

Materials design and selection for circular economy

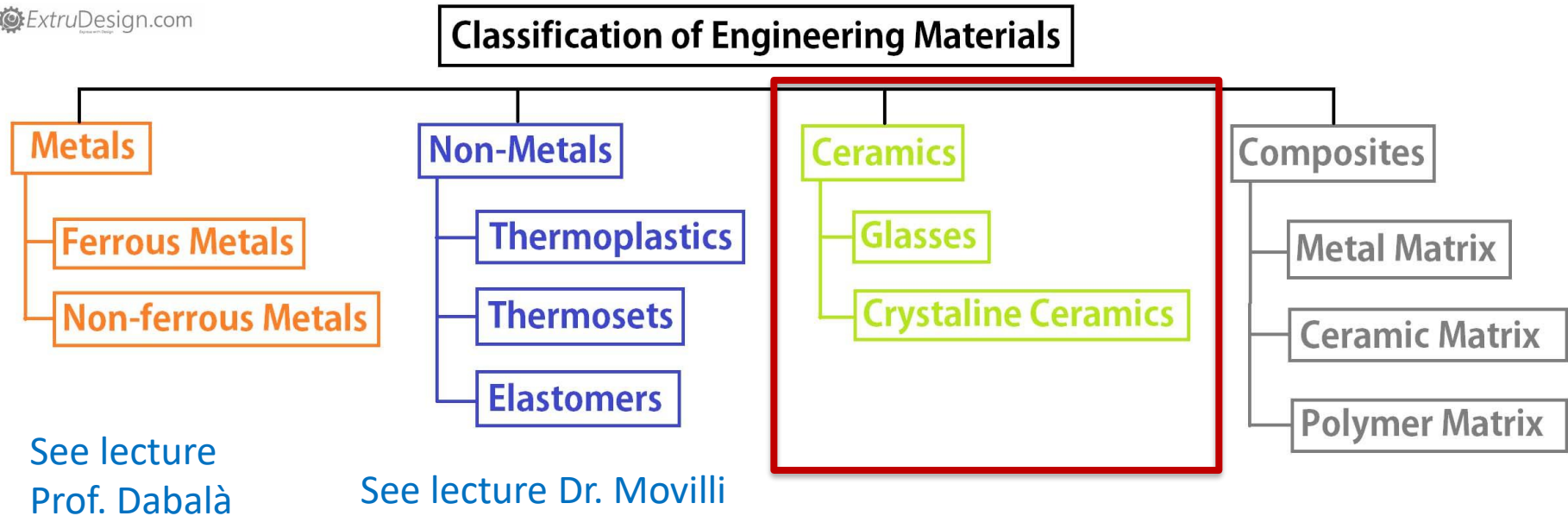
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www.chimica.unipd.it/silvia.gross

Classification of materials



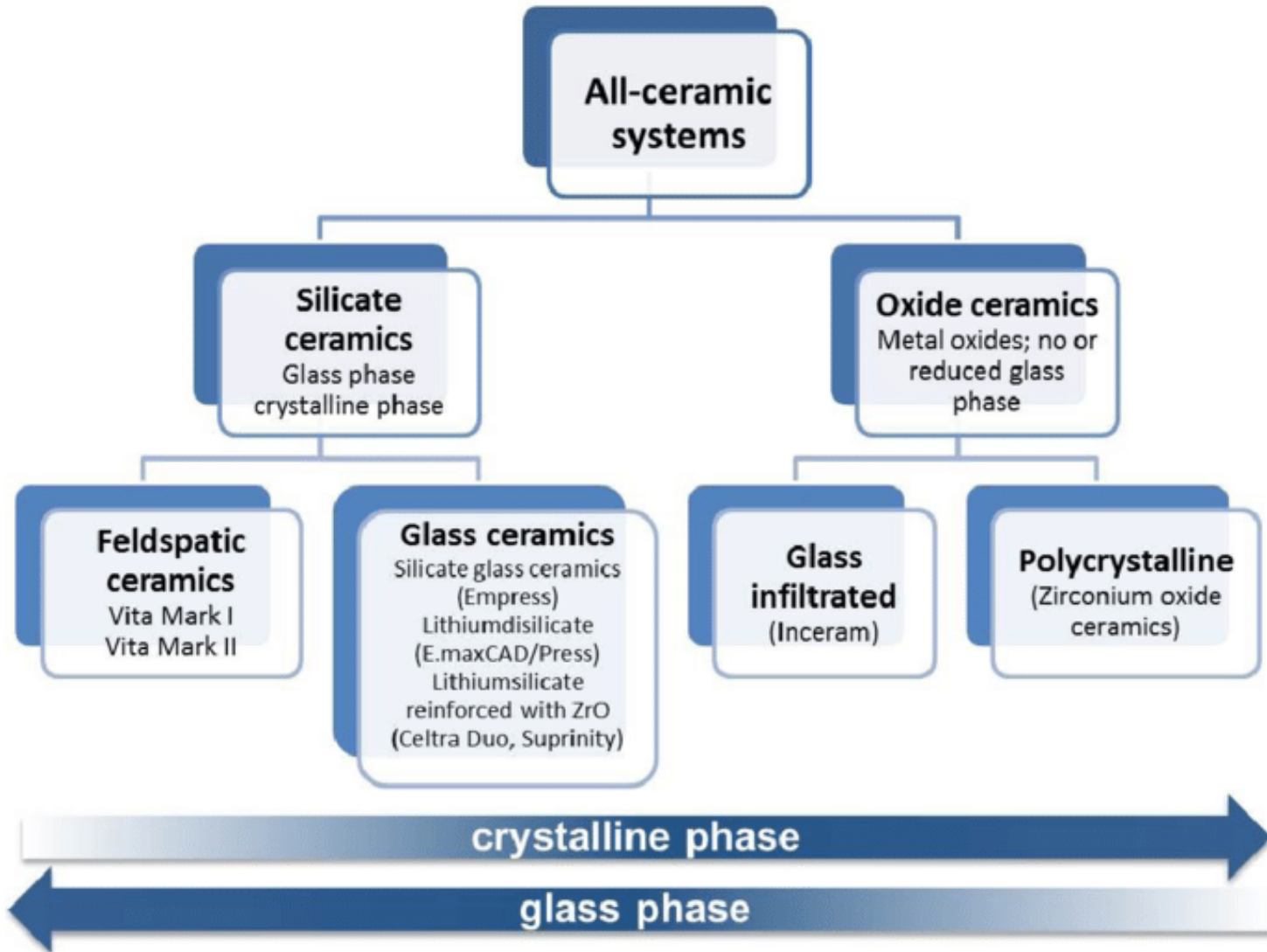
Source of the picture: <https://extrudesign.com/classification-of-materials-engineering-material-classification/>

Inorganic not (only) metallic materials

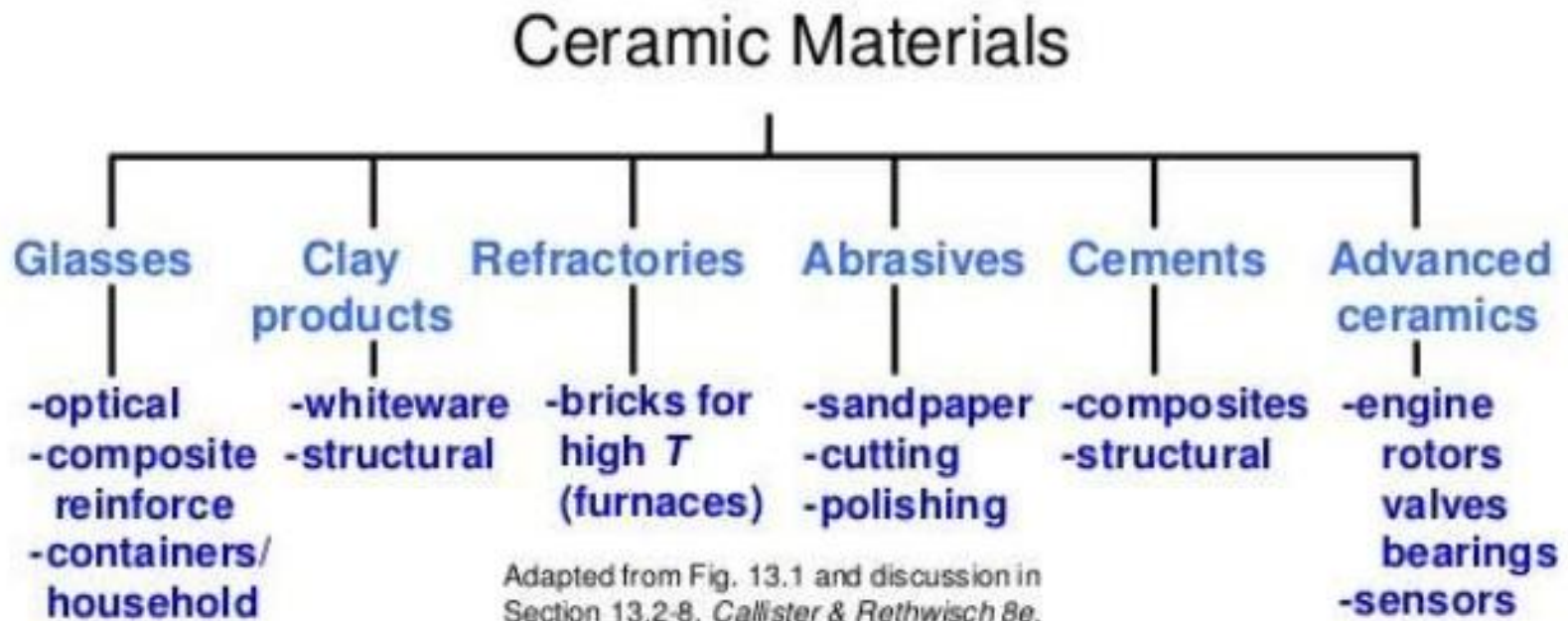
Handbook of Materials, Springer Verlag

- They contain metallic and non-metallic elements
- A ceramic is a material that is neither metallic nor organic. It may be crystalline, glassy or both **crystalline** and **glassy**.
- Inter-atomic bonding is ionic or covalent, and which are generally formed at high temperatures.
- Ceramics are typically hard and chemically non-reactive and can be formed or densified with heat.
- Ceramics are more than pottery and dishes: clay, bricks, tiles, glass, and cement are probably the best-known examples.
- Ceramic materials are used in electronics because, depending on their composition, they may be semiconducting, superconducting, ferroelectric, or an insulator.

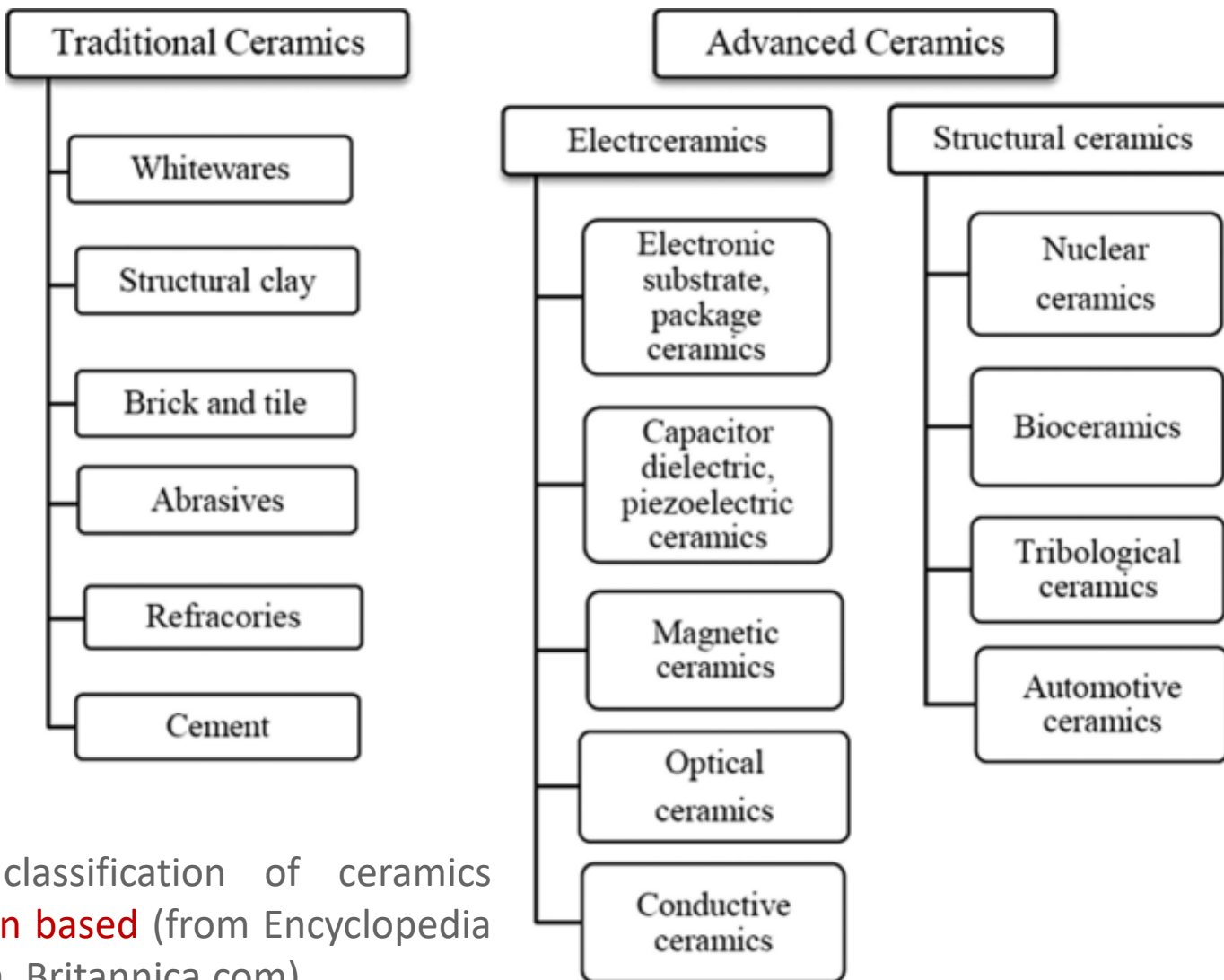
Ceramics materials



Classification of Ceramics

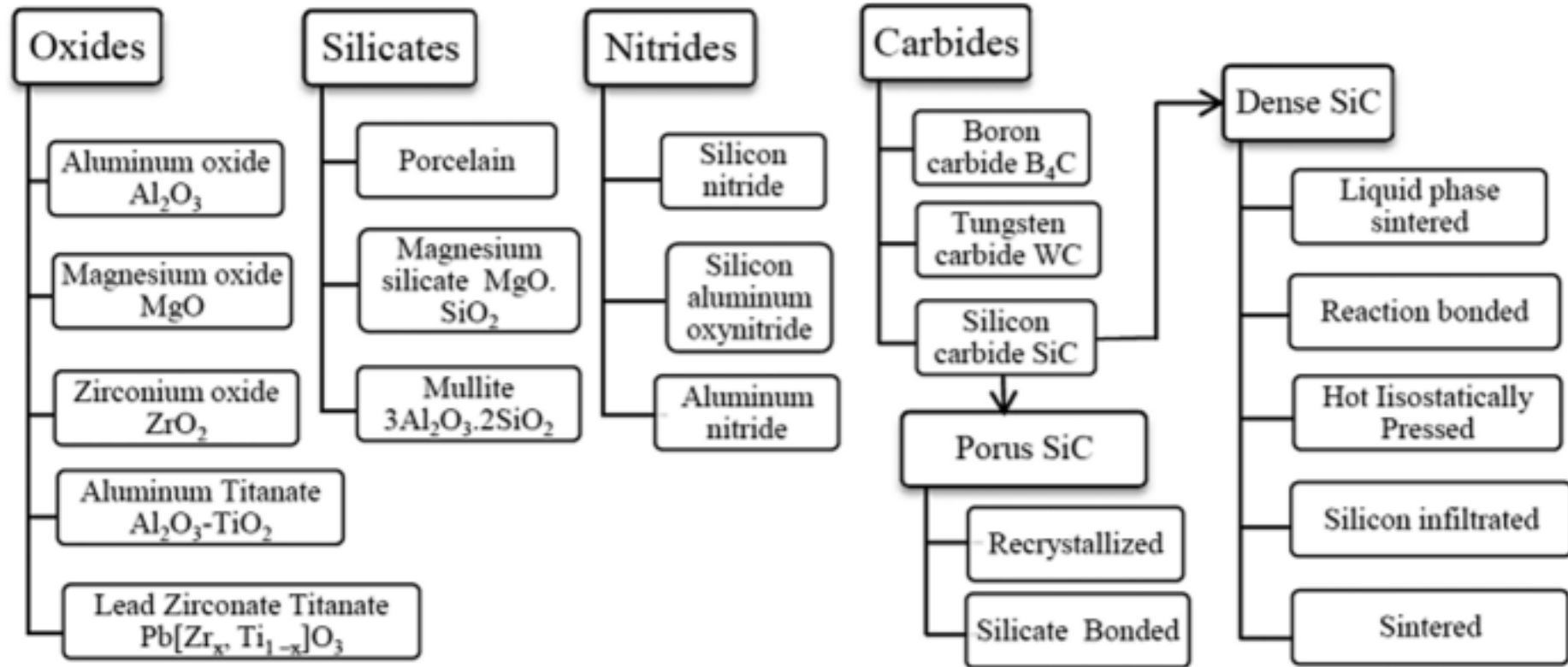


Ceramics materials



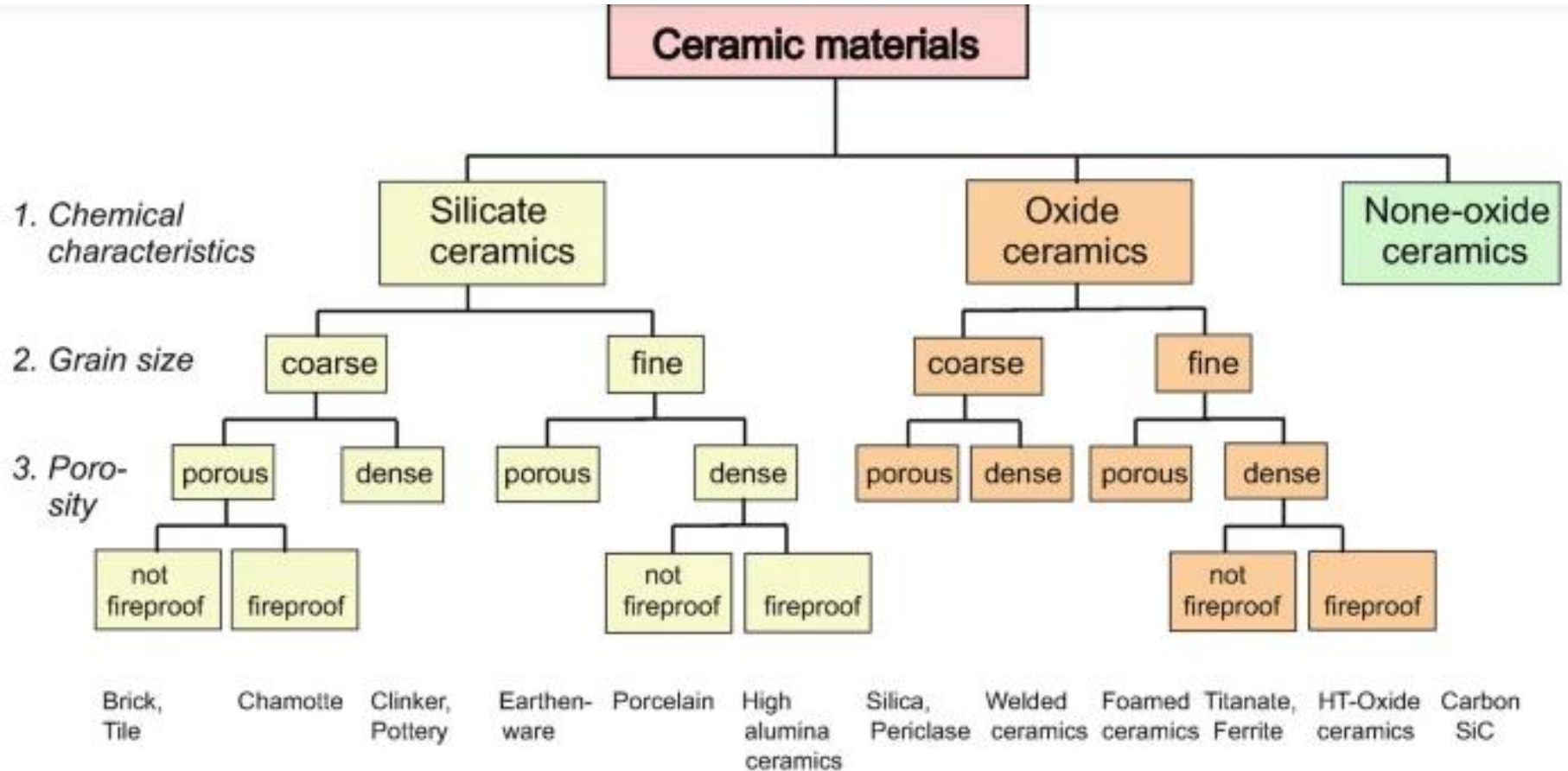
General classification of ceramics **application based** (from Encyclopedia Britannica. Britannica.com).

