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UNESCO
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2019 IYPT
International Year
of the Periodic Table
of Chemical Elements

The Elements: #22

Titanium (German: Titan)

„Element of Low Density and High Strength“

Titans:

Race of Greek Gods

Background

History of Titanium

1791 Titanium discovered by English chemist William Gregor in Ilmenite

1795 Impossible to isolate Ti from minerals → therefore called by Martin Klaproth in honor of Titans – gods of Ancient Greek mythology

1910 Finally isolated by heating titanium tetrachloride ($TiCl_4$)

WWII First applications: Parts of military aircrafts

1950s Still the most used alloy Ti-6Al-4V developed in Soviet Union, very soon also produced in United States

1950s Onward of applications in military and civilian aircraft industry and in space program

1960s Development and production of new alloys in USA, Russia, and Japan

Since 1990s Mass production in China

Background

Origin in Nature – Titania minerals

TiO_2	Rutil, Anatas, Brookit
$FeTiO_3$	Ilmenite
$CaTiO_3$	Perovskite
$CaTiO[SiO_4]$	Titanite

Rutile - TiO_2

Anatase - TiO_2

Ilmenite - $FeTiO_3$

Physical Properties

Relative atomic mass:	47.867 g/mol
Atomic radius:	147 pm
Density:	4.5 g/cm^3
Melting point:	1668 °C
Boiling point:	3287 °C
Electron configuration:	[Ar]4s^{2}3d^2
Oxidation states:	+4, +3, +2
Electronegativity:	1.3
Crystal structure:	hexagonal close packed (hcp)
Mohs hardness:	6.0
1st Ionisation energy:	658.8 kJ/mol
Stable isotopes:	Ti-46: 8.25 %
	Ti-47: 7.44 %
	Ti-48: 73.72 %
	Ti-49: 5.41 %
	Ti-50: 5.18 %

Synthesis and Purification of Titanium

Lab synthesis: $TiO_2 + 2\ CaH_2 \rightarrow Ti + 2\ H_2 + 2\ CaO$

Kroll process: $TiCl_4 + 2\ Mg \rightarrow Ti + 2\ MgCl_2$

Titanium is separated from the blend of Titanium, Magnesium dichloride, and Magnesium residues by high temperature vacuum sintering

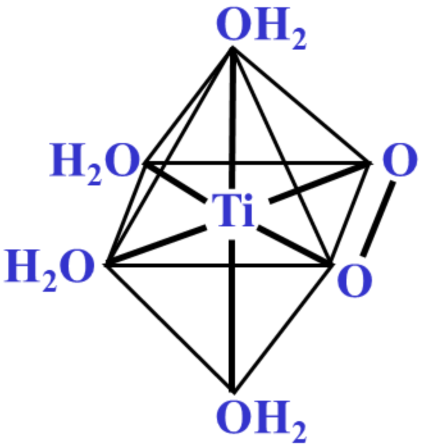
Magnesium dichloride is cleaved into Mg and Cl_2 by electrolysis. The resulting material is brittle and porous → Titanium sponge

Purification by Arkel-de Boer process:
$TiI_4 \leftrightarrows Ti + 2\ I_2$ (hot W-wire) $\Rightarrow$ Highly purified Titanium

Chemistry of Titanium

Titanium(IV) compounds

[Ar] configuration ⇒ most stable oxidation state, colourless
Ti^{4+} is small and highly charged ⇒ strongly polarising (high ion charge density)
$Ti^{4+} + 6\ H_2O \rightarrow 2\ H^+ + [Ti(OH)_2(OH_2)_4]^{2+}$ “cation base“
In aqueous solution, there are thus no Ti^{4+} cations but aqua hydroxo complexes that can be verified by the reaction with H_2O_2:



$[Ti(OH)_2(OH_2)_4]^{2+} + H_2O_2 \rightarrow [Ti(O_2)(OH_2)_4]^{2+} + 2\ H_2O$
(orange-yellow)

