CERIUM AND CERIUM COMPOUNDS

1. Introduction

Cerium [7440-45-1], Ce, at no. 58, is the most abundant member of the series of elements known as lanthanides. Lanthanide (Ln) is a collective name for the fifteen elements from at no. 57 (La) to 71 (Lu), also called the 4*f* elements. Rare-earth (RE) metal is the collective name for elements 21 (Sc), 39 (Y), plus 57 (La) to 71 (Lu). The label *light* is used herein for elements having atomic numbers from 57 to ~63 and the label *heavy* for numbers ~64 to 71.

Isolated first as an impure oxide in 1803, cerium was named after the earliest recognized asteroid Ceres. Cerium made its first contribution to chemical technology in the 1890s when, in Vienna, gas lights, using the Welsbach gas mantle based on a cerium-doped thorium oxide impregnated fabric, were introduced. Rapid widespread adoption of this form of illumination followed. Cerium still contributes to lighting in the 1990s but is now also to be found in automobiles, televisions, and other technologies.

Cerium, at wt 140.12; electron configuration [Xe] $4f^26s^2$; is characterized chemically by having two stable valence states, Ce^{3+}, cerous, and Ce^{4+}, ceric, for which the ionic radii are 114 pm and 97 pm, respectively. The easily accessible tetravalent ion is unique among the Ln series. Indeed, the ceric ion is a powerful oxidizing agent but when associated with the ligand oxygen, it is completely stabilized, and ceric oxide [1306-38-3], CeO_2, is the form of cerium most widely used. The most stable state for all lanthanides is a trivalent one, Ln^{3+}, having an electronic configuration of $[Xe]4f^n$; ie, for Ce^{3+}, $[Xe]4f^1$. The 4*f* electrons are in well-shielded inner orbitals not influenced by surrounding atoms, and hence the chemical behavior of all Ln^{3+} ions is very similar. The relative increased stability of empty $4f^0$, half-full $4f^7$, and completely full $4f^{14}$ shells, however, can, for certain elements, cause oxidation states other than three to be reasonably stable. Ce^{4+} has a $[Xe]4f^0$ configuration.

In bulk form cerium is a reactive metal that has a high affinity for oxygen and sulfur. It has a face centered cubic crystal structure, mp 798°C, bp 3443°C, density 6.77 g/mL, and a metallic radius of 182 pm. Detailed chemical and physical property information can be found in the literature (1,2).

Cerium ranks ca 25th in abundance in the earth's crust (3), and cerium, which occurs at 60 ppm crustal abundance, not lanthanum at 30 ppm, is the most abundant lanthanide.

2. Resources

There are few principal lanthanide deposits, and there are no minerals that are sources for cerium alone. All the lighter lanthanides occur together in any potential deposit, and processes separating the lanthanides are necessary to obtain pure cerium products.

Whereas certain rocks of igneous origin formed by melting and recrystallization can include minerals enriched in the lanthanides (4), cerium is usually present as a trace element rather than as an essential component. Only a few minerals in which cerium is an essential structure-defining component occur in economically significant deposits. Two minerals supply the world's cerium, bastnasite [68909-13-7], $LnFCO_3$, and monazite [1306-41-8], $(Ln,Th)PO_4$.

Bastnasite, a light Ln fluoride carbonate, occurs in an unusual type of magma-derived alkaline igneous rock in which the concentration of the Ln elements has been especially enhanced. These carbonatite magmas are produced when mantle rocks melt deep in the earth's crust in the presence of large amounts of carbonate. If fluoride ion is introduced during the ascent, the final stage of the emplacement can be specific lanthanide-containing fluorocarbonate minerals such as bastnasite.

Bastnasite has been identified in various locations on several continents. The largest recognized deposit occurs mixed with monazite and iron ores in a complex mineralization at Baiyunebo in Inner Mongolia, China. The mineral is obtained as a by-product of the iron ore mining. The other commercially viable bastnasite source is the Mountain Pass, California deposit where the average Ln oxide content of the ore is ca 9%. This U.S. deposit is the only resource in the world that is mined solely for its content of cerium and other lanthanides.

Monazite, a light lanthanide thorium phosphate, is found in many countries. It is an accessory mineral in granites, and because of a high specific gravity, on weathering of those primary rocks the mineral segregates out as placer deposits. Monazite-bearing beach and dune sand deposits occur in association with other heavy minerals such as ilmenite [12168-52-4], FeO_3Ti, zircon, and rutile [1317-80-2]. The 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 concentrates for the world market. Extensive deposits along the coast of western Australia are worked for ilmenite and are the primary source of world monazite. Other regions of Australia, along with India and Brazil, also supply the mineral. Because monazite contains thorium [7440-29-1], India and Brazil have embargoed its export for many years. In the United States, commerce in the mineral is regulated by the Nuclear Regulatory Commission.

Phosphate rock, mined widely throughout the world for its fertilizer value (see FERTILIZERS), in certain regions contains a few percent of lanthanides. For example, the apatite deposits in the Kola peninsula on the Russian/Finnish border. The Ln content is recoverable from the various processing residues, and because other Ln-containing minerals, such as loparite [12173-83-0], are also found there, the location supplies a significant part of the demand in Eastern Europe.

World mine production of contained Ln oxide was estimated at 119,000 t with ca 68% of this in China, mostly at Baiyunebo, ca 4.2% in the United States, and ca 22.6% in India (5).

3. Production

The production of cerium derivatives begins with ore beneficiation and production of a mineral concentrate. Attack on that concentrate to create a suitable mixed lanthanide precursor for later separation processes follows. Then, depending on the relative market demand for different products, there is either direct production of a cerium-rich material, or separation of the mixed lanthanide precursor into individual pure lanthanide compounds including compounds of pure cerium, or both. The starting mineral determines how the suitable mixed lanthanide precursor is formed. In contrast the separation technology, which involves liquid–liquid countercurrent extraction or solvent extraction (SX), for preparing the individual lathanides is essentially independent of the starting mineral (see EXTRACTION, LIQUID–LIQUID). Thus different feedstocks can ultimately be processed by the same separation routines and equipment.

3.1. Processing of Bastnasite. In the United States the ore is extracted by open-pit mining and the bastnasite fraction is separated by froth-flotation from other minerals including barite, calcite, strontium-containing materials, and quartz. The resulting bastnasite concentrate is a commercially available commodity. A typical analysis is given in Table 1. Bastnasite can be converted directly, without separating out the individual Ln, to other derivatives by dissolution in acid, such as sulfate or chloride, ie, $LnCl_3$/$RECl_3$. Bastnasite-derived rare-earth chlorides [68188-88-5] have a composition very similar to the analogous material produced from monazite.

The step used in California to crack or open the concentrate for further processing is to roast in air, whereby Ce^{3+} oxidizes to Ce^{4+}, then leach with HCl to produce an insoluble cerium-rich portion, cerium concentrate [68909-12-6], and a soluble cerium-poor lanthanum-rich fraction.

A typical analysis of the insoluble cerium concentrate portion is by wt%; CeO_2, ~62; other Ln oxides, ~10; CaO, 6; other oxides, ~4; and F^- ~10. The loss on ignition is about 8 wt%. Cerium oxide readily takes F^- ions into the lattice. The charge difference is then matched by some Ln^{3+} replacing Ce^{4+}.