Ceramics materials



General classification of ceramics **composition based** (from Encyclopedia Britannica. Britannica.com).

Ceramics materials



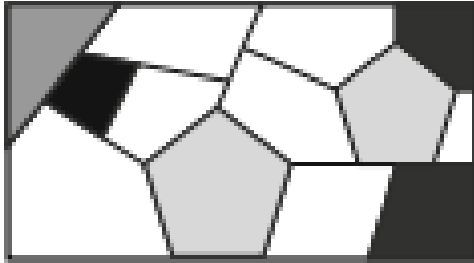
Introduction to Applied Mineralogy - Jens Götze, Matthias Göbbels, Springer ([available as e-book on CAB](#))

Metal-ceramics comparison

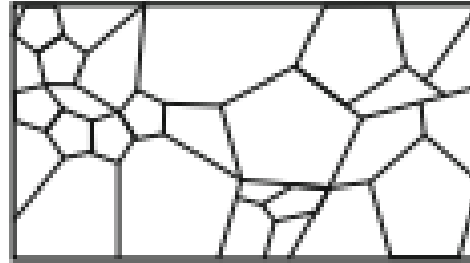
Property	Units	Ti 6Al 4V	316 SS	CoCr Alloy	TZP	Alumina
Young's modulus	GPa	110	200	230	210	380
Strength	MPa	800	650	700	900–1200	> 500
Hardness	HV	100	190	300	1200	2200

- Stiffness is comparable to the metal alloys
- The biggest problem is fracture toughness (sensitivity to flaws = **difetti**).
- Rigid plastics < Ceramics = Metals

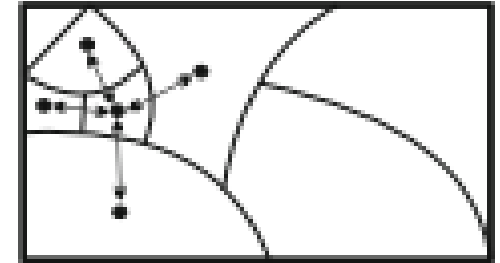
Ceramics microstructure



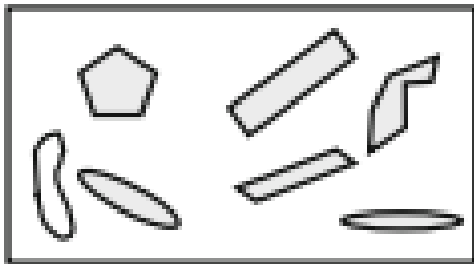
Phase fraction



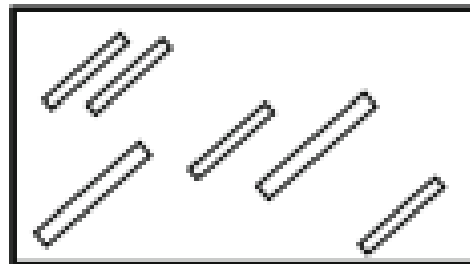
Grain size
Grain size distribution



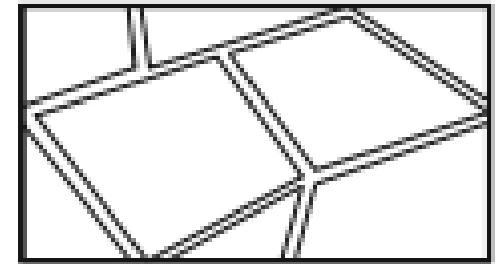
Spatial distribution
Relative position



Shape



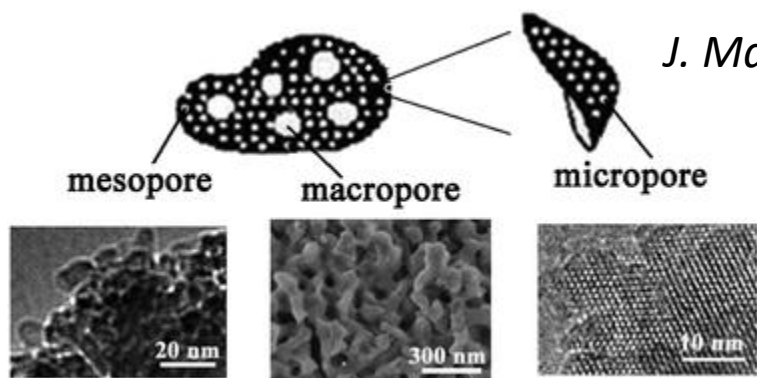
Orientation



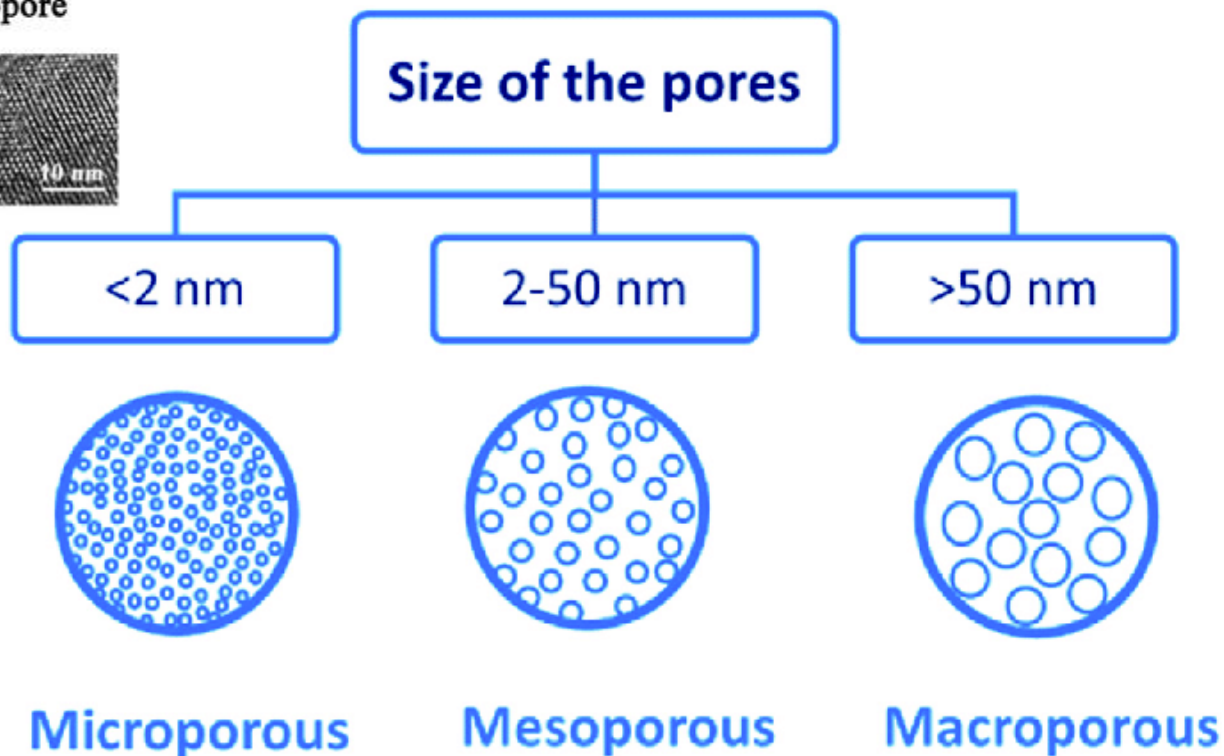
Specific interface

Parameters for quantitative microstructure description

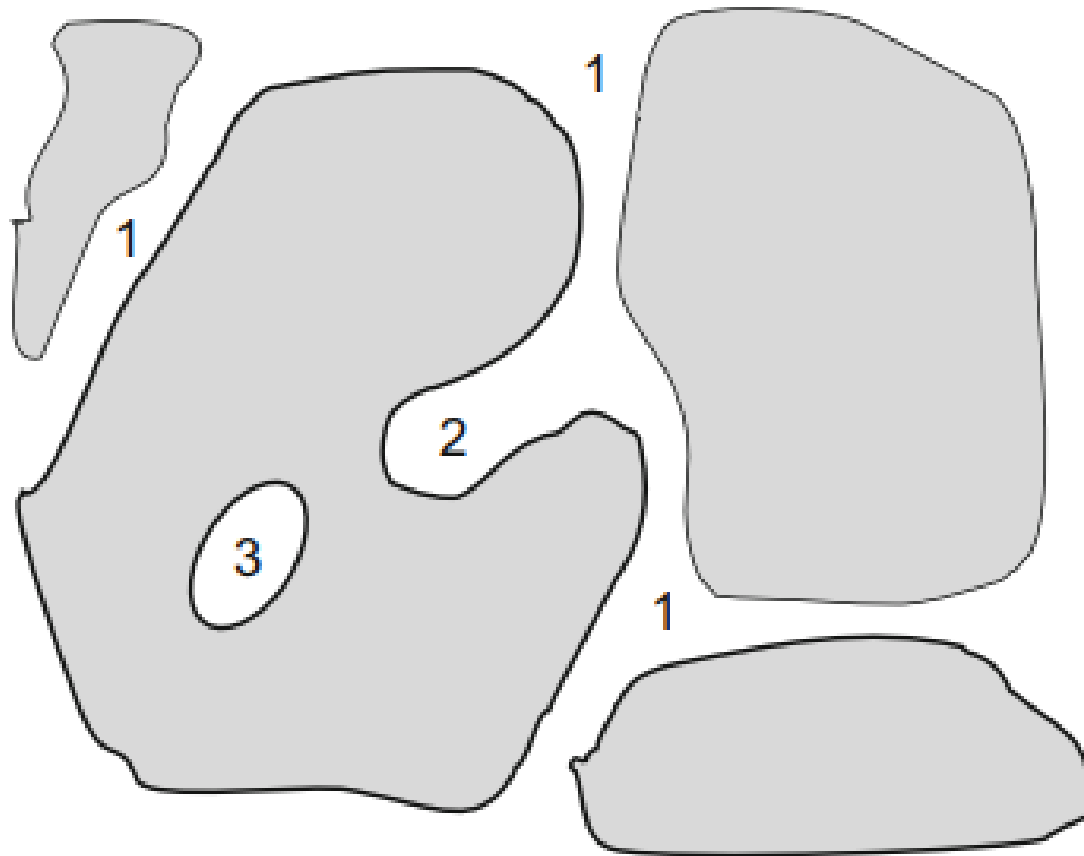
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J. Mater. Chem., 2011,21, 19395-19401



Source of the figure: ResearchGate. Available from:
https://www.researchgate.net/figure/Schematic-representing-difference-between-microporous-mesoporous-and-macroporous_fig6_349579616 [accessed 8 Oct 2024]

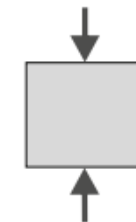


Schematic representation of porosity: 1 open, flow-through pores; 2 open, non-flow through pores (so-called blind pores); 3 closed pores

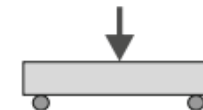
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Ceramics mechanical properties

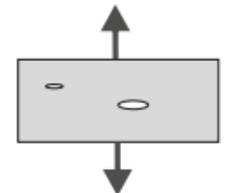
Material	Compressive strength in MPa
Coarse ceramics (bricks)	10–25
Refractory ceramics	30–100
Fine ceramics (porcelain)	400–600
Oxide ceramics	1000–3000
Granite	210–250
Basalt	160–190
Granulite	180–350
Marble	110–150
Sandstone (12% porosity)	10–40



Compression strength



Bending strength

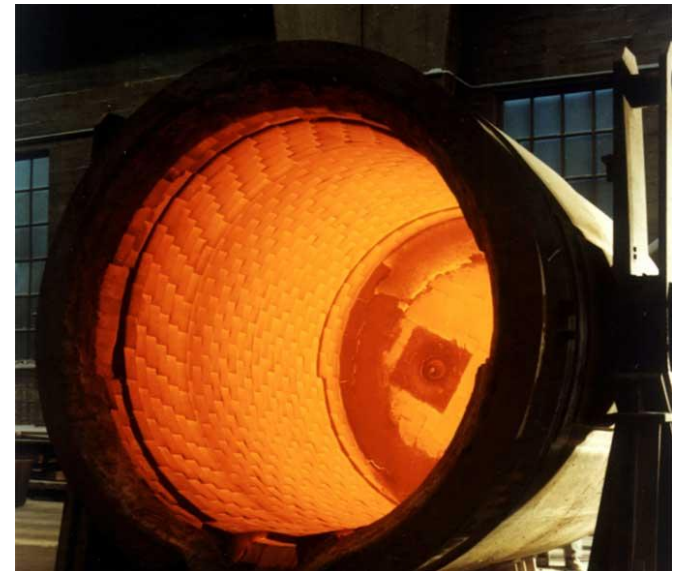


Tensile strength

Compressive strength of different materials

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Ceramics thermal properties: refractory materials



Ceramics thermal properties: refractory materials

Refractory Raw Materials

Types, Properties, and Applications



Alumina

Al_2O_3



Bauxite

$\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$



Chamotte

Calcined Fireclay



Chromite

FeCr_2O_4



Magnesia

MgO



Colemanite

$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$

Source: <https://www.metals-hub.com/en/blog/types-of-refractory-raw-materials/>

Ceramics thermal properties: refractory materials

Refractory materials are defined as high-temperature materials, both metallic and ceramic, designed to withstand extreme conditions, primarily used in applications such as furnaces and rocket technology, where durability and thermal efficiency are critical.

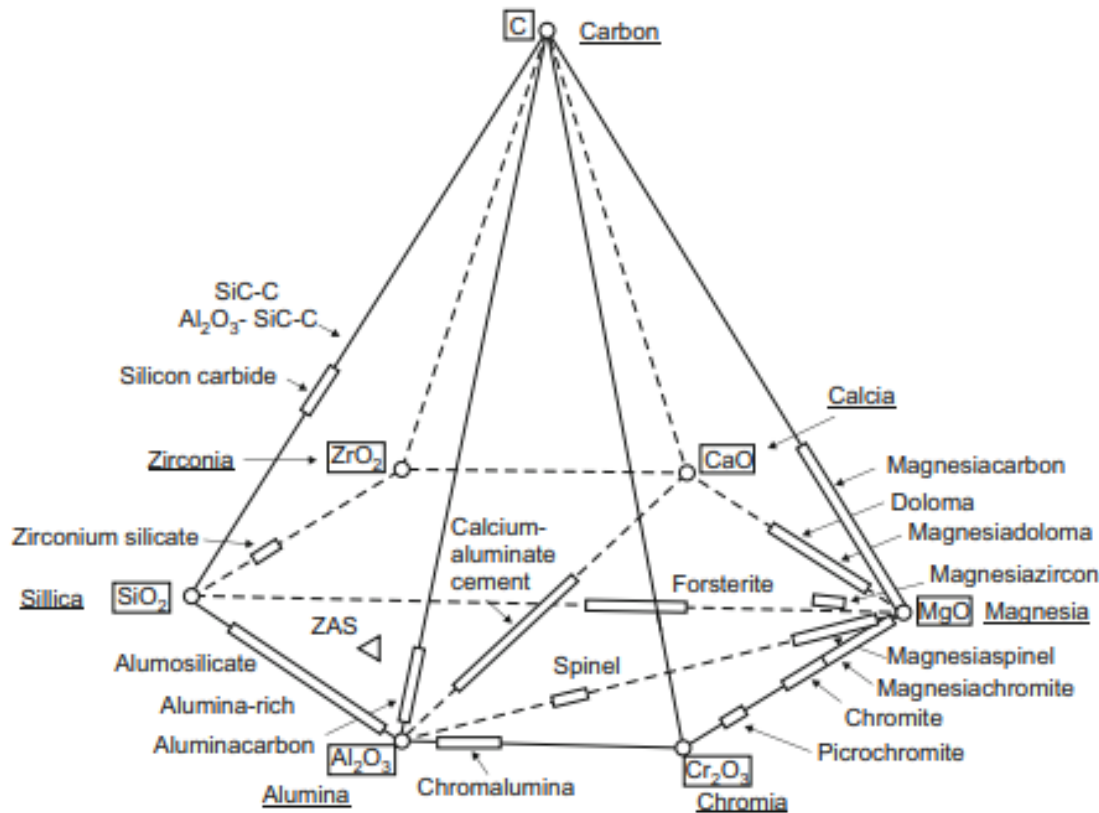
Refractories are thermally insulating materials known to withstand high temperatures without being degraded and are used for high-temperature applications

Sometimes they are classified into “refractory” and “high refractory”. They designate materials according to the characteristic of the occurrence of the first melt.

In the case of **refractory materials**, according to the definition, the first melt may only occur in the brick itself above 1450 °C without external chemical input.

For **high refractory materials**, this temperature is 1840 °C.

Ceramics thermal properties



Fundamental material pyramid with the position of the refractory materials.

Ceramic **refractory** materials are used in many ways in everyday life and in industry.

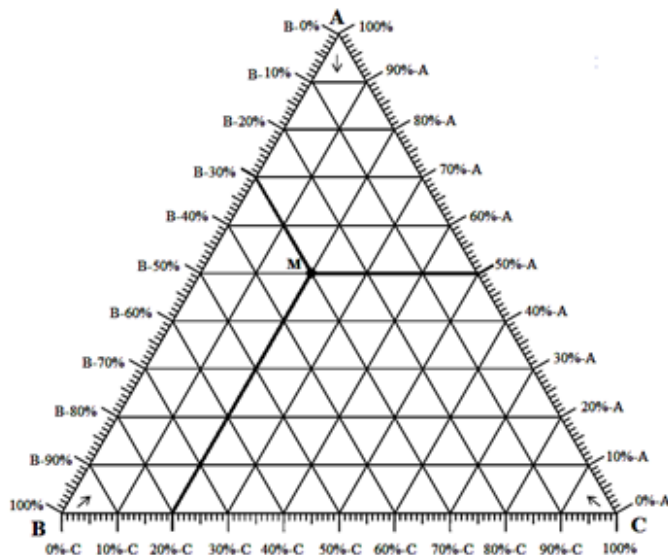
Fireclay bricks are found in open fireplaces or wood-burning stoves as lining in many homes

Practically all high-temperature processes in industry take place in reaction vessels lined with ceramic materials.

