Ceramics

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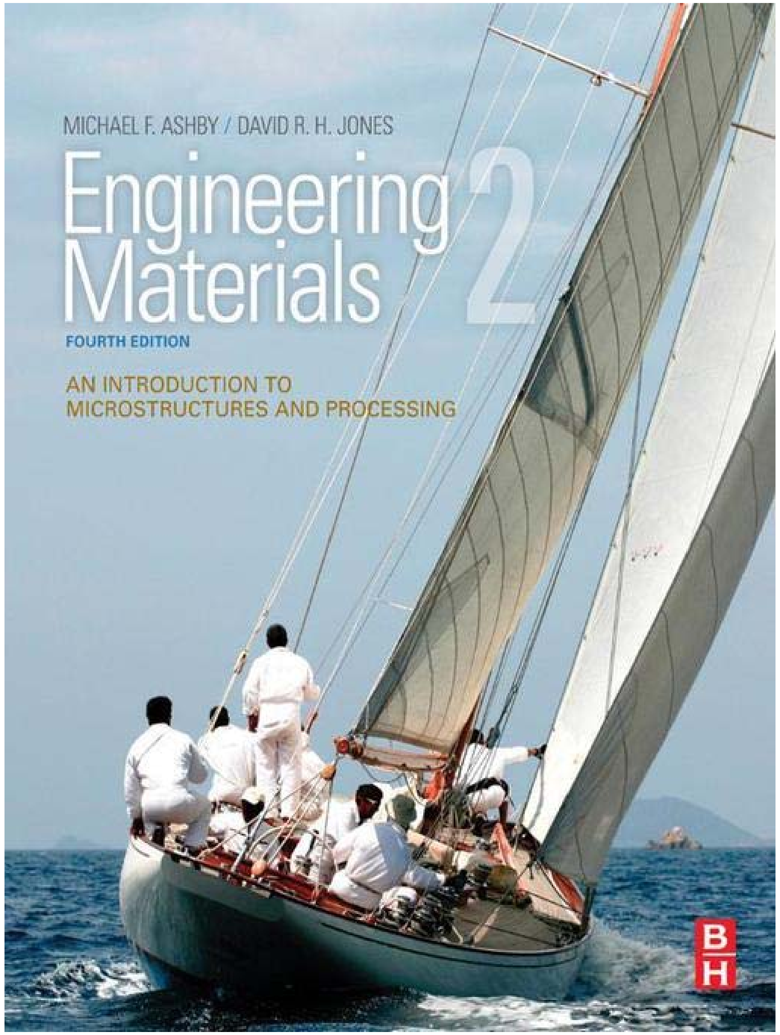
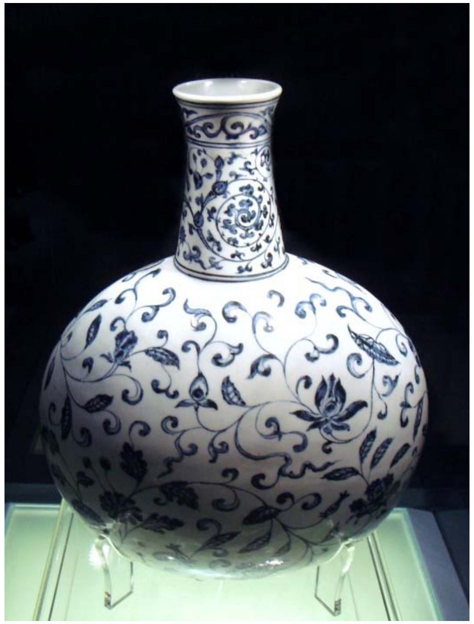
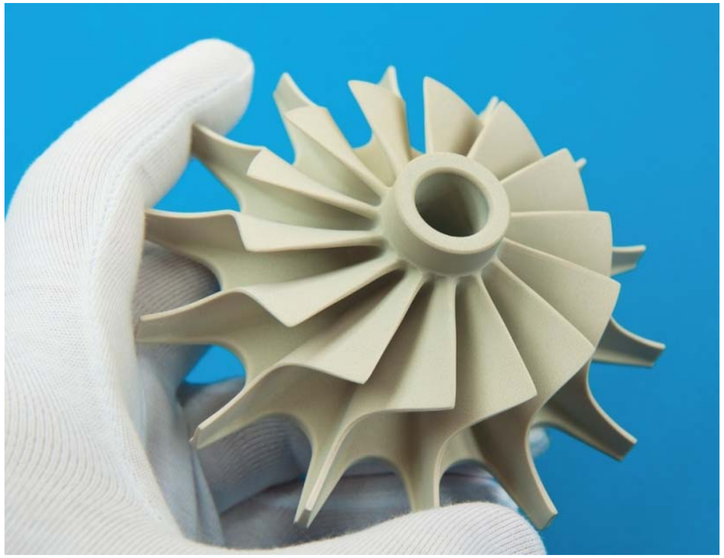
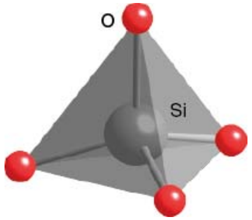
Reference Book



Chapters:
17-18-19



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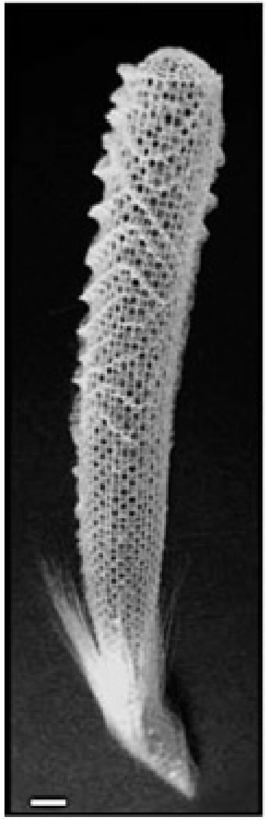
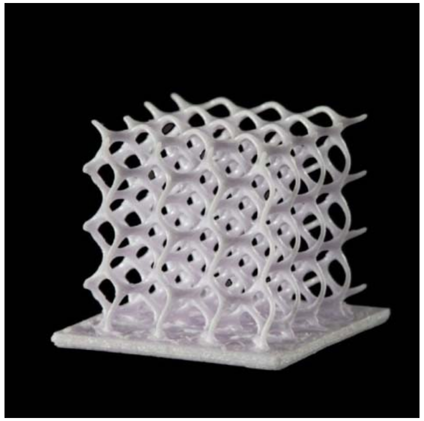




Ceramics

- Inorganic, non metallic solids
- Structure: crystalline, amorphous or a mixture of both
- Elements: oxygen, carbon or nitrogen + metals (aluminum or silicon)
- “keramikos” (of pottery): materials which are “fired” at high temperature (e.g., roof tiles made in terra-cotta)
- Includes naturally occurring materials such as rocks and stones
  - igneous → formed at high temperature
  - sedimentary → formed at low temperature, often by deposition / crystallization of water

Ceramics

- General features:
  - hard (diamond is the hardest material known)
  - inherently brittle
  - chemically stable
  - refractory (melt or soften at high temperature)
  - electrical insulators (carbon in the form of graphite is an exception)
  - Optically transparent (glass)

Ceramics

- Ceramic materials include 5 main classes:
  a) **Glasses**: all based on silica (SiO_2) with additions to reduce the melting point or to give other properties (reduce brittleness)
  b) **Traditional vitreous ceramics** (or clay products) used for plates, cups, sanitary ware, tiles, bricks, …
  c) **High-performance ceramics** developed within the last 60 years and finding increasing applications for resistance to wear, temperature and high biocompatibility
  d) **Cement and concrete**: complex ceramics with many phases, one (of the three) essential bulk material for civil engineering
  e) **Rocks and minerals** (including ice)

Glasses

- Based on silica (SiO_2 silicon dioxide)

  →[Si and O being the two most abundant elements in the earth's crust]

- Two primary interest: common window glass and temperature-resisting borosilicate glass

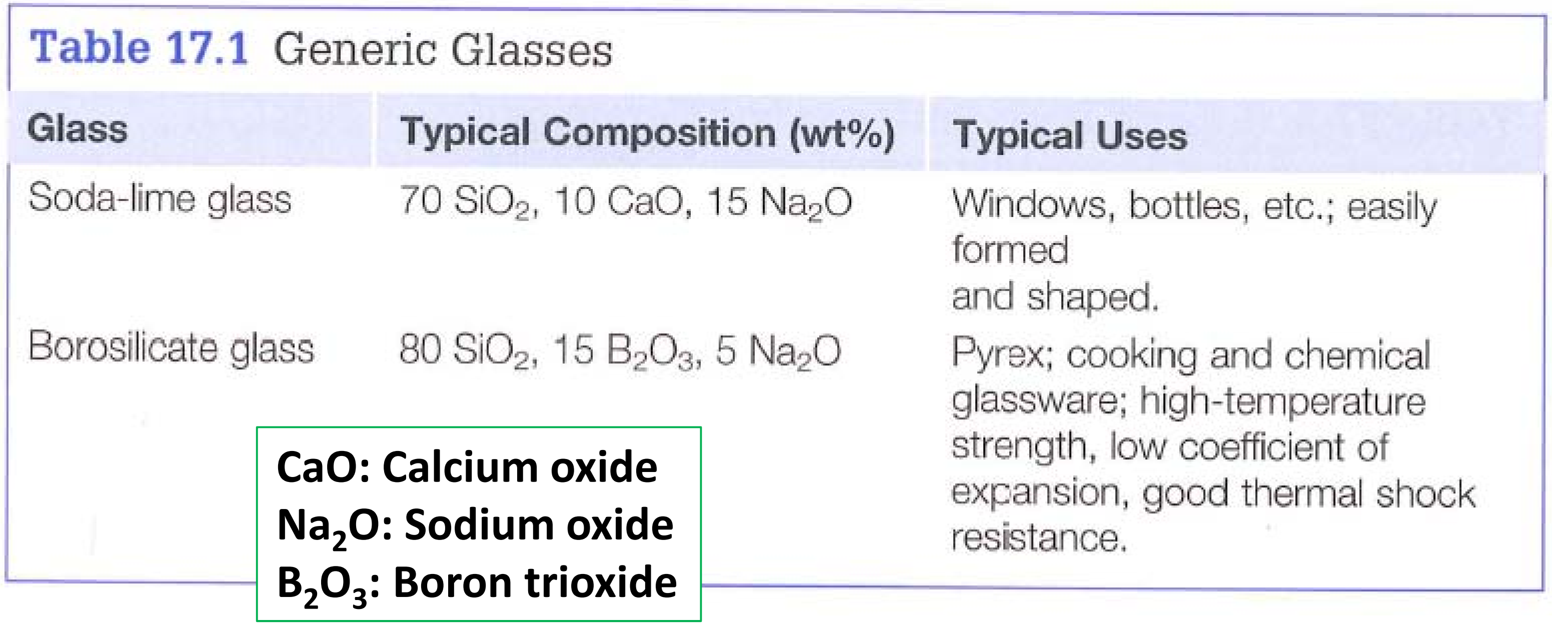
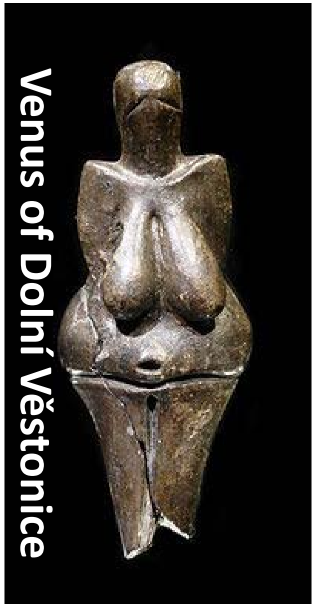


Table 17.1 Generic Glasses

Glass	Typical Composition (wt%)	Typical Uses
Soda-lime glass	70 SiO_2, 10 CaO, 15 Na_2O	Windows, bottles, etc.; easily formed and shaped.
Borosilicate glass	80 SiO_2, 15 B_2O_3, 5 Na_2O	Pyrex; cooking and chemical glassware; high-temperature strength, low coefficient of expansion, good thermal shock resistance.

CaO: Calcium oxide
Na_2O: Sodium oxide
B_2O_3: Boron trioxide

Vitreous Ceramics



- Pottery: present in our societies since ancient time (~**30.000** years BC)
- Thanks to pottery we know the state of development and cultures of ancient populations
- Process to make modern pottery, porcelain, tiles, … is not very different form 2000 years ago: the starting point is wet clay which is dried and fired.