The soluble fraction from the HCl leach, after a simple SX removal of heavy lanthanides, is either converted to a solid lanthanum concentrate [68188-83-0] or

Table 1. **Composition of Bastnasite Concentrate**[a]

Component	Composition, approx wt%
Lanthanides	
CeO_2	30
La_2O_3	20
Nd_2O_3	7
Pr_6O_{11}	2.4
other Ln	0.6
Non-Lanthanides	
SrO	5
CaO	4
BaO	1.5
F	5.5
SiO_2	1.5
PO_4	1
Fe_2O_3	0.5
SO_4	1

[a] Loss on ignition (carbonate) is 20%.

used as the feedstock for further separation processes to produce pure light lanthanide derivatives. The lanthanum concentrate is essentially a mixed lanthanide hydroxide chloride where the total Ln oxides is 80 wt%, Cl^- is 12 wt%, and the loss on ignition is 8 wt%. This material contains a small (12 wt%) percentage of cerium as CeO_2, and because lanthanum concentrate is consumed in quantity in fluid catalytic cracking (FCC) catalysts for gasoline production, it accounts for a portion of the net consumption of cerium. La_2O_3 is present at 46 wt%; the remaining 22 wt% consists of other lanthanides.

An alternative process for opening bastnasite is used in China: high temperature roasting with sulfuric acid followed by an aqueous leach produces a solution containing the Ln elements. Ln is then precipitated by addition of sodium chloride as a mixed sulfate. Controlled precipitation of hydroxide can remove impurities and the Ln content is eventually taken up in HCl. The initial cerium-containing product, once the heavy metals Sm and beyond have been removed, is a light lanthanide (La, Ce, Pr, and Nd) rare-earth chloride.

3.2. Processing of Monazite. Monazite, a by-product of the mineral–sands industry production of the economically more dominant minerals ilmenite, rutile, and zircon, is marketed worldwide as a concentrate in which the rare-earth oxide content is ~60%. The usual process to crack monazite is with alkali (6). After beneficiation, the monazite concentrate is finely ground and digested with an excess of caustic soda at ~150°C for several hours.

$$(\mathrm{Ln,Th})\mathrm{PO_4} + \mathrm{NaOH} \longrightarrow \mathrm{Na_3PO_4} + \mathrm{Ln(OH)_3} + \mathrm{Th(OH)_4}$$

A soluble sodium tripolyphosphate is produced as are insoluble lanthanide and thorium hydroxides (hydrated oxides).

The solids are treated with hydrochloric acid at 70°C at pH 3–4. The thorium hydroxide [13825-36-0] remains insoluble and can be filtered off. Small amounts of trace contaminants that carry through into solution, such as uranium and lead as well as some thorium, are removed by coprecipitation with barium sulfate in a deactivation step. The resulting product, after SX-removal of the heavy Ln fraction, is a rare-earth/lanthanide chloride, $LnCl_3 \cdot 6H_2O$. A typical analysis of this material gives from 22–25 wt% CeO_2, from 11–16 wt% La_2O_3, from 5–9 wt% Nd_2O_3, from 2–3 wt% Pr_6O_{11}, and from approximately 31 wt% chloride.

3.3. Production of Cerium Derivatives. Moderately pure (90–95%) cerium compounds can be made from rare-earth chloride through oxidation with, for example, hypochlorite to produce an insoluble cerium hydrate. The other lanthanides remain in solution. The hydrate, on calcination, converts to CeO_2.

$$2\,\mathrm{Ce(OH)_4}\; n\mathrm{H_2O(s)} \longrightarrow 2\,\mathrm{CeO_2} + 4\,n\mathrm{H_2O}$$

The cerium concentrate derived from bastnasite can also be upgraded by dissolution and controlled reprecipitation.

Ce(IV) extracts more readily into organic solvents than do the trivalent Ln(III) ions providing a route to 99% and higher purity cerium compounds. Any Ce(III) content of mixed lanthanide aqueous systems can be oxidized to

Ce(IV) and the resulting solution, eg, of nitrates, contacted with an organic extractant such as tributyl phosphate dissolved in kerosene. The Ce(IV) preferentially transfers into the organic phase. In a separate step the cerium can be recovered by reduction to Ce(III) followed by extraction back into the aqueous phase. Cerium is then precipitated and calcined to produce the oxide.

Solvent extraction (SX) is also the process for the commercial separation of the individual light lanthanides (7). Each SX step, using nitrate or chloride solutions as the aqueous phase and kerosene as the organic phase and using chelating agents (qv) as extractants, cuts the Ln series into two parts. Consequently cerium can also be recovered from the second step in the general sequential SX processing of the Ln(III) series.

4. Cerium(IV) Chemistry

The fluorite structure, which has a large crystal lattice energy, is adopted by CeO_2 preferentially stabilizing this oxide of the tetravalent cation rather than Ce_2O_3. Compounds of cerium(IV) other than the oxide, ceric fluoride [10060-10-3], CeF_4, and related materials, although less stable can be prepared. For example ceric sulfate [13590-82-4], $Ce(SO_4)_2$, and certain double salts are known.

The tetravalent ceric ion [16065-90-0], Ce^{4+}, is the only nontrivalent lanthanide ion, apart from Eu^{2+}, stable in aqueous solution. As a result of the higher cation charge and smaller ionic size, ceric salts are much more hydrolyzed in aqueous solution than those of the trivalent lanthanides.

$$[CeL_m(H_2O)]^n + H_2O \longrightarrow [CeL_m(OH)]^{[n-1]+} + H_3O^+$$

Ceric salt solutions are strongly acidic, basic salts tend to form readily, and there are no stable simple salts of weak acids.

The double salts, ceric ammonium nitrate [16774-21-3], $(NH_4)_2[Ce(NO_3)_6]$, and ceric ammonium sulfate [19495-85-3], $(NH_4)_2[Ce(SO_4)_3]$, are stable orange compounds prepared by dissolving freshly prepared hydrated oxide in excess of the appropriate acid and adding the correct amount of ammonium salt. Cerium(IV) is present in the anion, not the cation, of these salts. The crystal structure shows that the formal name should, for example, be diammonium hexanitratocerate. The solid sulfate analogues are correctly sulfatocerates. These complex anions and other similar species are stable in aqueous solutions. Chlorocomplexes of cerium(IV) are not as stable as nitrato or sulfato derivatives; the simple cerium tetrachloride [14986-52-8], $CeCl_4$, is unstable, because Cl^- is oxidized by Ce(IV), but salts of the hexachlorocerate ion [35644-17-8], $[CeCl_6]^{2-}$, having large cations, do exist. Ceric salts range from yellow through orange to red in color, depending on the anionic form. Ceric ion in a glass matrix absorbs in the ultraviolet portion of the spectrum but not in the visible; the precise details of the spectra depend on glass composition.

Cerium in the tetravalent state is a strong oxidizing agent and can be reduced by, eg, oxalic acid, halogen acids, ferrous salts, and hydrogen peroxide. The exact oxidation potential for the one-electron reaction of Ce(IV) to Ce(III) ranges from ca 1.3 V in 1 N HCl to ca 1.8 V in 6 N $HClO_4$ and it depends on which small anionic groupings are complexed to the tetravalent cerium. Aqueous solutions containing Ce(IV) species are stable, despite the lower electrode potential for the H_2O/O_2 couple (1.23 V), probably for kinetic reasons. Cerium(IV) oxidation is a valuable tool in organic chemistry (8) and can be used for quantitative volumetric oxidation reactions called cerate oxidimetry in analytical chemistry (9).