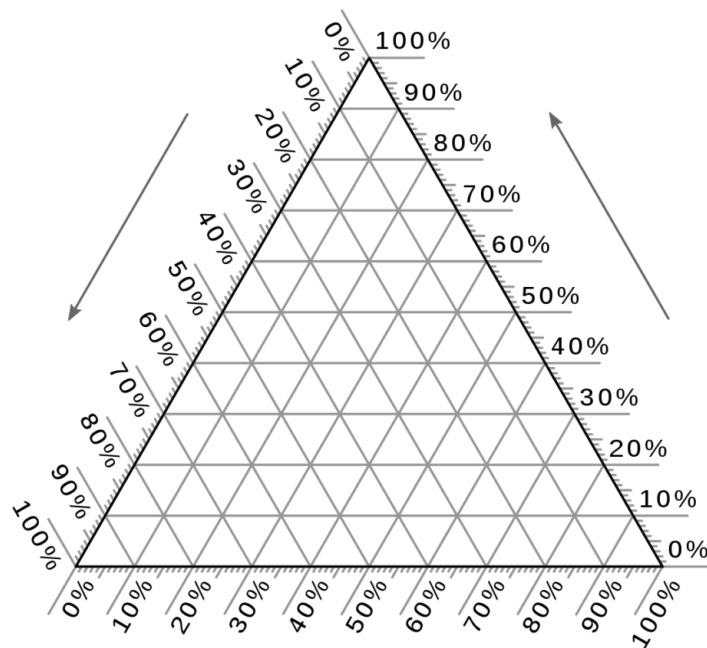
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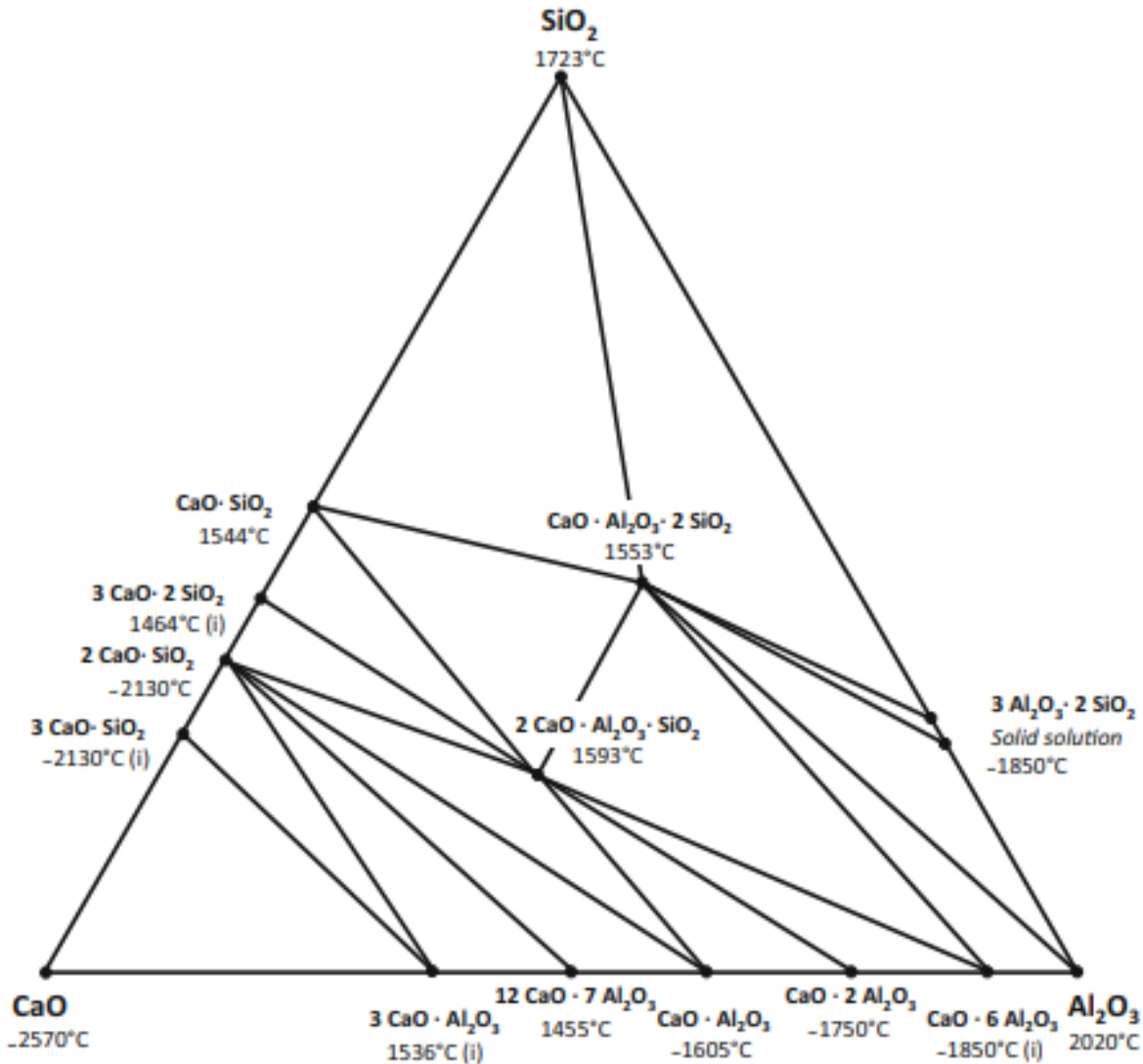
How to read a ternary diagram

(a)



Component	Weight% in mixtur (M)
A	50
B	30
C	20





The ternary system
CaO-Al₂O₃-SiO₂

Introduction to
Applied Mineralogy -
Jens Götze, Matthias
Göbbels, Springer
(available as e-book
on CAB)

Ceramics examples



How ceramics are produced

1. Compounding

- Mix and homogenize ingredients into a water based suspension = slurry or, into a solid plastic material containing water called a clay

2. Forming

- The clay or slurry is made into parts by pressing into mold (sintering). The fine particulates are often fine grained crystals.

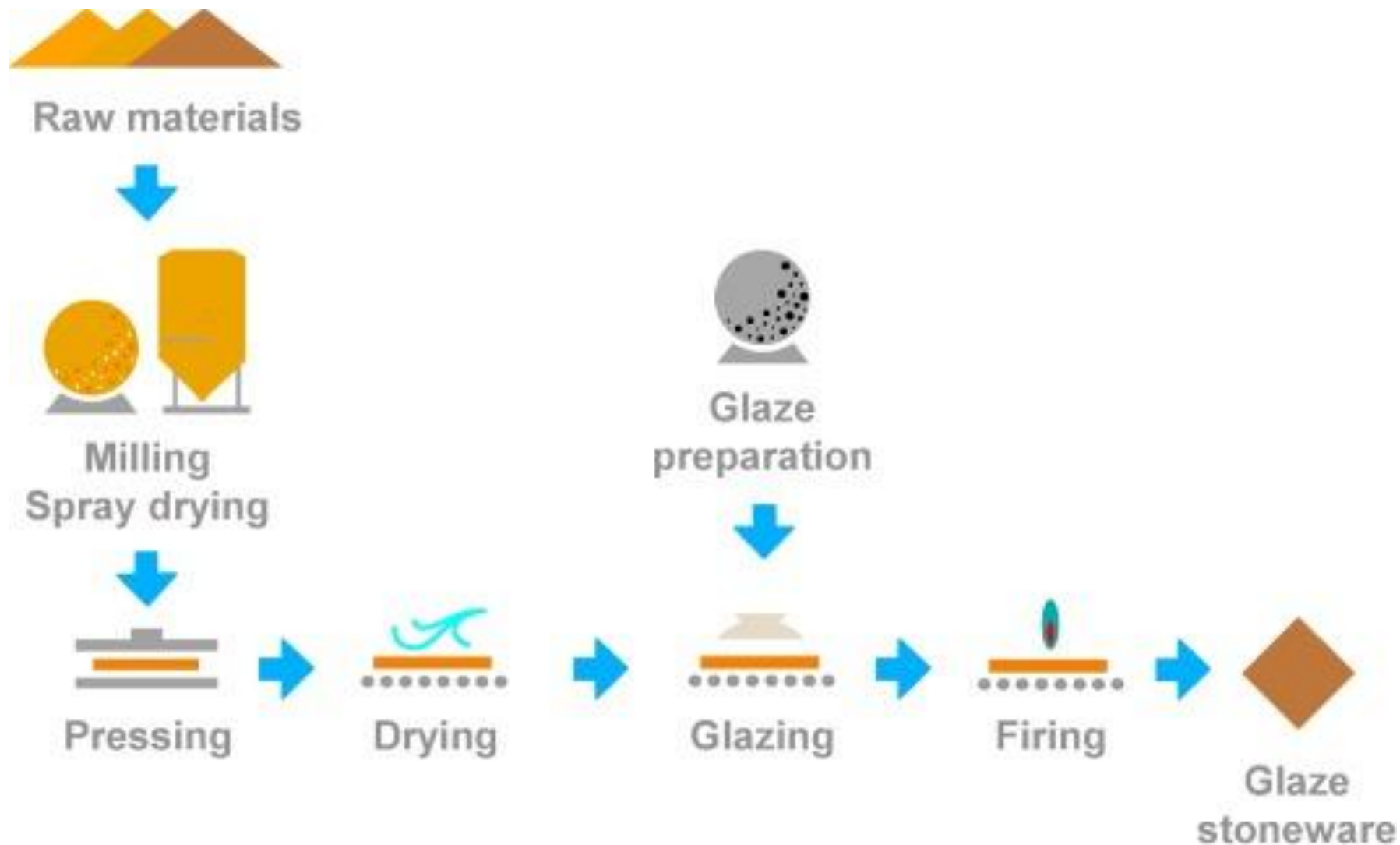
3. Drying

- The formed object is dried, usually at room temperature to the so-called "green" or leathery state.

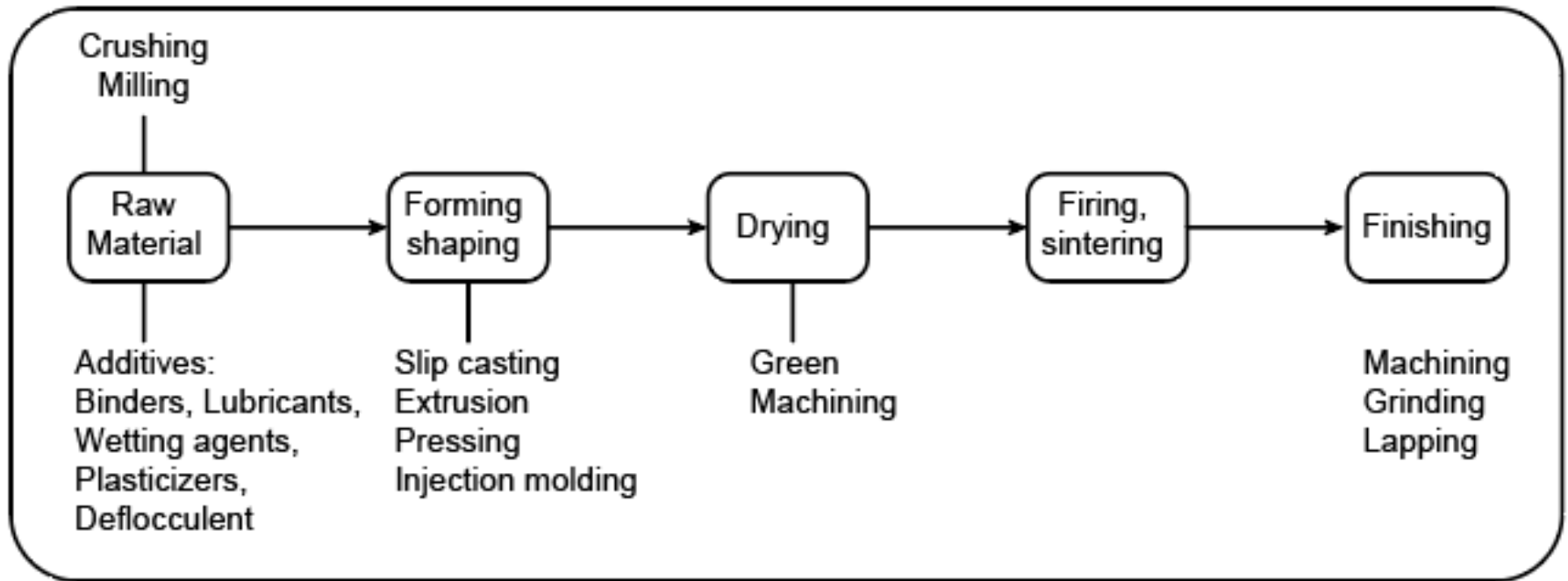
4. Firing

- Heat in furnace to drive off remaining water. Typically produces shrinkage, so producing parts that must have tight mechanical tolerance requires care.
- Porous parts are formed by adding a second phase that decomposes at high temperatures forming the porous structure.

How ceramics are produced



How ceramics are produced



Ceramics properties and uses

- Properties of ceramics arise from a combination of chemical bonding and the atomic defects and microstructure resulting from the fabrication techniques.
- The bonding, whether described as ionic or covalent, is strong, which ensures that the solids are chemically inert and often stable to high temperatures (refractory).
- Refractory ceramics are widely used in furnaces and other high-temperature equipment.
- The lack of free electrons endows basic ceramics with poor thermal and electronic conductivity. The chemical flexibility of ceramics, however, allows to be selectively doped with other ions.
- Ceramics do not deform very easily at ordinary temperatures, as strong chemical bonds must be broken and, unlike metals, dislocation movement

Properties

- high hardness
- higher strength and high temperature strength
- high strength to weight ratio
- biocompatibility
- lower thermal and electrical conductivity
- superior chemical stability
- wear resistance
- inertness

Uses

- insulators
- Resistors
- Piezoelectris materials
- Laser materials
- Memory devices
- Non linear optical materials
- Refractories
- capacitors

Ceramics fields of applications

Mechanical engineering. Cutting tools and dies, abrasives, precise instrument parts, molten metal filter, turbine engine components, low weight components for rotary equipment, wearing parts, bearings, seals

Aerospace: Fuel systems and valves, power units, low weight components, fuel cells, thermal protection systems, turbine engine components, combustors bearings, seals, and structures

Biomedical devices: bones and joints, fabrication of dental implants and restorations, acetabular cups, and femoral heads for total hip replacement, bone fillers, and scaffolds for tissue engineering, heart valves

Automotive: Heat engines, turbines, catalytic converters, drive train components, fixed boundary recuperators, fuel injection components, turbocharger rotors, low heat rejection diesels, water pump seal.

Ceramics fields of applications

Defense industry: Tank power trains, submarine shaft seals, improved armors, propulsion systems, ground support vehicles, military weapon systems, military aircraft (airframe and engine), wear-resistant precision bearings

Chemical processing engineering: bones and joints, catalysts and igniters, heat exchanger, reformers, refractories, and nozzle

Electrical, magnetic engineering: Memory element, varistor sensor, resistance heating element, integrated circuit substrate, multilayer capacitors

Nuclear industry: Nuclear fuel, nuclear fuel cladding, control materials, moderating materials

Oil industry: Bearings flow control valves, pumps, refinery heater, blast sleeves *Electric power generation:* Bearings ceramic gas turbines, high temperature components, fuel cells (solid oxide), filters *Optical engineering:* Laser diode, optical communication cable, heat-resistant translucent, porcelain, light-emitting diode

Thermal engineering: Electrode materials, heat sink for electronic parts, high-temperature industrial furnace lining

Ceramics materials

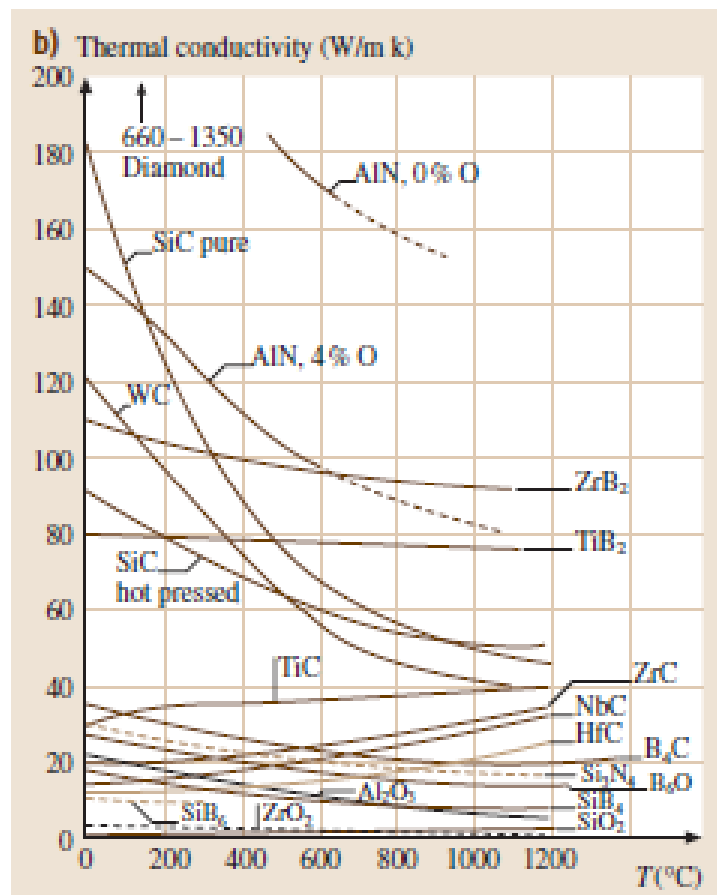
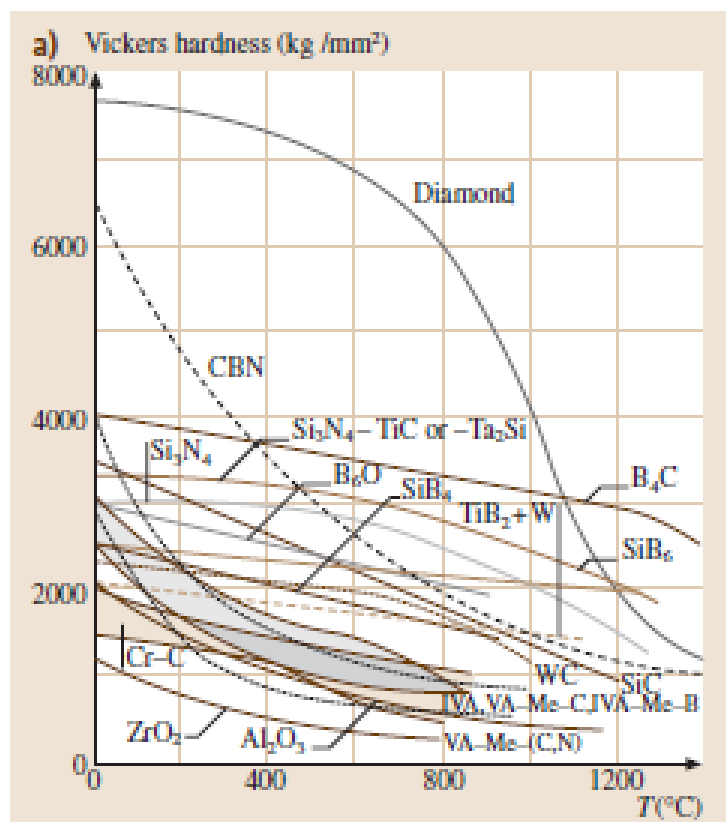
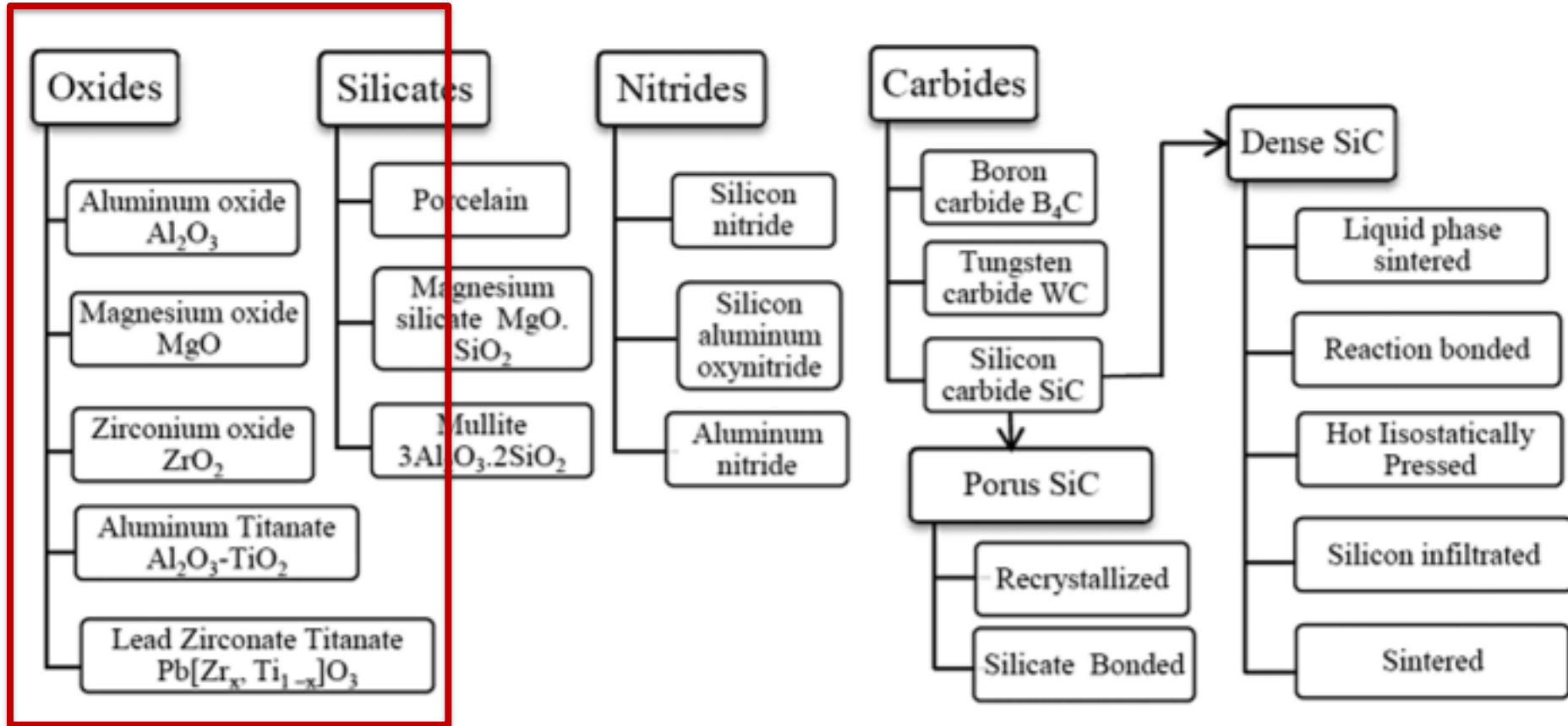