→ Structure: crystalline phase held together by a glassy (amorphous) phase based on silica (SiO_2). The glassy phase melt when the clay is fired and spreads around the surface of the inert (but strong) crystalline phase, acting as a "glue" among crystalline regions

Vitreous Ceramics

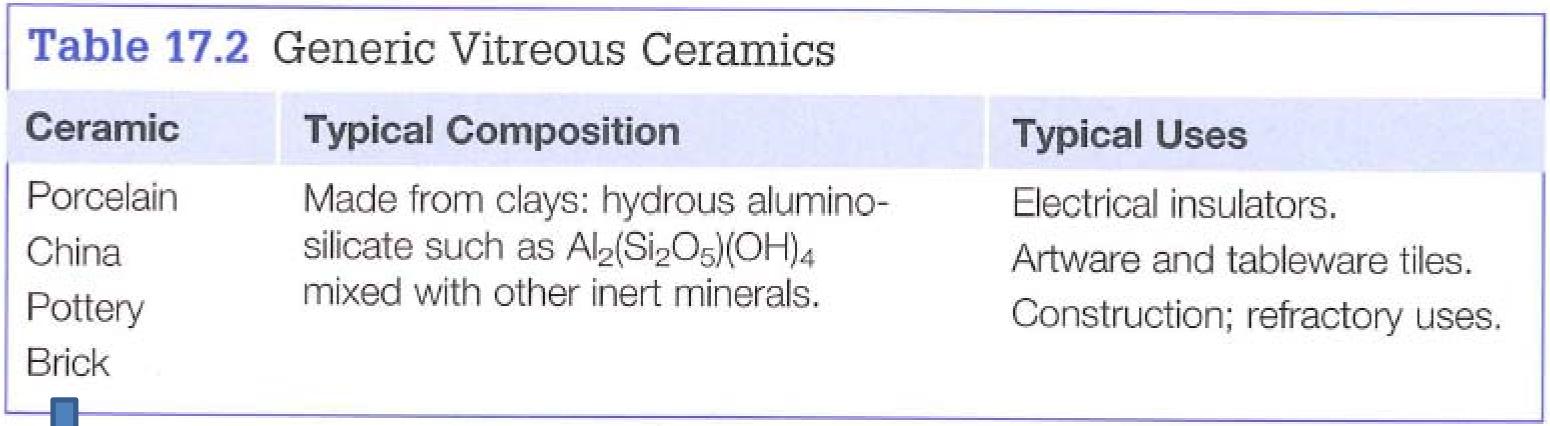
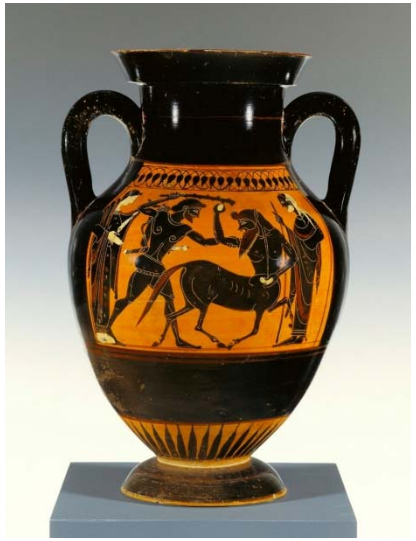


Table 17.2 Generic Vitreous Ceramics

Ceramic	Typical Composition	Typical Uses
Porcelain China Pottery Brick	Made from clays: hydrous alumino-silicate such as $Al_2(Si_2O_5)(OH)_4$ mixed with other inert minerals.	Electrical insulators. Artware and tableware tiles. Construction; refractory uses.

Depending on composition and firing conditions

Porcelain



Pottery

Brick

High-performance Engineering Ceramics

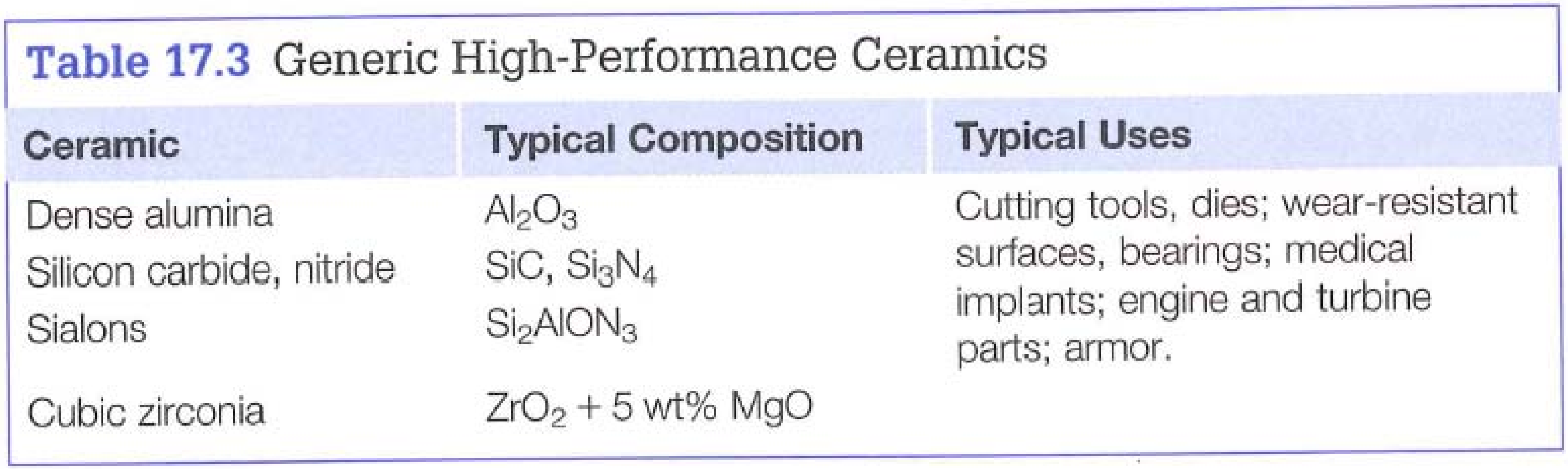


Table 17.3 Generic High-Performance Ceramics

Ceramic	Typical Composition	Typical Uses
Dense alumina	Al_2O_3	Cutting tools, dies; wear-resistant surfaces, bearings; medical implants; engine and turbine parts; armor.
Silicon carbide, nitride	SiC, Si_3N_4	
Sialons	Si_2AlON_3	
Cubic zirconia	$ZrO_2 + 5$ wt% MgO	

FROM: CERADYNE.COM

Natural Ceramics

- Stone: oldest of all construction materials (and most durable). Often the criteria used when design a material with stone are very similar to other ceramics.
- Ice: a unique natural ceramics. Its mechanical properties are of major importance in engineering applications such as the construction of offshore oil and gas rings in polar regions

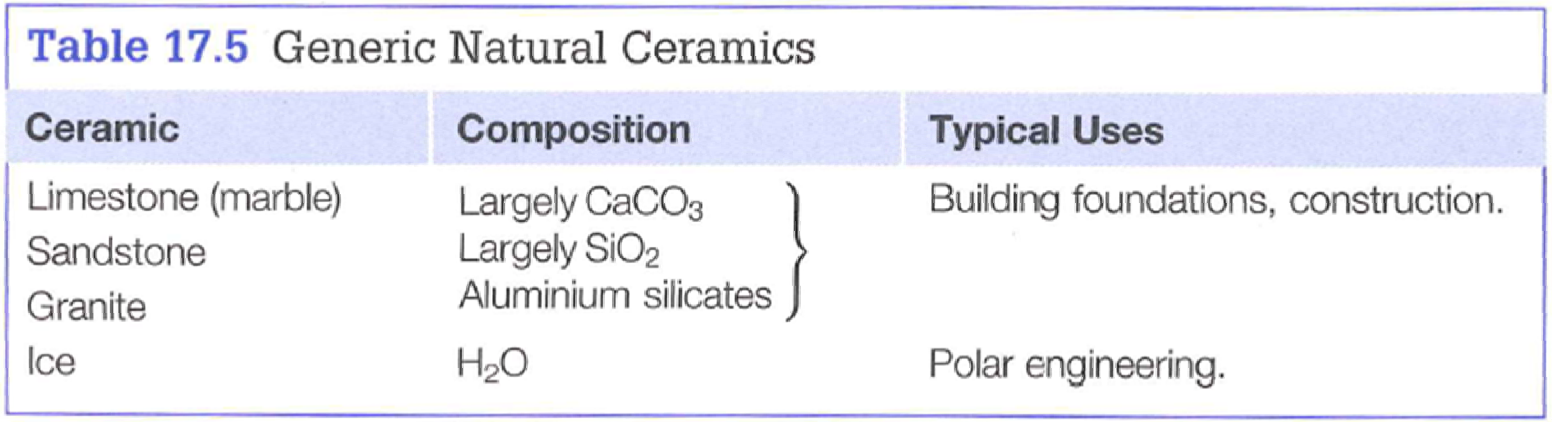


Table 17.5 Generic Natural Ceramics

Ceramic	Composition	Typical Uses
Limestone (marble)	Largely $CaCO_3$	Building foundations, construction.
Sandstone	Largely SiO_2	
Granite	Aluminium silicates	
Ice	H_2O	Polar engineering.

Cement and Concrete

- Cement an concrete are ubiquitously used in construction engineering (used as much as steel, brick and wood)
- **Cement**: mixture of lime (CaO), silica (SiO_2) and alumina (Al_2O_3)
- **Concrete**: sand and stone held together by cement

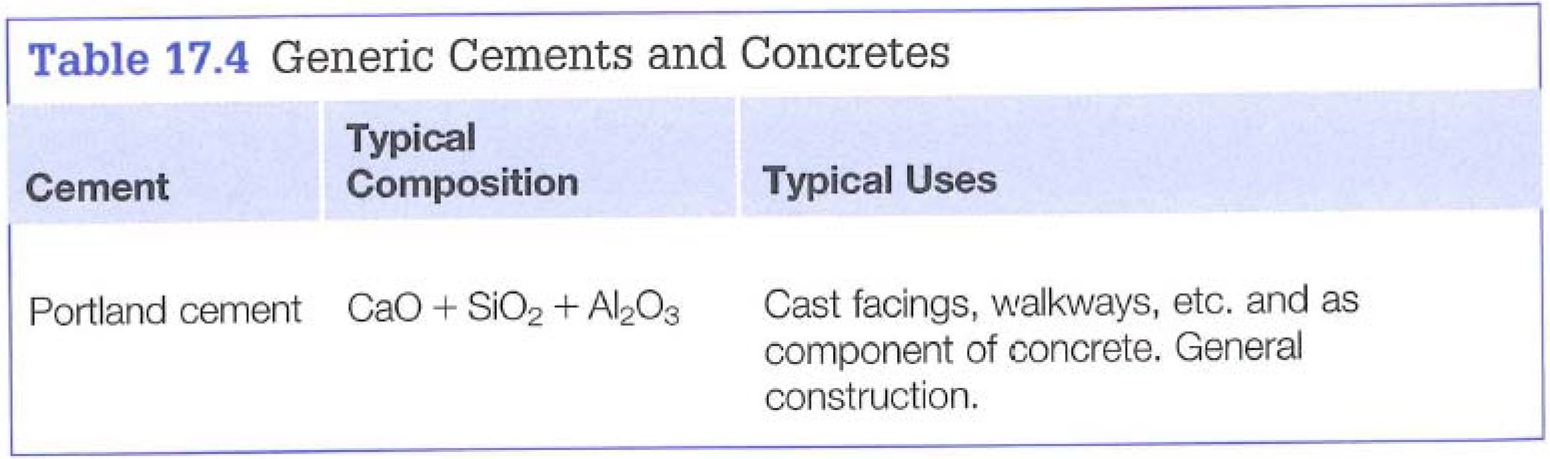


Table 17.4 Generic Cements and Concretes

Cement	Typical Composition	Typical Uses
Portland cement	$CaO + SiO_2 + Al_2O_3$	Cast facings, walkways, etc. and as component of concrete. General construction.