4.1. Cerium Oxide. The most stable oxide of cerium is cerium dioxide [1306-38-3], CeO_2, also called ceria or ceric oxide. When cerium salts are calcined in air or if oxygen is present, this tetravalent Ce(IV) oxide is formed, cerium sesquioxide [1345-13-7] Ce_2O_3, can be prepared in strongly reducing conditions but is unstable in air and water, readily converting to the dioxide. Cerium has one of the highest free energies of formation for an oxide. The dioxide is soluble in mineral acids but can prove difficult to dissolve unless a trace of reducing agent such as hydrogen peroxide is added.

Ceria has the fluorite (CaF_2) structure having eight-coordinate cations and four-coordinate anions. Under some circumstances it can exhibit large deviations from stoichiometry giving CeO_{2-x}, where x can be up to 0.3. The color of the oxide is sensitive not only to stoichiometry but also to the presence of other lanthanides. Pure CeO_2 is a very pale yellow but a slight trace (ca 0.02 wt%) of Pr results in a buff color attributable to Ce(IV)−Pr(III) transitions. Grossly nonstoichiometric ceria samples are reported to be blue.

Solid solutions of ceria with trivalent ions, eg, Y and La, can readily be formed. The M^{3+} ions substitute for the tetravalent Ce and introduce one oxygen vacancy for every two Ln^{3+} ions. The dopant ions and the oxygen vacancies form charge associates. The resulting defect-fluorites have good oxide ion conductivity and are novel solid electrolytes for temperatures above ∼600°C (10).

5. Cerium(III) Chemistry and Compounds

Cerium is strongly electropositive having a low ionization potential for the removal of the three most weakly bound electrons. The trivalent cerous ion [18923-26-7], Ce^{3+}, apart from its possible oxidation to Ce(IV), closely resembles, the other trivalent lanthanides in behavior.

The simple cerous salts can be prepared by dissolving the oxide, or preferably a more reactive precursor, in the appropriate acid or, when possible, produced by precipitation from solution. Upon crystallization a wide variety of hydrated species can result. These hydrates tend to be hygroscopic. Basic salts, eg, $Ce(OH)CO_3$, may be formed and these can be contaminants in the solid salts.

Ce(III) forms a water-insoluble hydroxide, carbonate, oxalate, phosphate, and fluoride; sparingly soluble sulfate and acetate; and soluble nitrate and chloride (and bromide). In solution the salts are only slightly hydrolyzed. The carbonate is readily prepared and is a convenient precursor for the preparation of other derivatives. The sparingly soluble sulfate and acetate decrease in solubility with an increase in temperature. Calcination of most Ce(III) salts results in CeO_2.

Cerous salts in general are colorless because Ce^{3+} has no absorption bands in the visible. Trivalent cerium, however, is one of the few lanthanide ions in which parity-allowed transitions between 4*f* and 5*d* configurations can take place and as a result Ce(III) compounds absorb in the ultraviolet region just outside the visible.

5.1. Hydroxide.

Freshly precipitated cerous hydroxide [15785-09-8], $Ce(OH)_3$, is readily oxidized by air or oxygenated water, through poorly defined violet-tinged mixed valence intermediates, to the tetravalent buff colored ceric hydroxide [12014-56-1], $Ce(OH)_4$. The precipitate, which can prove difficult to filter, is amorphous and on drying converts to hydrated ceric oxide, $CeO_2 \cdot 2H_2O$. This commercial material, cerium hydrate [23322-64-7], behaves essentially as a reactive cerium oxide.

5.2. Carbonate.

Hydrated cerous carbonate, $Ce_2(CO_3)_3 \cdot nH_2O$ when prepared under ideal conditions tends to crystallize as cerous carbonate octahydrate [16545-92-5], $n = 8$. The commercial product, prepared on a large scale by sodium carbonate addition, has a composition best represented as cerous carbonate trihydrate [64360-90-3], $n = 3$. Several other hydrates are known.

Temperature, pH, precipitation conditions, and the drying process determine the amount of water in the solid. In addition the species $Ce(OH)(CO_3) \cdot xH_2O$ and $Ce_2O_2(CO_3)$ may also be present. Thermal decomposition causes loss of crystallization water followed by the formation of ill-defined hydroxy- and oxy-species and eventually, at ~550°C, CeO_2. Discrete intermediates are not seen because of the concomitant oxidation of Ce(III) to Ce(IV).

5.3. Nitrate.

Cerium(III) nitrate hexahydrate [10294-41-4], $Ce(NO_3) \cdot 6H_2O$, is a commercially available soluble salt of cerium, and because of ready decomposition to the oxide, it is used, for example, when a porous solid is to be impregnated with cerium oxide. The nitrate is very soluble in water, up to about 65 wt%. It is also soluble in a wide range of polar organic solvents such as ketones, alcohols, and ethers.

5.4. Halides.

Cerous chloride hydrate [19423-76-8], $CeCl_3 \cdot nH_2O$, usually with $n \sim 6$, on heating tends to form cerous oxychloride [15600-64-3], CeOCl. The anhydrous cerous chloride [7790-86-5] can be made from the hydrated salt by suppressing oxyhalide formation during thermal dehydration by the presence of hydrogen chloride or ammonium chloride. The anhydrous salt is soluble in a variety of organic solvents, eg, alcohols and ethers, has mp 817°C, and can be volatilized at high temperatures in vacuum.

Precipitation of cerous fluoride [7758-88-5], CF_3, from aqueous solution by HF addition produces $CeF_3 \cdot nH_2O$, $n \sim \frac{1}{2}$, from which the anhydrous salt can be prepared by controlled dehydration. CeF_3, mp 1432°C, can also be prepared by reaction of a suitable precursor, such as carbonate, and ammonium bifluoride, NH_4HF_2. The anhydrous chloride and fluoride are potential precursors for cerium metal production. Cerous oxyfluoride [20901-12-6], CeOF, materials have novel ionic conductivity. The oxyfluoride and oxychloride are both high melting species that often form during halide salt calcination.

5.5. Carboxylates.

Cerium carboxylates, water-insoluble, can be made (11) by double decomposition and precipitation using water-soluble precursors, or by reaction of an insoluble precursor directly with the organic acid. Cerous oxalate [139-42-4], $Ce_2(C_2O_4)_3$, 2-ethylhexanoate (octanoate), naphthenate, and stearate are readily prepared.

5.6. Sulfides.

Several cerium sulfides have been characterized (12) including the expected cerium(III) sulfide [12014-93-6], Ce_2S_3. Cerium monosulfide [12014-82-3], CeS, and tricerium tetrasulfide [12185-95-4], Ce_3S_4, are also known. CeS (13), bronze in color with a metallic lustre, adopts the NaCl structure with the ions Ce^{3+}, S^{2-}, and one electron in a conduction band. This sulfide has a high (in the metallic range) electrical conductivity, a high thermal conductivity, a high (ca 2715 K) melting point, and good thermal shock resistance.

Cerium(III) oxysulfide [12442-45-4], Ce_2O_2S, is a high melting stable compound that precipitates out when steel is treated with a cerium-based metal to control sulfide inclusions. Its thermodynamic properties are well known and the Ce–O–S phase diagram has been determined (14).