Fig. 3.2-2a,b Temperature dependence of (a) the hardness and (b) the thermal conductivity of ceramic materials in comparison with diamond and cubic boron nitride (CBN) [2.3]

Ceramics materials



General classification of ceramics composition based (from Encyclopedia Britannica. Britannica.com).

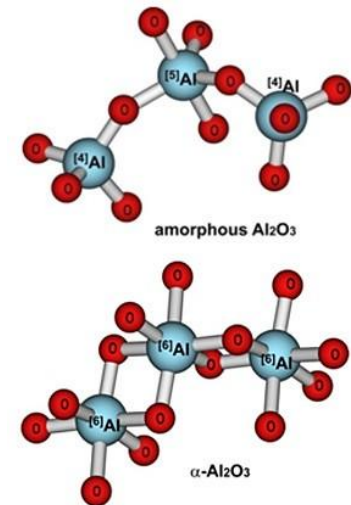
Ceramics materials: Al_2O_3

Most widely used either in pure form or as a raw material mixed with other oxides.

High hardness and moderate strength.

In its natural form, it contains varying amounts of impurities making it of non-uniform properties of unreliable behavior.

Al_2O_3 , as well SiC and many other ceramics, is now almost totally **manufactured synthetically** to control the quality. Synthetic alumina (first made in 1893) is obtained by fusion of molten bauxite (aluminum oxide ore), iron filings, and coke in electric furnaces. The material is then crushed, and mesh graded. Parts made from alumina are cold pressed and sintered to produce **white ceramics**. Their properties are enhanced by minor additions of other ceramics, such as titanium oxide and titanium carbide. The products are known as mullite (spinel), which are used as **refractory materials** for high temperature applications.

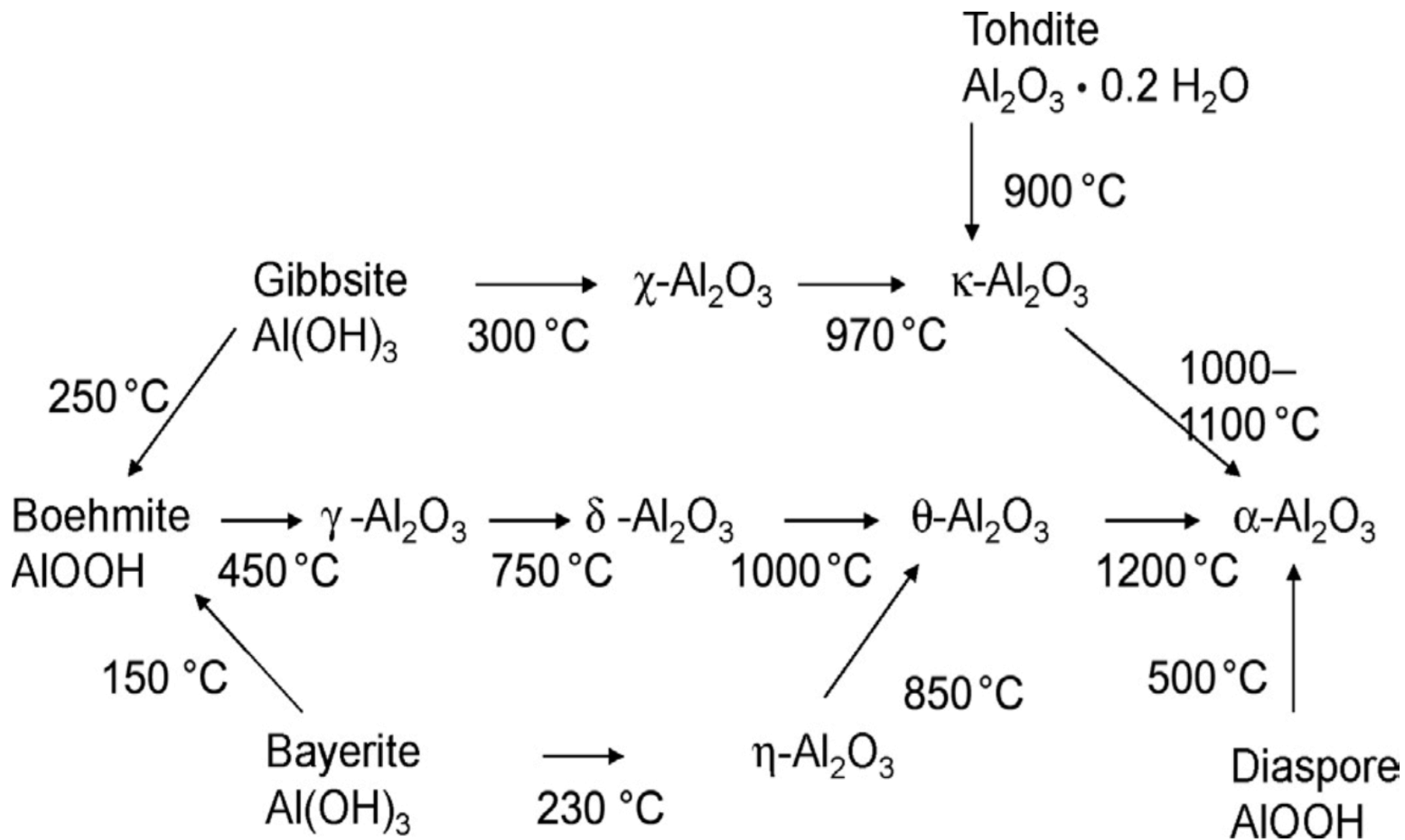


Ceramics materials: Al_2O_3

- single crystal alumina referred to as “Sapphire”
- “Ruby” is alumina with about 1% of Al^{3+} replaced by Cr^{3+} ; yields red color
- “Blue sapphire” is alumina with impurities of Fe and Ti; various shades of blue



Al_2O_3 polymorphs



Al₂O₃ polymorphs

Al ₂ O ₃ Polymorph	Characteristics	Stability T range [°C]
γ-Al ₂ O ₃	- Polymorph with the highest surface area (up to 300 m²/g) - Cubic disordered defective spinel crystal structure with Al³⁺ in O_h (ordered occupation of the sites) and T_d (anisotropic occupation of the sites)	400-600
δ-Al ₂ O ₃	- More organised structure compared to γ-Al₂O₃ - Cubic, closely packed oxygen sublattice similar to γ-Al₂O₃ → similar XRD patterns - Atomic ordering may depend on planar defects' density and distribution in original γ-Al₂O₃	600-1000
θ-Al ₂ O ₃	- Monoclinic structure, deriving from the spinel deformation - Isomorph of β- Ga₂O₃ - Completely ordered distribution of aluminium ions (50% in O_h and 50% in T_d)	1000-1200
α-Al ₂ O ₃ (corundum)	- Irreversible final thermodynamic stable phase after Al₂O₃ calcination - Rhombohedral crystal lattice, where oxide anions build up a compact hexagonal sublattice, in which Al³⁺ ions occupy 2/3 of the O_h interstitial sites	>1200

Table 1. Main characteristics of Al₂O₃ polymorphs

Ceramics materials: Al_2O_3

PROPERTIES

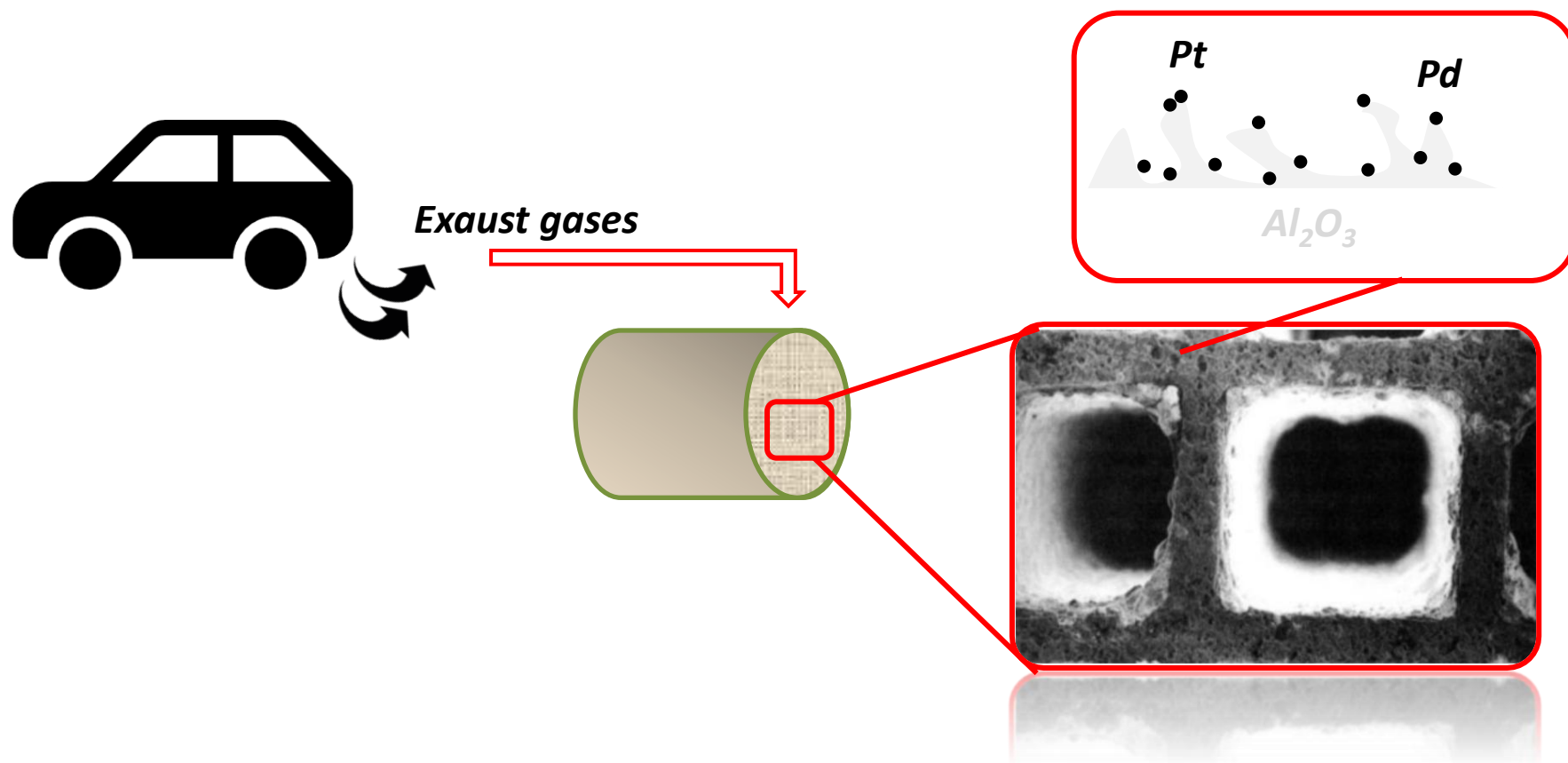
- dielectric and excellent thermal shock properties
- high thermal stability
- inert substance, and at room temperature, it is insoluble in all ordinary chemical reagents
- excellent wear resistance and can be polished to high surface finish
- biocompatible, atoxic

APPLICATIONS

- refractory material
- industrial abrasive material
- extrusion and sanding nozzles and for parts of machinery
- support for heterogeneous catalyst (e.g. in gas exhaust abatement)
- electronics industry for passive components such as interconnection, resistances, and capacitors, multi-layer interconnection circuits, materials for type II condensers, and hyper frequency resonators
- insulating material for applications in very high frequencies
- biomaterial in protheses
- enameling (i.e. coating given to the surface of insulators and other ceramic materials like tiles)

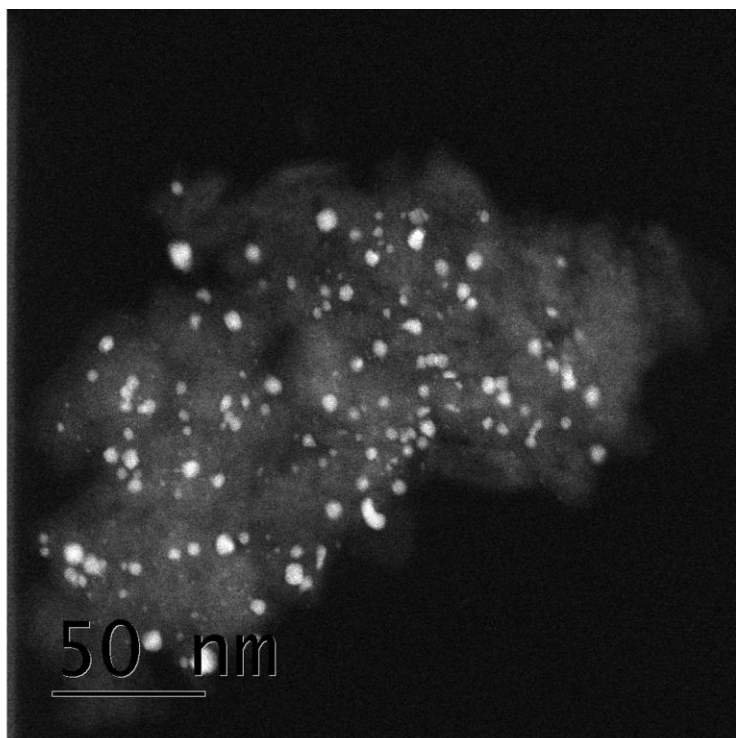
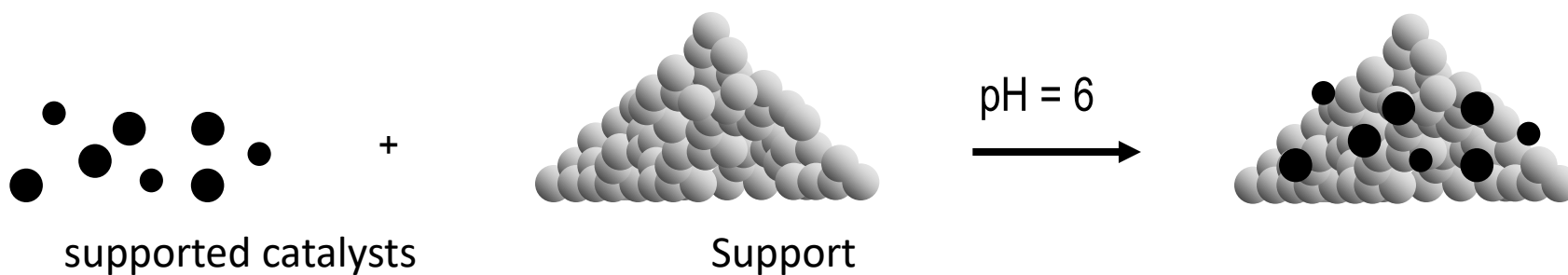
<https://www.preciseceramic.com/blog/uses-of-alumina-in-the-field-of-ceramics/>

Support for gas exhaust abatement



Handbook of Heterogeneous Catalysis, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2008**.