Treatment of TiO_2 with HNO_3 or H_2SO_4 yields double salts
$TiO_2 + H_2SO_4 \rightarrow TiO(SO_4) + H_2O$
$TiO_2 + 2\ HNO_3 \rightarrow TiO(NO_3)_2 + H_2O$
that contain polymeric Ti-O-Ti-O-Ti zig-zag chains

However, the reaction of Ti^{4+}-containing solutions with oxalates yield tetramers: $4\ [Ti(OH)_2(OH_2)_4]^{2+} + 8\ C_2O_4^{2-} \rightarrow [Ti_4O_4(C_2O_4)_8]^{8-}$

Applications

Overview

- **Aerospace industry - jet engines, aircraft construction (low specific density)**
- **Pipes – chemical and petrochemical industry (unaltered corrosion resistance)**
- **Part of deep-sea oil wells (low specific density, excellent corrosion resistance)**
- **Medicine – orthopedic implants, fixing devices (non-toxic metal and oxide TiO_2, high strength)**
- **Sporting goods – golf clubs, tennis rackets, bicycles (high strength accompanied by relatively low elastic modulus)**
- **Jewellery, architecture, outdoor equipment (high strength and high resistance)**

Applications

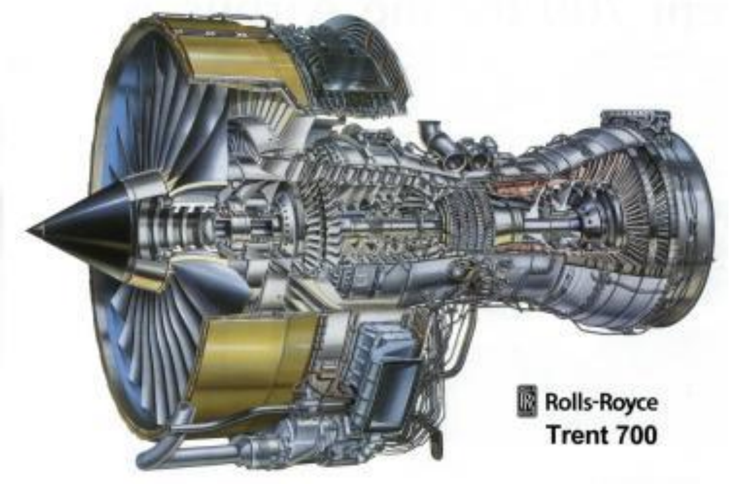
Aerospace industry

- **The first commercial application of titanium alloys since the mid of 1950s**
- **Ti content in aircraft construction**

  Airbus – 5 % of mass is Ti
  Boeing – 10 % of mass is Ti
  Carbon composite (Boeing 787 – Dreamliner) are used at the extent of aluminum – relative content of Ti is still growing
- **Aircraft engines**

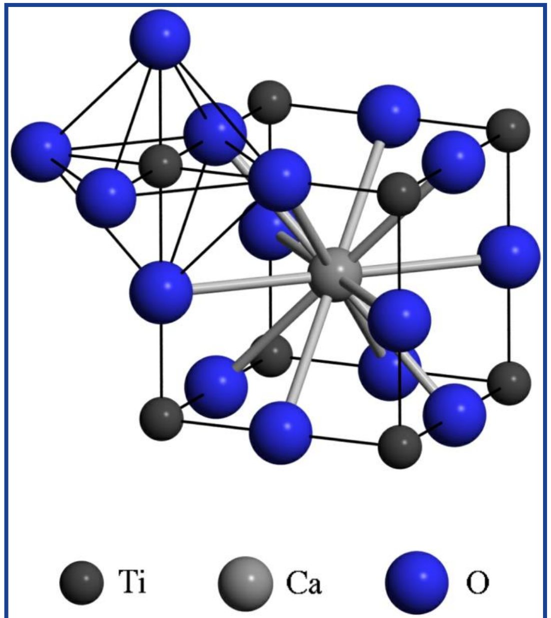
  25% of mass is Ti (service temperature up to 500 °C)