Ceramic Composites

- Often the great stiffens and hardens of ceramics are combined with the toughness of polymers and metals to form composite
- The hard phase (ceramics) gives stiffness and the soft phase (polymer) gives toughness
- Bone is a natural ceramics composite
- Synthetic ceramic-ceramic composites

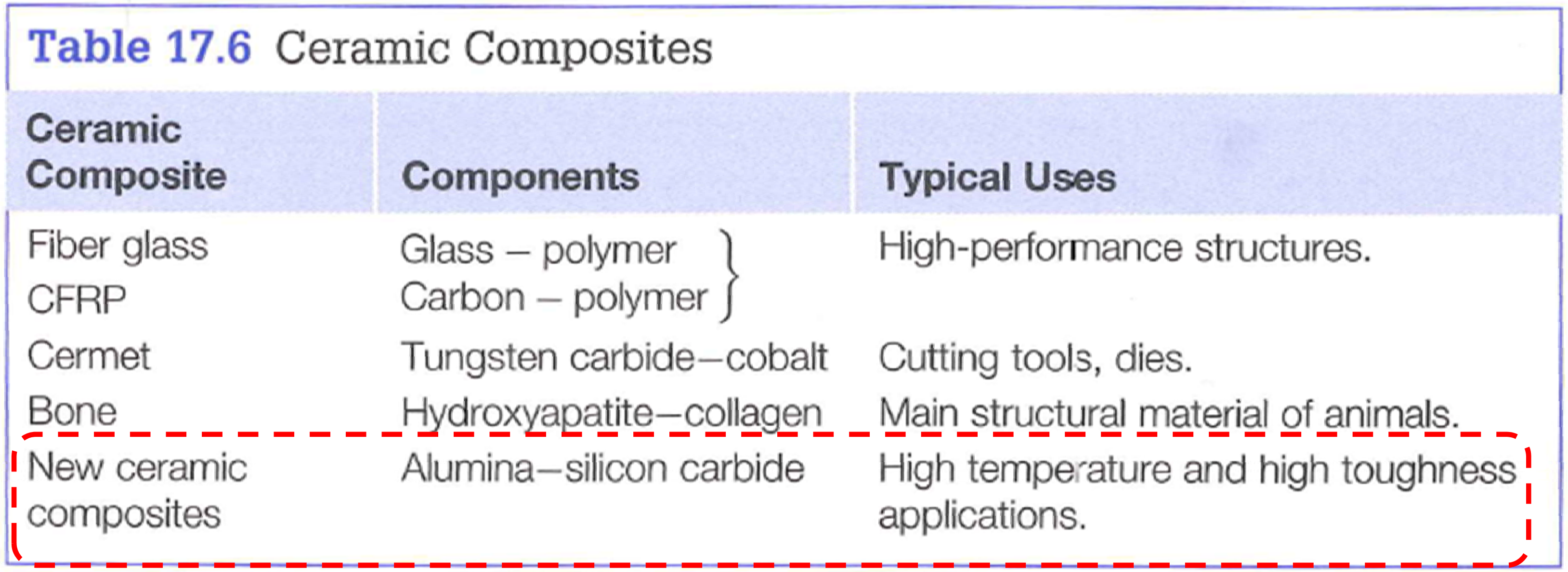
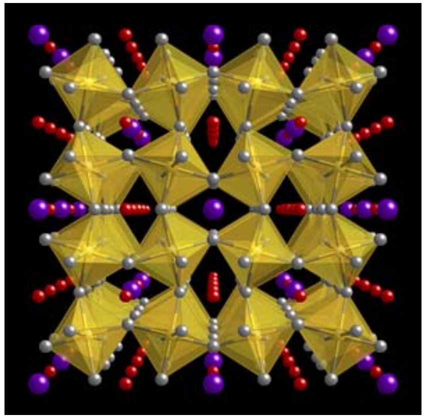


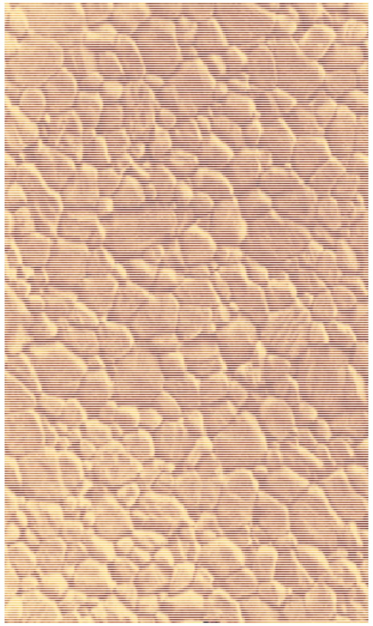
Table 17.6 Ceramic Composites

Ceramic Composite	Components	Typical Uses
Fiber glass	Glass – polymer	High-performance structures.
CFRP	Carbon – polymer	
Cermet	Tungsten carbide–cobalt	Cutting tools, dies.
Bone	Hydroxyapatite–collagen	Main structural material of animals.
New ceramic composites	Alumina–silicon carbide	High temperature and high toughness applications.

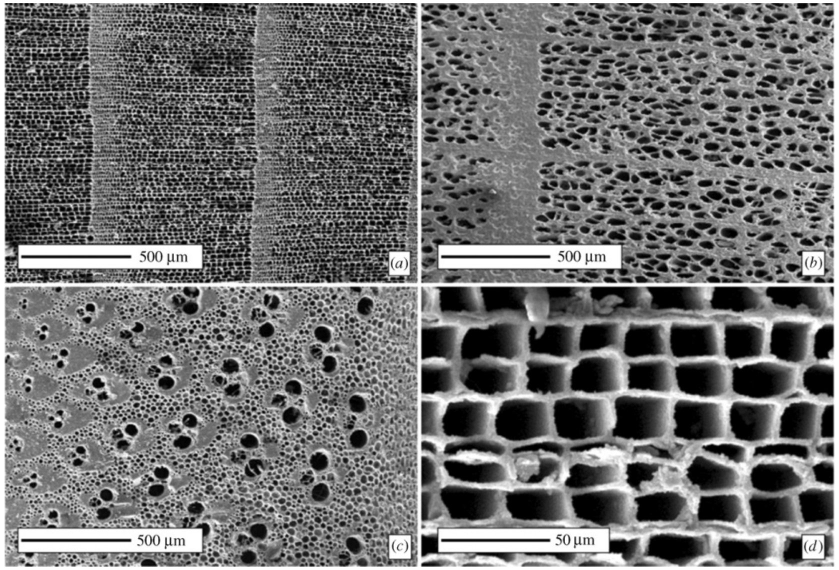
Ceramic Structures



0.1 – 1 nm



1 – 1000 nm

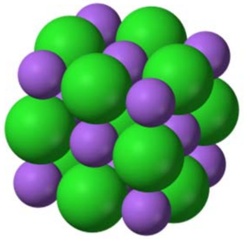


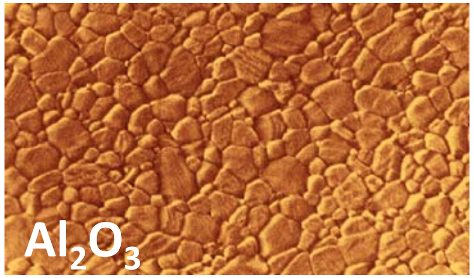
1 – 1000 µm

Ceramic Structures

Ceramic (like metals) has structural features at various length scales:

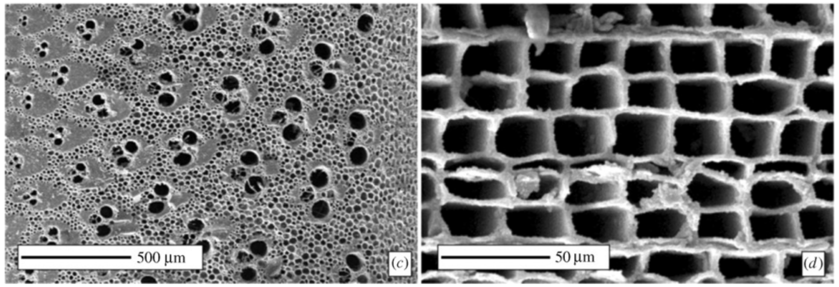
- structure at ~**10^{-10} m** (atomic scale): crystal or amorphous (glassy) structure





- structure at **10^{-9} – 10^{-6} m**: shape and arrangement of grains

- structure **10^{-6} – 10^{-3} m**: shape and size of pores



Ionic and Covalent Ceramics

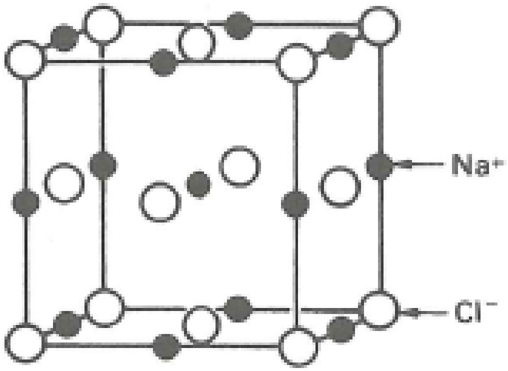
- Ceramics (predominantly) **ionic**:
  - **metal** + **nonmetal**
  - examples: sodium chloride (NaCl), magnesium oxide (MgO), alumina (Al_2O_3), zirconia (ZrO_2)
  - ionic bonding: metal and nonmetal have unlike electric charges → bonding mainly due to **electrostatic attraction** between unlike ions (Na^+, Cl^-)
  - packing: ions pack **densley** ($^+$ & $^-$ charges as close as possible) but with the constrain that ions of the same type must not touch

Ionic and Covalent Ceramics

- Ceramics (predominantly) **covalent**:
  - compounds of **two non-metals** (silica, SiO_2) or of **pure elements** (diamond or silicon)
  - covalent bonding: atoms bond by sharing electrons with the neighbors to give a **fixed number of directional bonds**
  - Packing: energy is minimize not by dense packing but by forming chains, sheets and three-dimensional networks (→ often non crystalline)
  - example: all commercial glasses have 3D amorphous networks based on silica (SiO_2)

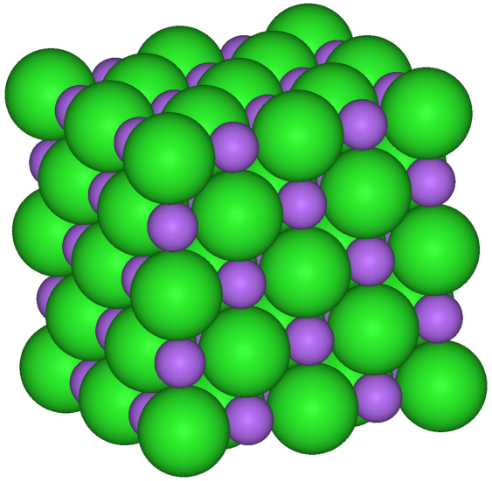
Simple Ionic Ceramic

- Sodium chloride (NaCl)
- Packing: maximum electrostatic interaction (high density & minimum energy) is achieved when each Na^+ is surrounded by 6 Cl^- and no Na^+ nearest neighbors (and vice versa)



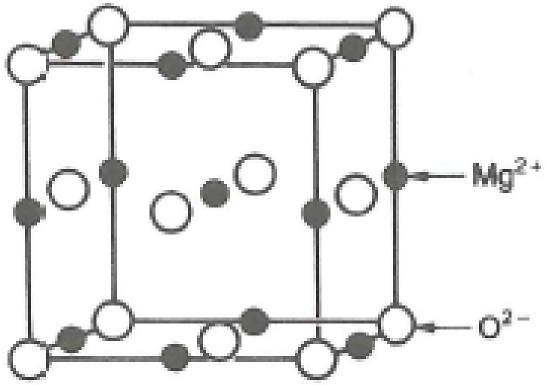
there is no better way of arranging single-charged ions than this

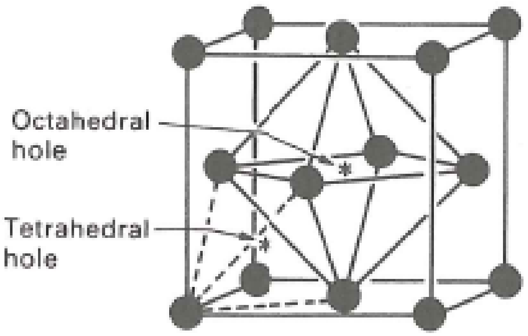
all ceramics with the formula AB have the rock salt structure



Simple Ionic Ceramic

- Magnesia (MgO) (engineering ceramics used as refractory in furnaces, melting point: 2000 °C)
- Alternative view of packing (useful to understand more complicated arrangements):
  - O^{2-} forms a f.c.c. (face centered cubic) packing
  - f.c.c. contains two sorts of interstitials holes: larger **octahedral** holes (one for each O^{2-}) and smaller **tetrahedral** holes (two for each O^{2-})

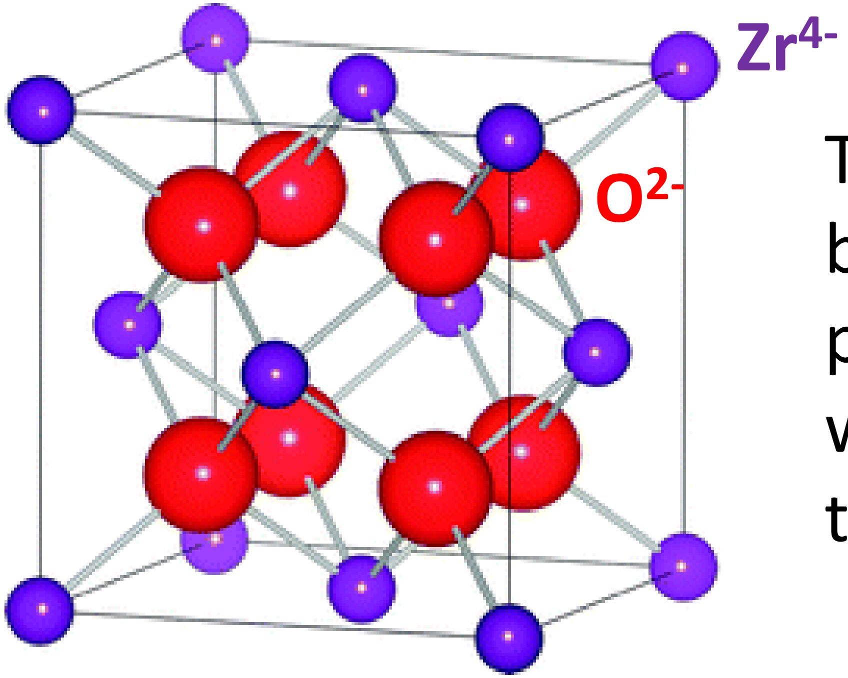




MgO can be interpreted as a f.c.c. packing of O^{2-} with a Mg^{2+} squeezed into the **octahedral holes**

