Cerium

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Cerium is a soft, ductile, silvery-white metallic chemical element with symbol **Ce** and atomic number 58. Tarnishing rapidly when exposed to air, it is soft enough to be cut with a knife. Cerium is the second element in the lanthanide series, and while it often shows the +3 state characteristic of the series, it also exceptionally has a stable +4 state that does not oxidise water. It is also traditionally considered to be one of the rare earth elements. Cerium has no biological role, and is not very toxic.

Despite always being found in combination with the other rare earth elements in minerals such as monazite and bastnäsite, cerium is easy to extract from its ores, as it can be distinguished among the lanthanides by its unique ability to be oxidised to the +4 state. It is the most common of the lanthanides, followed by neodymium, lanthanum, and praseodymium. It is the 26th most abundant element, making up 66 ppm of the Earth's crust, half as much as chlorine and five times as much as lead.

The first of the lanthanides to be discovered, cerium was discovered in Bastnäs, Sweden by Jöns Jakob Berzelius and Wilhelm Hisinger in 1803, and independently by Martin Heinrich Klaproth in Germany. It was first isolated by Carl Gustaf Mosander in 1839. Today, cerium and its compounds have a variety of uses: for example, cerium(IV) oxide is used to polish glass and is an important part of catalytic convertors. Cerium metal is used in ferrocerium lighters for its pyrophoric properties.

Characteristics

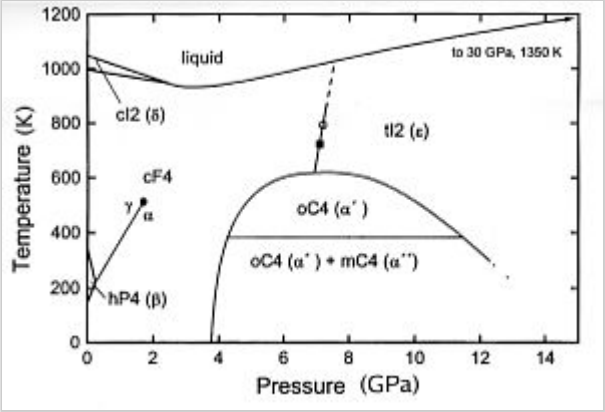
Physical

Cerium is the second element of the lanthanide series. In the periodic table, it appears between the lanthanides lanthanum to its left and praseodymium to its right, and above the actinide thorium. It is a ductile metal with a hardness similar to that of silver.[4] Its 58 electrons are arranged in the configuration [Xe]4f^{1}5d^{1}6s^2, of which the four outer electrons are valence electrons. Immediately after lanthanum, the 4f orbitals suddenly contract and are lowered in energy to the point that they participate readily in chemical reactions; however, this effect is not yet strong enough at cerium and thus the 5d subshell is still occupied.[5] Most lanthanides can only use three

Cerium, $_{58}$Ce

General properties	
Name, symbol	cerium, Ce
Appearance	silvery white
Cerium in the periodic table	
Atomic number (Z)	58
Group, block	group n/a, f-block
Period	period 6
Element category	□ lanthanide
Standard atomic weight (±) (A_r)	140.116(1)[1]
Electron configuration	[Xe] 4f^1 5d^1 6s^2[2]
per shell	2, 8, 18, 19, 9, 2
Physical properties	
Phase	solid
Melting point	1068 K (795 °C, 1463 °F)
Boiling point	3716 K (3443 °C,

electrons as valence electrons, as afterwards the remaining 4f electrons are too strongly bound: cerium is an exception because of the stability of the empty f-shell in Ce^{4+} and the fact that it comes very early in the lanthanide series, where the nuclear charge is still low enough until neodymium to allow the removal of the fourth valence electron.[6]



Phase diagram of cerium

Four allotropic forms of cerium are known to exist at standard pressure, and are given the common labels of α to δ:[7]

- The high-temperature form, δ-cerium, has a bcc (body-centred cubic) crystal structure and exists above 726 °C.
- The stable form below 726 °C to approximately room temperature is γ-cerium, with an fcc (face-centred cubic) crystal structure.
- The dhcp (double hexagonal close-packed) form of β-cerium is the equilibrium structure approximately from room temperature to −150 °C.
- The fcc α-cerium exists below about −150 °C; it has a density of 8.16 g/cm^3.
- Other solid phases occurring only at high pressures are shown on the phase diagram.
- Both γ and β forms are quite stable at room temperature, although the equilibrium transformation temperature is estimated at around 75 °C.[7]

	6229 °F)
Density near r.t.	6.770 g/cm^3
when liquid, at m.p.	6.55 g/cm^3
Heat of fusion	5.46 kJ/mol
Heat of vaporisation	398 kJ/mol
Molar heat capacity	26.94 J/(mol·K)

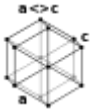
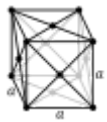
Vapour pressure

P (Pa)	**1**	**10**	**100**	**1 k**	**10 k**	**100 k**
at T (K)	1992	2194	2442	2754	3159	3705

Atomic properties

Oxidation states	**4**, **3**, 2, 1 (a mildly basic oxide)
Electronegativity	Pauling scale: 1.12
Ionisation energies	1st: 534.4 kJ/mol 2nd: 1050 kJ/mol 3rd: 1949 kJ/mol (more)
Atomic radius	empirical: 181.8 pm
Covalent radius	204±9 pm

Miscellanea

Crystal structure	double hexagonal close-packed (dhcp) β-Ce 
Crystal structure	face-centred cubic (fcc) γ-Ce 
Speed of sound	2100 m/s (at 20 °C)

