrogen halide, at temperatures between 800 and 1000°C.



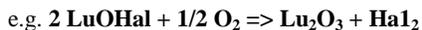
With the smaller lanthanide ions, e.g. Er to Lu and Y, a more complex oxyhalide, $\text{Ln}_3\text{O}_4\text{Cl}$, can be obtained by controlled decomposition of the oxychloride.

From **lanthanum** to **holmium** (along with **yttrium**) the resulting oxide chlorides crystallize in a tetragonal space group, isomorphous with BiOCl (PbFCl). The last members of the Ln series, Er, Tm, Yb and Lu, adopt a different oxychloride structure. In both structure types the semi-rigid $[\text{LnO}]_n^{n+}$ layer system with planes of M atoms on each side of an oxide plane, observed in many Ln oxy-compounds including **oxides**, can be seen. The layers of edge sharing OLn_4 tetrahedra are separated by halide ions.

On heating[1] the oxide chlorides of La - Ho will eventually decompose :



with the anhydrous halide volatilizing away. With the heavier-Ln's decomposition occurs at lower temperatures before the halide can become volatile and the oxyhalide tends to oxidize to oxide and release gaseous halogen.



The properties of several of the oxychlorides have been studied because of their potential as phosphor hosts; an active lanthanide ion such as Tb or Tm can easily be doped into the lattice to give luminescent behavior[2].

[1] The Thermal Stability of Lanthanide Oxide Chlorides, V.V. Bunda et al., Russ.J. Inorg. Chem., 1984, **29**(12),1741

[2] Terbium-Ion Activated Phosphors, G.Blasse and A-Bril, Philips Res. Rep., 1967, **22**, 481 Luminescence of Rare Earth Activated Lutetium Oxyhalide Phosphors, J.G.Rabatin, J.Electrochem.Soc., 1982, **129**(7), 1552

OXYFLUORIDES

The oxide, O^{2-} , and fluoride, F^- ions are isoelectronic and of very similar size. **Oxide** containing compounds of the lanthanides are very stable and it is therefore to be expected that comparable fluoride-containing materials will be stable provided the difference in negative charge causes no problems. Furthermore mixed O-F species, oxide fluorides or oxy- fluorides, will also be stable compounds. Indeed the processing of the fluoride-carbonate mineral **bastnasite** has to reflect these properties.

The oxyfluorides LnOF can be prepared[1]

- by heating the fluorides in air or water vapor
- by heating 1:1 ratio oxide/fluoride mixture in an inert atmosphere

Several of the Ln oxide fluorides adopt the fluorite, CaF_2 or CeO_2 , structure[2] with the fluoride and oxide ions occupying random anion sites. Sometimes the anions order and complex superstructures, based on the fluorite lattice, are formed. In addition non-stoichiometric $LnO_{1-x}F_{1+2x}$ compounds are known with excess fluorine that show an extended range of solid solubility.

The Ln Oxyfluorides as yet have no commercial significance on their own yet their properties[3] are of importance as possible intermediates in lanthanide **metal** production from the fluorides. In addition LnOF compounds show potential for oxide ion or fluoride-ion conductivity at high temperatures and could be of interest as solid electrolytes or as electrode coatings[4].

[1] Preparation and Reactions of Oxide Fluorides of the Transition Metals, the Lanthanides and the Actinides, J.H.Holloway and D.Laycock, Adv. Inorg. Radiochem., 1984, **28**, 73

[2] The Crystal Chemistry of Transition Metal Oxyfluorides, B.L.Chamberland, in "Inorganic Solid Fluorides", publ. Academic Press, 1985, p.205

[3] The High Temperature Thermodynamics of the La-O-F and Ce-O-F systems, Y.R.Hong et al., in "New Frontiers in Rare Earth Science and Applications, publ. Science Press, Beijing, China, 1985, p.1 1

[4] Preparation and Electrical Conductivity of Binary Rare Earth Metal Fluoride Oxides, M.Takashima et al., Solid State Ionics, 1987,**23**(1-2),99: Method of Producing Aluminum, Aluminum Production cell and Anode for Aluminum Electrolysis, J- J.Duruz, Eltech, Eur.Pat.appl., 0 192 603, publ. 27.08.86

OXYSULFIDES

All the elements of the Lanthanide series, along with **Yttrium**, can form compounds with the composition $\text{Ln}_2\text{O}_2\text{S}$ [1]. (The name usually used is *oxysulfide* but alternative names are *thio-oxide*, *sulfoxide*, or *oxide sulfide*; strict nomenclature would require the last term.) The oxysulfides can be considered as intermediates between the **oxides** and the **sulfides** of the corresponding elements; many features of their properties and structure reflect this. The oxysulfides, with melting points approaching 2000°C , have a greater thermal stability than the sulfides to oxidation but are less resistant than the oxides. In general the polycrystalline $\text{Ln}_2\text{O}_2\text{S}$ compounds, apart from $\text{Ce}_2\text{O}_2\text{S}$, are stable in air up to 500°C .

These $\text{Ln}_2\text{O}_2\text{S}$ materials, perhaps unexpectedly, account indirectly for a significant fraction of the world's use of the Lanthanide elements. The stable compounds resulting from the **Mischmetal** treatment of iron and steel are oxysulfides as is the red phosphor on almost all color TV screens and computer monitors. As a consequence, for this type of compound, much of the know-how regarding synthesis derives from the need to produce $\text{Y}_2\text{O}_2\text{S}$ for TV phosphors and other oxysulfides for X- ray screens. In contrast thermodynamic data comes from understanding the role of $\text{Ce}_2\text{O}_2\text{S}$ in steel treatment.

The oxide sulfides can be prepared [1], in principle, by either :

- introducing sulfur into an oxygen-containing compound e.g. with sulfur, CS_2 , H_2S , NH_4SCN etc., or
- reducing a sulfur-containing Lanthanide compound, e.g. reduction of sulfates or oxide sulfates with H_2 or CO .

The commercial production, for example, of $\text{Y}_2\text{O}_2\text{S}$ and $\text{Gd}_2\text{O}_2\text{S}$ involves the solid-state reaction, at $1100 - 1200^\circ\text{C}$, of the Ln oxide with a flux of sulfur and sodium carbonate [2], e.g. :

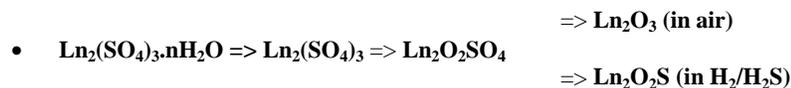


Polysulfides formed in the flux act as the sulfiding agent and, after reaction, the unwanted flux residue is removed by acid leaving a pure oxysulfide. Ln salts that decompose to oxide can also be used as precursors.

[1] Lanthanide Oxide Sulphides, Yu.L.Suponitskii et al., Russ.Chem.Rev., 1988, **57**(3), 209

[2] M.R.Royce et al., U.S.Patent 3,502,590,1970: Formation process of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}$ in a Preparation with Flux, O.Kanehisa et al., J.Electrochem.Soc., 1985, **132**(8), 2023

The alternative approach is the reduction of a sulfate, e.g. [3]:



The hydrated sulfate dehydrates on heating at 600 °C; an intermediate oxysulfate is then seen for some Ln's before conversion to the oxysulfide occurs at ≈1000 °C. Direct oxidation of the sulfide is also a preparative route but is difficult to control.

Ln compounds with a general formula (LnO)_nX often have as a general structural feature, layers of the planar poly- (LnO)_n⁺⁺ ion separated by layer(s) of the component X. This structure, found in the A- and B-type light lanthanide Ln₂O₃ oxides, is also to be seen in all the oxysulfides whatever the Ln. Sheets of (LnO) are separated by layers of S atoms with the Ln coordinated to four-O's from the polycation and three-S's.

The thermochemical properties of several of the light Ln oxysulfides have been studied [4] as a consequence of the compounds' importance in the mischmetal treatment of steel and iron. Phase stability diagrams at 1100 K have been determined [5] for La, Ce and Y in support of research into the high temperature desulfurization by lanthanide oxides of gaseous fuels and stack gases.

The gettering or trapping of sulfur contaminants during steel production is essential to control the steel's properties. The high affinity of the Ln elements for O and S ensures that "tramp" sulfur can be captured as an Ln oxysulfide. Furthermore the resulting oxysulfide remains solid even at molten steel temperatures and is present as innocuous inclusions. (In contrast manganese sulfide, for example, is liquid under those conditions and "strings" out, as steel is rolled, producing planes of weakness within the final product.)

[3] Preparation and Luminescence of Selected Eu³⁺-Activated Rare-Earth-Oxygen-Sulfur Compounds, J.W.Haynes and J.J.Brown, J.Electrochem.Soc., 1968, **115**(10), 1060

[4] Determination of the Standard Free Energies of Formation of Ce₂O₂S and Y₂O₂S at High Temperatures, R.ICDwivedi and D.A-R.Kay, J.Less-Comm.Met., 1984, **102**, 1: Thermodynamics of the Oxidation of Rare Earth Oxysulfides at High temperatures, R.ICDwivedi and D.A.R.Kay, Met.Trans.B, 1984, **15B**, 523: Electrochemical Determination of Standard Gibbs Free Energies of Formation of Rare Earth Oxysulfides and Oxysulfates, N.Fukatsu et al., J.Electrochem.Soc., 1985, **132**(9), 2258

[5] The Use of Re-O-S Phase Stability Diagrams in Gaseous Desulfurization and Iron and Steel Production, D.A-R.Kay et al., ???

PEROVSKITES

A very wide range of materials, many containing lanthanides, are known with the base-composition, ABO_3 , and perovskite-type structures[1]. Trivalent Ln^{3+} ions, with radii from ≈ 95 pm to ≈ 120 pm, readily form the A component while another cation, particularly from the first transition series, can be the smaller nominally-trivalent B ion, e.g. **chromites**, **cobaltates** and **manganites**. The structure contains octahedral BO_6 groups with the larger A ions surrounded by 12 O's.

Many changes, including non-stoichiometry, can be rung on the basic structure. The A site can be doped with another ion, e.g. M^{2+} ; the charge is balanced by a change of the valency of B, resulting in mixed valency for the B ion. The structure can stabilize a valence, e.g. Ni^{3+} , usually not easily obtained. In addition subtle structural changes can produce other crystal symmetries and differing behavior. The perovskite block, ABO_3 , also forms sub-units in more complex structures, e.g. $A_2BO_4 = AO / ABO_3$.

Interactions between the B ions can give rise to novel magnetic as well as unusual ionic and/or electronic conductivity behavior. Mixing B-ion contents can help optimize these properties. The potential to vary the Ln ion, and thus the A ion size, makes possible fine-tuning of structuresensitive properties. The net result is that $LnMO_3$ (M = transition metal) compounds are of interest in many developing technologies, such as electrocatalysis, high temperature electrodes and electrolytes, membranes for gas separation, and sensors. [2][3][4]

Perovskites can be prepared by high temperature solid-state reactions (if needed under reducing conditions) but, for close control of chemistry and particle morphology, co-precipitation or sol-gel type processes[5] are preferred.