Simple Ionic Ceramic

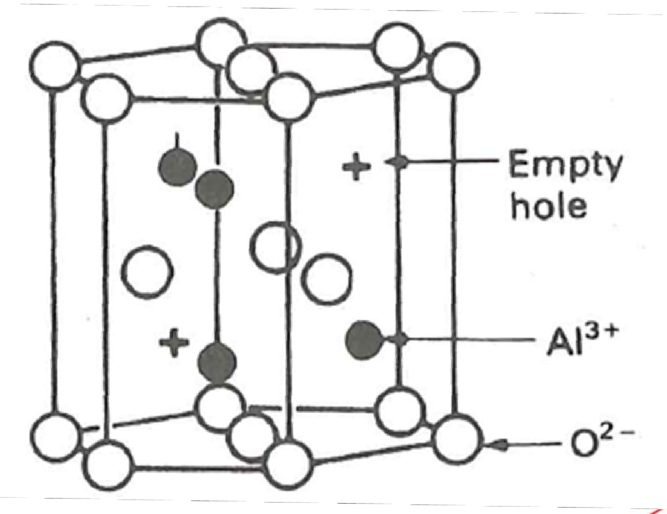
- Cubic zirconia (ZrO_2) (engineering ceramics of growing importance → similar to diamond but much cheaper)



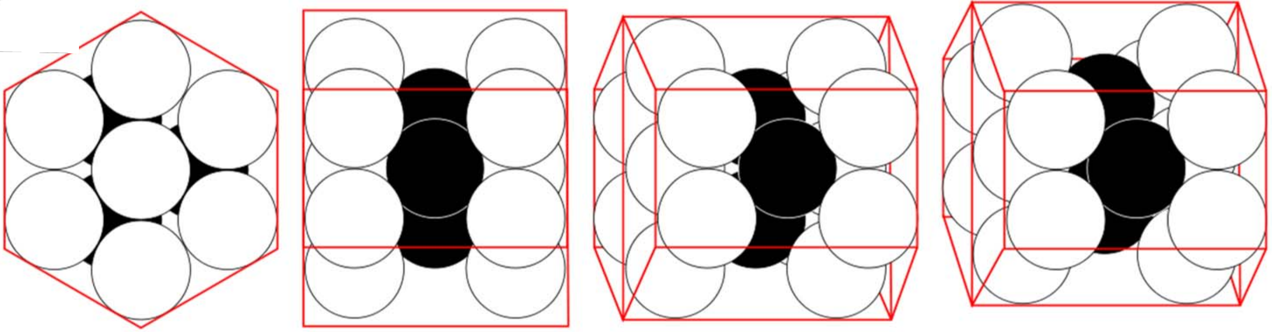
The structure of ZrO_2 can be described as a **f.c.c.** packing of Zr^{4+} (zirconium) with a O^{2-} squeezed into the **tetrahedral holes**

Simple Ionic Ceramic

- Alumina (Al_2O_3) (structural ceramics used for cutting tools, grinding wheels andas component in brick and pottery)



The structure of Al_2O_3 can be described as a **h.c.p.** (hexagonal close pack) packing of O^{2-} with Al^{3+} squeezed into the **octahedral hole**



hexagonal close pack (h.c.p.)

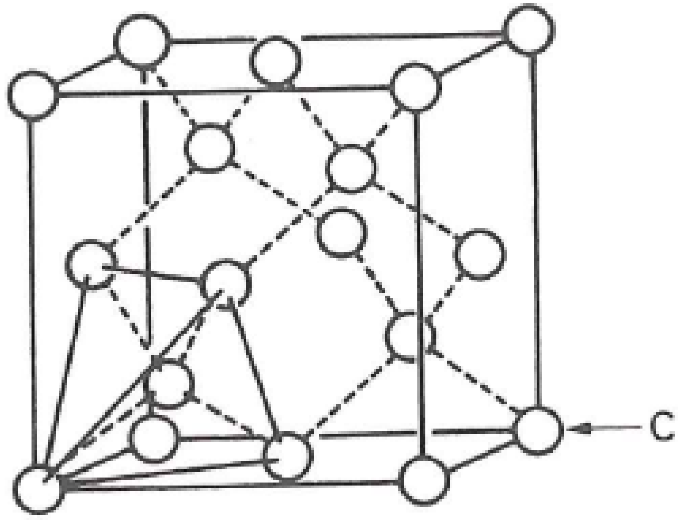
Simple Ionic Ceramic

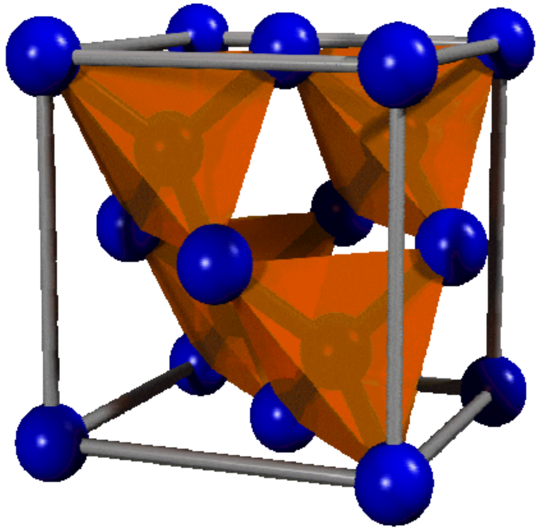
Crystalline Structure:

→ dense (f.c.c. or h.c.p.) of oxygen with various metal ions arranged (in an orderly fashion) in the octahedral or tetrahedral holes

Simple Covalent Ceramic

- Diamond (excellent strength, wear resistance & thermal conductivity)





Structure: each C atom is at the center of a tetrahedron with its four bonds directed to the four corners of the tetrahedron

Question: is the structure of diamond a closed-packed structure?

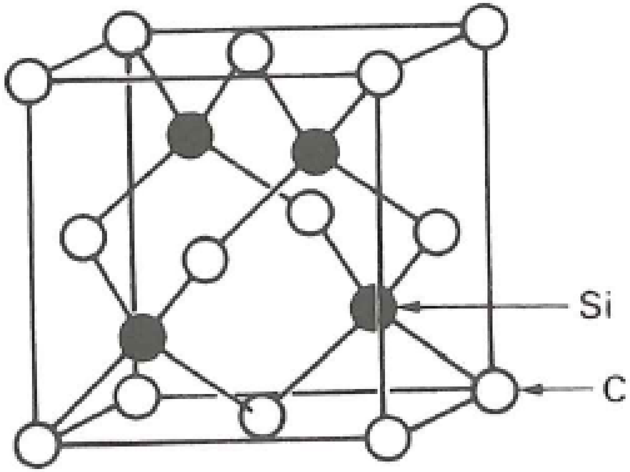
NO! neighbors are 4 (and not 12) → density is lower

Simple Covalent Ceramic

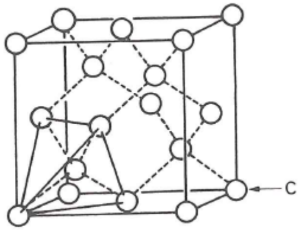
- silicon carbide (SiC) & silicon nitride (Si_3N_4)

very hard structural ceramics used for load bearing components such as engine parts and high temperature bearings

SiC (sphalerite structure)

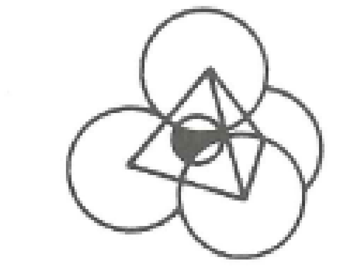


very similar to the structure of diamond but with every second C atom replaced by silicon

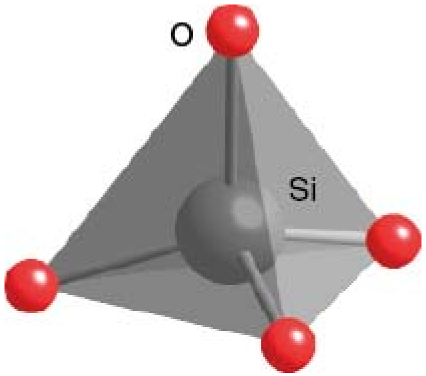


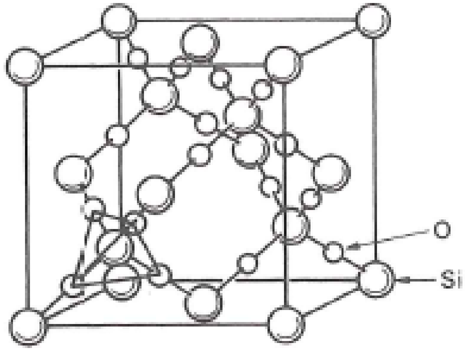
Silica and Silicates

- Silicates are main components in earth crust and also the most widespread raw material used by humans
- Basic “repeating” unit of silicates: tetrahedral units (1 silicon atom strongly bonded with 4 oxygen atoms)



(a) SiO_4 monomer





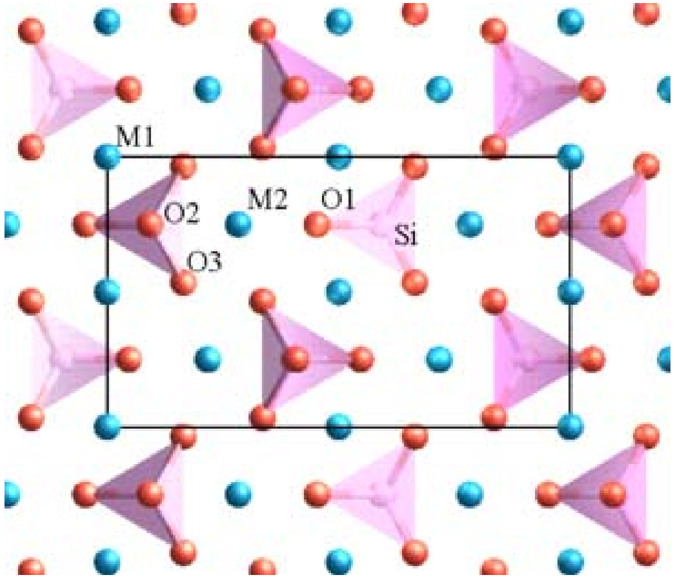
(c)

- “Silicate monomers” are linked to each other directly (pure silica) or indirectly via a metal ion (M link)
- Pure silica contains no M ions and every oxygen is a bridge between silicon atoms (diamond cubic structure with C replaced by SiO_4)

Silica and Silicates

"Polymerization" of silica:

- If silica is combined with metal oxide (MgO, CaO, Al_2O_3) such as: MO / $SiO_2 \geq 2 / 1$ → the resulting silicate is made up of several separate (SiO_4) monomers linked by the metal oxide molecules (e.g. olivine)

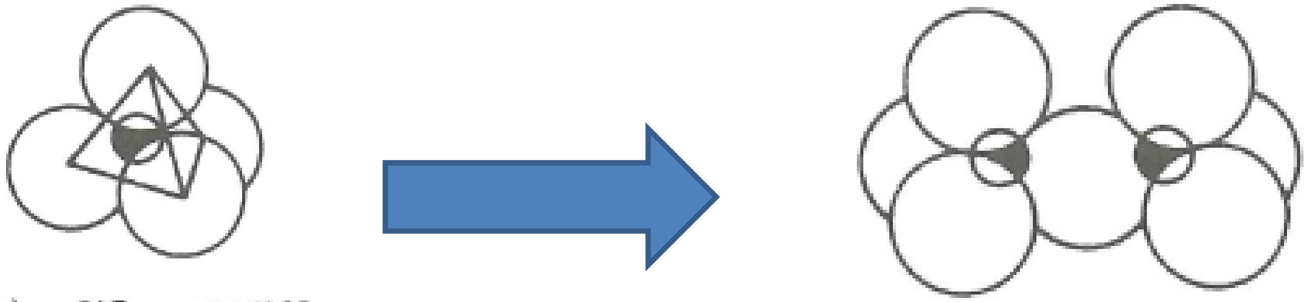


Oxygen is shown in red, silicon in pink, and magnesium/iron in blue. A projection of the unit cell is shown by the black rectangle.