Gas exhaust abatement: Al_2O_3



STEM-HAADF

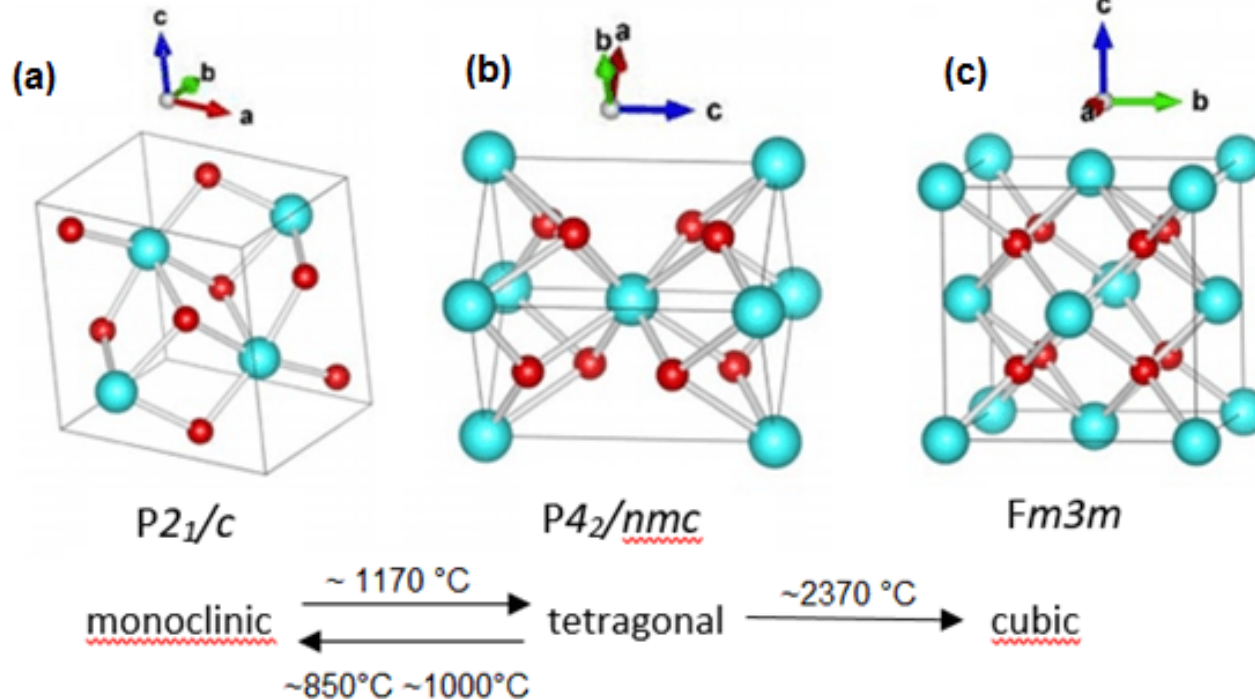
Supports for PM nanoparticles

- Al_2O_3
- SiO_2
- ZrO_2
- CeO_2
- Combination thereof

Ceramics materials: ZrO_2

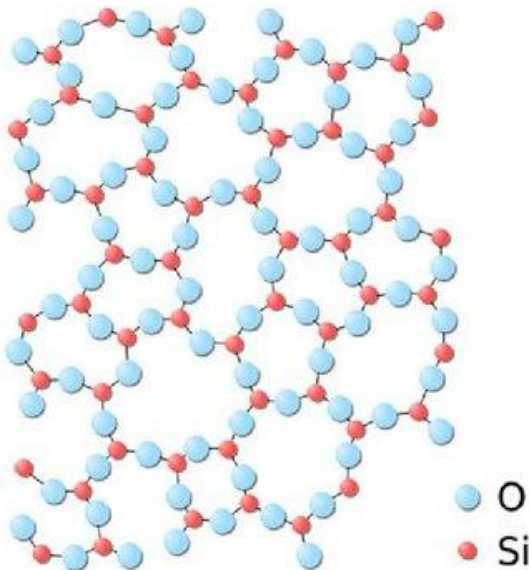
- zirconia
- refractory
- hard, tough

It is white in colour, has good toughness, good resistance to thermal shocks and corrosion, low thermal conductivity, and low coefficient of friction. A more recent development is **partially stabilized zirconia (PSZ), which performs more reliably than zirconia due to higher strength and toughness**. Typical applications of PSZ include dies for hot forming. Another important characteristic of PSZ is that its thermal conductivity is about one-third that of other ceramics. Consequently, it is suitable for heat engine components, such as cylinder liners and valve bushing. A new further development is transformation-toughened-zirconia (TTZ), which has higher toughness than that of PSZ.

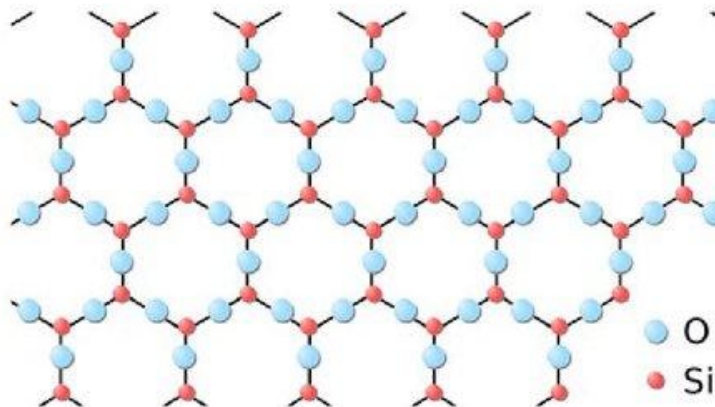


Ceramics materials: SiO_2

- Silica is the most abundant material on earth and it is the common name for inorganic ceramic materials composed of silicon dioxide (SiO_2)
- Different polymorphs with different thermal stabilities
- Silicon dioxide is the most commonly used insulator material in IC technology and in the other fields of silicon device fabrication.

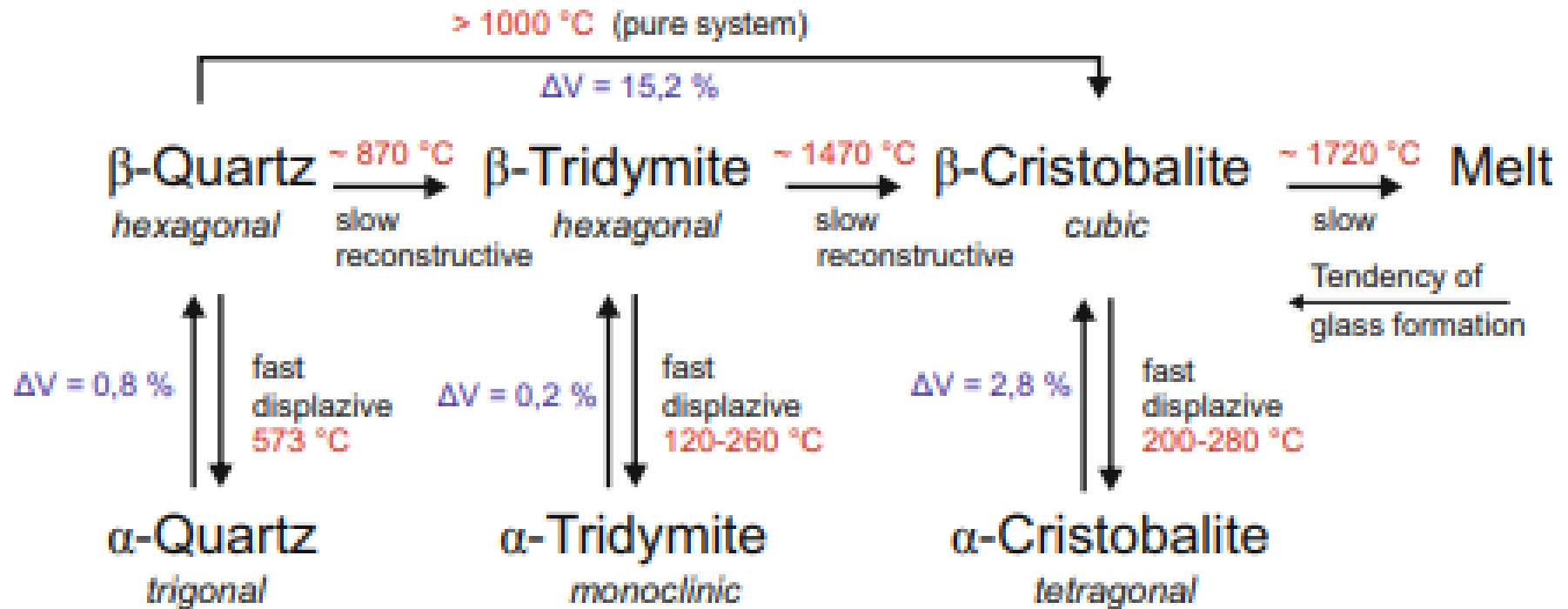


Glass



Quartz

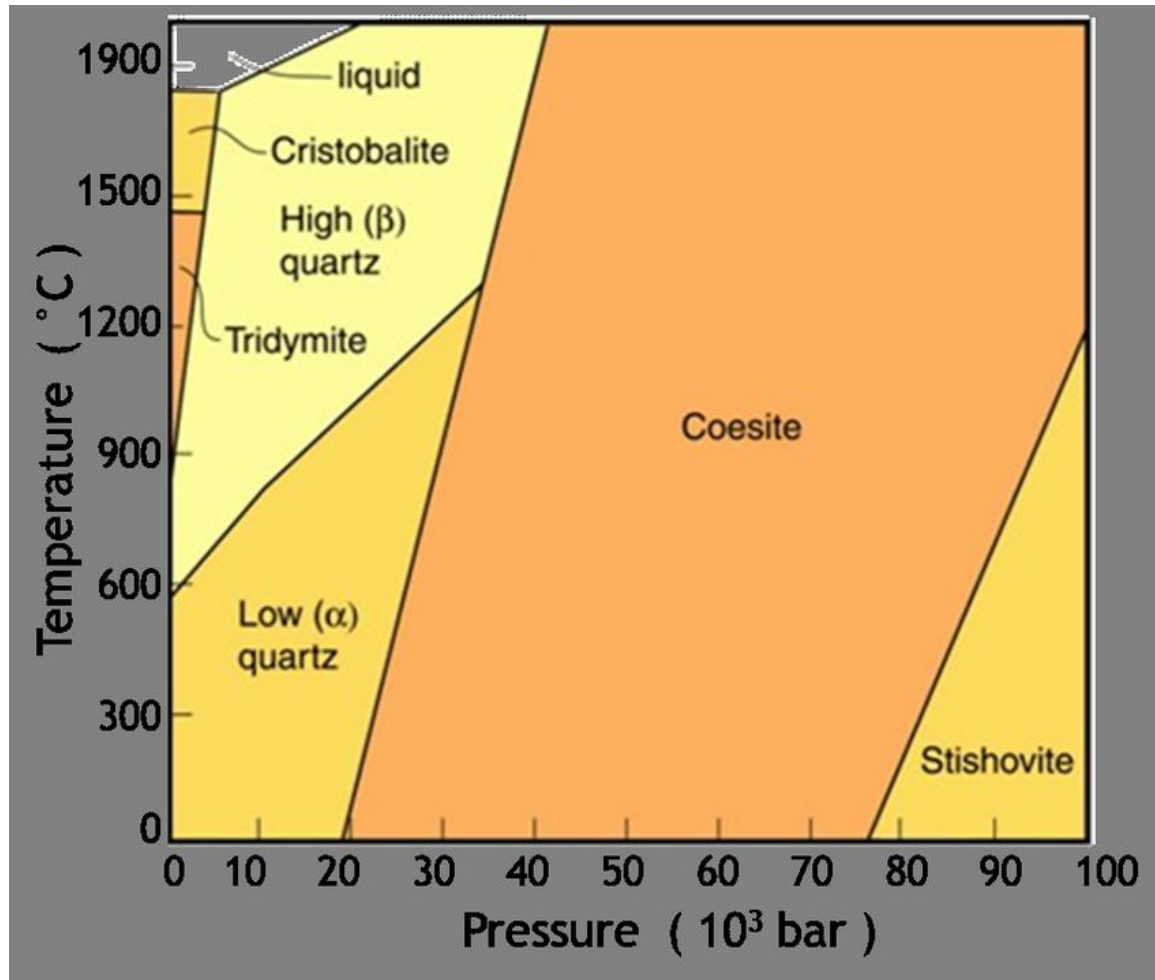
Silica polymorphs



The crystalline modifications of SiO_2 at normal pressure. α low-temperature modification, β high-temperature modification

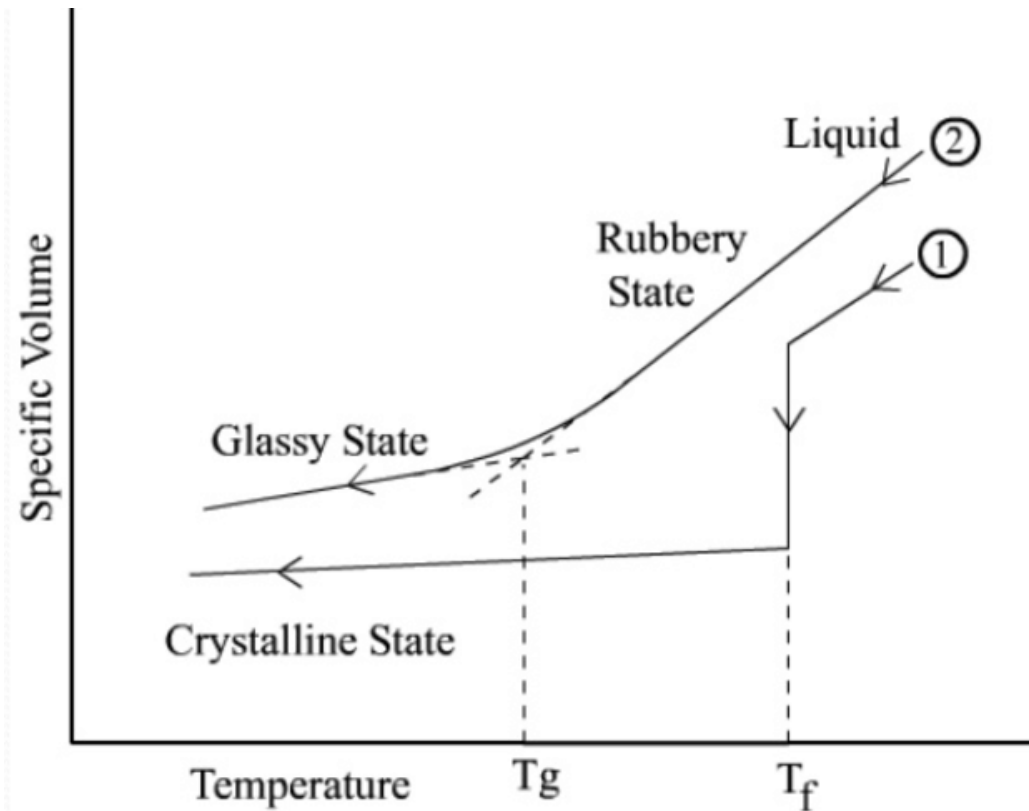
Introduction to Applied Mineralogy - Jens Götze, Matthias Göbbels, Springer ([available as e-book on CAB](#))

- Phase diagram of silica

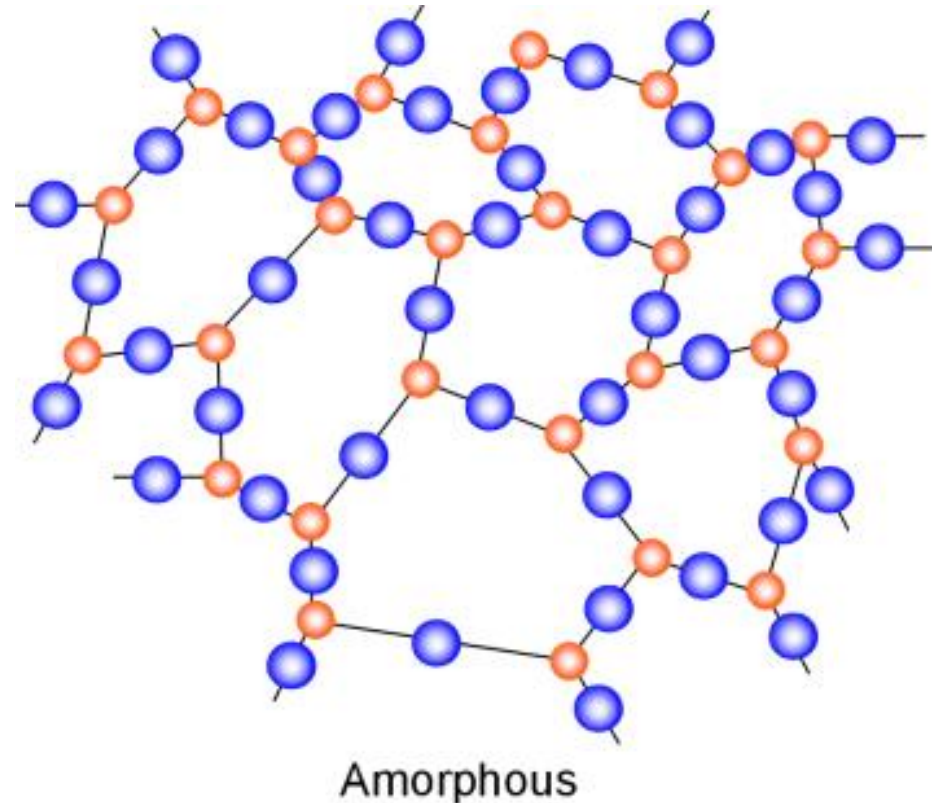
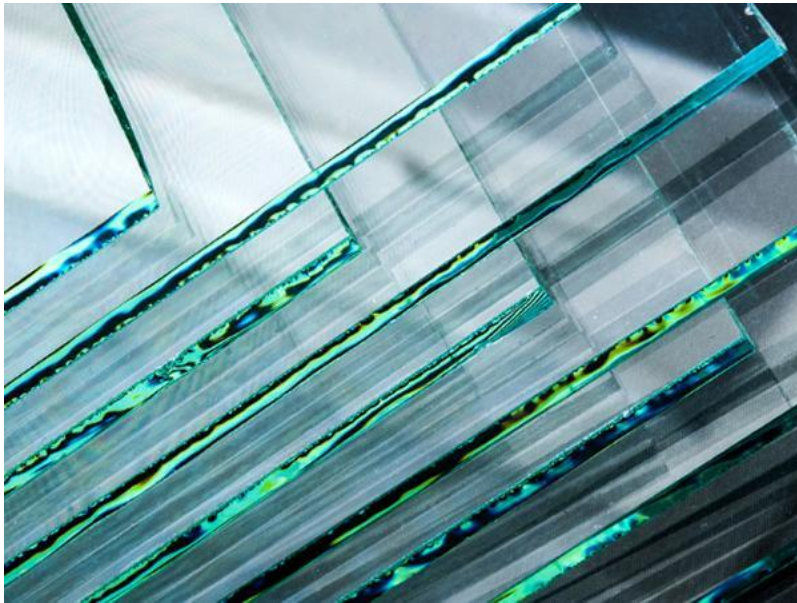


«an amorphous solid completely lacking in long range and periodic atomic structure and exhibiting a region of glass transformation reaction»

The glass transition is the phenomenon in which a solid amorphous phase exhibits more or less abrupt changes in derivative thermodynamic properties such as heat capacity or thermal expansion



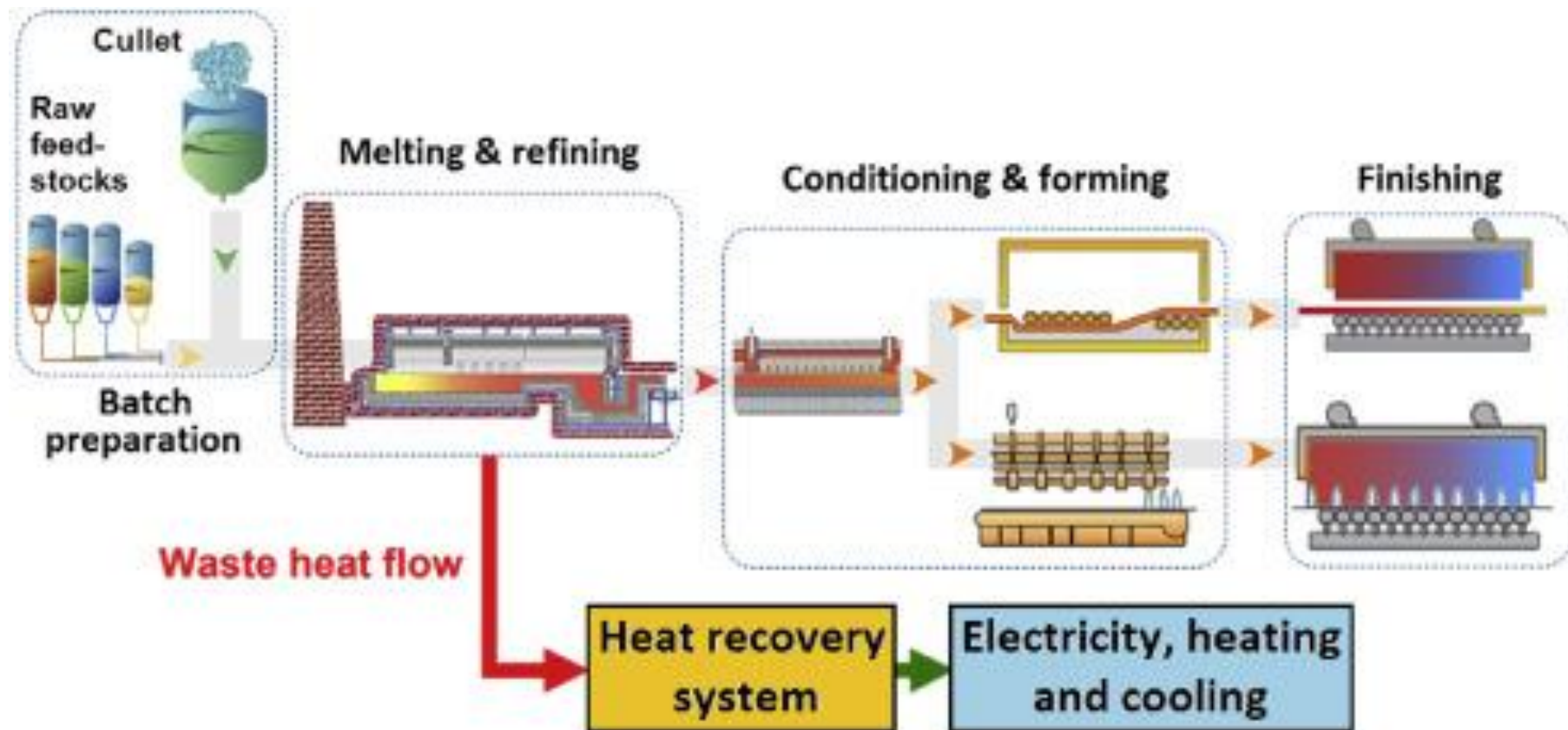
- (i) An inorganic solid material that is usually transparent or translucent as well as hard, brittle
- (ii) An inorganic product of fusion that has cooled from a melt to a rigid condition without crystallization;
- (iii) An amorphous solid.