Ln Perovskites $LnMO_3$	
<i>M ion</i>	<i>property & ref</i>
Sc	stability
Ti*	magnetic
V	electro-optic
Cr*	conductivity
Mn*	electrode, etc
Fe	catatysis[2]
Co*	catalysis, etc
Ni	catalysis[3]
*see entries in the Lanthology series	

[1] F.S.Galasso, *book*, Structure, Properties and Preparation of Perovskites-Type Compounds, 1969, publ. Pergamon : Stability and Thermodynamic Properties of Rare Earth Perovskites, J.-P. Coutures et al., High Temp. sc., 1980, **13**, 331

[2] Electrolytic Oxygen Evolution in Alkaline Medium on $La_{1-x}Sr_xFeO_{3-y}$ Perovskite Related Ferrites, A-Wattiaux et al., J.Electrochem.Soc., 1987, **134**(7), 1714

[3] Structure and Catalytic Activity of Perovskites La-Ni-O Supported on Alumina and Zirconia, A.K.Ladavos and P.J. Pomonis, Appl. Cat. B Envir., 1993, **2**, 27

[4] Perovskite Electrodes for Sensors, C.B.Alcock et al., Solid State Ionics, 1992, **51**, 281

[5] Precipitation of $LaNiO_3$ Powder from Co-precipitated Lanthanum Nickel Oxalates, J. Takahashi et al., J.Mat.Sci., 1990,**25**,1557: Modified Resin-Intermediate Processing of Perovskite Powders, L-W. Tai and P.Lessing, J.Mater.Res., 1992, **7**(2), 511

PHOSPHATES

The term "phosphate" usually is taken to refer to the orthophosphate LnPO_4 . However, in addition to this salt, several other compounds have been identified in $\text{Ln}_2\text{O}_3\text{-P}_2\text{O}_5$ systems [1], including metaphosphates, e.g. $\text{Ln}(\text{PO}_3)_3$, and pentaphosphates (or ultraphosphates) $\text{LnP}_5\text{O}_{14}$. Oxyphosphates, Ln_3PO_7 , are also known.

Lanthanide Orthophosphates			
Lanthanide	Compound	Structure Type Name as Mineral	Stability
La to Gd	LnPO_4	monazite	stable to $\approx 2000^\circ\text{C}$
Dy to Lu, Y	LnPO_4	xenotime	stable to $\approx 2000^\circ\text{C}$
La to Gd	$\text{LnPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	rhabdophane	converts to monazite $>> 500^\circ\text{C}$
Dy to Lu, Y	$\text{LnPO}_4 \cdot 2\text{H}_2\text{O}$	weinschenkite	converts to xenotims $>> 300^\circ\text{C}$

The table lists the crystalline species identified; the degree of hydration for the rhabdophane-type, given as 1/2, is variable. Both the two sparingly soluble hydrated compounds can precipitate out of aqueous solution but are rare in mineral guise because they readily decompose to the insoluble non-hydrated forms, the synthetic analogues of **Monazite** and Xenotime.

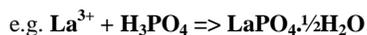
As the trivalent Ln ionic radius decreases from La to Lu there is a change in structural type with Dy and Tb sitting on the borderline for this transition. The larger Ln^{3+} ions take up a structure, Monazite, with an irregular nine-coordinated cation, whereas in Xenotime the heavier and smaller Ln ions become eight-coordinated by oxygen. (The Xenotime structure YPO_4 is identical to that of Zircon, ZrSiO_4 with an 8-coordinate metal.) In both phosphate types the somewhat-distorted tetrahedral PO_4 groups tie the structures together.

The orthophosphates, LnPO_4 , are commercially important materials and, as geologically occurring minerals, have provided a significant portion of the world's supply of lanthanides.

[1] The Systems $\text{Y}_2\text{O}_3\text{-P}_2\text{O}_5$ and $\text{Gd}_2\text{O}_3\text{-P}_2\text{O}_5$, D.Agrawal and FAHummel, J.Electrochem.Soc., 1980, 127(7), 1550 : Phase Equilibria in the System $\text{La}_2\text{O}_3\text{-P}_2\text{O}_5$, H.D.Park and E.R.Kreidler, J.Am.Ceram.Soc., 1984, **67**(1), 23 : ... in the System $\text{Nd}_2\text{O}_3\text{-P}_2\text{O}_5$, M-S.Wong and E.R.Kreidler, *ibid.*, 1987, **70**(6), 396

The LnPO₄ compounds can be prepared [2], for example, by :

- precipitation from aqueous solution,



- reaction of phosphoric acid, or ammonium phosphates,

with Ln salts such as the **oxide** or **carbonate**.

The exothermic reactions should be controlled by slurring the oxide or salt in water. The more complex phosphates, e.g. metaphosphates, can be made by the solid state reaction of the lanthanide salt and a phosphate source mixed in appropriate ratios.

In common with *all* Ln minerals, Monazite and Xenotime, in their naturally occurring forms, contain a "natural ratio" of many of the Ln elements, as well as other cations, and are not to be envisaged as pure compounds of any individual lanthanide. Monazite contains mainly light lanthanides whereas Xenotime is a source for Yttrium and heavy Ln's.

The monazite and xenotime structures have exceptional thermal stabilities and, probably, single-phase behavior up to their melting points[3] and indeed this, combined with a limited chemical reactivity, accounts for the difficulty of processing phosphate ores. (Ln phosphates have been suggested as hosts for the long-term storage of radio-active waste.)

The more complex phosphates on heating decompose to the orthophosphate, e.g. :

- $\text{La}_5\text{PO}_{14} \Rightarrow \text{La}(\text{PO}_3)_3 \Rightarrow \text{LaPO}_4$

The doped lanthanum salt, (La,Ce,Tb)PO₄, is now widely used as the preferred green-emitting phosphor for energy-efficient fluorescent lighting[4]. Ln phosphates have also been proposed as scintillators and laser hosts.

LnPO ₄ melting points °C	
<i>Monazite-type</i>	
La	2072
Ce	2045
Pr	1938
Nd	1975
Sm	1916
<i>Xenotime-type</i>	
Y	1995
Er	1896

[2] Syntheses of Rare-Earth Orthophosphates, Y.Hikichi et al., Bull.Chem.Soc.Jpn., 1978, **51**(12), 3645

[3] Melting Temperatures of Monazite and Xenotime, Y. Hikichi and Ts. Nomura, J.Am. Ceram. Soc., 1987, **70**(10), C-252

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

PRASEODYMIUM

In most compounds this element is trivalent like **Lanthanum** and, in chemical behavior, Pr(III) compounds closely resemble the analogous La(III) derivatives. Most Pr³⁺ salts are pale green due to strong absorption bands in the blue from 440 to 490 nm.[1] (Similar color and bands are seen in a glass matrix when Pr³⁺ is present.[2])

Most praseodymium salts when calcined in air produce, not a sesquioxide, Ln₂O₃, but a black material whose composition is best expressed as Pr₆O₁₁. The tetra-valent state of Pr is of just sufficient stability to form preferentially this oxide with mixed Pr valencies, charge transfer behavior and thereby an enhanced stability. (The Pr-O phase diagram is complex and several oxides, forming a homologous series, Pr_nO_{2n-2}, are known[3], each with a defect fluorite structure.) The Pr(IV) ion is only stable in a few solid compounds, all oxide and fluoride based. A pale green Pr₂O₃ oxide can be made under strongly reducing conditions but it is not stable in air.

Praseodymium forms ≈4 % of the lanthanide content of **bastnasite** but all that proportion is not recovered as a separated pure-Pr material because there is currently insufficient commercial demand. The element will be present in a small amount in almost all mixed-light-Ln derivatives, see **Lanthanum Concentrate**.

The most popular yellow ceramic pigment is a Pr-doped zircon[4] that is "cleaner" and "brighter" than alternatives probably due to the Pr-pigment having an optimum reflectance at ≈560 nm. In the preparation a "mineralizer", usually a metal halide MX, must be present to ensure complete reaction. Presumably the vapor phase

Pr	
Element	
Atomic Number	59
Atomic Weight	140.91
Electron configuration	[Xe]4f ⁴ 6s ²
Valency	3 (4)
Ionic radius for 8-coordination	113 pm
Magnetic moment	3.60 μB
metal	
Crystal Structure	Dhcp
Melting Point	931 °C
Boiling Point	3520 °C
Density	6.77 g/cm ³
Metallic Radius	183 pm

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

[2] Absorption Spectra of Praseodymium in Glass, A-Singh and P.Nath, Glass Ceram.Bull., 1983, **30**, 6

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

[4] Formation of Praseodymium-Doped Zircon Colors in Presence of Halides, R.A.Eppler, Ind.Eng. Chem.Prod.Res.Dev., 1971, **10**(3), 352 : Zirconia-based Colors for Ceramic Glazes, R.A-Eppler, Cer.Bull., 1977, **56**(2), 213

transport of Pr happens through the intermediacy of a transient PrMX_n complex. The cause of the coloration has been attributed solely to the Pr^{4+} ion stabilized in the host ZrSiO_4 but it is also possible that charge transfer bands contribute. The color of potential red pigments such as $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ [5] is certainly due to charge transfer bands associated with the Ce(IV)/Pr(III) system.[6]

A possible Pr(III)/Pr(IV) redox in a fluorite-related structure, with mobile oxide ions, indicates a potential for Pr in catalysis similar to that found for **cerium** in CeO_2 . As examples, the oxidative coupling of methane over doped Pr_6O_{11} shows a high selectivity to C_2 products[7] and the oxide Pr_4PdO_7 catalyzes the oxidation of natural gas fuels as well as having an excellent thermal stability and regenerative behavior[8].

On excitation the Pr^{3+} ion shows a variety of emissions depending strongly on the host lattice due to the strong influence of that lattice on the energy of the excited 4f5d level.[9] Pr-doped fluoride fibers have been proposed for optical amplification at 1310 nm for telecommunications; a system that could rival **Erbium**-doped fiber amplifiers. Another application of Pr-emission is in the scintillator $\text{Pr,Ce,F} : \text{Gd}_2\text{O}_2\text{S}$ for X-ray computed tomography[10]. Such scintillators need to be made as small translucent ceramics with an emitter with a very fast decay time, 5 μs for Pr^{3+} , and a wavelength matching the detector's sensitivity.