Silica and Silicates

“Polymerization” of silica:

- If MO / SiO_2 a bit less than 2 / 1 → formation of silica dimer (one oxygen is sheared between two tetrahedra).
  - This is the first step in the “polymerization” of the monomer to give chains, sheets and networks. The shared oxygen is called bridging oxygen

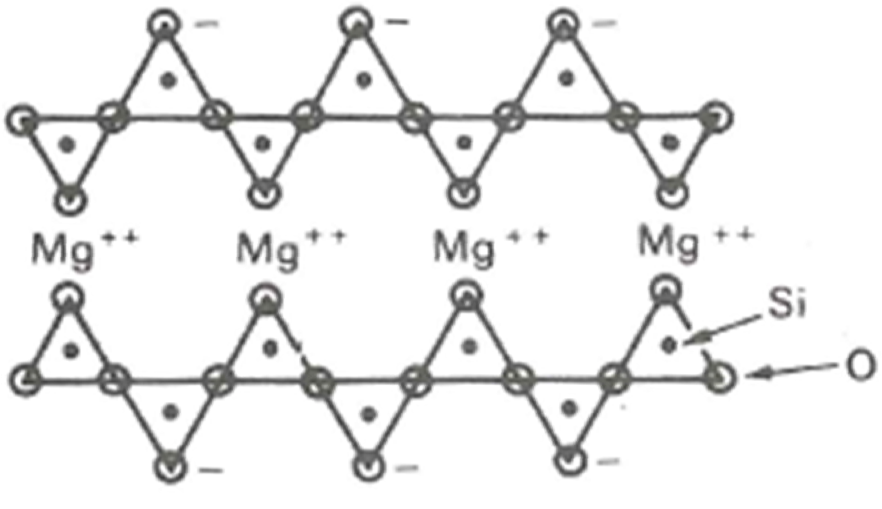


(a) SiO_4 monomer

SiO_7 dimer

Silica and Silicates: Chains

- With decreasing amount of metal oxide, the degree of polymerization increases and chains of linked tetrahedra form (like long chains of polymer but with a backbone of –Si-O-Si-O-Si-)
- In the chain, two oxygen of the tetrahedra are shared and the third oxygen forms ionic bonds between chains joined by metal oxide (MO) → fibrous silicates

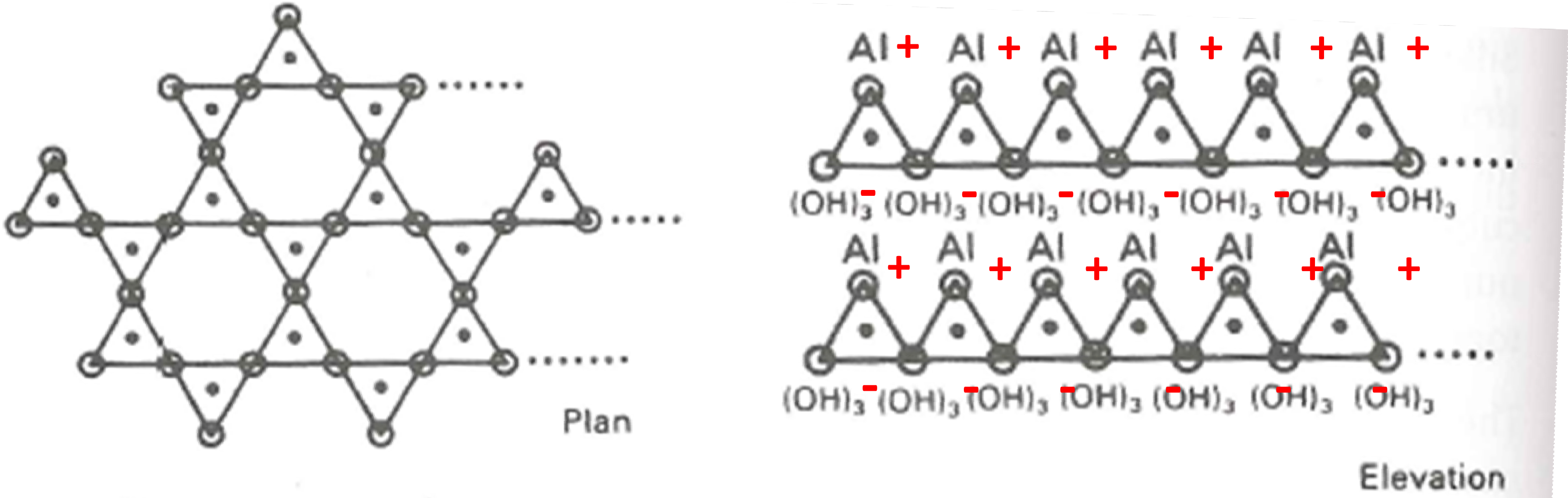


(c) Chain silicates (Enstatite, $MgSiO_3$)

Asbestos fibers

Silica and Silicates: Sheets

- If three oxygen of each tetrahedron are shared → formation of sheet structures (e.g. clay)

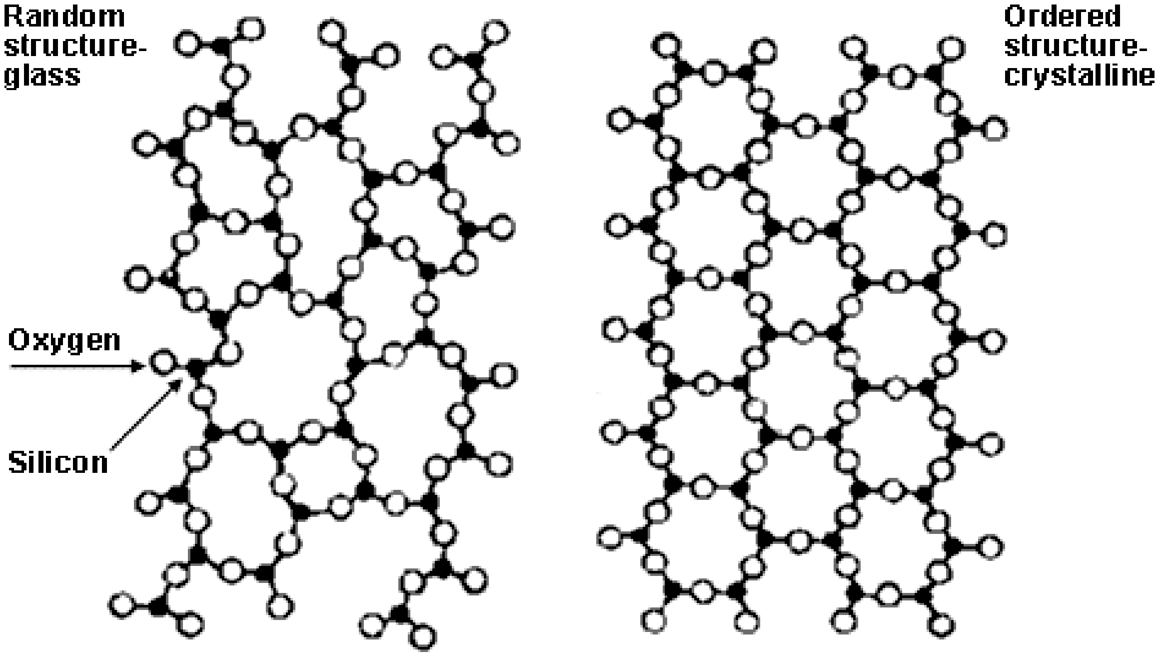


(d) Sheet silicate (clays)

- The additional MO attach to one side of the sheet (the side of the spare oxygen) → the sheet is polarized (positive charge on one surface and negative charge on the other) → layer of water between the sheets (give plasticity to clay as layers can slide over each other)

Silicate Glasses

- Commercial glasses are based on silica: they are made of the same SiO_4 tetrahedra of crystalline silicates BUT they are amorphous

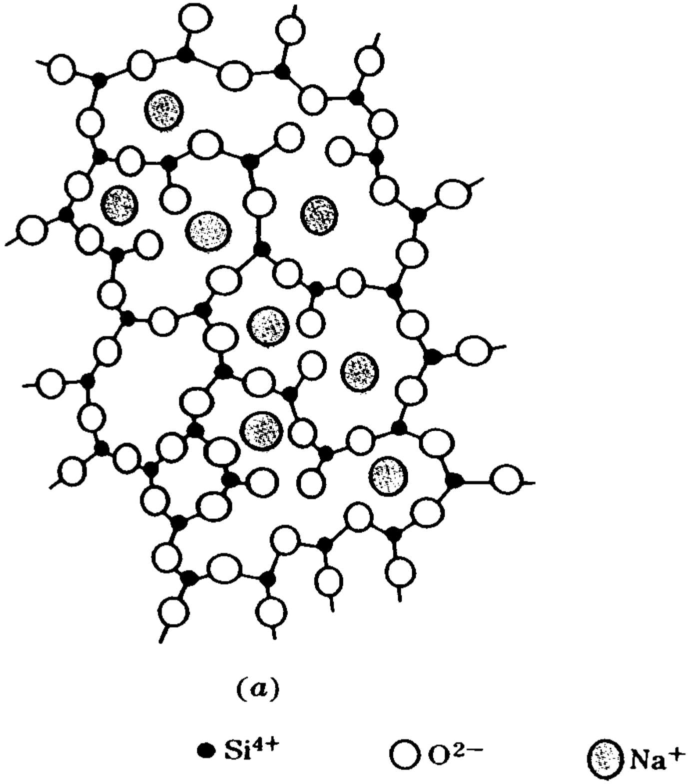


(Note: the fourth oxygen for each tetrahedra is not shown)

- The tetrahedra link at the corners to give a random network (bonding requirements are still satisfied)
- Pure silica forms a glass with high softening temperature (1200 °C), high strength and low thermal expansion BUT high viscosity → hard to work!

Silicate Glasses

- The viscosity can be reduced by introducing network modifiers (e.g. metal oxides Na_2O) which brake up the network by attaching to the oxygen of the tetrahedra
- The reduction in cross-linking soften the glass by reducing the glass temperature (temperature at which the glass is solid)
- Common window glass is 70% SiO_2 → it can be easily worked at 700 °C

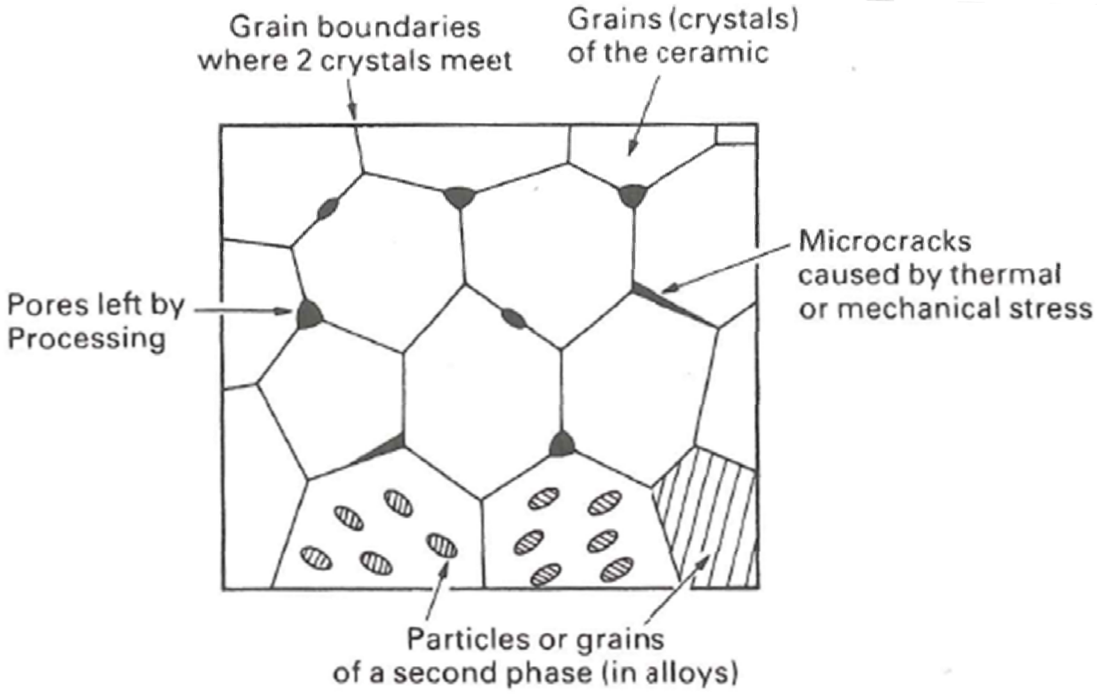


non-crystalline

- Pyrex glass is 80% SiO_2 (i.e. it contains less modifiers) but it requires higher temperatures (>800 °C) to work with

Microstructures of Ceramics

- Crystalline ceramics form **polycrystalline** microstructures (very like those of metals)



microstructural features of ceramics

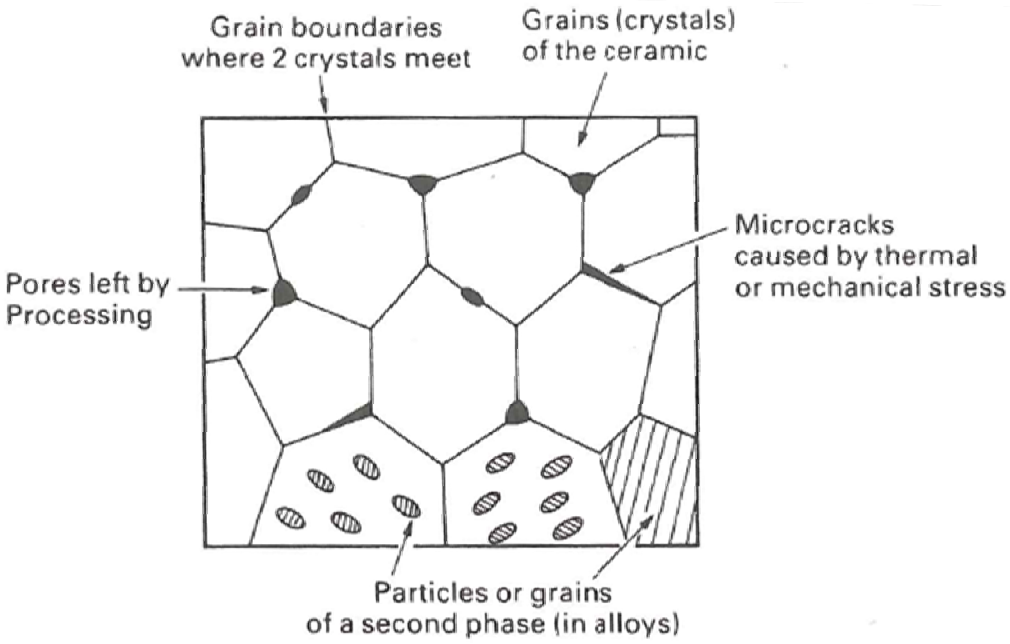
each grain is a fairly perfect crystal (ionic ceramic) meeting its neighbors at the grain boundaries

the structure at the grain boundaries is a bit more complicated as for metals since:

- ions with the same sign must avoid each other
- valence requirements must be met

Microstructures of Ceramics

- Most ceramics are not fully dense but have some porosity (up 20%)



microstructural features of ceramics

The pores weaken the material, however if they are well rounded, the stress concentration is small

More damaging is due to **cracks** (coming from processing or nucleated by differences in thermal expansion or modulus between grains or phases)

→ Recent developments in ceramics processing aim at reducing size and number of cracks and pores.