5.7. Miscellaneous Compounds. Among simple ionic salts cerium(III) acetate [17829-82-2] as commercially prepared, has $\sim 1\frac{1}{2}$ H_2O, has a moderate ($\sim$100 g/L) aqueous solubility that decreases with increased temperature, and is an attractive precursor to the oxide. Cerous sulfate [13454-94-9] can be made in a wide range of hydrated forms and has solubility behavior comparable to that of the acetate. Many double sulfates having alkali metal and/or ammonium cations, and varying degrees of aqueous solubility are known. Cerium(III) phosphate [13454-71-2], being equivalent to monazite, is very stable.

Derivatives such as borides, carbides, nitrides, and hydrides are best prepared by direct reaction between the elements. These metalloid-type compounds, which often show variable composition, are colored and sometimes semiconducting.

6. Metal

In bulk form cerium is a reactive metal. Pure metal is prepared by the calciothermic reduction of CeF_3.

$$2\,CeF_3 + 3\,Ca \longrightarrow 2\,Ce + 3\,CaF_2$$

A slight excess of calcium is used and the exothermic reaction, carried out in a tantalum crucible, is initiated at ~900°C. After physical separation of the upper layer of immiscible fluoride slag, vacuum distillation removes unreacted volatile Ca. Cerium can also be made by the electrolytic reduction of fused chloride.

On a fresh surface the metal has a steely lustre but rapidly tarnishes in air as a result of surface formation of oxide and carbonate species. For protection against oxidation the metal is usually stored in a light mineral oil. When made finely divided, eg, on being cut, it can be strongly pyrophoric, and, for this reason is used, as the ferro-alloy mischmetal, in lighter flints and ordnance. Cerium reacts steadily with water, readily dissolves in mineral acids, and is also attacked by alkali; it reacts with most nonmetals on heating.

Cerium metal has unique solid-state properties and is the only material known to have a solid–solid critical point. Three allotropes, α, β, γ, are stable at or close to ambient conditions and have complex structural interrelationships.

6.1. Mischmetal. Mischmetal [62379-61-7] contains, in metallic form, the mixed light lanthanides in the same or slightly modified ratio as occurs in the resource minerals. It is produced by the electrolysis of fused mixed lanthanide chloride prepared from either bastnasite or monazite. Although the precise composition of the resulting metal depends on the composition of chloride used, the cerium content of most grades is always close to 50 wt%.

An alternative commercial form of a metallic mixed lanthanide-containing material is rare-earth silicide [68476-89-1], produced in a submerged electric-arc furnace by the direct reduction of ore concentrate, bastnasite, iron ore, and quartz. The resulting alloy is approximately 1/3 mischmetal, 1/3 silicon, and 1/3 iron. In addition there are some ferro-alloys, such as magnesium–ferrosilicons, derived from cerium concentrate, that contain a few percent of cerium. The consumption of metallic cerium is overwhelmingly in the mixed lanthanide form in ferrous metallurgy.

7. Economic Aspects

The worldwide production of lanthanides in 2002 was 85,500 t (5), measured as contained Ln oxide. The primary sources are given in Table 2. The rise of Chinese lanthanide production during the 1980s has become a significant factor in the global market picture.

Forecast demand for rare earths is expected to grow at the rate of 4–9%/yr through 2007 (15).

Cerium is used in several forms other than as the pure oxide. Only a small fraction of the 80,000 ton Ln total is produced as separated, relatively pure individual Ln derivatives, cerium included. The bulk of the material is consumed as concentrates, cerium included.

Table 2. **2002 Lanthanide Production, t**[a]

Brazil	200
China	75,000
India	2,700
Malaysia	450
Sri Lanka	120
United States	5,000
former USSR	2,000

[a] As contained Ln oxide, wt approximate.

Table 3. **Commercially Available Cerium-Containing Materials and Uses**

Type	Material	Use	Cerium content
A	rare-earth chloride, mischmetal	FCC[a] catalysts iron metallurgy.	principal component[b]
B	lanthanum concentrate, La–Ln chloride	FCC[a] catalysts	minor component[b]
C	cerium concentrate	glass polishing, glass decolorizing	dominant element[c]
D	oxide, nitrate, metal	autoemission catalysts, etc	> ca 90 wt %
E	oxide, salts	luminescence, catalysts	> ca 99 wt %

[a] FCC = fluid catalytic cracking.
[b] Of mixed-lanthanide composition.
[c] In oxide-type compound.

Table 4. **U.S. Exports of Cerium Compounds by Country**[a,b]

Country[c]	2000 Gross weight, kg	2000 Value, $	2001 Gross weight, kg	2001 Value, $
Australia	5,630	39,000	2,740	15,400
Belgium	86,000	1,580,000	104,000	211,000
Brazil	205,000	337,000	241,000	486,000
Canada	201,000	1,520,000	300,000	2,640,000
France	124,000	515,000	121,000	401,000
Germany	832,000	2,460,000	518,000	1,900,000
Hong Kong	60,100	359,000	35,700	357,000
India	4,070	37,800	89,400	557,000
Japan	213,000	1,550,000	462,000	2,580,000
Korea, Republic of	1,150,000	4,950,000	1,080,000	4,900,000
Malaysia	178,000	889,000	122,000	594,000
Mexico	216,000	1,490,000	232,000	1,640,000
Netherlands	206,000	697,000	11,100	96,200
Singapore	15,100	83,100	13,600	69,900
South Africa	6,000	108,000	988	10,400
Taiwan	237,000	976,000	286,000	1,260,000
United Kingdom	133,000	400,000	386,000	703,000
other	172,000	997,000	477,000	1,700,000
Total	*4,050,000*	*19,000,000*	*4,490,000*	*20,100,000*
Total estimated equivalent rare-earth oxide (REO) content	*4,050,000*	*19,000,000*	*4,490,000*	*20,100,000*

[a] Ref. 16.

[b] Data are rounded to no more than three significant digits; may not add to totals shown.

[c] Harmonized Tariff Schedule of the United States category numbers.

The various cerium-containing derivatives available commercially are summarized in Table 3.

The average prices for imported cerium compounds, excluding cerium chloride increased to \$4.92/kg in 2001 from \$4.57/kg in 2000 (16).

U.S. exports of cerium compounds by country are listed in Table 4. U.S. imports for consumption of cerium products by country are listed in Table 5.

8. Analytical Methods

Preliminary separation of the lanthanides as a complete group is often possible by oxalate precipitation at low pH. In most cases direct calcination, at ~1000°C, of oxalate to the oxide provides a gravimetric determination of total Ln oxide content. If necessary controlled hydroxide precipitation can reject alkaline earths. The Ln oxide can be redissolved in strong acid and titrated against EDTA or other complexing agents. Depending on analytical procedures and on the sample it may be necessary to ensure that all the Ce is in one oxidation state, eg, 3+, by

Table 5. **U.S. Imports for Consumption of Cerium Compounds by Country**[a,b]

Country[c]	2000		2001	
	Gross weight, kg	Value, $	Gross weight, kg	Value, $
cerium compounds, including oxides, hydroxides, nitrates, sulfate chlorides, oxalates:				
Austria	49,600	468,000	59,000	439,000
China	3,470,000	13,500,000	4,060,000	14,000,000
France	2,390,000	7,130,000	1,240,000	6,650,000
Japan	410,000	7,820,000	288,000	6,500,000
other	134,000	561,000	115,000	737,000
Total	*6,450,000*	*29,400,000*	*5,760,000*	*28,300,000*
Total estimated equivalent rare-earth oxide (REO) content	*4,310,000*	*29,400,000*	*3,870,000*	*28,300,000*

[a] Ref. 16.