Amorphous: (i) Lacking detectable crystallinity; (ii) possessing only short-range atomic order; also *glassy* or *vitreous*

Glass-ceramic: Polycrystalline solids prepared by the controlled crystallization (devitrification) of glasses

How to obtain a glass: Traditional route



How to obtain a glass: Traditional route

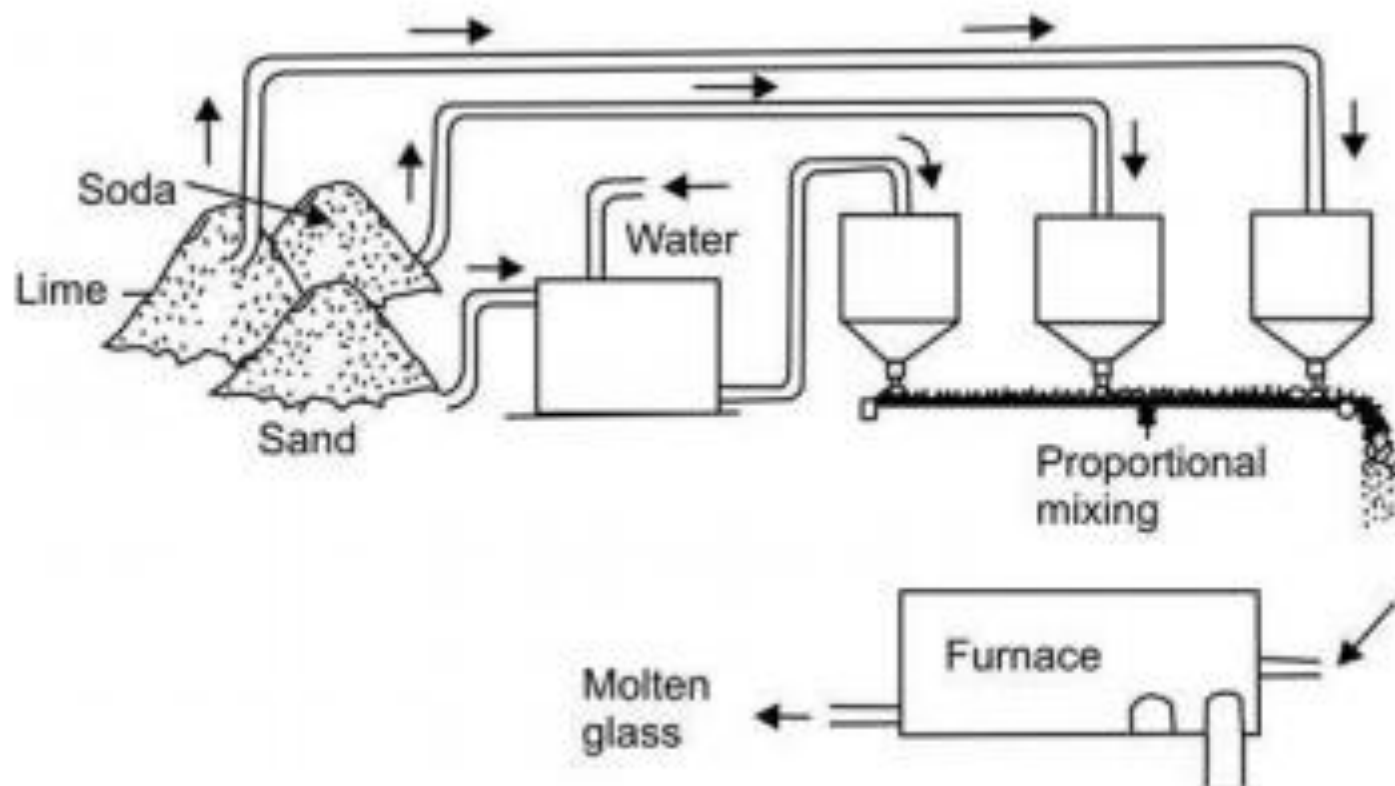
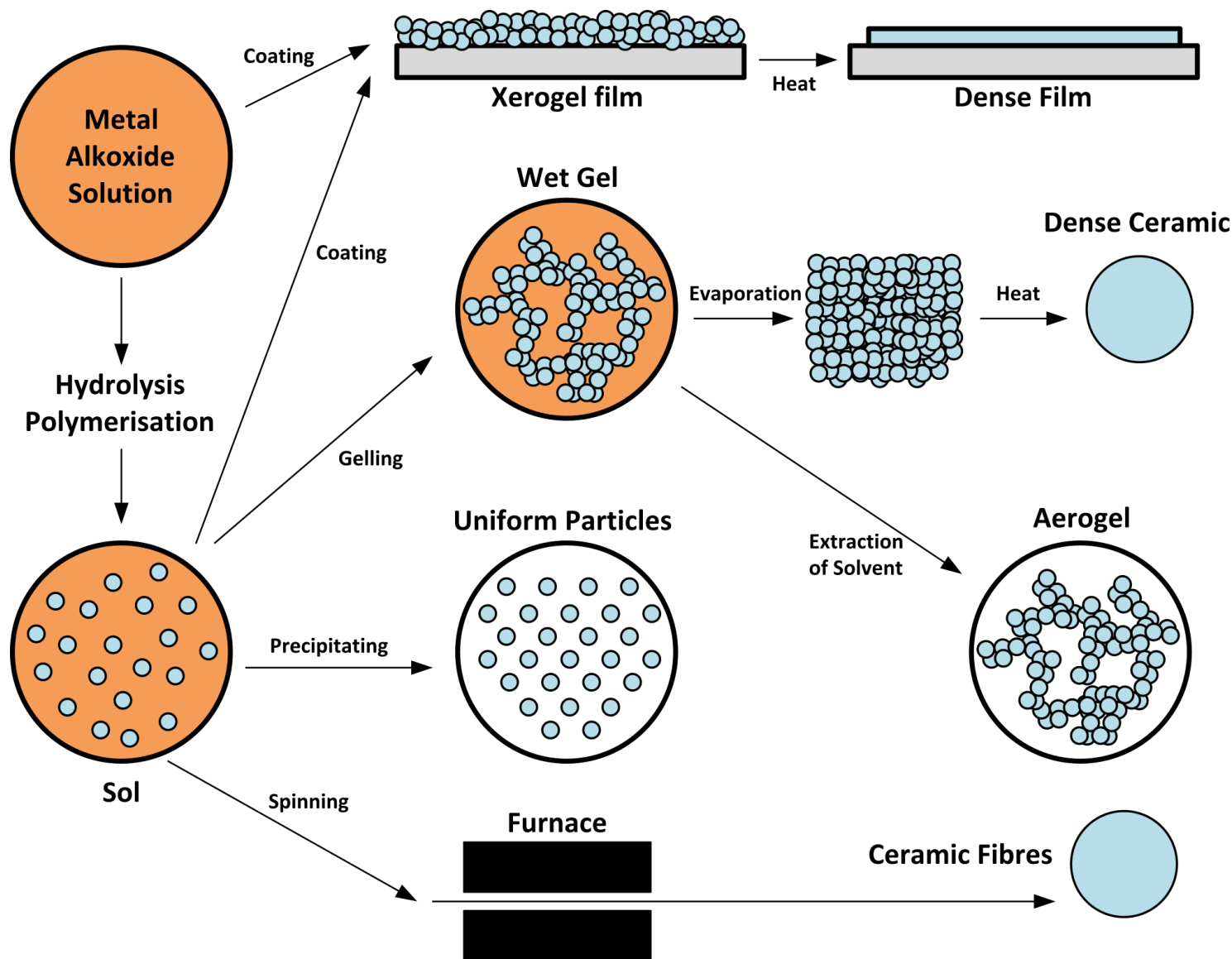
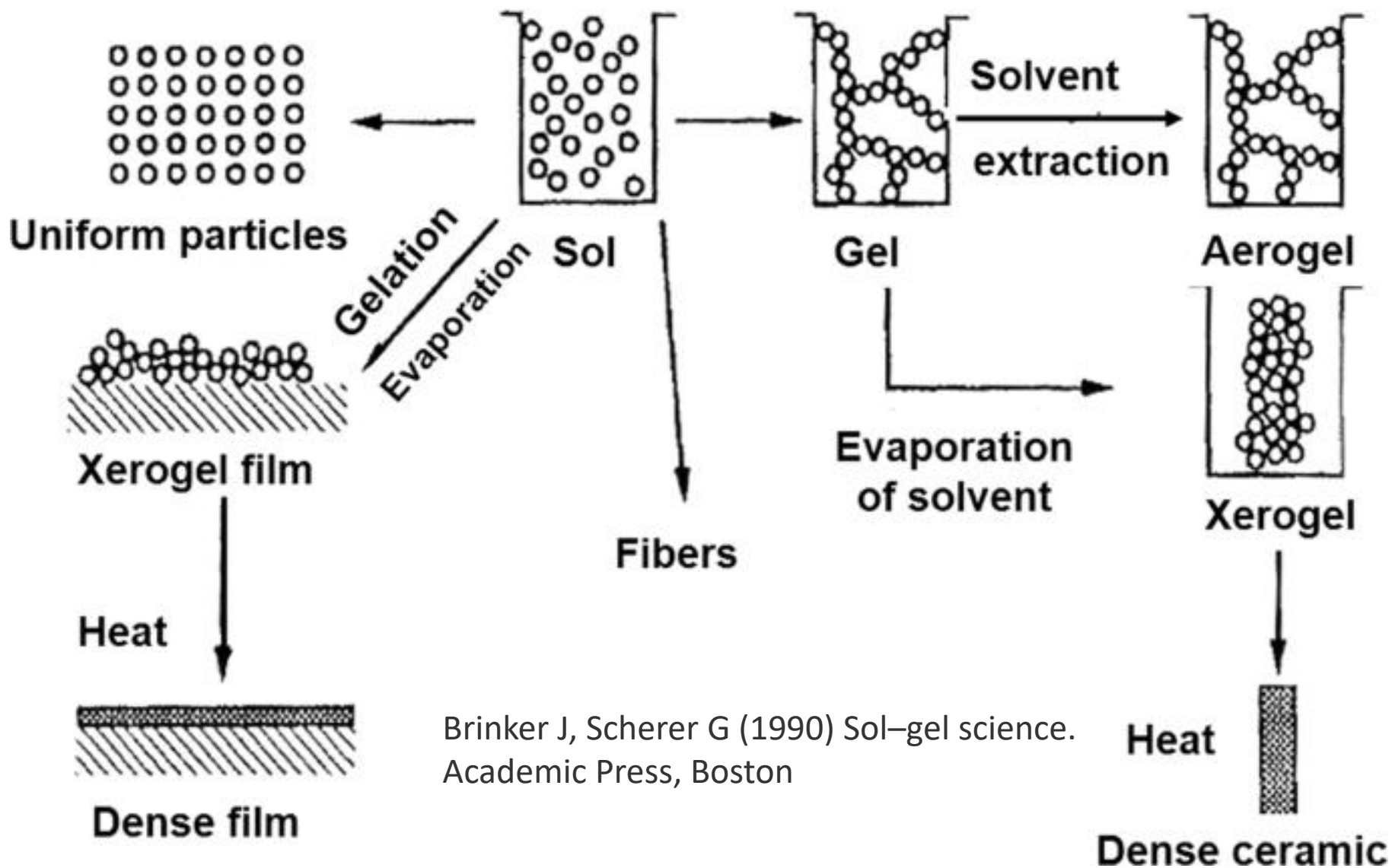


Fig. Glass Manufacturing Process

How to obtain a glass: sol-gel process



Sol-gel process



Brinker J, Scherer G (1990) Sol-gel science.
Academic Press, Boston

Gel

Non-fluid [colloidal network](#) or [polymer network](#) that is expanded throughout its whole volume by a fluid. Notes:

A gel has a finite, usually rather small, [yield stress](#).

A gel can contain:

- a covalent [polymer network](#), e.g., a [network](#) formed by [crosslinking](#) polymer chains or by non-linear [polymerization](#);

- a [polymer network](#) formed through the physical aggregation of polymer chains, caused by hydrogen bonds, [crystallization](#), [helix](#) formation, complexation, *etc*, that results in regions of local order acting as the [network](#) junction points. The resulting swollen [network](#) may be termed a [thermoreversible gel](#) if the regions of local order are thermally reversible;

- a [polymer network](#) formed through glassy junction points, e.g., one based on [block](#) copolymers. If the junction points are thermally reversible glassy domains, the resulting swollen [network](#) may also be termed a [thermoreversible gel](#);

- lamellar structures including mesophases, e.g., [soap](#) gels, [phospholipids](#) and clays;

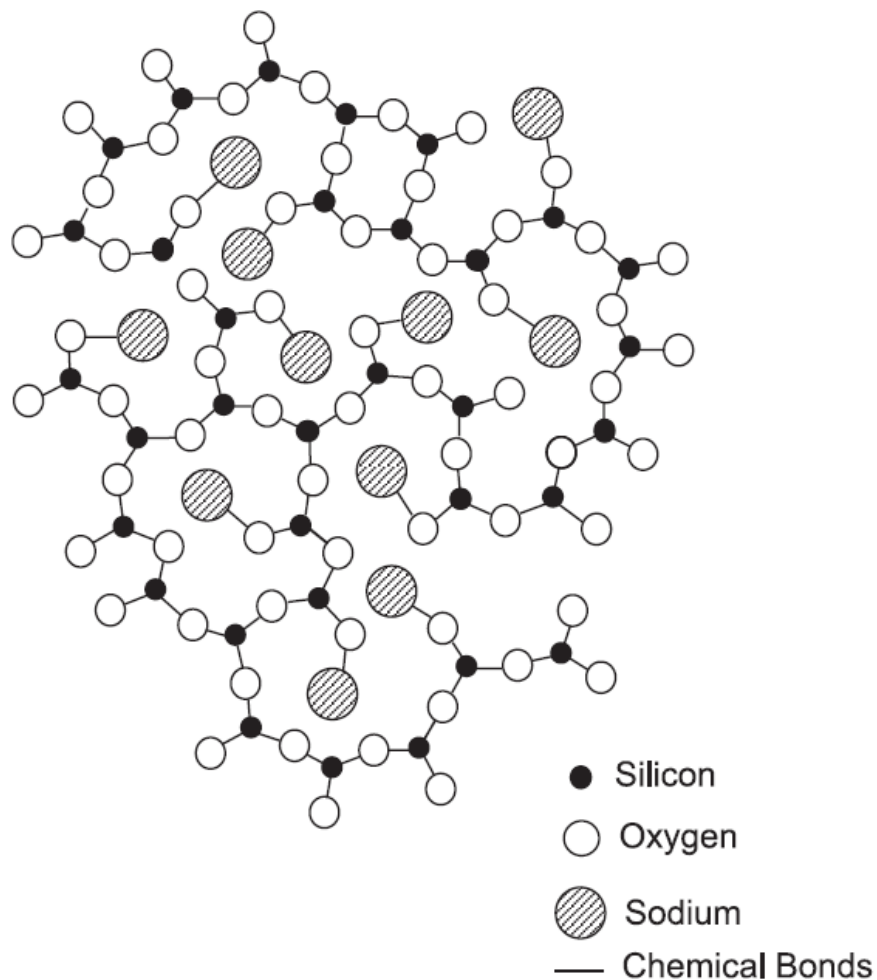
- particulate disordered structures, e.g., a flocculent precipitate usually consisting of particles with large geometrical [anisotropy](#), such as in V_2O_5 gels and globular or fibrillar protein gels.

Source: IUPAC

Sol

In a suspension (sol) solid particles are dispersed in a liquid; a colloidal suspension is one in which the size of the particles lies in the colloidal range.

Source: IUPAC



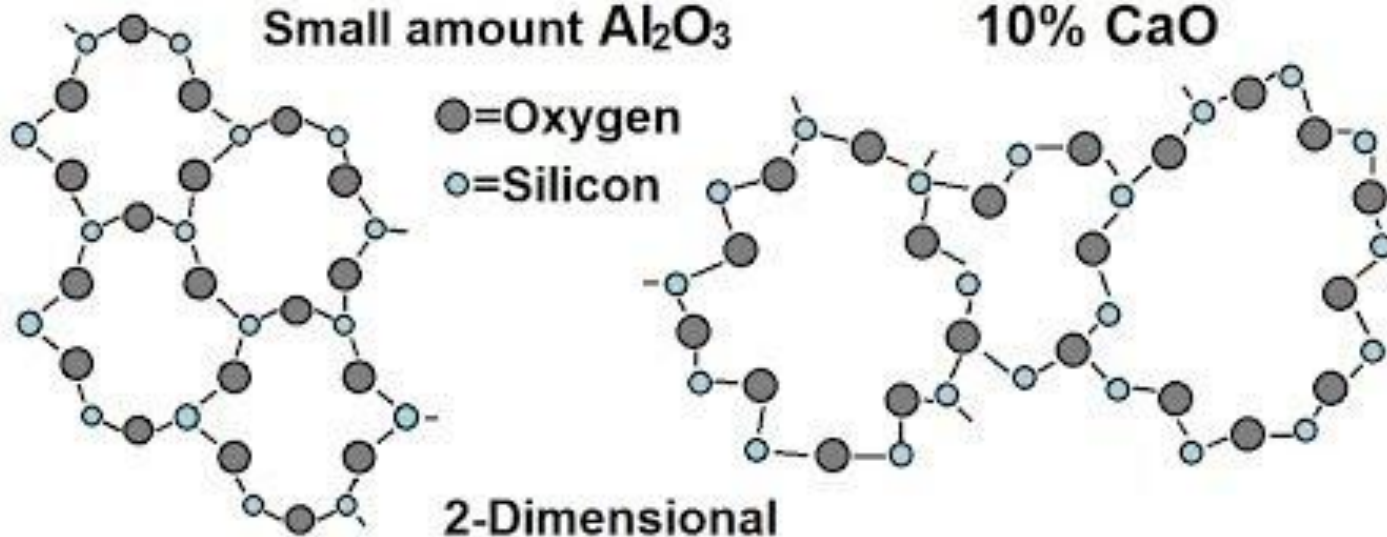
Idealized model of the amorphous atomic structure of a typical glass. There is no long-range order or orientation, and properties are isotropic.