Mechanical Properties of Ceramics

Elastic Moduli

- Ceramics (like metals but unlike polymers) have a well defined Young's modulus
- In ceramics moduli are higher than those of metals reflecting the higher stiffness of ionic (simple oxides) and covalent (silicates) bonding
- Since ceramics are composed of light atom (O, C, Si, Al) often not close-packed, they have small densities

Material	Modulus E [GPa]	Density ρ [kg/m³]	Specific modulus E/ρ
Steels	210	7.8×10^3	27
Al alloys	70	2.7×10^3	26
Alumina, Al_2O_3	390	3.9×10^3	**100**
Silica, SiO_2	69	2.6×10^3	27
Cement	45	2.4×10^3	19

→ very high specific modulus (often used in composites)

Hardness

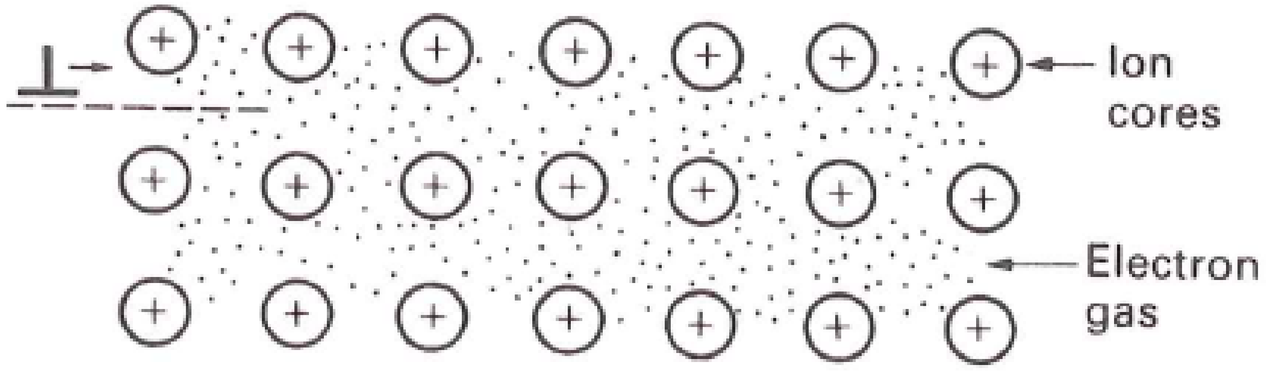
- Ceramics are the hardest of solids
- Corundum (a crystalline form of Al_2O_3), silicon carbide (SiC) and diamond (C) are used for abrasives

Pure Metal	H/E	Metal Alloy	H/E	Ceramics	H/E
Copper	1.2×10^{-3}	Brass (Cu Zn)	9×10^{-3}	Diamond	1.5×10^{-1}
Aluminum	1.5×10^{-3}	Dural (Al 4% Cu)	1.5×10^{-2}	Alumina	4×10^{-2}
Nickel	9×10^{-4}	Stainless steel	6×10^{-3}	Zirconia	6×10^{-2}
Iron	9×10^{-4}	Low alloy steel	1.5×10^{-2}	Silicon carbide	6×10^{-2}
MEAN	**1×10^{-3}**	MEAN	**1×10^{-2}**	MEAN	**8×10^{-2}**

- In metals, making alloys is a very efficient way to increase hardness and yield strength ($H \approx 3\sigma_y$)
- **Why do ceramics have such a high hardness ?**

Hardness & Lattice Resistance

- **Yielding** of ceramics or metals (e.g. in a tensile test or indentation test) implies the **movement of dislocations** through its structure
- Each yield test measures the “difficulty” of **moving material dislocations**
- Dislocations in metals (intrinsically soft materials):

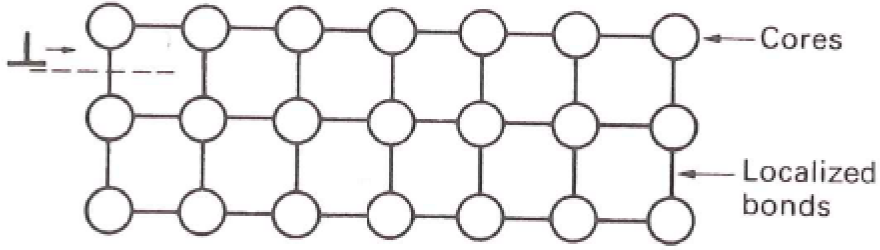


(a) Metal

- Electrons lost by metal atoms form a gas which moves freely around the ion cores
- Binding energy is due to electrostatic interaction between ions and the negative electron gas → bonds are not localized
- A travelling dislocation displays the atom above the slip plane over those below. This has only a small effect on electron-ion bonding → only a **small drag** on the moving dislocation → metals are **intrinsically soft**

Hardness & Lattice Resistance

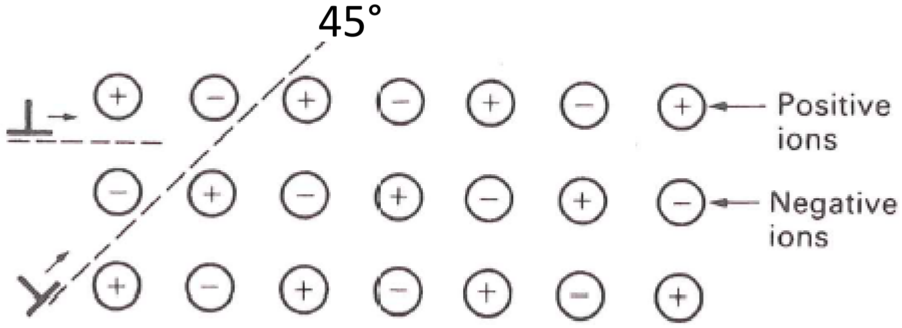
- Ceramics are **intrinsically hard**: ionic or covalent bonds present enormous lattice resistance to the motion of dislocation



(b) Covalent ceramic

Covalent ceramics

- Covalent bond is **localized**
  (e$^-$ are concentrated in the region between the bonded atoms)
- A moving dislocation must break and reform these bonds
  → **big drag** on moving dislocation



(c) Ionic ceramic

Ionic ceramics (NaCl)

- Electrostatic force
- crystal sheared on 45°: the like ions remain separated → **small drag**
- crystal sheared at 0°: it carries like ion in close contact → **big drag**

→ hardness of ionic ceramic is high BUT may be low if loaded along particular directions

Hardness & Lattice Resistance

- What about polycrystalline ceramics?

  → many slip phenomena are required and some of them may be hard

  → polycrystalline ionic ceramic is usually hard (but not as hard as covalent)

- In ceramics at room temperature the stress required to move dislocations is ~E/30 (in metals ~E/1000)

  → the yield strength of ceramics is very high: ~ **5 GPa**

- In ceramics the only way to measure yield strength is through indentation as in “standard” experimental testing ceramics will break before yielding

- In engineering design and materials selection with ceramics it is (almost) never necessary to consider plastic collapse as fracture will always occur first!

Brittle (or Fast) Fracture

- In brittle materials, the onset of brittle (or fast) fracture is given by:

$$\boxed{\sigma\sqrt{\pi a} = \sqrt{E\,G_c}}$$

"left side" of equation:
fracture will occur when in a material subject to a stress ***σ*** a crack reaches a critical size ***a***
OR when a material containing a crack of size ***a*** reaches a critical stress ***σ***

"right side" of equation:
depend only on material constants:
E: Young's modulus
G_C: energy to make a unit area of crack [KJ/m^2]

- The critical combination of stress and crack length at which a fast fracture will occur is a material constant $\sigma\sqrt{\pi a}$
- $\sigma\sqrt{\pi a} = K$ stress intensity factor [MN $m^{-3/2}$]
- $\sqrt{EG_c} = K_c$ critical stress intensity factor (or fracture toughness) [MN $m^{-3/2}$]

$$\boxed{K = K_c}$$

→ fracture will occur!!!

Fracture Strength of Ceramics

- The penalty of choosing a material with such high hardness is brittleness

  → the **fracture toughness of ceramics is low**

Material	**Fracture Toughness K_c [MN $m^{-3/2}$]**
Cement, ice	**0.2** MN$m^{-3/2}$
Traditional ceramics (brick, pottery, …)	0.5 -2 MN$m^{-3/2}$
Engineering ceramics (SiO_2, Al_2O_3, …)	**4** MN$m^{-3/2}$

Steel: ≈50 MPa $m^{1/2}$

- The low fracture toughness make ceramics a defect-sensitive material. Additionally, many ceramics contain cracks and flaws left by the production process (e.g. voids left between particles from which ceramics is fabricated)
- The tensile strength of ceramics is determined by the low fracture toughness K_c (material property) in combination with the length of the cracks (due to manufacturing or handling).

If the longest microcrack within a sample has length of $2a_m$, the **tensile strength** is:

$$\sigma_{TS} \approx \frac{K_c}{\sqrt{\pi a_m}}$$

Fracture Strength of Ceramics

- Exercise: compute the size of the typical larger crack-like defects in some ceramics knowing the tensile strength and the toughness:

Engineering ceramics: σ_{TS}= 200 MPa; K_c =2 $MNm^{-2/3}$
Pottery, brick and stones: σ_{TS}= 20 MPa; K_c =1 $MNm^{-2/3}$
Cement: σ_{TS}= 2 MPa; K_c =0.2 $MNm^{-2/3}$