Permanent magnets based Praseodymium, a lanthanide more abundant than **Samarium**, have the potential to be comparable in properties to the well recognized samarium-cobalt material, SmCo_5 . Certain oxides, added as powders (up to 1 wt %) prior to sintering, can suppress the formation of undesirable impurity phases. The added oxide reacts with any excess Ln in the starting alloy composition and keeps the overall Pr : Co ratio down to the desired 1 : 5. One esoteric use of this element is in the intermetallic PrNi_5 that has made possible the attainment of ultra-low temperatures, in the micro-Kelvin range[11]. The ^{141}Pr nuclei have the requisite novel magnetic properties.

[5] Optical Properties of $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ Powders and their Applications to the Coloring of Ceramics, R.Olazcuaga et al., J.Solid State Chem., 1987, **71**, 570

[6] Charge-Transfer Spectra of Tetravalent Lanthanide Ions in Oxides, H.E.Hoefdraad, J.Inorg.Nucl.Chem., 1975, **37**, 1917

[7] Methane Conversion, AM.Gaffney (Arco), U.S.Patent, 4,499,323, 12 Feb. 1985

[8] Praseodymium-Palladium Binary Oxide, Catalyst Compositions containing the Same, and Methods of Use, T.C.Chou et al.(Engelhard), U.S.Patent 5,102,639, 7 April 1992.

[9] Chemistry and Physics of R-Activated Phosphors, G.Blasse, in "Handbook on the Physics and Chemistry of Rare Earths", ed. K.A.Gschneidner and L.Eyring, publ. North-Holland, 1979, Vol.4, p.237

[10] A Scintillator $\text{Gd}_2\text{O}_2\text{S} : \text{Pr, Ce, F}$ for X-Ray Computed Tomography, H. Yamada et al., J.Electrochem.Soc., 1989, **136**(9), 2713

RESOURCES

For significant resources to exist then geological fractionation processes will need to have improved on the inherent crustal **abundance**. Two common geochemical processes, hydrothermal activity and differentiation by magmatic recrystallization, however tend - for the lanthanides - to oppose each other. Minerals enriched in the lanthanide elements nevertheless are known[1] and have created lanthanide rich deposits although only a few major commercially significant sources are recognized[2].

Minerals containing lanthanides can be categorized, according to total Ln content, as having,

- very low Ln concentrations, a group with many common rock-forming minerals, or
- minor amounts of these elements, not as essential constituents, with ≈ 200 minerals known to have a Ln content of $> 0.01\%$, or
- major, usually essential - that is structure determining - Ln contents. (Recent listings[3] describe >70 discrete minerals under this heading.)

Lanthanides Mineral Resources (by tonnage)	
major	Bastnasite
moderate	Monazite
	Loparite ion-adsorption
minor	Xenotime
	Apatites
potential	Eudialyte
	Brannerite

The Ln-elements are the major, structure-determining, elements in some magma-derived minerals. In one unusual type of deposit the concentration of the Ln-elements has been especially enhanced. *Carbonatite* magmas form when mantle rocks melt deep in the earth's crust with large amounts of carbon dioxide present. This magma type occasionally rises to the surface to produce alkaline igneous rocks. If fluoride enters during the ascent specific Ln-fluoride carbonate minerals, e.g. **Bastnasite**, are formed.

Currently the two major sources in the world for the lanthanides are two bastnasite deposits, one at Mountain Pass, California, U.S.A., the other at Bayun-obo, Inner Mongolia, China. The U.S.A. mine is devoted solely to the Ln's whereas the chinese deposit is mined primarily for iron ore.

[1] The Not-So-Rare Earths, G.KMuecke and P.Möller, Sci.Amer., 1988, **258**(1), 72

[2] Rare Earths, Enter the Dragon, M.O'Driscoll, Industrial Minerals, 1988(11), 21

[3] Crystal Structures of Rare-Earth Minerals, R. Miyawaki and I. Nakai, Rare Earths (publ. Jpn. Rare Earth Soc.), 1987, **11**, 1 : Mineralogy of the Rare Earth Elements, A.M.Clark, in Rare Earth Element Geochemistry, ed. P. Henderson, publ. Elsevier, 1984, 1

Other significant bastnasite deposits are known[4], e.g Wigu, Tanzania, and elsewhere in Africa, but none are in commercial production.

Certain igneous rocks, made by repeated processes of melting and recrystallization, can include minerals enriched in the lanthanides and **yttrium**. The Ln's can substitute in crystal structures for a variety of large positive ions, not only those also triply charged, and can be found in many complex mineral compositions. The reduction in ionic radius from La at the beginning of the Ln-series, to Lu at the end, can create a crystal structure change along the series and a separation into light lanthanide and heavy-lanthanide counterparts.

The light-lanthanide **phosphate, Monazite**, has a heavy-lanthanide analogue, Xenotime, both of which are lanthanide resources with the Monazite being available in much larger quantities. Monazite is a common component in "heavy" beach sands and found throughout the world, particularly along coast lines in Australia, Brazil and India. This heavy mineral has been released from a primary source by weathering and concentrated, by wave-action over long periods of time, into placer deposits. In addition to beach sand deposits, Monazite is also found in high grade inland deposits such as the Mt. Weld intrusion near Perth in Western Australia.[5]

Xenotime, an Yttrium-heavy-Ln phosphate, comes from Malaysia, Thailand or China. Both phosphates are recovered as by-products of mining for other more economically dominant materials, titanium / zirconium and tin minerals respectively.

Some minerals mined, for example, for their Uranium or Niobium content, can also serve as lanthanide sources. Uranium mines in Canada have supplied, as by-product, yttrium-enriched concentrates for further processing. Similar resources, complex heavy-element mineralizations, are known in countries such as Brazil and Australia. A cerium-rich Loparite, $(Ln,Na,Ca)(Ti,Nb)O_3$, is currently mined in Russia's Kola peninsula, adjacent to Finland, and supplies the bulk of the CIS demand for Ln's.[6]

The Ln's, in geochemical environments, occur as Ln^{3+} cations of ≈ 100 pm radius, i.e. comparable size to Ca^{2+} . If the charge disparity is balanced elsewhere, Ln's can partially replace the ubiquitous divalent calcium. Some Ca phosphates, e.g. apatites where the Ln proportion is a percent or more, are potential lanthanide resources. If the parent phosphate is mined for fertilizer then the by-products provide a source of Ln's, e.g. the Kola peninsula apatite that complements Loparite as a Ln resource.

[4] Economic Geology of the Rare Earth Elements, A.N.Mariano, Rev. Mineral., 1989, **21**, 308

[5] Mt. Weld Rare Earths Project, D. Kingsnorth, Aus.IMM Bull., 1992, **8**, 13

[6] Rare Earths Industry of Today in the Commonwealth of Independent States, V.D.Kosynkin et al., J. Alloys Comp., 1993, **192**, 118

RESOURCES

Significant new resources are the **ion-adsorption ores** processed by China. These were created by the weathering of primary granitic-type rock followed by the capture of soluble Ln species by adsorption on clays. Ideal climatic conditions for this process evidently occurred in southern china, especially Jiangxi province, where there are many such deposits. The weathering process modifies the proportions of the various lanthanides present and can reduce the **Cerium** content compared to the source rock. These ores, with compositions dependent on location, are relatively rich in Y and the mid-Ln's such as Eu Sm and Gd, and, although of overall low-Ln content, are easily processed. They now supply a major portion of the world's yttrium and heavy lanthanides.

The mineral, *Eudialyte*, an acid-soluble calcium-zircon silicate, is also a potential Yttrium source. Significant deposits have been identified in Russia, U.S.A. (New Mexico), U.S.A., Greenland and elsewhere. Deposits of several other minerals, such as *Brannerite*, *Gadolinite* and *Euxenite*, particularly in Canada and Australia, have been examined as potential yttrium (and lanthanide) sources. These minerals contain a variety of large polyvalent ions, among them yttrium and some heavy lanthanides. The complexity of the ore bodies and of the mineral compositions however gives major processing problems. A simple physical route, or an inexpensive chemical crack, to a good grade concentrate is difficult to find.

World reserves have been estimated as ≈ 85 million tonnes[7], more than 1,000 times current annual consumption. Total production of lanthanide (rare earth) oxides (LnO's) in 1991 was $\approx 70,000$ tons, 35 % from China and 35 % from the United States, with the bulk of the world's supply of Ln's being met by the mineral Bastnasite. In that year, of China's $\approx 25,000$ tons LnO, only 900 tons came from monazite whereas 6,100 were apparently derived from the new "ion-adsorption" source. Direct comparison between production and consumption quantities is obscured by stockpiling of partially processed ores.

The major factor in world markets during the '80's has been the development of ion-adsorption ores in China and a drive by the chinese to increase exports in order to obtain foreign currency.[8] They have increased production by an order of magnitude and become the major supplier to many markets outside the U.S. in particular to Japan. The steady production increase by China, and their increased overseas marketing with province competing against province, caused significant declines in the price of high-purity materials and major problems for the market-economy producers.

[7] Rare Earth Metals, J.B.Hedrick, U.S.Dept Interior, Mineral Commodity Summaries, 1991, 128

[8] The Rare Earth Industry: A World of Rapid Change, P.Falconnet, J. Alloys Comp., 1993, **192**, 114

SAMARIUM

Samarium **metal** is made directly from the oxide by reaction with, for example, lanthanum; vaporization of the volatile Sm drives the reaction to completion. The room-temperature structure of the metal is unusually complex, due to involvement of the f-orbitals in the bonding.

Introduction of the intermetallics SmCo_5 and $\text{Sm}_2\text{Co}_{17}$, as permanent magnet materials [1] created a significant market for samarium. These Sm-Co compounds are made by a reduction-diffusion process whereby Sm_2O_3 is converted directly to the Sm-transition metal alloy, Sm-metal is not isolated; see **metals**.

The magnetic strength of the Sm-Co compounds arises predominantly from the cobalt atoms but the role of Sm is crucial in determining that property. In essence Sm helps define an anisotropic structure "locking" the cobalt moments in place and making demagnetization impossible.

Although now over-shadowed by the Nd-Fe-B materials, a market niche remains for the high-temperature-stable (Curie temperature ≥ 700 °C) Sm-based magnet alloys, particularly in microwave applications. A recently discovered ternary Sm-transition metal system, $\text{Sm}_2\text{-Fe}_{17}\text{-N}_{\approx 3}$, also offers potential as a permanent magnet material[2].