Blackbird SR-71



Applications

Perowskites ABX_3



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- $CaTiO_3$, $SrTiO_3$, $BaTiO_3$, $PbTiO_3$, KIO_3, $LaCoO_3$, ...
- Cubic primitive unit cell, i.e. $\alpha = ß = \gamma = 90°$, $a = b = c$
- Corner connected TiO_6-octahedra
- Me^+, Me^{2+}, Me^{3+} occupy twelvefold coordinate voids

Ferroelectrics

- Possess areas (domains) in the crystal which are uniformly polarised in one spatial dimension
- These domains exhibit a permanent dipole moment
- Throughout the whole crystal, the differently polarized domains are distributed statistically $\Rightarrow$ compensation dipole moments
- When introduced to an electrical field, the dipole moments are going to align themselves
  $\Rightarrow$ The orientation partly persists even after the cut-off of the electrical field (storage effect)
  $\Rightarrow$ Ferroelectricity (cooperative phenomenon)
- $BaTiO_3$ is particularly strong ferroelectric ($\varepsilon \sim 1000$) $\Rightarrow$ application in capacitor ceramics

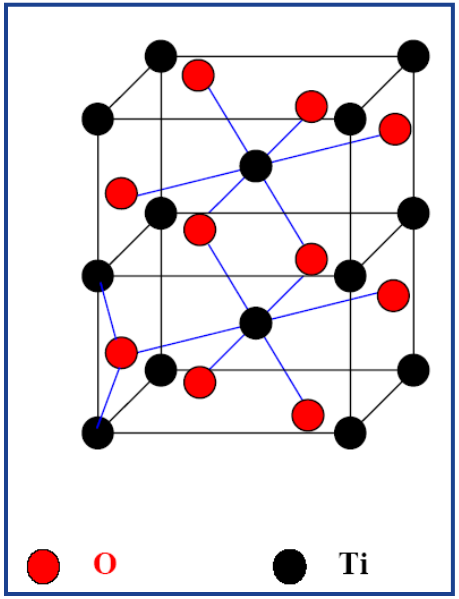
Applications

Titanium dioxide TiO_2

Structure
- Ti is coordinated octahedrally by Oxygene
- 3 modifications: rutile, brookite, anatase

⇒ Different connectivity of TiO_2-octahedra

Rutile structure

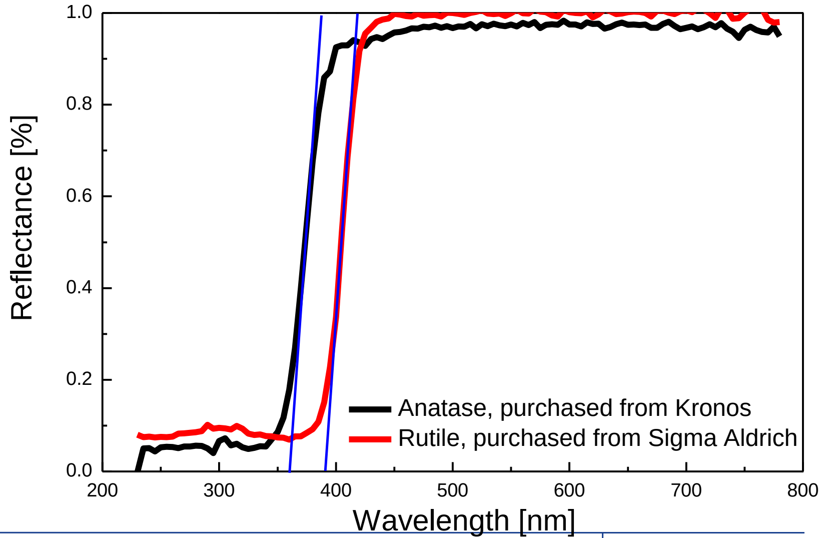


Properties
- Photocatalytic activity: Anatase

  $TiO_2 + h\nu \rightarrow TiO_2^*(e^- + h^+)$

  $TiO_2^*(e^- + h^+) + A + D \rightarrow TiO_2 + A^- + D^+$
- High refractive index: Rutile