$$\boxed{\sigma_{TS} \approx \frac{K_c}{\sqrt{\pi a_m}}}$$

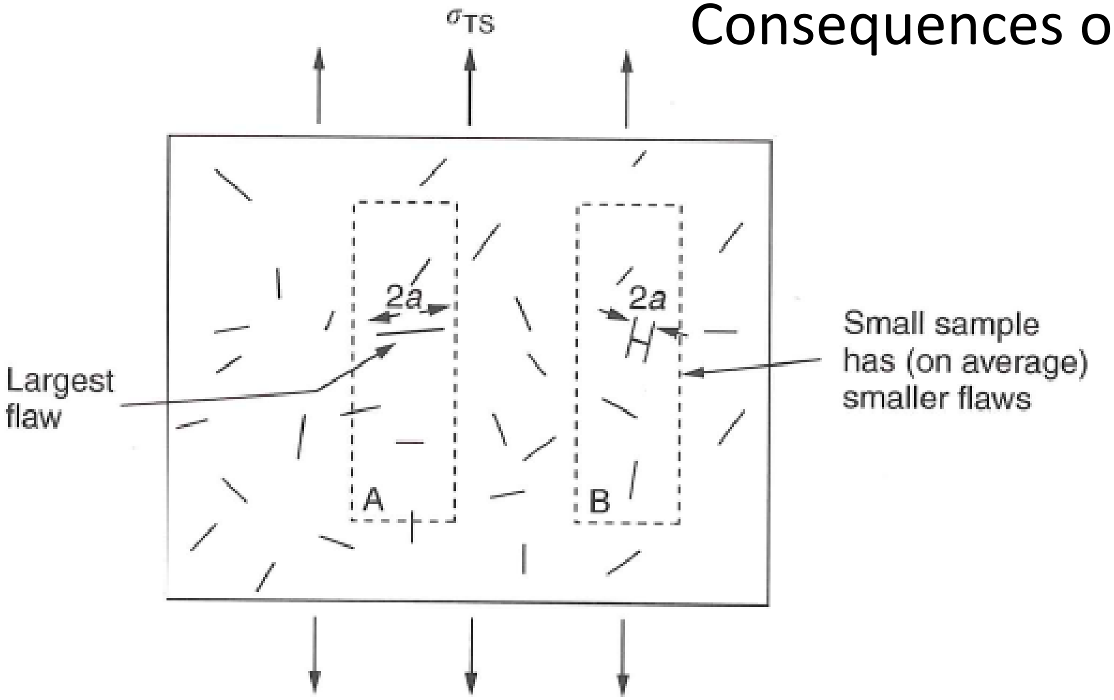
The Statistics of Strength

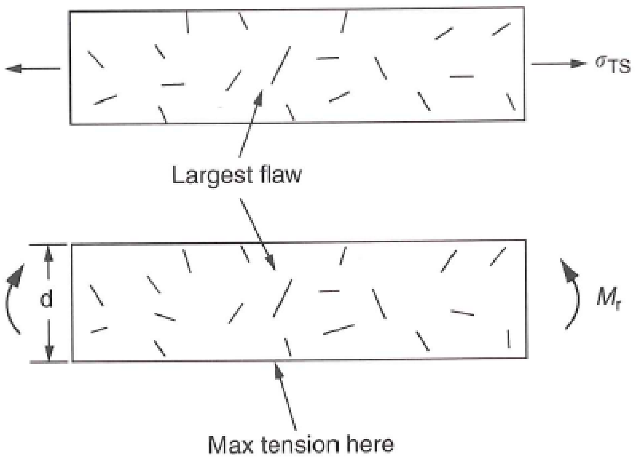
- Due to the presence of multiple defects, when using a brittle material (like ceramics) for load-bearing applications it is **NOT POSSIBLE** to be certain that it will not fail, even if the stress is lower than the tensile strength
- Although when we test one sample of ceramics we will get one single value of tensile strength, **there is no single value** for the tensile strength but only a **distribution of strength**

→ when selecting ceramics materials (e.g., high performance ceramics) for load-bearing applications it is necessary to specify an acceptable **survival probability** rather than an acceptable maximum stress!!!

The Statistics of Strength

Consequences of crack lengths distributions





1) Two nominally identical piece of ceramics (e.g., A and B) can have great differences in tensile strength (up to a factor of 2) → there is a **probability of strength**
2) A larger sample will fail at a lower stress than a small one → **volume dependence** of strength
    2.1) Brittle materials appear to be stronger in bending than in tension:
        → the max stress is carried by a small portion of the material

The Weibull Distribution

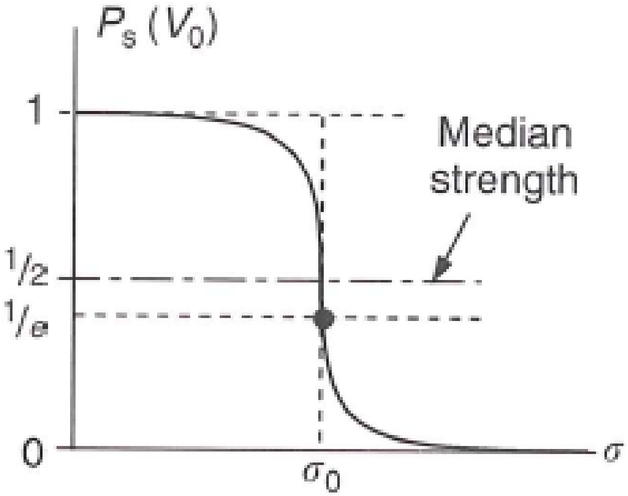
How do we handle the statistics of strength? How do we define the strength of ceramics → Weibull

- Survival probability $\mathbf{P_s(V_0)}$: fraction of identical samples (each of volume V_0) which survive loading to a tensile stress σ

$$P_s(V_0) = exp\left\{-\left(\frac{\sigma}{\sigma_0}\right)^m\right\}$$

m, σ_0: constants

$\boxed{\sigma_0}$



if σ = 0 → $P_s(V_0) = 1$

if σ → ∞ → $P_s(V_0) = 0$

if σ = σ₀ → $P_s(V_0) = \frac{1}{e} = 0.37$

σ_0 is the tensile stress that allows 37% of samples to survive

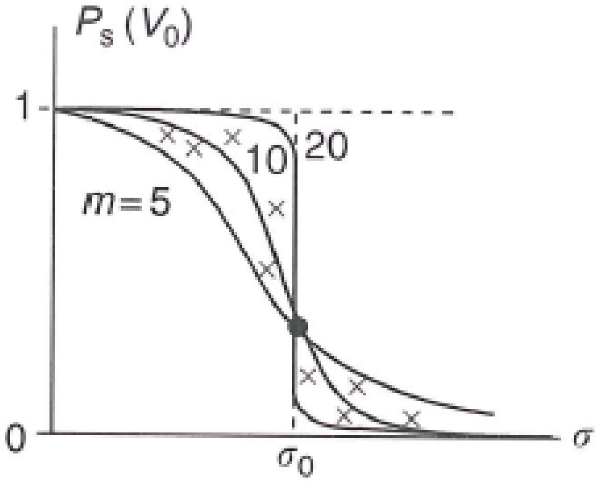
The Weibull Distribution

How do we handle the statistics of strength? How do we define the strength of ceramics → Weibull

- Survival probability $\mathbf{P_s(V_0)}$: fraction of identical samples, each of volume V_0, which survive loading to a tensile stress σ

$$P_s(V_0) = exp\left\{-\left(\frac{\sigma}{\sigma_0}\right)^m\right\} \quad m, \sigma_0\text{: constants}$$

m: Weibull modulus



the lower *m* the greater the variability of strenth

- chalk: m=5
- engineering ceramics (SiC, Al_2O_3. Si_3N_4): m=10
- steel: m=100

if m>20 we can assume the material has a single well-defined value of strength

values of m and σ_0 can be found by performing testing on a large number of samples of volume V_0

The Weibull Distribution

We have defines the dependence of survival probability P$_s$ on stress, what about volume dependence?

The probability that *n* identical samples of volume V_0 will survive a tensile stress *σ* is:

$$\{P_s(V_0)\}^n$$

If we stuck toghter the samples to give a single sample of volume $V=nV_0$:

$$P_s(V) = \{P_s(V_0)\}^n = \{P_s(V_0)\}^{\frac{V}{V_0}} \quad \Longrightarrow \quad \boxed{P_s(V) = exp\left\{-\frac{V}{V_0}\left(\frac{\sigma}{\sigma_0}\right)^m\right\}}$$

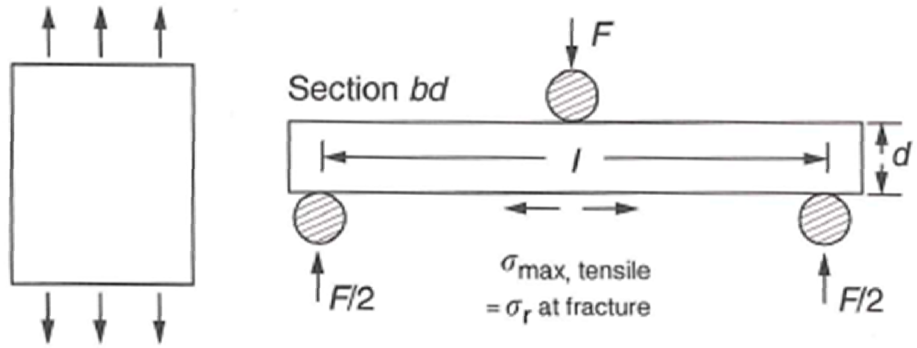
material selection equation

If the stress is not constant (as in a simple tensile test) but varies with position through the composite:

$$\boxed{P_s(V) = exp\left\{-\frac{1}{V_0}\left(\frac{1}{\sigma_0}\right)^m \int_V \sigma^m dV\right\}}$$

The Modulus of Rupture

- It is difficult to perform tensile tests on brittle material as samples break prematurely when they are gripped on a tensile machine
  [contact stress >> fracture strength]
- The preferred method to test ceramics in tension is 3-point bending test (and also 4-point bending)



measured quantity: <u>modulus of rupture</u>

$$\boxed{\sigma_r = \frac{3Fl}{2bd^2}}$$

In general the modulus of rupture is larger than the tensile strength since:

1) only half of the sample is subjected to tension (the other part is in compression)
2) peak tensile stresses are located on the lower surface (just below the loading point), everywhere else tensile stresses are lower

modulus of rupture / tensile strength relationship:

$$\boxed{\sigma_{TS} = \frac{\sigma_r}{\{2(m+1)^2\}^{1/2}}}$$

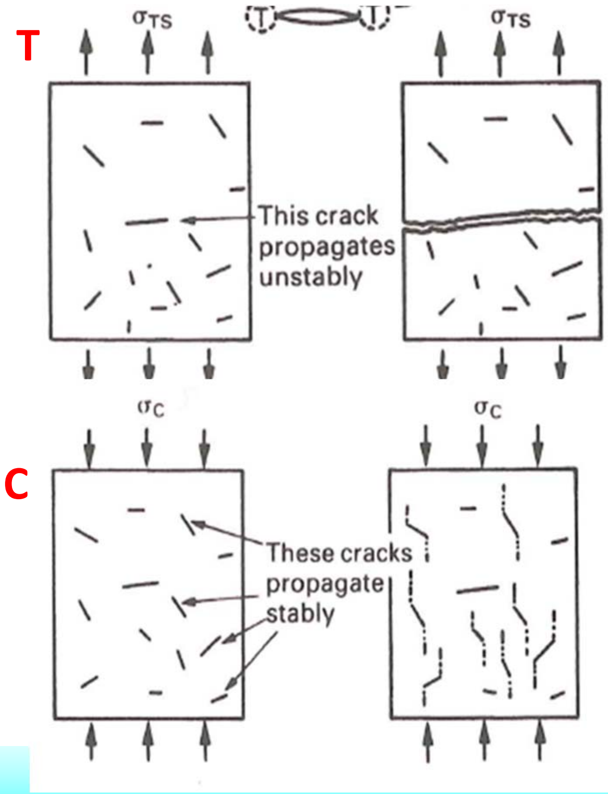
Compressive Strength

- Many ceramics carry load in compression (hence avoiding the uncertainties associated with tensile loading)
- To measure compressive strength σ_C we can perfrom a compression test (often used cement and concrete samples)

measured quantity: <u>compressive strength</u> σ_C

for brittle materials : $\sigma_C \neq \sigma_{TS}$

$$\boxed{\sigma_C \approx 15\,\sigma_{TS}}$$



- tensile fracture: rapid unstable propagation of one crack (usually the largest)
- compressive fracture is not caused by the rapid unstable propagation of one crack but by the **slow extension of many cracks** to form a crushed zone
- cracks propagates **stably** and twist out from their original orientation to propagate **parallel to the loading axis**

- compressive fracture is not caused by the rapid unstable propagation of one crack but by the **slow extension of many cracks** to form a crushed zone

- it is not the size of the largest crack that matters but that of the average $\bar{a}$

$$\sigma_{TS} \approx \frac{K_c}{\sqrt{\pi a_m}} \qquad \sigma_C \approx 15\,\frac{K_c}{\sqrt{\pi \bar{a}}}$$

Thermal Shock Resistance

- A sudden change in temperature can fracture ceramics
- Thermal shock resistance is measured by dropping a piece of slowly heated ceramics in cold water. The maximum temperature drop ΔT it can survive measured the thermal shock resistance

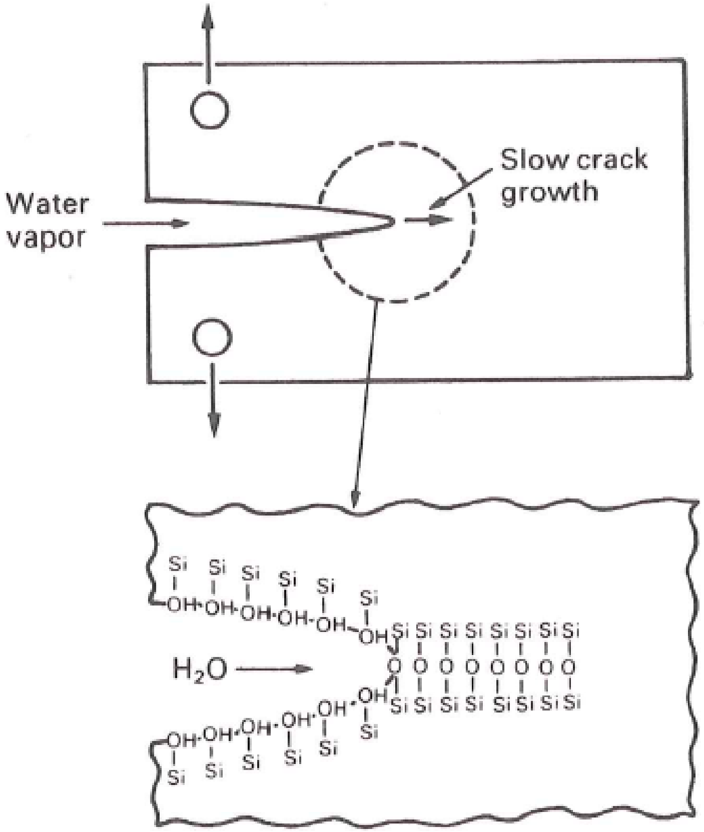
$$\boxed{\Delta T \approx \frac{\sigma_{TS}}{\alpha E}}$$