The chemical behavior in aqueous systems of Samarium is intermediate between that of **Yttrium** and **Neodymium**. Nevertheless, the moderate stability - albeit less than Eu(II) - of Sm(II) differentiates Samarium from most other Ln's. The iodide, SmI_2 [3], in THF is a stable versatile reagent in synthetic organic chemistry where its oxophilic nature makes possible a wide variety of organic-molecule trans

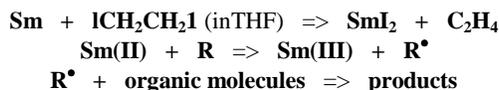
Sm	
Element	
Atomic Number	62
Atomic Weight	150.4
Electron configuration	$[\text{Xe}]4f^66s^2$
Valency	3 (2)
Potential $E_{\text{M(III)/M(II)}}$	-1.55 V
Ionic radius for 8-coordination	108 pm
Magnetic moment	0.85 μB
metal	
Crystal Structure	Complex
Melting Point	1074 °C
Boiling Point	1794 °C
Density	7.52 g/cm ³
Metallic Radius	180 pm

[1] Permanent Magnets, J.J.Becker, Scientific American, 1970(December), 92 : RETM_5 and $\text{RE}_2\text{TM}_{17}$ Permanent Magnets Development, K.Kumar, J.Appl.Phys., 1988, **63**(6), R13

[2] Intrinsic Magnetic Properties of New Rare-Earth Iron Intermetallic Series, J.M.D.Coey et al., J.Mag.Magnetic Mat., 1991, **101**, 310

[3] SmI_2 : A Most Useful Material, S-H. Wang, Rev. Inorg. Chem., 1990, **11**, 1

formation reactions.[4] Transfer of a single electron from Sm^{2+} , forms, in situ, a reactive organic radical that reacts further.



Samarium has a weak spectral absorption band close to 400 nm that causes, in glass, a pale yellow color at high concentrations. There are other absorption bands around 950 and 1100 nm, hence its use in filter glasses that surround Neodymium laser rods to pass the pumping light energy but to absorb stray emission from the laser rod and improve operating efficiency.

The oxide, as usually prepared, has the $\text{C-Ln}_2\text{O}_3$ type structure although the B-type arrangement can also be obtained. Similar to several Ln oxides Samarium oxide forms stable complex titanates that have useful dielectric properties suitable for capacitors, particularly at microwave frequencies.[5] The essential compound is probably a ternary oxide phase with a 1:1:~5, Ba:Sm:Ti, composition.

Samarium-doped cerium oxide has, relative to **cerium oxide** alone, enhanced electronic and oxide ion conductivity[6] and has been proposed as a component, $[\text{CO}_2]_{0.8}[\text{SmO}_{1.5}]_{0.2}$ for solid oxide fuel cells that can operate at temperatures as low as 800 °C[7].

[4] Preparation of Divalent Ytterbium and Samarium Derivatives and their Use in Organic Chemistry, H.B.Kagan and J.L.Namy, in Handbook on the Physics and Chemistry of Rare Earths, ed. K.A.Gschneidner and L.Eyring, publ. North Holland, 1984, Vol. 6 Ch. 50, 525: Divalent Samarium Compounds : Perspectives for Organic Chemistry, H.B.Kagan, New J.Chem., 1990, **14**, 453

[5] Microwave Dielectric Properties of (Ba,Sr)O-Sm₂O₃-TiO₂ Ceramics, S.Nishigaki et al., Cer.Bull., 1987, **66**(9), 1405 : Reaction Sequence and Effects of Calcination and Sintering on Microwave Properties of (Ba,Sr)O-Sm₂O₃-TiO₂ Ceramics, J.- M.Wu et al., J.Am.Ceram.Soc., 1990, **73**(6), 1599

[6] Oxygen Ion Conductivity of the Ceria-Samarium Oxide System with Fluorite Structure, H.Yahiro et al., J. Appl. Electrochem., 1988, **18**, 527

[7] High Performance Catalyzed Reaction Layer for Medium Temperature Operating Solid Oxide Fuel Cells, M. Watanabe et al., J. Electrochem. Soc., 1994, **141**(2), 342

SILICATES

Within the binary $\text{Ln}_2\text{O}_3\text{-SiO}_2$ system several lanthanide silicates have been identified[1]. The 1:1 compounds display two different crystal structural types, the change occurring around Tb and Dy; both 1:1 structures are stable up to 1950°C.

Ln ₂ O ₃ : SiO ₂ Compounds		
1:1	Ln ₂ O (SiO ₄)	oxy-Orthosilicates
7:9	Ln _{<5} O (SiO ₄) ₃	"apatite" silicates
1:2	Ln ₂ (Si ₂ O ₇)	di-orthosilicates

The apatite-silicates form, for all Ln's, one type of cation-deficient structure with a composition best expressed as $\text{Ln}_{3.33}[\]_{0.67} \text{Ln}_6(\text{SiO}_4)_6 \text{O}_2$ with defects on the Ln site. This large-cation structure is very stable with the light-Ln-members melting without decomposition near 1900°C. For the diorthosilicates, with discrete Si_2O_7 anions, at least seven different structures are recognized.

Trace amounts of Ln's are present in many complex silicates found in nature. In some minerals the Ln elements occur in significant quantities and define the structure. Although potential resources, e.g. for Sc, none are currently processed on any scale.

Lanthanide Mineral Silicates	
Examples	
Allanite	(Ce,Ca,Y) ₂ M ₃ (SiO ₄) ₃
Eudialyte	(Ca,Na,Ce) ₅ (ZrFe) ₂ (Si ₆ O ₂₀)
Gadolinite	(Y,Ln) ₂ Fe Be ₂ Si ₂ O ₁₀
Thortveitee	(Sc,Y) ₂ Si ₂ O ₇

Ln silicates can act as specialized phosphor hosts. Ce- and Tb- Yttrium orthosilicates are commercial phosphors that also have potential for projection TV's[2]. The crystals are grown from the oxides in a suitable flux, e.g. Bi_2O_3 . The $\text{Ce:Y}_2\text{Si}_2\text{O}_7$ material with a high efficiency and a very fast decay time, < 200 nanoseconds, also has a specialized CRT use. Other silicate phosphors, e.g. $\text{Ce:Gd}_2\text{SiO}_5$, are potential scintillators for positron emission imaging and gamma-ray detection.

For soda-lime silicate glasses the lanthanides are important additives to provide behavior such as u.v. absorption (Ce) or coloration (Nd,Pr). Furthermore, for these glasses, **Cerium concentrate** is used for decolorization during production and also as the basis for the best polishing agents known.

[1] The Crystal Chemistry of the Rare Earth Silicates, J.Felsche, Structure and Bonding, **13**, 100, publ., Springer 1973 : Rare Earth Silicates, I.A.Bondar, Ceramics Int., 1982, **8**(3), 83) : Compound Formation in the $\text{Ce}_2\text{O}_3\text{-SiO}_2$ System, H.A.M. van Hal and H.T.Hintzen, J.Alloys Comp., 1992, **179**, 77

[2] Single Crystal Rare-Earth Doped Yttrium Orthosilicate Phosphors, J.Shmulovich et al., J.Electrochem.Soc., 1988, **135**(12), 3141

SILICIDES

A metallic mixed-lanthanide-containing material, a ferro-silicon alloy called *rare-earth silicide*, is produced in a submerged electric arc furnace by the direct reduction of **bastnasite** concentrate, together with iron ore and quartz. The resulting alloy is approximately 1/3 **mischmetal**, 1/3 silicon, and 1/3 iron and is used as an additive to alloy steels[1] and to cast irons[2]. (No benefit can be gained by separating the lanthanide precursor into individual Ln's prior to reduction as there is no major difference in behavior between different lanthanides. In ferrous metallurgy, silicon is often present in the final product.)

Rare Earth Silicide	
Typical Analysis %	
Fe	≈33
Ce	≈16
La	≈11
Nd	≈2
misc Ln's	≈2
Si	≈33

The silicide additives provide lanthanides that, in cast irons, can control morphology of the precipitated graphite that defines the iron's properties. However, such control is now more economically supplied by Mg and the role of the Ln's has become that of specialist additive within such silicides. Some magnesium ferro-silicon alloys contain ≈1 % of **Cerium**, derived from cerium concentrate. The Cerium's role is particularly to capture, probably as intermetallics, contaminants such as lead and bismuth[3] and to increase the number of nuclei on which graphite grows.

Several discrete intermetallic compounds of Ln and Si, e.g. Ln_5Si_3 , LnSi , and LnSi_2 — in which the Si atoms form a three dimensional network— and other compositions, are known, e.g. for Cerium[4] and **Gadolinium**[5]. The properties of some such materials are of interest for the behavior of micro-electronic devices based on Si-SiO₂ systems. Lanthanide silicides are possible low-resistance contacts with silicon. Deposition of a thin film of say La, followed by a diffusion reaction in-situ, creates a silicide barrier that has a desirable low or high Schottky barrier, depending on the nature of the Si substrate.[6]

[1] Reducing Temper Embrittlement by Lanthanide Additions, C.I.Garcia et al., J.Metals, 1985, **37**, 22

[2] The Role of Rare Earth Elements in the Production of Nodular Iron, H.F.Linebarger et al., in "Industrial Applications of Rare Earth Elements" ed. K.A.Gschneidner, ACS Symposium 164, pub Am.Chem.Soc., 1981, 19

[3] Neutralization of the Deleterious Effects of Bismuth and Lead in Gray Cast Iron by Lanthanide Additions, D.M.Stefanescu et al., in "Advanced Casting Technology", Conf.Proc., Publ. ASM, 1986, 167

[4] The Cerium-Silicon System, A.B.Gokhale et al., Bulletin Alloy Phase Diag., 1989, **10**(1), 73

[5] The Gadolinium-Silicon System, *ibid.*, 1988, **9**(5), 574

[6] Rare Earth Silicide Schottky Barriers, R.D.Thompson, U.S.Patent, 4,394,673, 19 July 1983

SOLVENT EXTRACTION

Some text books still imply that the lanthanides and yttrium are all produced by ion exchange technology. Not so. Only a few heavy lanthanides are purified commercially on a small scale by ion exchange. For large-scale production the chosen path is **solvent extraction**, usually in nitrate solutions[1]. Furthermore, once the starting precursor has been prepared, this separation technology is independent of starting mineral and different feedstocks can ultimately be processed by the same separation routines and equipment.

The liquid-liquid counter-current two-phase extraction procedure, commonly referred to as solvent extraction (SX), rely on the differential partitioning of metal soluble complexes between immiscible aqueous and organic phases. The organic phase acts as a diluent for the extractant that may be selective towards cationic, neutral or anionic species. The reagents used are :

- as extractants, or complexing agent, organic phosphates, carboxylic compounds, etc.,
- as the aqueous phase, acidic solutions, e.g. nitric,
- as the organic phase, commercial aliphatic or aromatic solvents.