Amorphous solids → Not crystalline

Quartz
100% SiO_2

Pyrex
60-90% SiO_2
10-25% B_2O_3
Small amount Al_2O_3

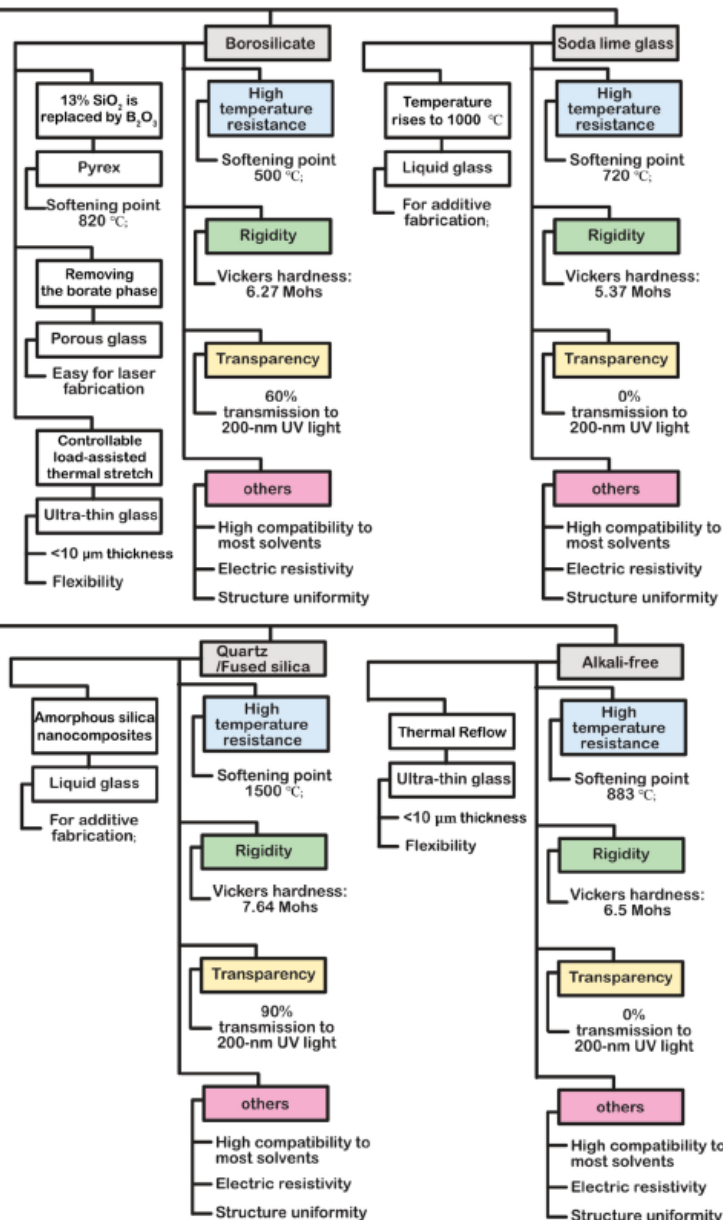
Soda lime glass
75% SiO_2
15% Na_2O
10% CaO



Glass families

Families of glasses.

Source of the picture: Tang et al. Sensors and Actuators: B. Chemical 339 (2021) 12985



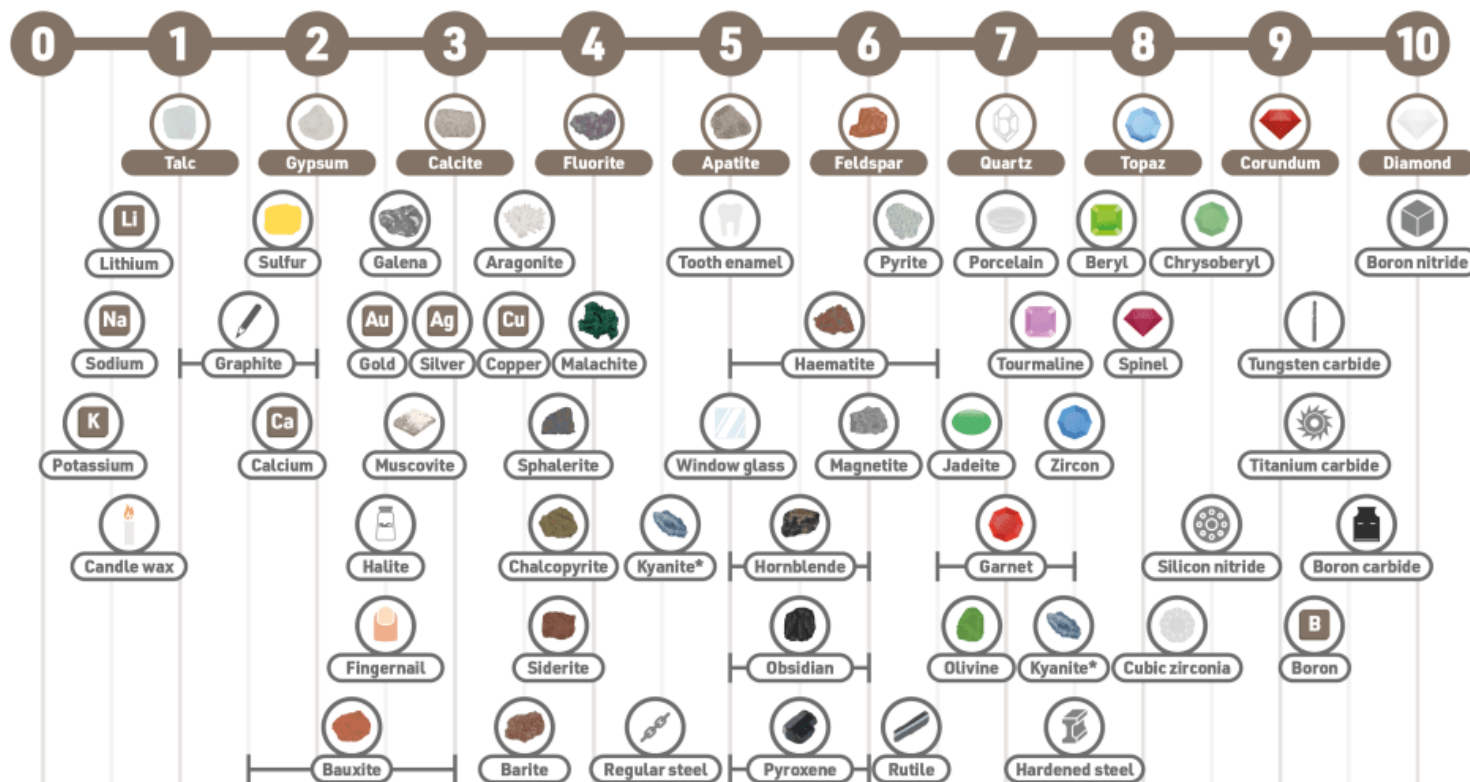
Mohs Hardness Mineral Scale

Mineral	Mohs Hardness	Observations
Talc	1	Easily scratched by fingernail
Gypsum	2	Can be scratched by fingernail
Calcite	3	Easily scratched with sharp metal edge
Flourite	4	Can be scratched with sharp metal edge
Apatite	5	Can be scratched with sharp metal edge, not easily
Orthoclase	6	Cannot be scratched with sharp metal edge, can scratch glass with difficulty
Quartz	7	Easily scratches glass
Topaz	8	Very easily scratched glass
Corundum	9	Cuts glass
Diamond	10	Used as a glass cutter

The Mohs Mineral Hardness Scale



German Geologist Friedrich Mohs introduced the Mohs hardness scale in 1812. It is based on the ability of one mineral to scratch another: a mineral that scratches another will be above that mineral in the scale. The scale is a relative ranking, with no fixed difference in hardness between each point on the scale.



* Kyanite's hardness differs depending on the direction in which it is tested – softer when tested parallel to crystals, and harder when tested perpendicular.

Soda-lime glass is an amorphous mixture of mainly SiO_2 (~75 %) with a small amount of **sodium, calcium, aluminum, potassium and sulphur dioxide**. Its heat and chemical resistance are lower than those of borosilicate glass, due to the substitution of boric oxide for soda and lime in the composition.

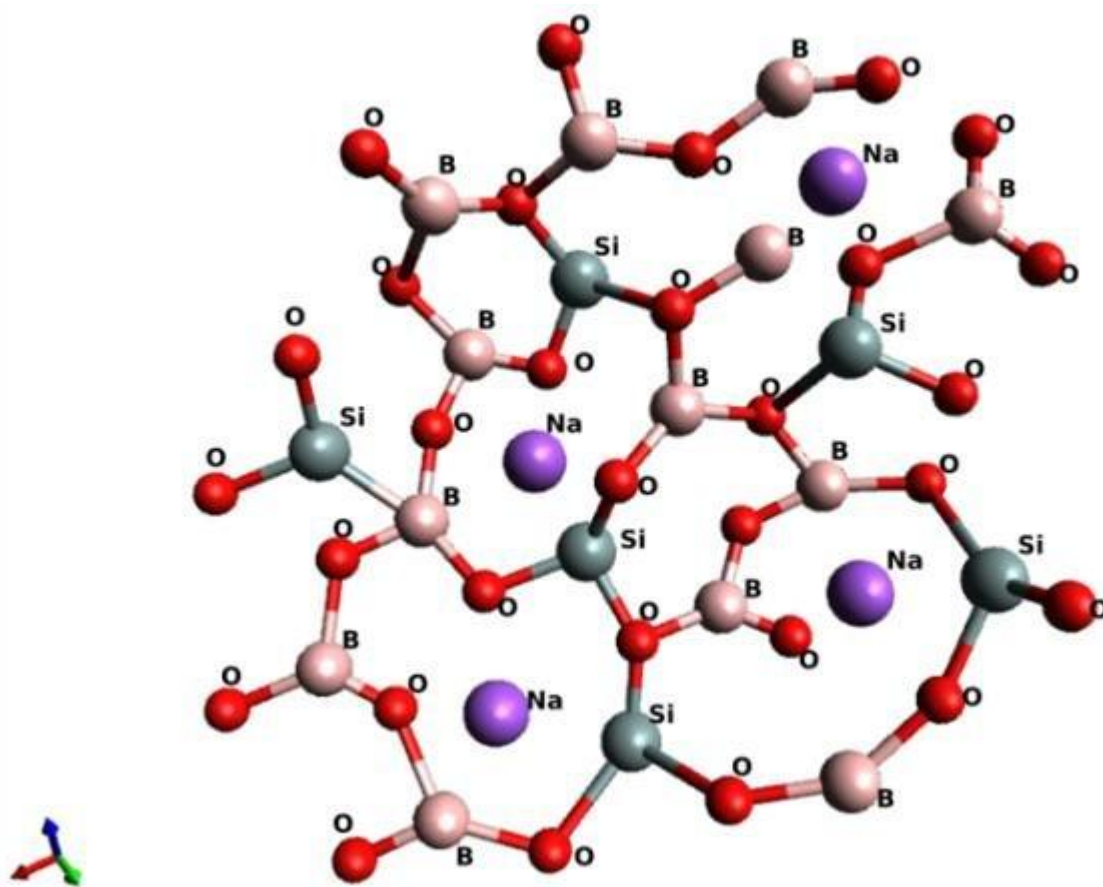
Compared to borosilicate (Pyrex) and fused silica, soda lime glass has a higher proportion of non-silicate elements and therefore has more plastic deformation processes along the slip line and tends to show ductile erosion behaviour.

Borosilicate glass is one of the earliest types of glass applied in the fabrication of biochips, the main components of which are **silica and boron trioxide** (at least 5%).

Borosilicate glass is widely applied as a base plate for microfluidic devices due to its chemical resistance to liquids, which has been used for cell culturing or chemical synthesis.

Tang et al. Sensors and Actuators: B. Chemical 339 (2021) 12985

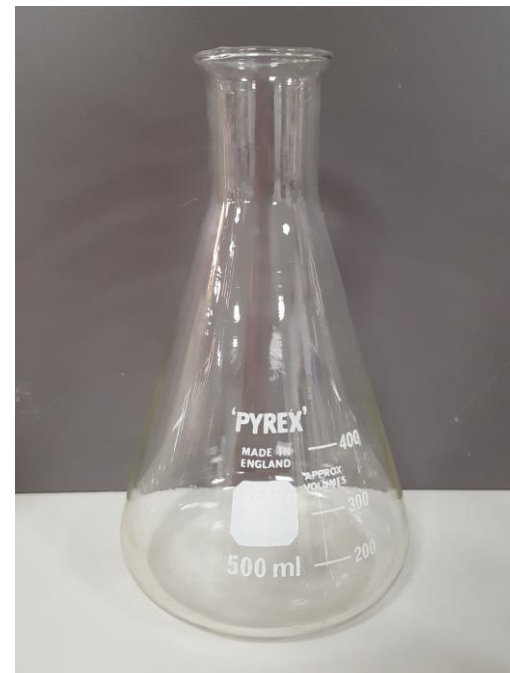
Borosilicate glass



Schematic representation of the structure of network formers and network modifier in borosilicate glass. Source of picture: S, Does & C, et al. (2019). Blucher Proceedings X Encontro Científico de Física Aplicada Effect of thermal treatment on morphological properties of borosilicates glass doped with silver.

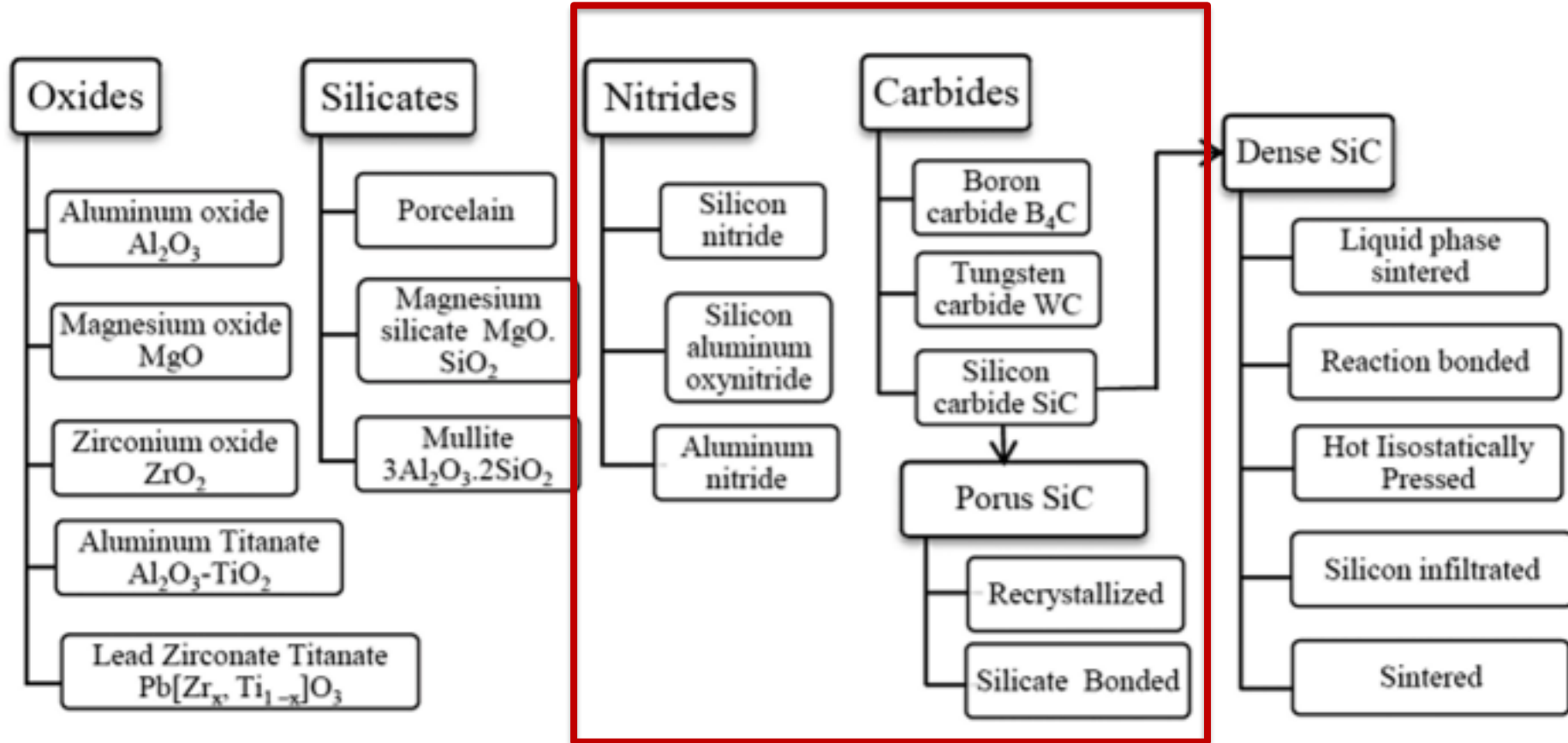
Pyrex glass, one of **commercial borosilicate glasses**, is mainly composed of SiO_2 (~81 %). Compared to borosilicate glass, pyrex has changed its chemical composition or provided some process, for example, a small amount of SiO_2 is replaced by B_2O_3 (13 %).

As a result, pyrex glass has a **low thermal expansion coefficient of $3.3 \times 10^{-6} \text{ K}^{-1}$ to 400°C** , which is similar to that of silicon. But glass has a lower thermal conductivity ($1 \text{ W/m}\cdot\text{K}$) than silicon ($146 \text{ W/m}\cdot\text{K}$). **Highly thermally stable (up to 820°C)**.



Alkali-free glass, free of alkali oxides and composed of 15–25% Al_2O_3 , 52–60% SiO_2 , and about 15 % alkaline earths, has a very high transformation temperature and softening point.

Ceramics materials: non oxide



General classification of ceramics composition based (from Encyclopedia Britannica. Britannica.com).

Carbides

Carbides are the main precipitate product of carbon, either as primary MC-type carbides, where M is a metal component, or as secondary carbides.

From: [Welding and Joining of Aerospace Materials, 2012](#)

Ceramics materials: carbides and nitrides

Table 1. Fundamental properties of selected transition metal carbides/nitrides. Values are for room temperature and stoichiometric composition. Reproduced with permission from ref. [14].

Compound	Density [g cm ⁻³]	Microhardness [GPa]	Melting point [°C]	Young's modulus [GPa]	Heat conductivity [W m ⁻¹ K ⁻¹]	Linear thermal expansion coefficient [(10 ⁻⁶) K ⁻¹]	Electrical resistivity [μΩ cm]
Carbides							
TiC	4.93	28	3067	450	28.9	8.5	100
ZrC	6.46	25	3420	350	24.6	7.5	75
HfC	12.3	20	3930	420	25.1	6.1	67
VC _{0.88}	5.36	26	2650	430	26.8	7.2	69
NbC	7.78	18	3610	340	27.0	6.6	20
TaC	14.48	16	3985	290	22.1	6.3	15
Cr ₃ C ₂	6.68	27	1810	380	14.0	10.3	75
Mo ₂ C	9.18	17	2520	530	15.0	7.8	57
WC	15.72	23	2776	707	19.0	3.9	17
Nitrides							
TiN	5.39	17	3050	420	29	9.9	27
ZrN	7.32	15	3000	460	11	7.8	24
HfN	13.83	18	3330	380	11	8.5	27
VN	6.04	5.7	2350	380	11	10.8	65
NbN	8.16	11	Decomposes	360	3.8	10.2	60
TaN	15.9	32	Decomposes	—	—	8.0	—
CrN	6.14	13	Decomposes	450	—	—	—

Ceramics materials: carbides and nitrides

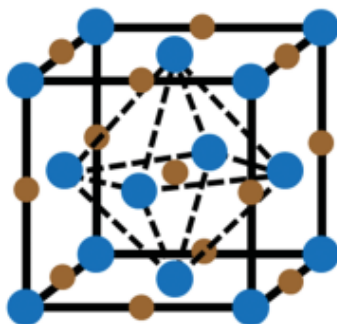
a

IVB	VB	VIB	VIIB	VIII B		
Ti*	V	Cr	Mn	Fe	Co	Ni
Zr	Nb	Mo	Tc	Ru	Rh	Pd
Hf	Ta	W	Re	Os	Ir	Pt

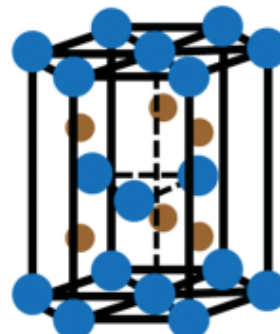
	MC/MN		M_3C_2/M_3N_2		M_3C/M_3N
	MC_{1-x}/MN_{1-x}		M_2C/M_2N		M_3N
	No stable carbide/nitride				

*Titanium carbides can be also attributed to MC_{1-x}

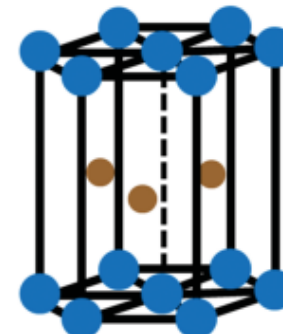
b



Face-Centered Cubic (fcc)



Hexagonal Closed Packed (hcp)



Simple Hexagonal (hex)

Ceramics materials: carbides

Tungsten carbide consists of WC powder with cobalt (Co) as binder. Co has a major influence on the properties of this ceramic. Toughness increases with Co content, whereas both hardness and strength decrease.