[b] Data are rounded to no more than three significant digits; may not add to totals shown.

[c] Harmonized Tariff Schedule of the United States category numbers.

using a reducing agent such as ascorbic acid. The ceric content can be determined by oxidation of Ce^{3+} to the tetravalent state by persulfate or bismuthate then titrating the resulting Ce^{4+} with standard ferrous ammonium sulfate. Qualitative colorimetric tests are also possible.

Several instrumental methods are available for quantitative estimation of from moderate to trace amounts of cerium in other materials. X-ray fluorescence is widely available, versatile, and suitable for determinations of Ce, and any other Ln, at percent levels and lower in minerals and purer materials. The uv-excited visible luminescence of cerium is characteristic and can be used to estimate Ce content, at ppm levels, in a nonluminescing host. X-ray excited optical luminescence (17), a technique especially appropriate for Ln elements including cerium, relies on emissions in the visible, and also measures ppm values. Atomic emission spectrometry is applicable to most lanthanides, including Ce (18). The precise lines used for quantitative measurement must be chosen with care, but once set-up the technique is suitable for routine analyses.

9. Health and Safety Factors

In general the lanthanides, including cerium, have a low toxicity rating (19), especially when they are present in material having low aqueous solubility. Cesium resembles aluminum in its pharmacological action as well as in its chemical properties. The insoluble salts such as the oxalates are stated to be nontoxic even in large doses. The greatest exposures are likely to be during manufacture of cerium. Exposed workers have experienced sensitivity to heat, itching, and skin lesions (20). When orally administered poor absorption from the gastrointestinal tract tends to result in the lanthanides generally having little effect. The anion is often an important determinant in toxicity.

Cerium is a strong reducing agent. There is a moderate explosion hazard when cerium in the form of dust is exposed to flame. There is also a moderate fire hazard since cesium ignites spontaneously in air at 150–180°C (20).

Historically the use of monazite, a thorium-containing mineral, as the principal lanthanide resource led to confusion regarding the relation between radioactivity and the lanthanides. Inadequate separations produced Th-contaminated Ln products. Modern processing technology results in products that meet all regulatory requirements.

10. Uses

The technological applications of cerium rely predominantly on its high thermodynamic affinity for oxygen and sulfur, potential redox chemistry involving cerium(III) and cerium(IV), and the absorption/excitation energy bands associated with its electronic structure. Uses may be categorized as occurring in metallurgy (qv), glass (qv) and ceramics (qv), catalysis (qv), and chemicals, plus phosphors/luminescence.

The purity of the cerium-containing materials depends on the application as indicated in Table 3, and purity can mean not only percentage of cerium content but also absence of unwanted components. For some uses, eg, gasoline production catalysts, the lanthanides are often used in the natural-ratio without separation and source literature for these applications often does not explicitly mention cerium. Conversely, particularly in ferrous metallurgy, cerium is often assumed to be synonymous with rare-earth or lanthanide and these terms are used somewhat interchangeably.

10.1. Metallurgical Applications. *Steel.* Mischmetal (MM) and other cerium-containing ferro-alloys are used to improve the physical properties of high strength/low alloy (HSLA) steels (21). Cerium is added primarily to provide sulfide shape control but also as a deoxidizer or desulfurizer because steel quality is improved when the oxygen and sulfur content is minimal. Nonmetallic inclusions, particularly of certain sulfides, can deform at high working temperatures. These platelike inclusions produce layers of weakness and hence undesirable mechanical properties in the final steel. When added to the molten steel, cerium and other lanthanides combine avidly with oxygen and sulfur, even reducing other oxides and sulfides originally present, to form high melting, hard Ln oxysulfides and oxides, which do not deform later during rolling of the steel. In addition these same inclusions can provide nuclei during solidification that promote a fine-grained final product.

Modern steelmaking technology, with an emphasis during production on low levels of oxygen and sulfur, results in cleaner steels. This, together with the general downturn in steel production in the western economies, has resulted in a significantly reduced demand for mischmetal in the steel industry. In contrast, in China, which has abundant Ln reserves and less advanced steelmaking technology, mischmetal consumption in steel treatment amounts to about 75% of their Ln production.

Cast Iron. Cast irons contain carbon (qv) as the main alloying element, are heterogeneous in microstructure, and form an extensive family of materials that includes gray iron, compacted graphite, and ductile iron. The key to obtaining distinctive differences in properties between individual cast-iron types is the control of the carbon content and especially control of the morphology that graphitic carbon precipitates assume in the final product. Crystal morphology depends on tramp elements bound to the growing crystallite surfaces.

The lanthanides, and in particular cerium, are used (22) to provide this graphite morphology control, for example to produce spherulitic or vermicular crystallites. The elements are usually added as silicides or in various ferro-alloys with cerium as the principal lanthanide. The function of cerium and all the lanthanides is probably to remove free oxygen and sulfur from the melt through formation of stable lanthanide oxysulfides, akin to the role in steel technology; to initiate the special carbon crystal growth by nucleation on those oxysulfide compounds; and to tie up undesirable tramp elements, eg, Pb and Sb, as intermetallics.

Lighter Flints and Getters. Traditionally the item most widely associated with cerium has been the pyrophoric iron-mischmetal (~60%) alloy for lighter flints, in limited use. Similar low vapor pressure reactive alloys based on cerium, such as Th_2Al-MM, can also be used as getters for electronic equipment and vacuum tubes (see ELECTRONIC MATERIALS; VACUUM TECHNOLOGY).

Super Alloys. Super alloys are nickel- or cobalt-based alloys that are exceptionally heat-resistant and are used, for example, in gas turbine engines in aircraft (see COBALT AND COBALT ALLOYS; NICKEL AND NICKEL ALLOYS). One operating problem, caused by the repetitive cycling from ambient up to high temperature, is the tendency for the essential protective oxide skin on the metal surface to spall off. Several commercial alloys have ~0.05 wt% pure cerium that significantly improves this oxidation resistance, provides creep resistance, and confers a longer operating life (23). This alloy property improvement probably comes from the trapping of trace unwanted sulfur impurities from the metal crystallite boundaries plus a modification to the diffusion mechanism for oxide skin growth. The oxide skin formed at high temperatures shows less tendency to spall off when cerium is present in the alloy.

Aluminum Alloys. Aluminum alloy systems, under development for use at higher temperatures than is normally possible with aluminum, can be made by rapid solidification powder metallurgy processes (see ALUMINUM AND ALUMINUM ALLOYS; HIGH TEMPERATURE ALLOYS). The novel compositions produced have additive element concentrations, eg, of cerium, beyond those possible using conventional ingot metallurgy. One of the most promising of the lightweight alloys is an Al-8.3Fe-4.0Ce (wt%) material, having excellent properties in the 230°C to 340°C range (24).