A component, say Ln_A is distributed between the two phases and will have a distribution coefficient, measured at equilibrium :

$$D_A = (\text{Concentration in organic phase}) / (\text{Concentration in aqueous phase})$$

For two components, Ln_A and Ln_B , both distributed between the organic and aqueous phases, a separation factor can be defined:

$$\beta^A_B = D_A/D_B$$

The closer this factor approaches '1' the more difficult it will be to separate those two elements. The degree of separation is maximized by optimization of operating conditions. To achieve any relatively complete separation, i.e for two lanthanides adjacent in the Periodic Table in order to produce material of 99.99% or higher purity for the one element without contamination by the other, many SX cells must be linked

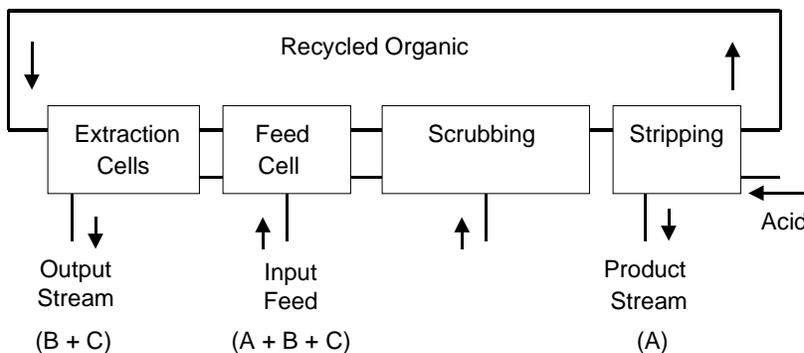
[1] Solvent Extraction Used in Industrial Separation of Rare Earths, C.G.Brown and L.G.Sherrington, J.Chem.Tech.Biotechnol., 1979, **29**, 193 : Discovery and Commercial Separations, J.Kaczmarek, in "Industrial Applications of Rare Earth Elements", ed. K.A.Gschneidner, ACS Symp. 164, publ. Am.Chem.Soc., 1981, p.135

SOLVENT EXTRACTION

in series into a chain. The aqueous feed flows one way while the organic flows the other. In commercial practice 50 or more cells will form a circuit. The most difficult separation tends to be that between Nd and Pr, and, in SX behavior, Yttrium fits into the Ln series near Dy or Ho.

Passing a mixed-Ln-and-Y feedstock through an SX circuit will result in a cut into two fractions. A single element could be cut off from one end of the group or, alternatively, the mixed feedstock can be split into two fractions, each still containing several elements. The choice will depend on economics, on the relative demand for the mixture or the single element. Different processors may well follow different steps to reach an individual pure element although using the same precursor concentrate.

Liquid-Liquid Counter-Current Extraction Simplified SX-Circuit



The diagram indicates the material flow paths within a typical SX circuit. Here the desired product, A, is preferentially concentrated in the organic phase and, after removal of the "contaminants" B and C in the scrub section, is stripped from the organic by an acid stream.

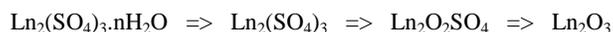
SULFATES

Lanthanide sulfates can be prepared by addition of **hydroxide, carbonate** or other salts to sulfuric acid. They can form, on crystallization into a solid phase, a wide range of hydrates, $\text{Ln}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, [1] with n varying from 1 to ≈ 8 , with the octahydrate the species often obtained under equilibrium conditions. Simple lanthanide sulfates are moderately soluble in water and acid [2], from $\text{La} \approx 40 \text{ gm/l}$ to $\text{Lu} \approx 400 \text{ gm/l}$ (at 20°C), with - for most Ln's - solubility *decreasing* with *increasing* temperature.

Many Ln(III) double sulfates, with alkali metal and ammonium cations such as $\text{Ln}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, are known with varying degrees of aqueous solubility. These so-called "pink" salts have been explored - because their solubility changes as a function of the Ln - as intermediates in processes to effect a rough separation between lights and heavies. Other salts such as acid sulfates, e.g. $\text{Ce}_2(\text{SO}_4)_3 \cdot m\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$, and hydroxysulfates, $\text{La}(\text{OH})\text{SO}_4$, have been characterized. Much published knowledge in this area arose from the initial atomic energy project work on rare earth separation. Sulfuric acid processing can be used for the processing of **bastnasite** and **monazite**.

Cerium(IV), ceric, forms a stable sulfate, $\text{Ce}(\text{SO}_4)_2$, that is strongly acidic in solution due to hydrolysis. The double salt, ceric ammonium sulfate, is a stable orange compound with Ce(IV) present in the *anion*, not the cation. The crystal structure shows this, and related compounds, to be truly sulfatocerates, e.g. $[(\text{NH}_4)_2] [\text{Ce}(\text{SO}_4)_3]$; these complex anions are very stable in aqueous systems. **Europium(II)** forms a nearly insoluble salt, EuSO_4 , that provides a chemical step for the purification of europium.

Upon heating the Ln sulfates, water of hydration is lost but discrete intermediate hydrates are not necessarily seen. The anhydrous sulfate is formed at temperatures in the range 250 to 400°C . At higher temperatures, approaching 850°C , an oxysulfate, is produced that is stable up to $\approx 1200^\circ\text{C}$, before ultimately converting to the oxide. The precise temperatures at which the intermediates appear vary from lanthanide to lanthanide.



The oxysulfate phase, $\text{Ln}_2\text{O}_2\text{SO}_4$, is known for all lanthanides, all with the same structure based on layers of $[\text{LnO}]_n^{n+}$ composition separated by $[\text{SO}_4]^{2-}$ groups.

[1] Properties of various Cerium Sulfates, O.V.Govorukhina et al., Russ.J.Inorg.Chem., 1984, **29**(6), 822

[2] Solubility of some Lanthanide Sulfates in Polycomponent Systems containing H_2SO_4 , D.S.Todorovsky et al., Monats. Chemie, 1993, **124**, 673

SULFIDES

For Ln_2S_3 systems, with Ln^{3+} , several polymorphs are possible and, although the possible existence of products such as $\text{Ln}_{10}\text{S}_{14}\text{O}$ can confuse analysis, the various structures have been characterized.[1] In general, in lanthanide sulfides, tetravalent Ln ions are not found (unlike the oxides) whereas divalent Ln, unstable in oxides, is more stable in sulfide systems ; the sulfide anion is less electronegative than its oxide counterpart. Polysulfides and more complex compositions are possible.

Non-stoichiometric compositions readily form and, in particular, materials can have a composition range from Ln_2S_3 through to Ln_3S_4 , the single phase Th_3P_4 structure being maintained throughout the range. (The generic formula is $\text{Ln}_{3-x}[\]_x\text{S}_4$ where [] is a vacancy site and x varies from 0 to 0.333.) The one extreme, Ln_2S_3 , is an insulator, intermediates are semi-conducting, and the other extreme, Ln_3S_4 , is metallic [2]. (This conductivity behavior underlies the sulfide's potential in high temperature thermo-electric conversion, heat to electricity, for power sources in space.[3]) The cerium sulfides that have been characterized include not only the compound Ce_2S_3 , expected for Ce^{3+} and S^{2-} , but also a black Ce_3S_4 and CeS .

CeS [4], bronze in color with a metallic lustre, adopts the NaCl structure with Ce^{3+} , S^{2-} and one electron in a conduction band. This sulfide has a high electrical conductivity (in the metallic range), a high thermal conductivity, a high melting point (≈ 2715 K) plus good thermal shock resistance and, in addition, it is machineable like a metal.

The red Ce_2S_3 is comparable in color to cadmium sulfide derivatives and it has been proposed as a pigment to replace those cadmium derivatives[5]. The composition of the cerium sulfides can be fine-tuned, like the cadmium compounds to optimize coloring power etc.

[1] Sulfides, Selenides and Tellurides, J.Flahaut, in "Handbook on the Physics and Chemistry of Rare Earths", ed. K.A.Gschneidner et al., Vol.4, 1 (Chap. 31), publ. North-Holland 1979

[2] High-Temperature Thermo-dynamic Properties of Alpha and Gamma Lanthanum Sesquisulfides and Related Compounds, T.Amano et al., J.Appl. Phys., 1986, **59**(10), 3437

[3] Thermoelectric Efficiency of Rare Earth Sesquisulfides, S.M.Taher and J.B.Gruber, Mat.Res.Bull., 1981, **16**, 1407 ; Thermoelectric Properties of Lanthanum Sulfide, C.Wood et al., J.Appl.Phys., 1985, **58**(4), 1542

[4] Synthesis of CeS and Interactions with Molten Metals, O.H.Krikorian and P.G.Curtis, High Temp. High Press., 1988, **20**, 9

[5] Compositions based on Rare Earth Sulfides, their Manufacture, Pigments containing Sulfides, and Use of the Pigments, T.Chopin et al., Eur.Patent Appl., 545746, 9 June 1993

The thermochemistry of CeS, along with other Ln sulfides, has been studied [6] because of its possible role in steel treatment by mischmetal. It has one of the greatest - most negative - free energies of formation for sulfides and has been proposed as a containment material for very reactive molten metals such as uranium and titanium.

Possible preparation methods for Ln sulfides include :

- direct reaction between the elements,
- high temperature sulfidation of anhydrous salts by H₂S,
- low temperature sulfidation in oxygen-free organic media,
- disproportionation between Ln metal and lead sulfide.

One potential problem is the formation of the very stable **oxysulfide**, e.g. Ce₂O₂S due to water or oxygen contamination in the starting reactants. The oxysulfide content can be reduced by high temperature reduction with carbon.

Many ternary sulfides, M_xLn_yS_z, are known[1] where M can be mono-, di-, or higher valent. The compound, CaLa₂S₄, and similar materials have been extensively studied[7] because of their optical transparency from the visible out to 14 μ in the infrared. They are physically robust and are potential windows for use with i.r. sensors. This type of ternary sulfide can be prepared by, e.g. :

- firing in H₂S of mixed oxides and carbonates,[8] or
- reaction of alkoxides with H₂S in organic solvents[9].

[6] Thermochemistry of The Rare Earth Carbides, Nitrides and Sulfides for Steelmaking, K.A.Gschneidner et al., Report IS-RIC-5, publ. 1971, Rare-Earth Information Center, Iowa State University, Ames, IA, available from Molycorp

[7] Physical Properties of Ternary Sulfide Ceramics, D.L.Chess et al., Mat.Res.Bull., 1984, **19**, 1551 New Far Infra-red Window Materials -from Zinc Sulphide through Calcium Lanthanum Sulphide to Diamond, J.A-Savage, Glass Technol., 1991, **32**(2), 35

[8] Processing Ternary Sulfide Ceramics : Powder Preparation, Sintering and Hot-Pressing, D.L.Chess et al., J.Am.Ceram.Soc., 1983, **66**(1), 18

[9] Preparation of Calcium Lanthanum Sulfide Powders via Alkoxide Sulfurization, Y.Han and M.Akinc., J.Am.Ceram.Soc., 1991, **74**(11), 2815

TERBIUM

The Tb(IV) state has just sufficient stability to cause the oxide, formed in air on calcination of most salts, to be Tb₄O₇ and not the expected Ln₂O₃. This solid, due to the dual valence ions, Tb³⁺ and Tb⁴⁺, creating a strong charge-transfer color, is chocolate brown. No simple salts of Tb(IV), however, are known; terbium's chemistry, mainly due to Tb(III), resembles that of **yttrium** and the other heavy lanthanides.