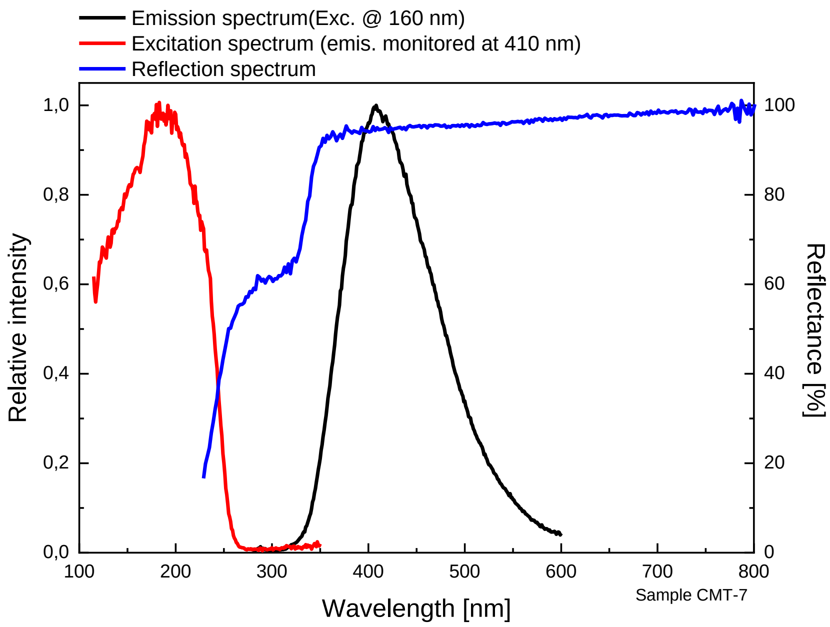
Modification	E_g [eV]	E_g [nm]	n
Anatase	3.5	360	2.55
Rutile	3.2	390	2.79



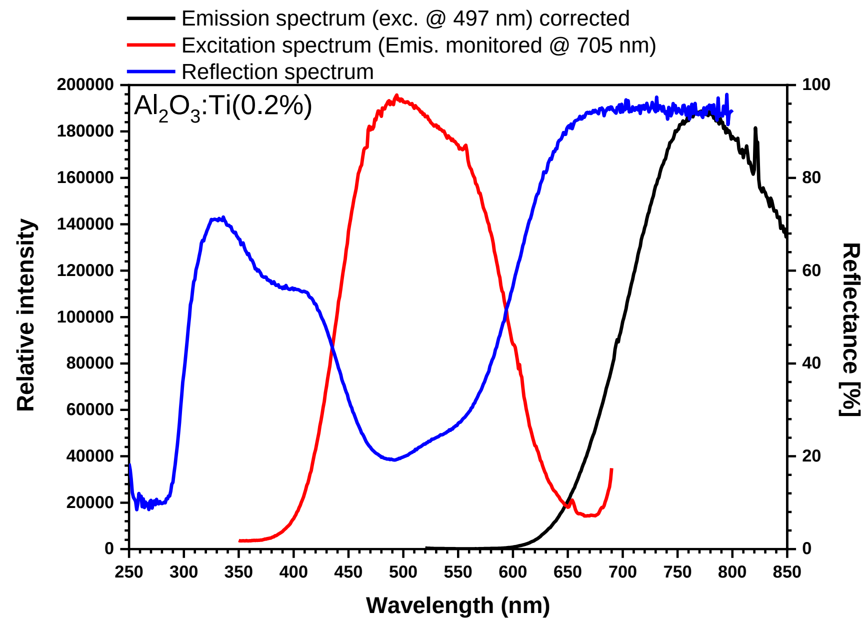
Applications

Solid state compounds doped by Ti cations show strong luminescence

$CaMgSi_2O_6$:Ti



Al_2O_3:Ti



Sapphire as a gain medium for tuneable solid state laser