The technique of rapid solidification enables relatively large amounts of insoluble metallic elements to be finely dispersed within atomized powders. Upon freezing very small intermetallic particles are formed, resulting, after further processing, in a high volume fraction of finely dispersed particles within the aluminum matrix and hence a dispersion strengthened alloy. The intermetallic phases, or possibly oxidic species, responsible for the dispersion strengthening are probably binary Al-Fe and ternary Al–Fe–Ce compounds.

Chromium Plating. Chromium is deposited onto many consumer articles and industrial items to provide decoration as well as corrosion resistance. The chromium coating is produced by an electroplating (qv) process from an aqueous solution containing a chromium salt. Chromium cannot easily be plated directly from Cr(III), however, because of the high stability of the aquo-ion $[Cr(H_2O)_6]^{3+}$. It needs to be present as Cr(VI), which can be reduced to Cr(O), ie, chromium metal, through the intermediary of a protected Cr(III) species avoiding the formation of the stable hexaaquochromium(III) ion. The plating solutions must contain an anion, such as fluoride, to stabilize the active Cr(III) intermediate and prevent the aquo-ion from forming. It has proved difficult to maintain a stable F^- concentration. The addition of cerous ions, Ce^{3+}, as cerium fluoride added directly to the plating bath, gives a self-regulating electrolyte (25). The solubility of cerous fluoride is nearly independent of the temperature of the plating solution within the practical range. By ensuring that excess, undissolved CeF_3 is always present, the fluoride ion concentration can be closely controlled and quality plating achieved.

Welding Electrodes. The electrodes used in certain welding (qv) technologies, such as inert gas tungsten-arc welding, contain a finely dispersed oxide distributed throughout the tungsten matrix. These oxide particles give an arc-strike reliability to the electrodes at lower voltages than tungsten alone can provide. Cerium oxide, at 2 wt% loading, provides an alternative to thorium oxide, a common additive that is being phased out for environmental reasons (26).

10.2. Glass and Ceramic Applications. *Glass Polishing.* The most efficient polishing agent for most commercial glass compositions is cerium oxide (27). This application consumes, either as a moderately pure oxide or as a cerium oxide-dominated concentrate, a significant portion of the cerium products produced annually. Commercial glass polishes (qv) are based on cerium oxide powders having defined particle sizes and controlled dispersibility in aqueous systems. The polishing process requires water, and it is a softer hydrated surface layer that is removed or reformed. In general, the polishing agent should have a Mohs' hardness of ~6.5, close to the hardness of most glasses. Cerium oxide slurried in water contains the potential polyvalent cerium atom, and redox reactions from the Ce(IV)/Ce(III) couple may well provide chemical assistance in breaking up the silicate lattice. Transient formation of complexed groupings consisting of $\cdots$Ce–O–Si$\cdots$ has been suggested.

The cerium concentrate derived from bastnasite is an excellent polish base, and the oxide derived directly from the natural ratio rare-earth chloride, as long as the cerium oxide content is near or above 50 wt%, provides an adequate glass polish. The polishing activity of the latter is better than the CeO_2:LnO ratio suggests. Materials prepared prior to any Ln purification steps are sources for the lowest cost polishes available used to treat TV face plates, mirrors, and the like. For precision optical polishing the higher purity materials are preferred.

A cerium-based abrasive material for producing a highly accurate polished surface and improved grindability has been reported (28).

Glass Decolorization. An important use for cerium compounds is the decolorization of glass. The dominant glass produced is the soda lime-type made from inexpensive raw materials, the purity of which determines the color of the finished product. One common impurity from silica sand, iron, is a moderately strong colorant in glass and as little as 0.01 wt% can be visually detected. The coloration caused by iron results from absorption of both the ferric and ferrous ions. Glass can be decolorized without changing the total iron content by keeping all the iron in the Fe^{3+} state by addition of Ce^{4+} to the glass bath.

Cerium(IV) oxidizes ferrous ion to ferric and the cerium ions are stable under the conditions of a molten silicate–glass bath. Furthermore, cerium itself has no absorption in the visible region. Economical additions of cerium, as cerium concentrate, enable the efficient use of raw materials containing trace quantities of iron (29).

Ultraviolet Absorption. The damage sunlight causes materials from near uv (300–400 nm range) radiation, can be limited by screening out the damaging radiation through the incorporation of components that absorb at those wavelengths. Cerium(IV) in particular makes glass opaque to near uv radiation but shows no absorption in the visible; cerium(III) has similar behavior (30). Cerium-doped glass has applications in several areas, eg, medical glassware, display case glass windows, etc.

The photostability of pigments can be enhanced by surface additives that increase the provision of recombination centers for the photoproduced charge carriers that would otherwise cause chemical damage. The surface additive must be a one-electron redox couple and be present in both valence states. Cerium, through the Ce(III)/Ce(IV) interconversion, can provide this protective process, giving pigments lightfastness. The rate at which certain pigments, such as titanium dioxide, darken on exposure to light can be reduced by producing a precipitated cerium salt coating on the pigment particles (31).

Radiation-Resistant Glass. Television glass faceplates are subjected to electron bombardment by high energy electrons, particularly with the high tube voltages needed for color displays. Over time this bombardment causes discoloration or browning of the glass because of the creation of color centers, an effect which is suppressed by the addition of up to 1 wt% or so of cerium oxide to the glass. A similar suppression of gamma-ray induced discoloration is also possible and cerium-containing glasses are used in the construction of viewing windows in hot-cells in the nuclear industry. The suppression mechanism in both instances is believed to depend on the presence of both Ce^{3+} and Ce^{4+} ions within the glass lattice (32).

Photo-Sensitive Glass. On exposure to strong light, certain glass formulations develop a latent image that can, in a later step, be converted into a permanent structural or color change. This type of glass contains cerium ions that absorb ultraviolet radiation and release electrons into the glass matrix. Heat treatment causes these electrons to migrate to silver ions, also present, that initially form silver specks that in turn nucleate the crystal growth of other compounds within the glass (33). Highly detailed patterns can be produced that are not only decorative but also can help create masks, spacers, and the like for electronic uses.

Opacifier in Enamels. Cerium oxide has a high (~2.2) refractive index and is a potential opacifying agent (34) in enamel compositions used as protective coatings on metals. In addition to a high thermal stability, ceria has only one crystallographic form throughout the range of temperatures met during enameling. Opacity in porcelain enamels refers to the desired white cover-coat surface and is created when the opacifier, the oxide, precipitates out as micrometer-sized crystals during the firing on of the enamel (see ENAMELS, PORCELAIN, OR VITREOUS).

Zirconia Ceramics. Zirconia, ZrO_2, the high temperature engineering ceramic, needs an additive to produce components having high strength and toughness (see ADVANCED CERAMICS). A so-called phase stabilizer is added in order to maintain a portion of the ZrO_2 as dispersed particulates of the tetragonal phase within the matrix cubic phase at ambient temperatures. Addition of ~12 mol% of CeO_2, for example, to zirconia produces a material having exceptional toughness and good strength (35,36). Cerium oxide-doped zirconia is also used in thermal barrier spray coatings on metal surfaces (37) such as aircraft engine parts in order to reduce the high temperatures to which the metal substrate would be exposed (see METAL SURFACE TREATMENTS).