One characteristic property, a green emission band - after u.v. excitation - centred around 545nm, is used for phosphors in energy- efficient fluorescent lamps that convert the mercury arc u.v. into visible light [1][2]. Tb's green emission is employed in materials such as

- **Tb: (La,Ce)PO₄**
- **Tb: CeMgAl₁₁O₁₉**
- **Tb: (Ce,Gd)MgB₅O₁₀**

Terbium also responds efficiently to X-ray excitation and the Tb-doped **oxysulfide** of **gadolinium** is currently the most popular X-ray phosphor[3]. In addition several CRT phosphors contain Tb, for example, the high intensity green emitter needed for projection television can be a Tb:YAG, or a Tb:Y₂SiO₅ material[2][4].

Magneto-optic recording of data is possible on suitable metallic films; Tb transition metal alloys, such as Tb-Fe-Co's, are so used[5]. Another metallic use is in Magneto-strictive alloys, Tb-Dy-Fe, that change dimensions in magnetic fields[6].

Tb	
element	
Atomic Number	65
Atomic Weight	158.92
Electron configuration	[Xe]4f ⁹ 6s ²
Valencies	3 (4)
Ionic radius for	
8-coordination	104 pm
Magnetic moment, Tb ³⁺	9.72 μB
Tb ⁴⁺	7.86 μB
metal	
Crystal Structure	hcp
Melting Point	1356°C
Boiling Point	3230°C
Density	8.23 g/cm ³
Metallic Radius	178 pm

[1] Phosphors based on Rare Earths, A New Era in Fluorescent Lighting, B.M.J.Smets, Mater. Chem. Phys., 1987, **16**, 283 : Green-luminescent (La,Ce)PO₄:Tb Phosphors for Small Size Fluorescent Lamps, N.Hashimoto et al., J.Lumin., 1991, **48 & 49**, 893

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

[3] New X-Ray Phosphors, L.H.Brixner, Mater.Chem.Phys., 1987, **16**, 253

[4] Optimizing β-Y₂SiO₅:Tb for Projection Television Applications, C.R.Ronda et al., J.Alloys Comp., 1993,**192**,55

[5] Media for Erasable Magneto-optic: Recording, P.Hansen et al., IEEE Trans Magn., 1989, **25**, 4390

[6] The Development of Highly Magneto-strictive Rare Earth-Iron Alloys, D.C.Jiles, J.Phys.D:Appl.Phys., 1994,**27**, 1

THULIUM

Thulium, the rarest of the "abundant earths", is a typical heavy lanthanide with chemistry similar to **Yttrium**. Its most specific property is, upon appropriate excitation, an emission in the blue. The luminescence of Tm, for example, under X-ray excitation is in the near u.v (≈ 375 nm) and blue (≈ 465 nm), closely matching the sensitivity of normal photographic film. As Tm:LaOBr, it is used in sensitive X-ray phosphors to reduce X-ray exposure.[1]

Another luminescence application is as Tm-doped CaSO₄, in dosimeters for radiation measurement. Incorporated in personal badge detectors, it makes possible the precise measurement of low radiation doses in the ≈ 0.1 mR to ≈ 50 R range[2].

Ln halides emit, at high temperatures, many spectral lines and are added to metal halide discharge lamps. The aim of the emission is to reproduce closely - within the visible but not outside that region - a black body spectrum. Thulium-sodium iodide mixtures, at milligrams per lamp, provide high luminous efficiencies and good color rendition[3] probably through transient formation of a ternary iodide.

A flat panel CRT display based on electroluminescence depends critically on developing a bright blue emitter. Although thulium, as the TmF₃:ZnS phosphor, has the right wavelength[4] it does not yet have the luminance / brightness required.

Tm	
Element	
Atomic Number	69
Atomic Weight	168.93
Electron configuration	[Xe]4f ¹³ 6s ²
Valencies	3
Ionic radius for	
8-coordination	99 pm
Magnetic moment	7.56 μ_B
metal	
Crystal Structure	hcp
Melting Point	1545°C
Boiling Point	1950°C
Density	9.32 g/cm ³
Metallic Radius	175 pm

[1] J.G.Rabatin, U.S.Patent 3,677,743, 1971 : Rare Earth X-Ray Phosphors for Medical Radiography, J.G.Rabatin, in "Industrial Applications of Rare Earth Elements", ed. K.A.Gschneidner, ACS Symp. 164, publ. Am.Chem.Soc., 1981, p. 135; New X-Ray Phosphors, L.H.Brixner, Mat.Chem.Phys., 1987, **16**, 253

[2] The Use of Metal Filters to Flatten the Energy Response of CaSO₄ : Tm TL Dosemeters, and to Provide Spectral Information, KStammers et al., Rad.Prot.Dos., 1991, **36**(1), 23

[3] Spectral Properties of Metal Halide Alamps with Rare Earth Iodide or Sc-Iodide and Sodium Iodide, P.Tielemans et al., Lighting Res.Tech., 1985, 1985, **17**, 79 : Measurement of Enhanced Thulium Abundance in Metal Halide Discharge Lamps, M.J.Shea et al., in "High Temperature Lamp Chemistry", Vol 93-16, publ. Electrochem.Soc., 1993

[4] Preparation and Photoluminescence of Thulium-Activated Zinc Sulfide Films, B.T.Collins et al., J.Electrochem.Soc., 1991, **138**(11), 3515

TITANATES / TITANIUM DIOXIDE

Within the $\text{Ln}_2\text{O}_3 / \text{TiO}_2$ systems, several compounds containing Ln^{3+} , Ti^{4+} and O^{2-} , have been recognized[1], the more important are listed in the box. The Pyrochlore structure, for $\text{Ln}_2\text{Ti}_2\text{O}_7$ species, occurs only with the smaller Ln ions; the L_2T_9 compound can approach an LT_4 composition.

Ln ₂ O ₃ : TiO ₂ Compounds			
Formula	Oxide Ratio (Abbreviation)	Structure Type	Ln Range for Stability
$\text{Ln}_4\text{Ti}_9\text{O}_{24}$	L_2T_9	(complex)	
$\text{Ln}_2\text{Ti}_2\text{O}_7$	LT_2	Pyrochlore	Ln = Sm to Lu, Y
$\text{Ln}_2\text{Ti}_2\text{O}_7$	LT_2	(several)	Ln = La to Nd
Ln_2TiO_5	LT	(several)	

L = Ln_2O_3 ; T = TiO_2

These compounds can be prepared by the high-temperature solid-state reaction of mixed **oxides** or **carbonates**, or by firing of coprecipitated material obtained, for example, by the "Pechini" citrate-process. (The stability of *tetravalent Cerium* causes, on firing, a brannefite-type $\text{Ce}^{4+}\text{Ti}_2\text{O}_6$ compound to form.[2]) Possible lattice vacancies plus the potential for variable valency with titanium means that Ln-Ti-O systems will, in general, be structurally complex.

In the systems $\text{Ln}^{3+}\text{-Ti}^{3+}\text{-O}$, with *trivalent* titanium, an isostructural series of Compounds for Ln = La to Tm, plus Y, with the **perovskite**, ABO_3 , structure is formed.[3] (The compound EuTiO_3 , due to the stability of *divalent Europium*, is Eu(II)-Ti(IV)-O_3 .) These perovskites have a range of novel and complex magnetic and electrical properties. Metallic and semi-conducting behavior are possible. Virtually every type of magnetic phenomena, e.g ferro-, ferri-, antiferro-, and para-magnetism, can be found in the series.[3]

[1] Lanthanide Titanates, L.G.Shcherbakova et al., Russ.Chem.Rev. (Engl. ed.), 1979, **48**(3), 423

[2] Crystal Chemistry of Cerium Titanates, Tantalates and Niobates, R.S.Roth et al., Mat.Res.Bull., 1977, **12**,1173

[3] The Rare-Earth Titanium(III) Perovskite Oxides - An Isostructural Series with a Remarkable Variation in Physical Properties, J.E.Greedan, J.Less-Common Met., 1985, **111**, 335

TITANATES, TITANIUM DIOXIDE

Lanthanide titanates can display unusual electrical properties[4] and, mainly in ternary systems, are used in various electronic ceramic compositions. Barium Lanthanide Titanates, especially those containing **Neodymium**, are the basis of the dielectric formulations increasingly used in multi-layer capacitors.[5] These materials have high dielectric constants, low loss factors and temperature-independent dielectric constants. Within the BaO-TiO₂-Ln₂O₃ systems (Ln = La, Nd, and Sm) 1:3:1 and 1:(≈4 - ≈5):1 compounds have been identified and it is probable that these species account for the desirable dielectric properties.

Doping of the common titanate, BaTiO₃, by other ions is used to create and control physical properties. Introduction of a small fraction, ≈1 %, of trivalent La, into this titanate can cause the resistivity to increase by several orders of magnitude near the titanate's Curie temperature, ≈100 °C.[6] These materials are used as thermistors for the protection of electrical equipment.

The high refractive index of titanium dioxide makes it a superb white pigment. However it is photosensitive and u.v. radiation will cause degradation. Lightfastness can be improved by coating the surface with a cerium derivative that strongly absorbs the ultra-violet.[7]

[4] A new Ferroelectric:La₂Ti₂O₇, S.Nanamatsu et al., *Ferroelectrics*, 1974, **8**, 511; La₂Ti₂O₇ Ceramics, P.A. Fuierer and R.E.Newnham, *J.Am.Ceram.Soc.*, 1991, **74**(11), 2876

[5] Defect Structure and Dielectric Properties of Nd₂O₃-Modified BaTiO₃, A.Shaikh and R.W.Vest, *J.Amer.Ceram.Soc.*, 1986, **69**(9), 689 ; Microwave Dielectric Properties of (Ba,Sr)O-Sm₂O₃-TiO₂ Ceramics, S. Nishigaki et al., *Am.Ceram.Soc.Bull.*, 1987, **66**(9), 1405 ; Synthesis and Characterization of Barium Lanthanum Titanates, J.P.Guha, *J.Am.Ceram.Soc.*, 1991, **74**(4), 878

[6] The PTC Effect of Barium Titanate, J.Daniels et al., *Philips Tech.Rev.*, 1978/79, **38**(3), 73

[7] Titanium Dioxide Pigment coated with Cerium Cations, selected Acid Anions and Alumina, H.W.Jacobson, U.S. Patent, 4,737,194, 12 April 1988

TOXICOLOGY

In general all the lanthanides are considered as having a low toxicity rating[1][2] and this is especially so when they are present in material with a low aqueous solubility. When orally administered poor absorption from the gastro-intestinal tract tends to result in the lanthanides having little effect. (Solubility is a critical aspect of the oral bioavailability of a material and the nature of the anion is often the important determinant of a material's toxicity.) For comparison the oral toxicity of lanthanide oxides is apparently comparable to that of common table salt[3] and this low toxicity of the Ln's has led to their use as markers in nutritional studies.