Cerium has a variable electronic structure. The energy of the 4f electron is nearly the same as that of the outer 5d and 6s electrons that are delocalised in the metallic state, and only a small amount of energy is required to change the relative occupancy of these electronic levels. This gives rise to dual valency states. For example, a volume change of about 10% occurs when cerium is subjected to high pressures or low temperatures. It appears that the valence changes from about 3 to 4 when it is cooled or compressed.[8]

At lower temperatures the behavior of cerium is complicated by the slow rates of transformation. Transformation temperatures are subject to substantial hysteresis and values quoted here are approximate. Upon cooling below −15 °C, γ-cerium starts to change to β-cerium, but the transformation involves a volume increase and, as more β forms, the internal stresses build up and suppress further transformation.[7] Cooling below approximately −160 °C will start formation of α-cerium but this is only from remaining γ-cerium. β-cerium does not significantly transform to α-cerium except in the presence of stress or deformation.[7] At atmospheric pressure, liquid cerium is more dense than its solid form at the melting point.[4][9][10]

Isotopes

Naturally occurring cerium is made up of four isotopes: ^{136}Ce (0.19%), ^{138}Ce (0.25%), ^{140}Ce (88.4%), and ^{142}Ce (11.1%). All four are observationally stable, though the light isotopes ^{136}Ce and ^{138}Ce are theoretically expected to undergo inverse double beta decay to isotopes of barium, and the heaviest isotope ^{142}Ce is expected to undergo double beta decay to ^{142}Nd or alpha decay to ^{138}Ba. Additionally, ^{140}Ce would release energy upon spontaneous fission. None of these decay modes have yet been observed, though the double beta decay of ^{136}Ce, ^{138}Ce, and ^{142}Ce has been experimentally searched for. The current experimental limits for their half-lives are:[11]

^{136}Ce: $>3.8\times10^{16}$ y
^{138}Ce: $>1.5\times10^{14}$ y
^{142}Ce: $>5\times10^{16}$ y

thin rod	
Thermal expansion	γ, poly: 6.3 µm/(m·K) (at r.t.)
Thermal conductivity	11.3 W/(m·K)
Electrical resistivity	β, poly: 828 nΩ·m (at r.t.)
Magnetic ordering	paramagnetic[3]
Young's modulus	γ form: 33.6 GPa
Shear modulus	γ form: 13.5 GPa
Bulk modulus	γ form: 21.5 GPa
Poisson ratio	γ form: 0.24
Mohs hardness	2.5
Vickers hardness	210–470 MPa
Brinell hardness	186–412 MPa
CAS Number	7440-45-1
History	
Naming	after dwarf planet Ceres, itself named after Roman deity of agriculture Ceres
Discovery	Martin Heinrich Klaproth, Jöns Jakob Berzelius, Wilhelm Hisinger (1803)
First isolation	Carl Gustaf Mosander (1838)
Most stable isotopes of cerium	

All other cerium isotopes are synthetic and radioactive. The most stable of them are ^{144}Ce with a half-life of 284.9 days, ^{139}Ce with a half-life of 137.6 days, ^{143}Ce with a half-life of 33.04 days, and ^{141}Ce with a half-life of 32.5 days. All other radioactive cerium isotopes have half-lives under four days, and most of them have half-lives under ten minutes.[11] The isotopes between ^{140}Ce and ^{144}Ce inclusive occur as fission products of uranium.[11] The primary decay mode of the isotopes lighter than ^{140}Ce is inverse beta decay or electron capture to isotopes of lanthanum, while that of the heavier isotopes is beta decay to isotopes of praseodymium.[11]

iso	NA	half-life	DM	DE (MeV)	DP
^{134}Ce	syn	3.16 d	ε	0.500	^{134}La
^{136}Ce	0.186%	is stable with 78 neutrons			
^{138}Ce	0.251%	is stable with 80 neutrons			
^{139}Ce	syn	137.640 d	ε	0.278	^{139}La
^{140}Ce	88.449%	is stable with 82 neutrons			
^{141}Ce	syn	32.501 d	β−	0.581	^{141}Pr
^{142}Ce	11.114%	is stable with 84 neutrons			
^{143}Ce	syn	33.039 d	β−	1.462	^{143}Pr
^{144}Ce	syn	284.893 d	β−	0.319	^{144}Pr

The great rarity of the proton-rich ^{136}Ce and ^{138}Ce is explained by the fact that they cannot be made in the most common processes of stellar nucleosynthesis for elements beyond iron, the s-process (slow neutron capture) and the r-process (rapid neutron capture). This is so because they are bypassed by the reaction flow of the s-process, and the r-process nuclides are blocked from decaying to them by more neutron-rich stable nuclides. Such nuclei are called p-nuclei, and their origin is not yet well understood: some speculated mechanisms for their formation include proton capture as well as photodisintegration.[12] ^{140}Ce is the most common isotope of cerium, as it can be produced in both the s- and r-processes, while ^{142}Ce can only be produced in the r-process. Another reason for the abundance of ^{140}Ce is that it is a magic nucleus, having a closed neutron shell (it has 82 neutrons), and hence it has a very low cross-section towards further neutron capture. Although its proton number of 58 is not magic, it is granted additional stability, as its eight additional protons past the magic number 50 enter and complete the 1 $g_{7/2}$ proton orbital.[12] The abundances of the cerium isotopes may differ very slightly in natural sources, because ^{138}Ce and ^{140}Ce are the daughters of the long-lived primordial radionuclides ^{138}La and ^{144}Nd.[11]

Bibliography

- Wikipedia: Cerium