Optical Coatings. Thin surface coatings are applied to optical components to improve performance. Wideband antireflection coatings for the visible and ir regions need materials with a refractive index of ~1.5 for the best efficiency. Cerium fluoride, a stable material resistant to humidity damage, has a suitable index, 1.63 in the visible, 1.59 in the infrared, and is transparent over the range 0.5 μm to 5 μm. It is one of the compounds used to build up the multilayers deposited on lenses, sensors, and the like.

10.3. Catalytic and Chemical Applications. *Cracking Catalysts* Several catalysts used to convert crude oil to lower molecular-weight fractions, such as gasoline, contain lanthanides including cerium (38). Within the United States alone ~500 of FCC are consumed per day. An FCC unit has a lower reactor temperature and a higher regenerator temperature; the catalyst circulates between the two. FCC catalysts contain crystalline zeolites and additives embedded in an inert matrix. The zeolite, a special alumino–silicate with organic molecule-sized pores, requires cations within those pores for charge neutrality, to give catalytic reactivity in the reactor and to provide thermal stability in the regenerator.

Large highly charged ions, such as La^{3+} or Ce^{3+}, bound within the zeolite pores create a high electric field gradient strong enough to dissociate adsorbed water and provide a high surface acidity. The Ln content can reach up to 10 wt% or higher by weight of the zeolite, but not all FCC catalysts contain lanthanides. Catalysts with a range of Ln content are made, each designed to meet specific refinery needs. Cerium, because of the potential availability of the Ce^{4+} state that tends to hydrolyze at the ion-exchange pH used, is often partially removed from the precursor solutions.

The lanthanides, be they La, Ce, or others, are used to give high cracking activity to the catalysts, especially to produce low octane fuel from heavy crude oil feedstocks. Consumption of lanthanides, and hence of cerium, in FCC catalysts has altered during the decade of the 1980s because of increased demand for high octane fuels, greater feedstock availability of lighter crudes, and changes in catalyst technology. FCC Ln demand reached a peak in ~1984 when one-third of all Ln consumption was in FCC.

This trend has influenced the supply and availability of cerium, particularly in comparison to the availability of lanthanum-rich cerium-poor materials. The increase in Ln demand for FCC catalysts up to the mid-1980s, together with the need to separate out cerium in order to make the La-rich Ce-poor compositions increasingly preferred, led to a glut of Ce-based raw materials at that time.

Emission Control Catalysts. There is strong demand for cerium as one of the catalytically active components used to remove pollutants from vehicle (autoexhaust) emissions (16,39). The active form of cerium is the oxide that can be formed *in situ* by calcination of a soluble salt such as nitrate or by deposition of slurried oxide (see EXHAUST CONTROL, AUTOMOTIVE).

The most widely used exhaust control device consists of a ceramic monolith with a thin-walled open honeycomb structure. The accessible surface of this monolith system is increased by applying a separate coating, a wash coat, of a high surface area material such as gamma-alumina with the catalytically active species impregnated into this washcoat. The catalyst needs to oxidize hydrocarbons, convert CO to CO_2, and reduce NO_x. The whole system forms a catalytic converter that, suitably encased, is placed between the engine and the muffler/silencer unit.

In addition to platinum and related metals, the principal active component in the multifunctional systems is cerium oxide. Each catalytic converter contains 50–100 g of finely divided ceria dispersed within the washcoat. Elucidation of the detailed behavior of cerium is difficult and complicated by the presence of other additives, eg, lanthanum oxide, that perform related functions. Ceria acts as a stabilizer for the high surface area alumina, as a promoter of the water gas shift reaction, as an oxygen storage component, and as an enhancer of the NO_x reduction capability of rhodium.

The tendency for high surface area gamma-alumina to sinter and lose that crucial area during high temperature operation is retarded by the intimate addition of several percent of cerium oxide. The mechanism is still under debate but may involve a surface LN–aluminate species on the alumina.

An oxygen storage component stores oxygen under lean operating conditions, ie, fuel-poor/air-rich, and releases it under fuel-rich, air-poor conditions to continue the oxidation of unburnt hydrocarbons and the removal of carbon monoxide even when there is insufficient gaseous oxygen. CeO_2 readily provides elemental oxygen by going nonstoichiometric to CeO_{2-x} in those air-poor portions of the exhaust cycle and then reoxidizing to CeO_2 during the air-rich period. The role of the cerium oxide however is more complex than just this oxygen storage capability. Overall ceria in autoexhaust catalysts provides better low temperature performance.

A process for the treatment of gases with a high oxygen content, with a view to controlling nitrogen oxide emissions, using a catalytic composition comprising cerium oxide and/or zirconium oxide has been reported (40).

Combusion Additives. The ability of cerium oxide to act as an oxidizing agent underlies the potential use of various cerium derivatives as additives to aid combustion (see COMBUSTION TECHNOLOGY). Diesel exhaust often contains unburnt carbonaceous material as particulate matter, and in order to reduce particle emissions the exhaust can be passed through a ceramic trap, a closed honeycomb. In order to extend the lifetime of these traps and to reduce the temperature needed for regeneration, a cerium carboxylate, in particular cerium naphthenate, can be used as an additive to the fuel (41). The cerium compound, dissolved in the fuel at a concentration equivalent to around 25–50 pmm by weight of oxide, is transformed within the engine into CeO_2, which in turn is trapped in the so-called trap oxidizer. This finely divided oxide, thoroughly dispersed throughout the trap, produces conditions under which continuous regeneration effectively occurs; burn-off happens at a lower temperature because CeO_2 catalyzes the carbon combustion.

Sulfur Oxide Removal. In the refinery catalytic cracking process (FCC) sulfur-containing crude oil fractions can give rise to sulfur oxide in the gases emitted under the oxidizing conditions in the high temperature (750°C) regenerator unit. An additive to the actual FCC catalyst can capture this regenerator-SO_x as sulfate and later release, in the cracking, (reducing) region, a more easily trapped form of sulfur, H_2S. Several catalyst additives containing cerium and/or lanthanides can act as the SO_x control agent by forming a stable sulfate that is reducible at the operating temperatures of the riser reactor.

Cerium oxide acts as a catalytic oxidizer in a spinel-based additive (42) that aids SO_2 to SO_3 conversion and promotes the required sulfate formation. Bastnasite itself is the most economical source of cerium and can be used directly at ~1% as the capture additive (43).

Polymerization Initiator. Some unsaturated monomers can be polymerized through the aid of free radicals generated, as transient intermediates, in the course of a redox reaction. The electron-transfer step during the redox process causes the scission of an intermediate to produce an active free radical. The ceric ion, Ce^{4+}, is a strong one-electron oxidizing agent that can readily initiate the redox polymerization of, for example, vinyl monomers in aqueous media at near ambient temperatures (44). The reaction scheme is

$$\textit{Initiation} \quad RH + Ce^{4+} \longrightarrow \text{complex} \longrightarrow R\cdot + H^+ + Ce^{3+}$$

$$\textit{Propagation} \quad R\cdot \longrightarrow R - M\cdot \longrightarrow R - M - M\cdot \text{ etc}$$

where the monomer M can be methylmethacrylate, acrylamide, etc (see ACRYLAMIDE).

Cellulose and similar materials are polyhydric alcohols having hydroxyl groups that can react with ceric ions. The resulting macroradicals provide active sites for the polymerization of monomer with the special advantage that the radicals remain attached to the backbone polymer and hence copolymerization can occur without homopolymer being formed. Ceric ions can initiate graft polymerization of vinyl monomers onto wool, starch, cotton, and the like thereby modifying the properties of the natural polymer in order to, for example, improve mechanical strength.