The inhalation toxicology of lanthanides has been studied but often using specific non-natural radio-active species in order to investigate effects that would arise from nuclear-fall-out. In addition the past use of monazite, a thorium-containing mineral as the major resource led to confusion regarding the relation between radio-activity and the lanthanides; inadequate separations in the past produced Th- contaminated Ln- products. Current processing technology for mineral recovery and for lanthanide separation results in products that meet all regulatory requirements.

"The very few human studies [regarding inhalation] that showed any medically significant effects were the result of essentially unmitigated chronic exposures over long periods of time. These studies were further confounded by other factors (e.g. smoking and exposure to other toxic substances)." [4] "It is also obvious from epidemiologic data that, when compared to other well-documented fibrogenic dusts such as quartz and silica, rare earths display only mild pathogenic potential." [5] These two quotes from recent publications summarize the accepted medical view. Material safety data sheets for lanthanide products, as regards inhalation exposure, tend to recommend for **TLV-TWA** (Threshold limit value-Time weighted average) values the widely used nuisance-dust limits.

[1] Pharmacology and Toxicology of the Rare Earth Elements, T.J.Haley, J.Pharm-Sc, 1965, **54**, 663 : Toxicity, T.J.Haley, in "Handbook on the Physics and Chemistry of Rare Earths", ed. K.A.Gschneidner and L.Eyring, publ. North-Holland, 1979, vol.4, Ch. 40: Rare Earths in Biological Systems, P.H.Brown et al., *ibid*, 1991, vol.13 : Toxicity of Rare Earths, P.Arvela, *Prog. Pharmacology*, 1979, **2**(3), 69

[2] Institut Francais de Toxicologie, Oxyde de Cerium : Essais de Toxicite Aigue par Vois Orale et Percutanée chez le Rat, Rapport 301229, 1/1983; Oxyde de Cerium : Essais de Toxicite Aigue par Vois Respiratoire chez le Rat, Rapport 302217, 2/1983; Oxyde de Cerium : Tests de Tolerance Locale chez le Lapin, Rapport, 302314

[3] DHHS-NIOSH, Registry of Toxic Effects of Chemical Substances, DHHS-NIOSH Publication 86-103, 1986

[4] A Review of the Literature on the Toxicity of Rare-Earth Metals as it pertains to the Engineering Demonstration System Surrogate Testing, P.H.Wald and V.A.Mode., publ. Lawrence Livermore National Laboratory, January 1990, UCID-21823 Rev. 1 (avail. NTIS)

[5] Pulmonary Toxicity of Stable and Radio-active Lanthanides, P.J.Haley, *Health Physics*, 1991, **61**(6), 809

YTTERBIUM

In broad chemical behavior this element resembles **Yttrium** and the heavy lanthanides. This penultimate member of the lanthanide series, however, has a moderately stable divalent state, Yb^{2+} , with a full-shell $4f^{14}$ electron configuration. Yb(II) is less stable than Eu^{2+} but comparable to Sm^{2+} in behavior, e.g.[1].

As elemental metal, Yb has low melting and boiling points plus a large metallic radius, all due to the presence of divalent, rather than trivalent, atoms. The **metal** can be prepared by **oxide** disproportionation using Yb oxide and another Ln such as La or Ce, and then purified by vacuum sublimation. Unlike **Europium metal**, Yb metal is relatively inert in air due to a stable, C-type structure, oxide surface film. The metal when subject to very high stresses increases its electrical resistance by an order of magnitude and is used in stress gauges to monitor ground deformations caused, for example, by nuclear explosions[2].

Ytterbium, as Yb^{3+} , has a single dominant spectral *absorption* band, independent of the environment, in the infra-red, at ≈ 985 nm[3]. The selective *emission* at this wavelength, can be used, through coupling to silicon photocells, for the direct conversion of radiant energy to electricity.[4] Because of the similarity between Yb and Y, Yb-stabilized ZrO_2 (YbSZ) resembles YSZ and, indeed, Yb offers longer life to thermal barrier coatings than Yttrium if a bond coating of a MCrAlYb alloy, in place of MCrAlY, is used.[5]

Yb	
Element	
Atomic Number	70
Atomic Weight	173.04
Electron configuration	$[\text{Xe}]4f^{14}6s^2$
Potential $E_{M(\text{III})/M(\text{II})}$	-1.33 V
Valencies	3 (2)
Ionic radius for	
8-coordination	98 pm
Magnetic moment	4.54 μB
metal	
Crystal Structure	fcc
Melting Point	819°C
Boiling Point	1196°C
Density	6.97 g/cm^3
Metallic Radius	194 pm

[1] Preparation of Divalent Ytterbium and Samarium Derivatives and their Use in Organic Chemistry, H.B.Kagan and J.L.Namy, (Ch.50), p. 525 in Vol. 6, Handbook of the Physics and Chemistry of Rare Earths, ed. K.A.Gschneidner and L.Eyring, publ. 1984, North-Holland

[2] Piezoresistance Response of Ytterbium Foils Gauges Shocked to 45 kbar in Fused Silica Matrix, N.S.Brar and Y.M.Gupta, J.Appl.Phys., 1987,**61**(4), 1304

[3] High-Temperature Spectral Emittance of Oxides of Erbium, Samarium, Neodymium and Ytterbium, G.E.Guazzoni, Appl.Spect., 1972, **26**(1), 60

[4] Solar Radiation Conversion System, E.Kittl, U.S.Patent 3,929,510 30 December 1975 : Thermophotovoltaic Technology, R.E.Nelson, U.S.Patent 4,584,426 22 April 1986

[5] Advanced Thermal Barrier System Bond Coatings for Use on Nickel-, Cobalt- and Iron-based Alloy Substrates, S.Stecura, Thin Solid Films, 1986, **136**, 241 : Thermal Barrier Coating System, S.Stecura, U.S. Patents, 4,485,151, 27 November 1984 and 4,535,033 13 August 1985

YTTRIUM

Yttrium is inherently more **abundant** than the *heavy* lanthanides, resembles them in properties, occurs with them in nature, and hence dominates minerals containing that selection of Ln elements. (The term "heavy lanthanide" here is taken to mean ≈Tb to Lu.)

Yttrium is recovered to a small extent from the two main minerals supplying lanthanides, **Bastnasite, Monazite** and also from Xenotime. Within recent years, however, the processing in China of **ion-adsorption ores** has come to dominate the Yttrium supply position.

These ores contain the Y^{3+} (and Ln^{3+}) ions captured on aluminosilicates, and have been created by the weathering over geological time of primary minerals. Several deposits of this type are known with a variety of compositions; there is no single typical analysis but they tend to be yttrium dominated. These ores are treated by simple leach technology to bring the Ln ions into solution.

Other potential resources include a Brannerite-type mineral derived as a Uranium-mining by-product concentrate, and the mineral Eudialyte, a complex silicate, found in several locations, e.g. Russia, in large quantities. The complex mineralization of many of these alternative resources and the consequent extreme difficulty in economically extracting the yttrium content makes such sources currently not viable.

Despite several major uses - and activity due to superconductivity research - Yttrium is not recovered in the same quantities as the *light* (La to Nd) lanthanides. World-wide ≈600 tonnes (counted as oxide) of yttrium are currently produced whereas >60,000 tonnes of light lanthanides (as oxide) are recovered.

Separation of yttrium from the heavy lanthanides by a single discrete process is not possible. It needs to be recovered by counter-current liquid-liquid extraction processes, **solvent extraction** (SX), that rely on the differential partitioning of complexes between an organic phase and an aqueous phase.

Y	
Element	
Atomic Number	39
Atomic Weight	88.906
Valency	3
Ionic radius for 8-coordination	102 pm
metal	
Crystal Structure	Hcp
Melting Point	1522°C
Boiling Point	3338°C
Density	4.47 g/cm ³
Metallic Radius	180 pm

Y Sources	
<i>Y content as % of total Ln-and-Y in concentrates</i>	
Bastnasite	0.1 %
Monazite	2.1 %
Xenotime	≈60 %
ion-adsorption	varied

Compound	Ideal Formula	Formula Weight	% Oxide	% Element
Oxide	Y ₂ O ₃	225.81	100	78.7
Acetate	Y(CH ₃ COO) ₃ .4H ₂ O	338.10	33.4	26.3
Carbonate	Y ₂ (CO ₃) ₃ .3H ₂ O	411.85	54.8	43.2
Chloride	YCl ₃ .6H ₂ O	303.35	37.2	29.3
Fluoride	YF ₃ .3H ₂ O	199.94	56.5	44.5
Hydroxide	Y(OH) ₃ .3H ₂ O	193.97	58.2	45.8
Nitrate	Y(NO ₃) ₃ .6H ₂ O	383.01	29.5	23.2
Oxalate	Y ₂ ((COO) ₂) ₃ .9H ₂ O	604.00	37.4	29.4
Sulfate	Y ₂ (SO ₄) ₃ .8H ₂ O	593.98	38.0	29.7

After SX purification, in order to obtain high purity - 99 % and higher - materials, it is usual to precipitate the oxalate and then calcine at ≈ 1000 °C. The resulting **yttrium oxide** is the most readily commercially available pure compound of yttrium. (Other compounds such as nitrate, acetate and chloride are available as well as the elemental form, the metal.)

Yttrium is trivalent in its chemical compounds whose properties are very similar to those of heavy lanthanide analogues[1]. In particular the closest similarity is with **Dysprosium**, a consequence of the ionic radii Y(III) and Dy(III) being nearly the same. The exact position of equivalence does however vary, depending on the property underlying the comparison.[2] Data for some common compounds are recorded in the table.

[1] Thermochemical Properties of Yttrium, Lanthanum and the Lanthanide Elements and Ions, L.R.Morss, Chem. Rev., 1976, **76**(6), 827

[2] The Position of Yttrium within the Lanthanides with respect to Unit Cell Volumes of Isostructural Compounds as an Indication of Covalency in Lanthanide Compounds, S.Sierkierski, J.Solid State Chem., 1981,**37**,279

It forms aqueous-insoluble **oxides, oxalates, hydroxides, carbonates** and **phosphates** as well as soluble **nitrates** and **chlorides**. The **sulfates** and **acetates** are more soluble for Y and the heavies than for the light lanthanides. In comparison to **lanthanum**, the carbonate and oxalate tend to be solubilized in the presence of excess anion, presumably stable species such as $Y(C_2O_4)_n^-$ exist. Double salts also tend to be more soluble for Y and the heavies than for La and the lights.

The element Y has an exceptionally high thermo-dynamic affinity for oxygen, free energy of formation 1817 kJmol^{-1} , probably the greatest of any element.[3] The property underlies many of yttrium's uses not only as the **yttrium oxide** but also as the metal. Yttrium is the active component in the MCrAlY family of alloys used in high temperature oxidizing environments. The trace of Y present enhances the stability of the alumina/chromia oxide coating by improving resistance to spalling. It has been suggested that yttrium "getters" sulfur at the oxide crystallite interfaces[4]. The gettering effect of Yttrium has also been used in discharge lamps[5]. The affinity for hydrogen can provide a chemical-trap method for removing trace amounts of hydrogen from molten alkali metal circuits in certain nuclear reactors.