α coefficient of thermal expansion

- ΔT: 80 °C (ordinary glass) - 500 °C (Si_3N_4 silicon nitride)
- high-performance engineering ceramics: small α and high σ_{TS} → can be quenched suddenly through several hundred degrees without fracturing

Time Dependence of Strength

- Some ceramics may exhibit sudden disintegration (e.g. car windshield or bottles)
- Typical behavior of most oxide (glass) due to slow growth of surface microcracks caused by the chemical interaction between ceramics and the water (or water vapor) in the environment



- water that reaches the crack tip reacts with molecules (forms hydroxide, OH^-) and breaks the typical Si-O-Si bonds
- when the crack has reached the critical length for failure (at the given stress level), the part fails suddenly and catastrophically
- typical behavior of *toughened glass* as it contains internal stresses that can drive crack growth
- from a mechanical viewpoint it resembles fatigue failure → static fatigue

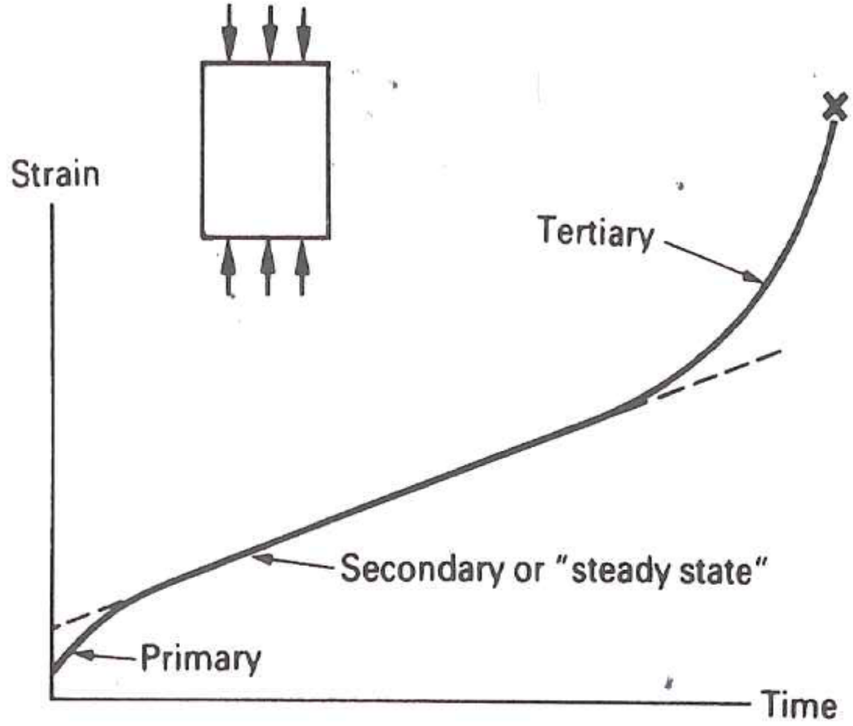
$$\boxed{\left(\frac{\sigma}{\sigma_{TS}}\right)^{n} = \frac{t\ (test)}{t}}$$

n: “slow crack growth exponent”
n (oxides @ room T): 10-20
n (carbides): 100

standard test to measure σ_{TS} takes a time t(test)
σ is the stress safely supported for a time t

Creep of Ceramics

- Ceramics creep when they are hot: T > 1/3 T_M T_M=melting temperature ($\sim$ 2000 °C engineering ceramics)
- Creep curve (similar as in metals):



3 creeps regions:

primary: $\dot{\varepsilon}$ (strain rate) decreases with time

secondary: steady-state creep

$$\dot{\varepsilon} = A\sigma^n exp\left(-\frac{Q}{RT}\right)$$

A, n: creep constants
R: universal gas constant
Q: activation energy for creep

tertiary: strain rate increases till fracture

→ Engineering design against creep is based on creep equation of secondary phase
→ Creep at low temperature is highly relevant for ice

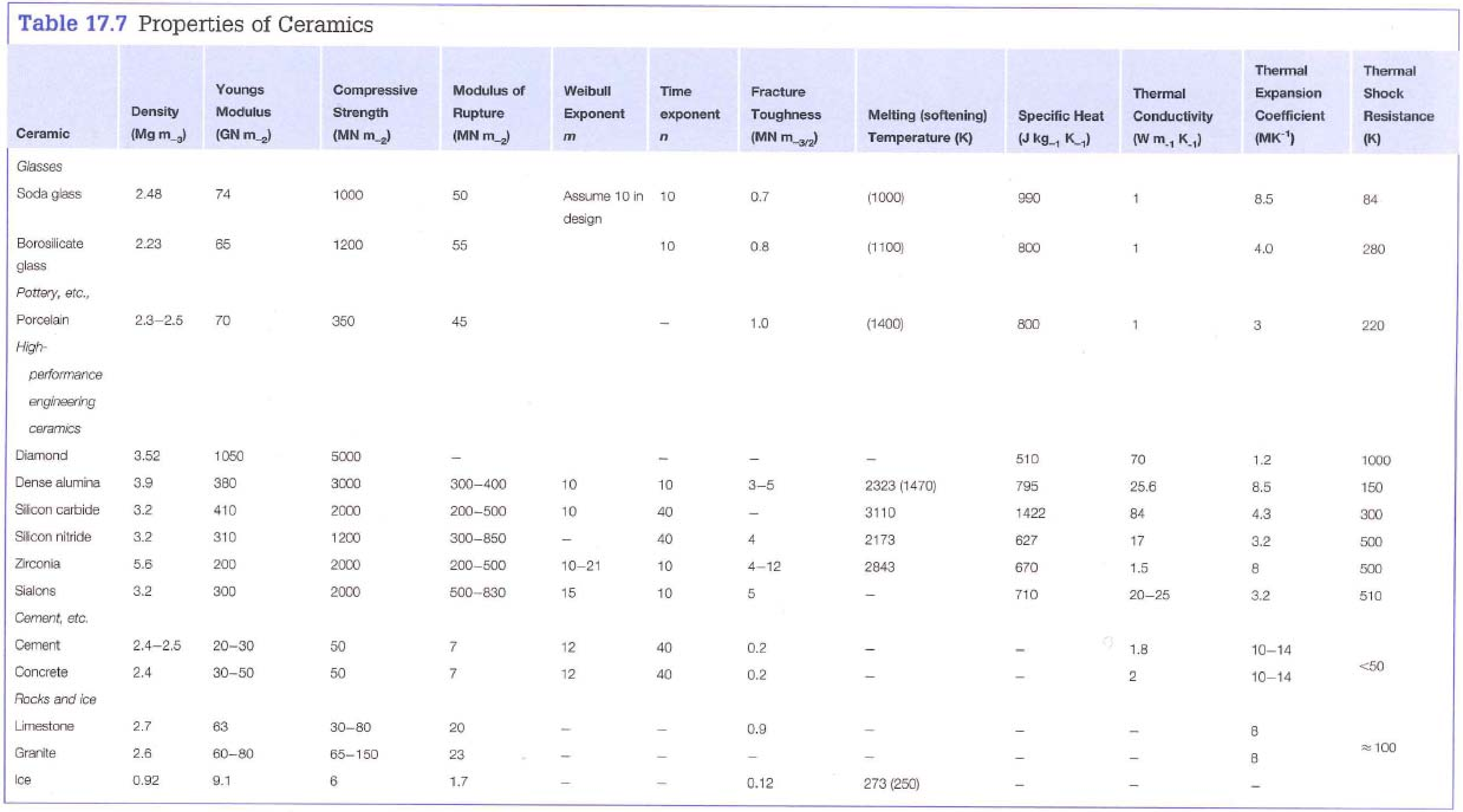
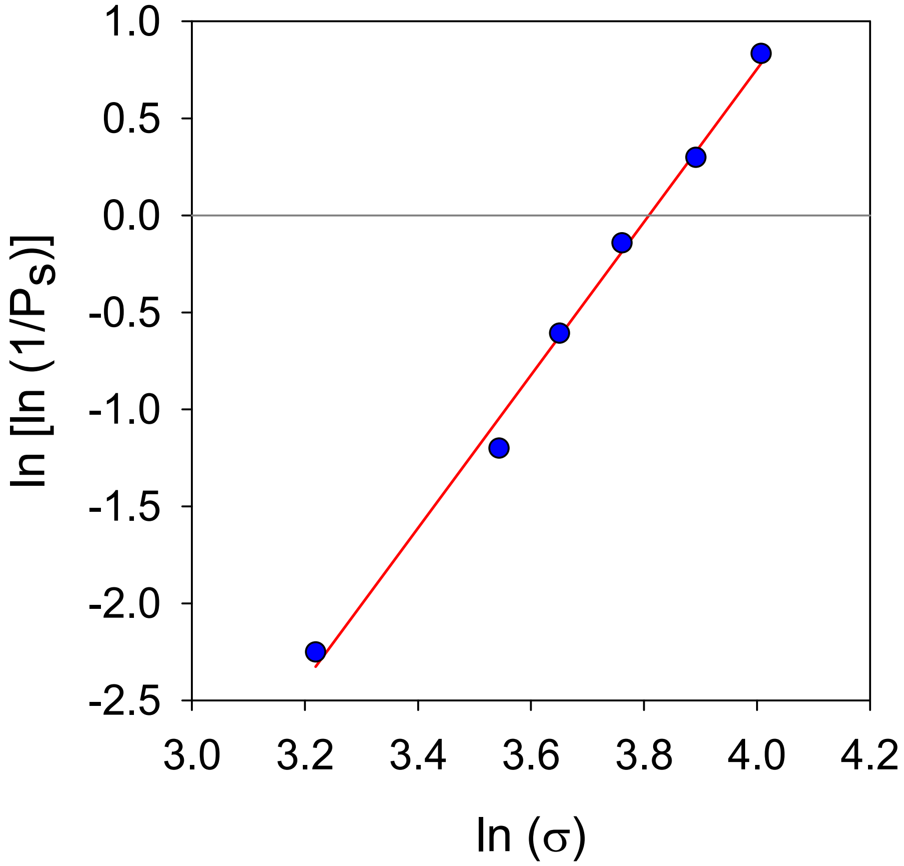


Table 17.7 Properties of Ceramics

Ceramic	Density (Mg m_{-3})	Youngs Modulus (GN m_{-2})	Compressive Strength (MN m_{-2})	Modulus of Rupture (MN m_{-2})	Weibull Exponent m	Time exponent n	Fracture Toughness (MN $m_{-3/2}$)	Melting (softening) Temperature (K)	Specific Heat (J kg_{-1} K_{-1})	Thermal Conductivity (W m_{-1} K_{-1})	Thermal Expansion Coefficient (MK^{-1})	Thermal Shock Resistance (K)
Glasses												
Soda glass	2.48	74	1000	50	Assume 10 in design	10	0.7	(1000)	990	1	8.5	84
Borosilicate glass	2.23	65	1200	55		10	0.8	(1100)	800	1	4.0	280
Pottery, etc.,												
Porcelain	2.3–2.5	70	350	45		–	1.0	(1400)	800	1	3	220
High-performance engineering ceramics												
Diamond	3.52	1050	5000	–		–	–	–	510	70	1.2	1000
Dense alumina	3.9	380	3000	300–400	10	10	3–5	2323 (1470)	795	25.6	8.5	150
Silicon carbide	3.2	410	2000	200–500	10	40	–	3110	1422	84	4.3	300
Silicon nitride	3.2	310	1200	300–850	–	40	4	2173	627	17	3.2	500
Zirconia	5.6	200	2000	200–500	10–21	10	4–12	2843	670	1.5	8	500
Sialons	3.2	300	2000	500–830	15	10	5	–	710	20–25	3.2	510
Cement, etc.												
Cement	2.4–2.5	20–30	50	7	12	40	0.2	–	–	1.8	10–14	<50
Concrete	2.4	30–50	50	7	12	40	0.2	–	–	2	10–14	
Rocks and ice												
Limestone	2.7	63	30–80	20	–	–	0.9	–	–	–	8	≈ 100
Granite	2.6	60–80	65–150	23	–	–	–	–	–	–	8	
Ice	0.92	9.1	6	1.7	–	–	0.12	273 (250)	–	–	–	

Weibull Plot



$$ln\left[ln\left(\frac{1}{P_s}\right)\right] = 3.94\ ln(\sigma) - 15, \qquad r^2 = 0.99$$

m $\approx 3.94; \sigma_0 \approx 45$