Dehydrogenation, Ammoxidation, and Other Heterogeneous Catalysts. Cerium has minor uses in other commercial catalysts (45) where the element's role is probably related to Ce(III)/Ce(IV) chemistry. Styrene is made from ethylbenzene by an alkali-promoted iron oxide-based catalyst. The addition of a few percent of cerium oxide improves this catalyst's activity for styrene formation presumably because of a beneficial interaction between the Fe(II)/Fe(III) and Ce(III)/Ce(IV) redox couples. The ammoxidation of propylene to produce acrylonitrile is carried out over catalytically active complex molybdates. Cerium, a component of several patented compositions (46), functions as an oxygen and electron transfer through its redox couple.

Lubrication Additive. Cerium fluoride, CeF_3, can be used as an additive to lubricant formulations to improve extreme pressure and antiwear behavior (47). The white solid has a crystal structure that can be pictured as [CeF] layers separated by [F] atom sheets, a layer structure analogous to that of MoS_2, a material that CeF_3 resembles in properties.

Carbon Arcs. An electric arc struck between two rods of carbon can be a source of very intense light approximating sunlight in quality. The efficiency with which the input electrical energy is converted to the radiant visible energy can be enhanced by making the electrode rod with a core of lanthanide fluoride, $(Ce,Ln)F_3$. The function of the cerium and other lanthanides is to increase the light's intensity by the absorption of energy resulting in excitation of the Ln atoms to higher energy states. These excited atoms then emit light, falling back to their normal ground energy states. The atomic emission spectra of cerium and other lanthanides have many lines in the visible.

Paint Driers and Polymer Additives. Paints based on alkyd resins (qv) dry by the oxidation and cross-linking of unsaturated side chains. Metal catalysts are included in paint formulations to promote this drying. Cerium carboxylates, eg, the naphthenate, are used as through driers, ie, to promote drying in the body of the paint film rather than at the film's surface (48).

Silicones are oligomers and polymers, with good high temperature stability, based on the siloxane –O–Si–O–Si– backbone that itself is insensitive to oxidative scission, a degradation mechanism common to –C–C–C– backbone polymers. The oxidative stability, however, of the side chain groupings can remain a weak point for the molecule. Additives, in particular cerium derivatives (49), can improve properties. Metal soaps, such as the cerium octanoate, blended into the polymer can enable, for example, silicone fluids to be used at 250°C. Thermal degradation proceeds through free-radical reactions and the function of the cerium is, through the potential one-electron redox Ce(IV)/Ce(III) system, to mop up these radicals. Low levels of additive are effective because the behavior of cerium appears to be catalytic. Any Ce(III) formed is reoxidized back to the active Ce(IV) by the slow diffusion of oxygen/air through the silicone.

10.4. Phosphor/Luminescence Applications.

Fluorescent Lighting Phosphors. Fluorescent lighting relies on phosphors to convert the efficient low pressury mercury-arc emission at 254 nm in the ultraviolet into energy emitted within the visible spectrum, 400 nm to 700 nm. Until the mid-1970s the phosphors of choice were halophosphates and others that produced an essentially continuous broad white-light spectrum. It was shown then that, for the visual perception of white, three line-emitting phosphors would suffice. Such a blend of three phosphors, with narrow line emissions centered at ~450, ~550, and ~610 nm, is not only more efficient in converting input electrical energy to output luminance but can also provide excellent color rendition. Cerium is an essential component in these new generation phosphors that have made possible the so-called tricolor lamps, essential for energy efficient and compact fluorescent lighting (50).

The role of cerium in these lighting phosphors is not as the emitting atom but rather as the sensitizer. The initial step in the lighting process is the efficient absorption of the 254 nm emission; Ce^{3+}, with broad absorption bands in the uv, is very suitable. This absorbed energy is then transferred to the sublattice within the crystalline phosphor; eventually the activator ion is fed and emission results. Cerium, as a sensitizer ion, is compatible in crystal lattices with other lanthanide ions, such as Eu and Tb, the usual activator atoms.

The precise choice of compound for the phosphor depends on a complex interplay of symmetry, interatomic spacing, stability, etc in the crystal structure. The initial green emitting phosphor was the aluminate $Ce_{0.67}Tb_{0.33}MgAl_{11}O_{19}$. More recently the choice has been a $(La_{0.4}Ce_{0.45}Tb_{0.15})PO_4$ compound and in addition a borate, $(Ce,Gd,Tb)MgB_5O_{10}$, is also now used.

Another Ce-containing fluorescent lighting phosphor is $Y_3Al_5O_{12}$:Ce used in some blends to convert energy from the otherwise unwanted 435 nm mercury line from the blue into the yellow, lowering the color temperature of the light. This same garnet phosphor is also used in high pressure mercury discharge lamps for the same effect.

Cathode Ray Tube Phosphors. The cerium atom, upon excitation by energetic cathode ray electrons, produces a characteristic emission (luminescence) that is usually in the blue to ultraviolet region, the precise wavelength depending on the symmetry and nature of the ions immediately surrounding the Ce atom in the host lattice. The Ce^{3+} emission is highly efficient, is broadband in character, and corresponds to a $5d-4f$ transition. Because the transition is allowed the emitting energy level has a very short ($\sim$50 ns) lifetime and the luminescence decays very rapidly. This property underlies the use of some cerium-containing phosphors in specialized cathode-ray tube applications (51).

Beam-indexing display tubes require phosphors that emit ultraviolet when struck by an electron beam. The phosphor needs a high efficiency and an extremely fast decay time; the preferred material is cerium doped ($\sim$2 atomic%) yttrium diorthosilicate, Ce:$Y_2Si_2O_7$, having a peak emission at 380 nm. A flying-spot scanner images a transparent film and converts the image to an electronic signal with a very fast phosphor covering the whole visible spectrum. Two cerium-containing components, a garnet, Ce:$Y_3Al_5O_{12}$, and a silicate, Ce:Y_2SiO_5, the first emitting in the range 500–650 nm and the second over the range 370–500 nm, are combined to give the correct phosphor properties.

Cando-Luminescence, Gas Mantles. The role of a gas mantle is to produce visible radiation, in excess of the expected black-body thermal radiation, from an impinging gas flame. The closely woven fabric is impregnated with the nitrate solution that decomposes on heating to leave the oxide mantle adopting the fine structure of the textile yet having reasonable mechanical stability. The resulting oxide $Ce_{0.01}Th_{0.99}O_2$ has a broad emission band centered around 500 nm covering most of the visible; the trace of cerium moves the emission from the violet end into the visible and hence the emission becomes more pleasing to the eye. In addition it is probable that ceria is acting catalytically to ensure complete combustion.

10.5. Electrorheological Fluids. Researchers have used cerium and titanium dioxide to make an improved electrorheological (ER) fluid. Using an electric field, ER fluids have variable viscosity, stiffness, and heat transference. Under an electric field, the particles in the ER fluid are polarized and organize into chain structures. This increases its viscosity. Cerium-doped titanium dioxide in dimethylsilicone oil had a shear stress five to six times higher than pure titanium dioxide. Potential applications of these fluids are in viscous clutches, variable-cushion shock absorbers, and other variable coupling devices (52).

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