The superconducting properties of the Y-Ba-Cu-O system have led to an immense amount of research and associated publications. A variety of processes for the preparation of these and similar materials are now known. Many properties, in addition to superconductivity-related behavior, have been investigated. Yttrium's chemical and physical behavior in many compounds is now better understood and may well lead to other uses in addition to ceramic superconductors.

[3] Thermochemistry of the Rare Earths, Part I Rare Earth Oxides etc., K.A.Gschneidner et al., Report IS-RIC-6, publ. Rare Earth Information Center, Iowa State University, Ames Iowa, 1973 (available from Molycorp)

[4] A Relationship between Indigenous Impurity Elements and Protective Oxide Scale Adherence, J.G.Smeggil et al., Metall. Trans.A, 1986, **17A**, 923

[5] A Getter for Metal-Iodide High Pressure Mercury Vapour Lamps, G.Kuus, Philips Tech.Rev., 1975, **35**(11),354

YTTRIUM OXIDE

The very stable oxide, Y_2O_3 , known as *yttria*, adopts the "bixbyite" structure (C-type Ln_2O_3) that resembles that of fluorite (CaF_2 and CeO_2) but with one quarter of the anions removed in an ordered manner[1].

Resistance to aggressive chemical attack at high temperatures and its thermal stability underlie many uses[2]. Others depend on the creation of stable defined crystal structures with specialized properties. The fluorescent light over-head, the computer's color display and the oxygen sensor controlling a car's fuel consumption depend on this element. It is essential, for example, for CRT phosphors, for microwave garnet crystals, for certain lasers and for several high performance ceramics.

Yttrium Oxide, Y_2O_3	
Chem. Abs. No.	1314-36-9
Formula weight	225.81
<i>Properties</i>	
Crystal Structure	C-type Ln oxide
Melting Point	2703 K (2430 C)
Density	5.03 gcm^{-3}
Specific Heat	$\approx 450 \text{ jkg}^{-1}K^{-1}$
Thermal Expansion	$8 \times 10^{-6} K^{-1}$
Thermal Conductivity	$\approx 16 \text{ Wm}^{-1}K^{-1}$
Dielectric Constant	$\approx 12 (10^2 - 10^6 \text{ Hz})$

Yttrium oxide, as usually prepared (doped or undoped), has a particle size averaging several microns and may contain strong agglomerates. Finer materials, e.g. sub-micron sized and desirable for some ceramic applications listed below, can be made by methods such as homogeneous precipitation in situ through the slow hydrolysis of ureas or the controlled hydrolysis of yttrium organometallic compounds.[3] The increasing demand for doped yttrium oxide in fluorescent lighting phosphors[4], see below, has brought with it the direct production of those doped materials as coprecipitates without the intermediate formation of pure Y_2O_3 .

Yttria ceramics can be used, for example, as crucibles for melting reactive metals and as nozzles for jet casting molten alloys[5]. The benefits of yttria are also obtained by coating Y_2O_3 on other substrates. The precision investment casting of titanium utilizes the oxide as the first, the face, coat on the exposed surface of the casting mold.

[1] The Binary Rare Earth Oxides, L.Eyring, in "Handbook on the Physics and Chemistry of Rare Earths", ed. K.A.Gschneidner and L.Eyring, 1979, Vol.3, publ. North Holland, 337

[2] Yttria as a Ceramic, B.T.Kilbourn, 1993 (leaflet with references) Molycorp, White Plains, U.S.A.

[3] Synthesis and Properties of Y_2O_3 Powder Obtained by Different Methods, B.Djuricic et al., J.Eur. Ceram.Soc. 1992, **9**, 75

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

[5] High Density Yttria for Ceramic Applications, A-L.Micheli et al., J.Amer.Ceram.Soc. 1992, **75**(3), 709

Plasma spraying of yttria powder onto less stable but more economical materials, e.g. graphite, can produce suitable crucibles, e.g. for containing reactive molten metals.

Yttria can be sintered, with the aid of lanthanum oxide or other additives, to produce a transparent material suitable for optical windows that are transparent from 280nm out into the infrared near 8000nm[6]. In addition yttria is being explored as the envelope material for discharge lamps[7].

The sintering of powder precursors to prepare high-temperature structural ceramics benefits from additives to achieve a near-100% ideal density. Such aids work by the transient formation of an intermediate phase and the solution / precipitation of the dominant material. Yttrium oxide is the preferred additive for sintering Si_3N_4 [8], AlN, Si-Al-O-N's[9] and it also used for such species as MgO and SiC.

Zirconia can be stabilized against destructive phase transformations by the addition of another oxide, e.g. a few mole percent of yttria can create yttria-stabilized-zirconia (YSZ). Variations of such a material are used as plasma-spray coated thermal barrier coatings to prevent metal surfaces from degradation at high temperatures, e.g. on surfaces exposed to jet engine temperatures. Tough zirconia ceramics are sintered fine-grained tetragonal ZrO_2 polycrystals (TZP's) containing ≈ 3 mole percent of yttria that can be used as cutting tools and engine components. In addition higher Y_2O_3 loadings in ZrO_2 with enhanced oxide ion conductivity form the oxygen sensors used to monitor exhaust gas compositions of vehicles.

Microwave communication relies on devices made from yttrium iron garnets YIG's, in which the magnetically active iron atoms are locked into the garnet structure $\text{Y}_3\text{Fe}_5\text{O}_{12}$. These devices can be magnetically tuned for frequency selection[10].

The crystal structure of Y_2O_3 readily accepts similarly sized Ln ions such as europium; the dopants can be chosen to provide visible emission upon excitation by energy sources such as electron or ultra-violet radiation. (Yttrium has no emissions because it has no low-lying energy levels.) The phosphor $\text{Eu:Y}_2\text{O}_3$ gives the red to almost all television and color CRT's. Other specialized CRT phosphors, for example for projection television, are based on such compounds as yttrium aluminum garnet, YAG, $\text{Y}_3\text{Al}_5\text{O}_{12}$.

[6] Controlled Transient Solid Second Phase Sintering of Yttria, W.H.Rhodes, J.Am.Ceram.Soc., 198 **64**(1), 13; Lanthana-Doped Yttria, A New Infra-Red Window Material, W.H.Rhodes et al., SPIE Pro 1986, **693**, 12

[7] Sodium Resistance of Certain Refractory Materials for Use in High Pressure Sodium Vapo Discharge Lamps, Y. Tsukuda, J.Canad.Ceram.Soc., 1982, **51**, 16

[8] High Performance Silicon Nitride Materials, C.Boberski et al., Angew.Chem.Int.Ed.Adv.Mater., 1992, **28**(11), 1560

[9] SiAlON Ceramics, T.Ekström, J.Am.Ceram.Soc., 1992, **75**(2), 259

[10] YIG Filters, P. Röschmann, Philips Tech.Rev., 1971, **32**, 322; Magnetically Tuneable Oscillators Oscillators and Filters, H.Tanbakuchi et al., IEEE Trans.Magn., 1989, **25**(5), 3248

YTTRIUM OXIDE

The widespread introduction of energy efficient fluorescent lighting has become possible by the use of phosphors emitting close to the three prime wavelengths of red, blue and green. Here the red comes from $\text{Eu:Y}_2\text{O}_3$. (The other colors also use lanthanide-containing materials.)[11]

A recently introduced X-ray phosphor is yttrium tantalate, YTaO_4 . The garnet, YAG, is also used as the host for neodymium in Nd:YAG lasers. Most of these yttrium containing compounds are made by high temperature reactions of yttria with the appropriate oxide, a fluxing agent being beneficial.

A dispersion of fine particle yttria within an alloy substrate can increase the metal's strength. Such oxide dispersion strengthened (ODS) materials can be prepared by mechanical alloying, by ball milling directly the metal powder and $\approx 1\%$ of a suitable small crystallite size yttrium oxide powder. The resulting alloys show an enhanced resistance to deformation as a consequence of the Y_2O_3 particles blocking incipient cracks. Such nickel-based super alloys are used, for example, in the hot sections of military jet engines as components subject to $\approx 1250^\circ\text{C}$ conditions.

[11] Phosphors based on Rare-Earths, A New Era in Fluorescent Lighting, B.M.J.Smets, Mat.Chem.Phys., 1987, **16**, 283

ZIRCONATES, ZIRCONIUM OXIDE

This section covers compounds within the Ln-Zr-O system and Ln-doped ZrO₂'s.

Ln₂Zr₂O₇ compounds, (1:2, La₂O₃:ZrO₂) can be made by a solid state reaction between the oxides or, preferably, by variations on the sol-gel Pechini process with citric acid and glycol.[1] The structures found, pyrochlore and fluorite, are very closely related[2] and, indeed, which structure is formed depends on the temperature reached during preparation. Ln zirconates are of interest for catalytic[3] and conductivity[4] properties. However, although defect fluorites can be good ionic conductors, ordering of the O₂₋ vacancies in the pyrochlore (A₂B₂O₈₋₁) version of fluorite, (A₂B₂O₈≡O₂) limits this potential.

Lanthanide Zirconates Ln ₂ Zr ₂ O ₇		
<i>Ln-range</i>	<i>Structure type</i>	<i>Relation to Fluorite</i>
La - Eu Tb - Er	Pyrochlore "Fluorite"	O-ordered vacancies O-substoichiometric

ZrO₂'s doped with the Ln's or Y can show exceptional mechanical and electrical properties[5]. The cations of the Ln's and Y can substitute for Zr₄₊ in the zirconia lattice. Charge compensation is made possible through the formation of oxygen vacancies; this influences ionic and electrical conductivity.

Depending on the amount of dopant present the zirconia can be partially or full stabilized. Sub-micron grain size, tetragonal-phase Y₂O₃-zirconia (Y-TZP) ceramic exhibit a high fracture toughness[6] and are used for wear components; yttria dopin is ≈3 mol % in order to confer mechanical strength. In the fully stabilized form, YSZ's materials are the solid electrolyte in oxygen sensors for exhaust emission control. With ceria a higher doping, ≈12 mole %, is needed to give doped zirconias exceptional fracture toughness and hardness[7]. A significant use of Ln-doped ZrO₂'s is plasma-spray coatings for protection of metal surfaces at very high temperatures.

- [1] Preparation of La₂Zr₂O₇ by Sol-Gel Route, H.Kido et al., J.Am.Ceram.Soc., 1991,**74**(2),422:Phase Relationships and Conductivity of Sr- and La-Zirconates, F.W.Poulsen et al., Solid State Ionics, 199 **53-56**,777
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