Titanium carbide consists of TiC powder with nickel, and molybdenum as binder. It is not as tough as WC, but harder.

Silicon carbide (SiC) has good wear, thermal shock, and corrosion resistance. It has low coefficient of friction and retains its strength at elevated temperature. It is suitable for high temperature components in heat engines and is also used as an abrasive. Synthetic SiC is made from silica sand, coke, and small amounts of nail and saw dust, in a similar way to that of synthetic Al_2O_3 .



WC



Ceramics materials: nitrides

Cubic boron nitride (C-BN) is the second hardest known substance after diamond. It does not exist in nature and was first made synthetically in the 1970s, with similar techniques as synthetic diamond.

Titanium nitride (TiN) is extensively used as coatings on cutting tools to improve tool life due to its low coefficient of friction.

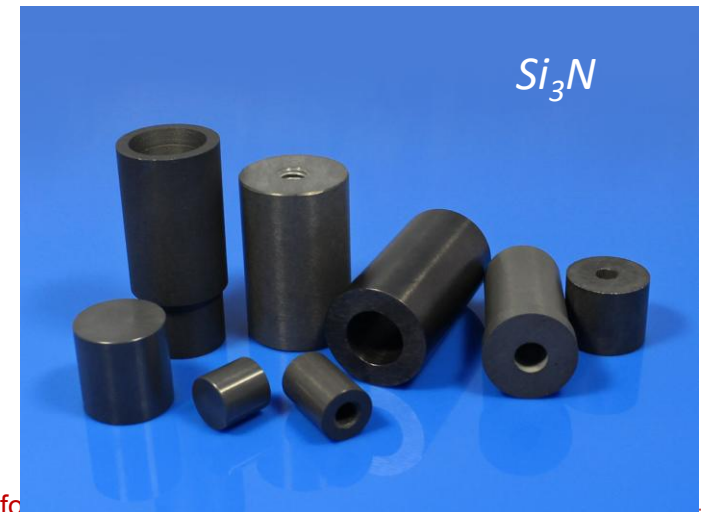
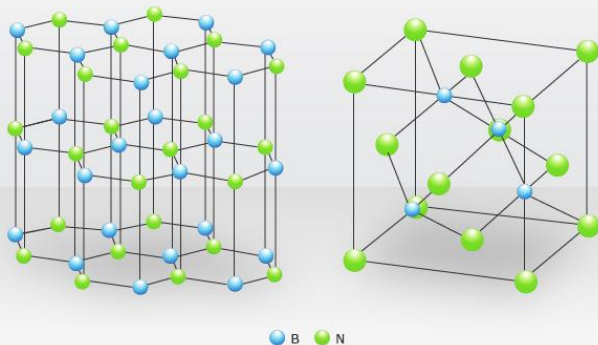
Silicon nitride (Si_3N_4) has high creep resistance at elevated temperatures, low thermal expansion, and high thermal conductivity. Hence, it resists thermal shocks. Therefore, it is suitable for high temperature applications, such as in automotive engines and gas turbine components, bearings, and components for the paper industry.

Sialon and cermets are used as materials for cutting tools and cutting tips for machining DTC materials.

Boron nitride

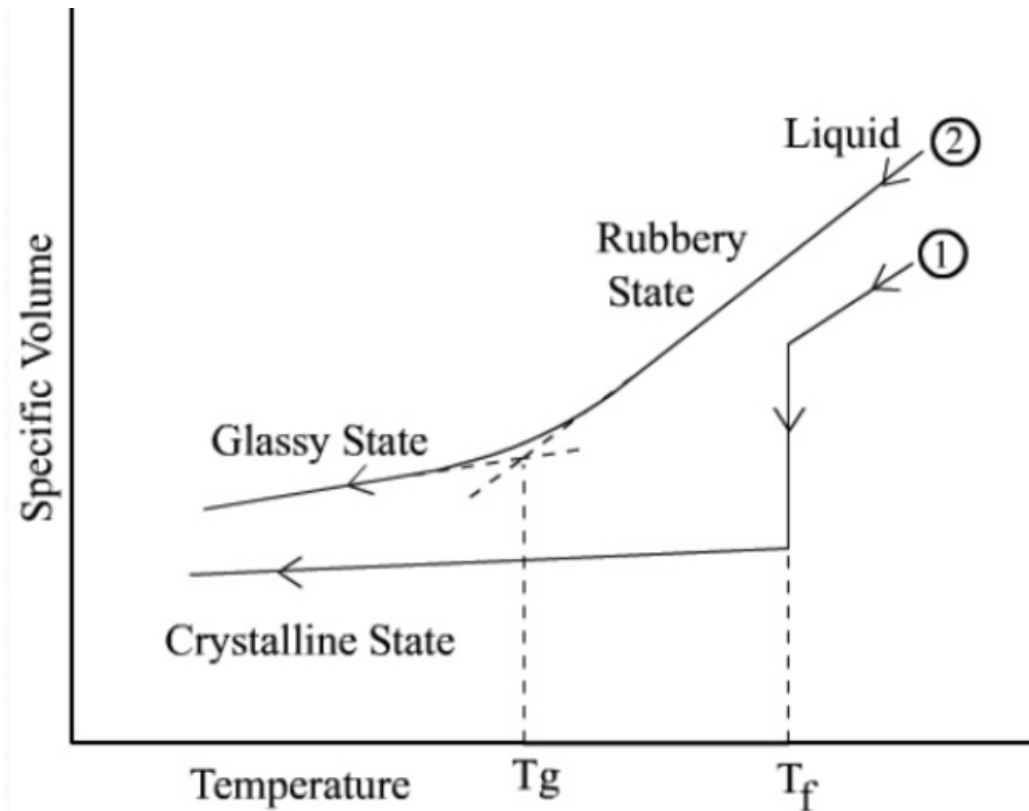
Hexagonal boron nitride

Cubic boron nitride

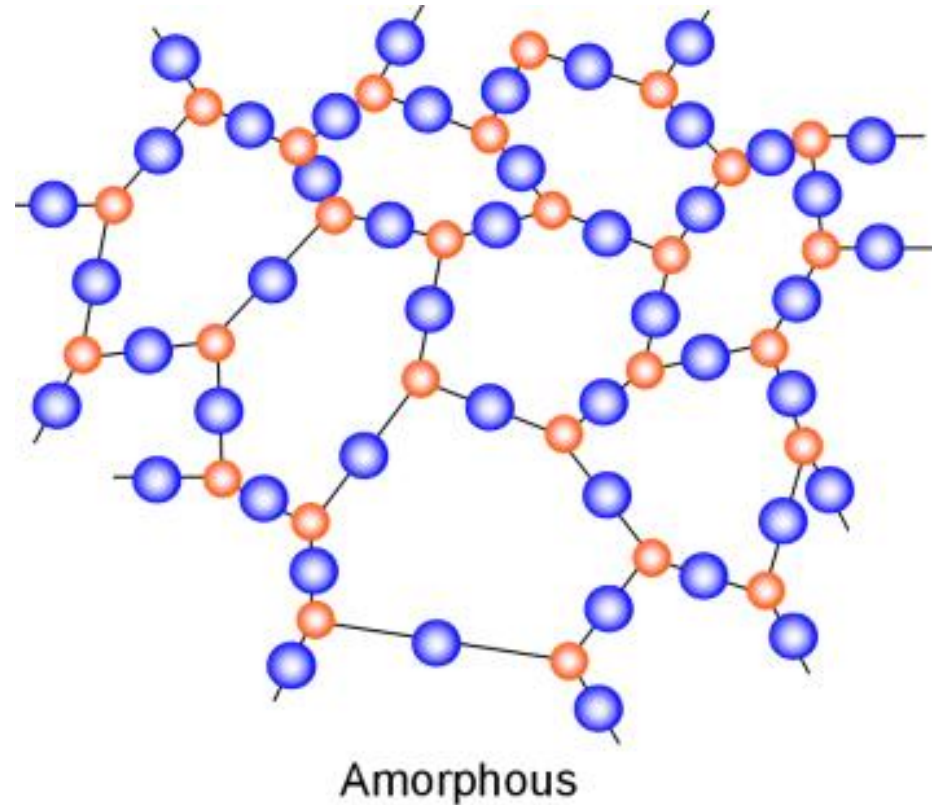
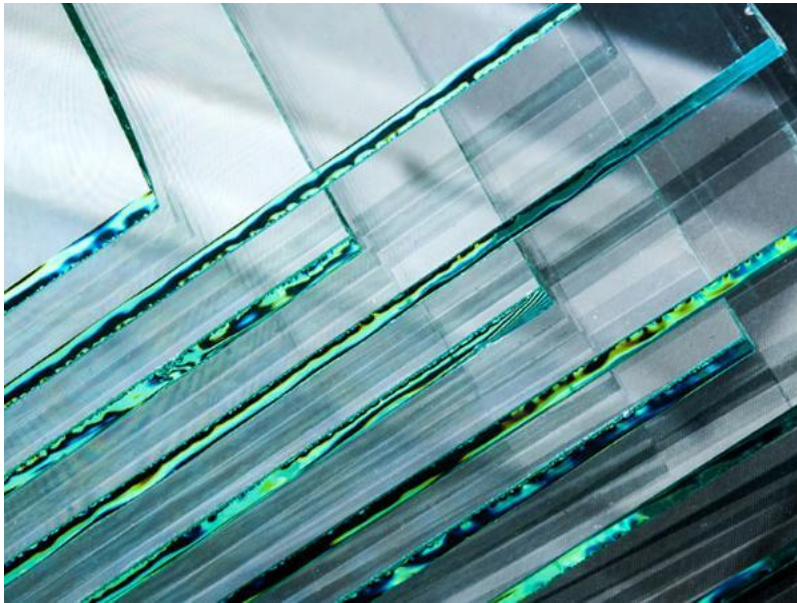


«an amorphous solid completely lacking in long range and periodic atomic structure and exhibiting a region of glass transformation reaction»

The glass transition is the phenomenon in which a solid amorphous phase exhibits more or less abrupt changes in derivative thermodynamic properties such as heat capacity or thermal expansion: when an amorphous material changes from a solid state to a liquid state on heating or from a liquid to a solid-like state on cooling.



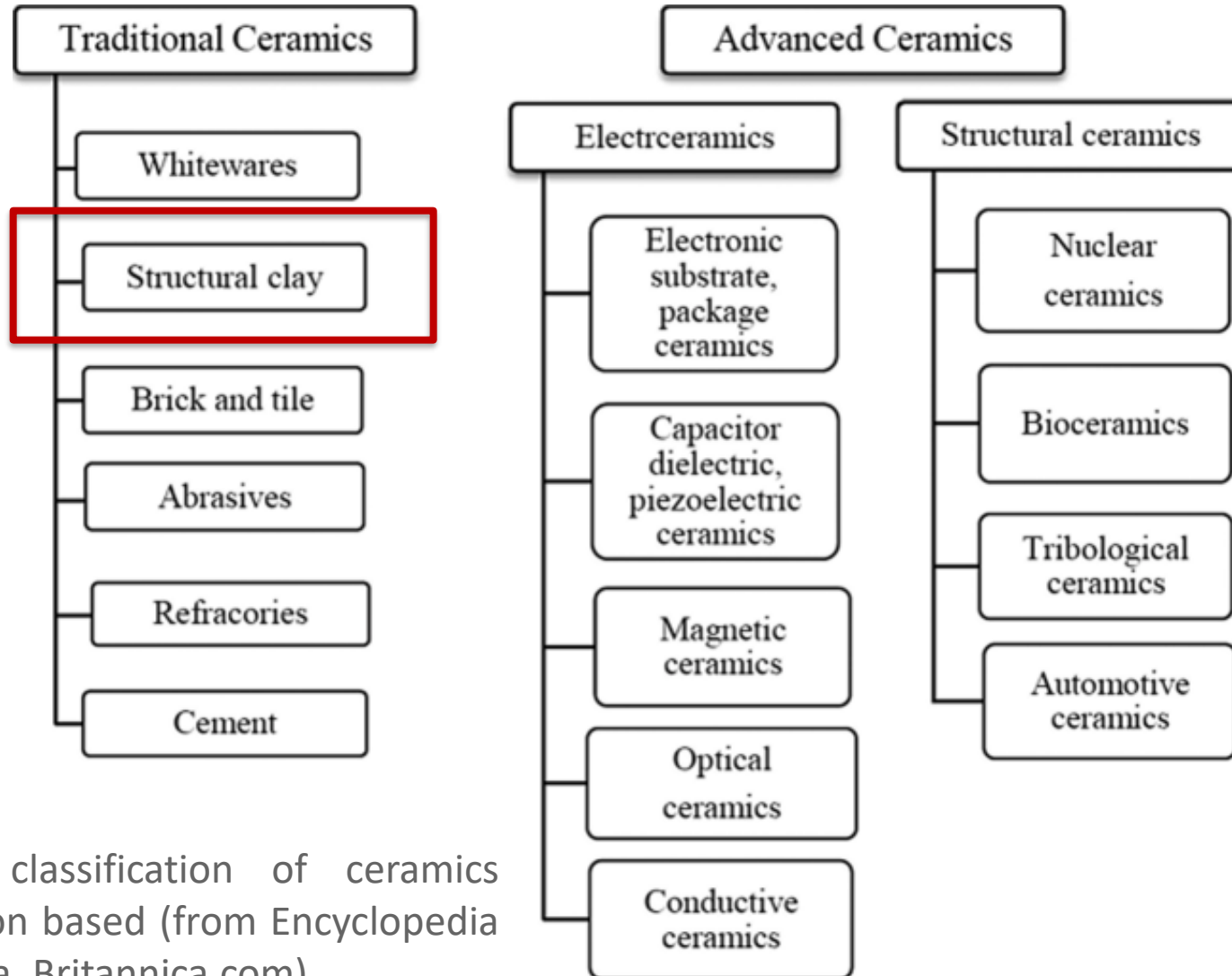
- (i) An inorganic solid material that is usually transparent or translucent as well as hard, brittle
- (ii) An inorganic product of fusion that has cooled from a melt to a rigid condition without crystallization;
- (iii) An amorphous solid.



Amorphous: (i) Lacking detectable crystallinity; (ii) possessing only short-range atomic order; also *glassy* or *vitreous*

Glass-ceramic: Polycrystalline solids prepared by the controlled crystallization (devitrification) of glasses

Ceramics materials



General classification of ceramics application based (from Encyclopedia Britannica. Britannica.com).

The term "clay" is applied both to:

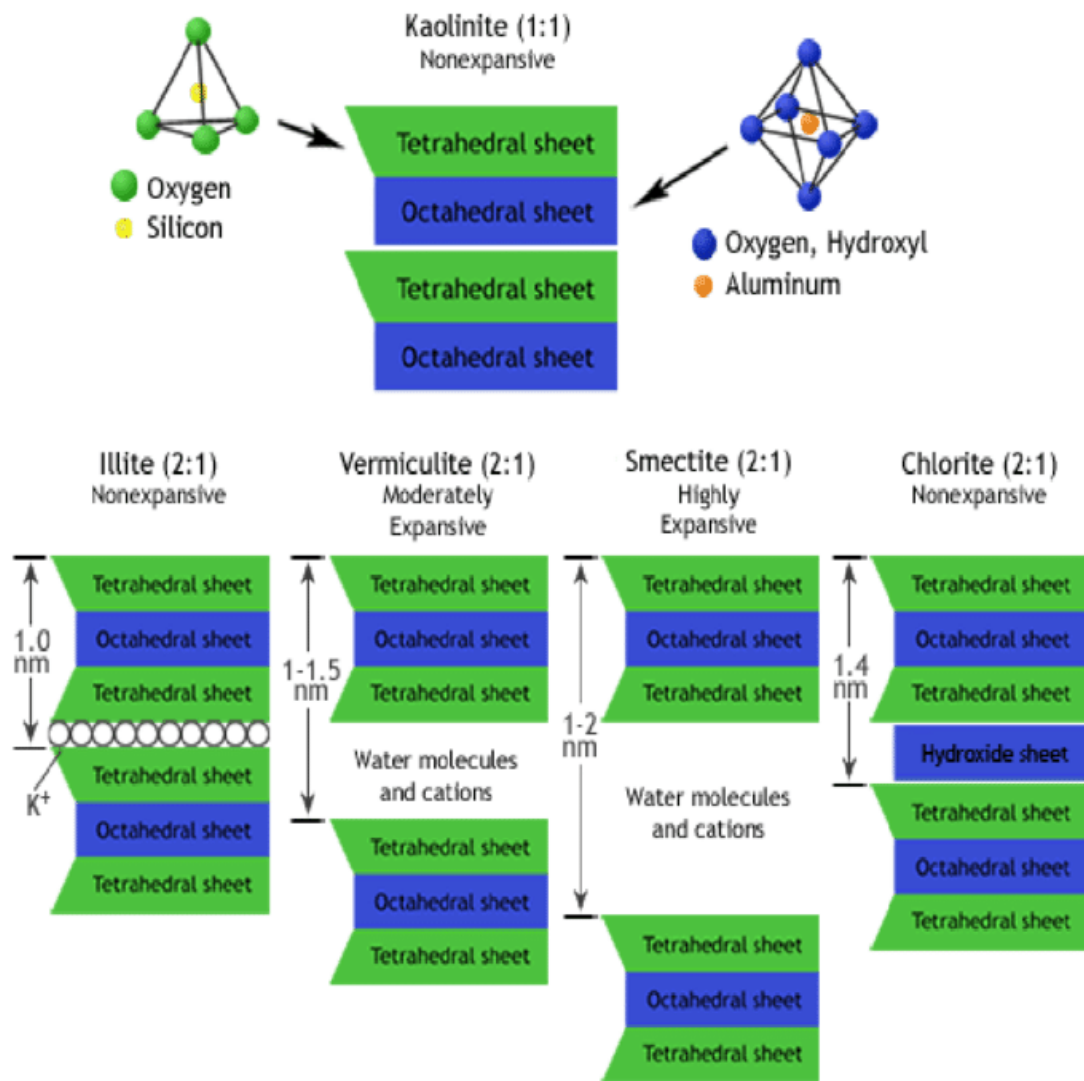
- materials having a particle size of less than 2 micrometers and to
- family of minerals that has similar chemical compositions and common crystal structural characteristics.
- Clay minerals have a wide range of particle sizes from 10's of angstroms to millimeters.
- Clays may be composed of mixtures of finer grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate, and metal oxides. Clays and clay minerals are found mainly on or near the surface of the Earth.

U.S. Geological Survey

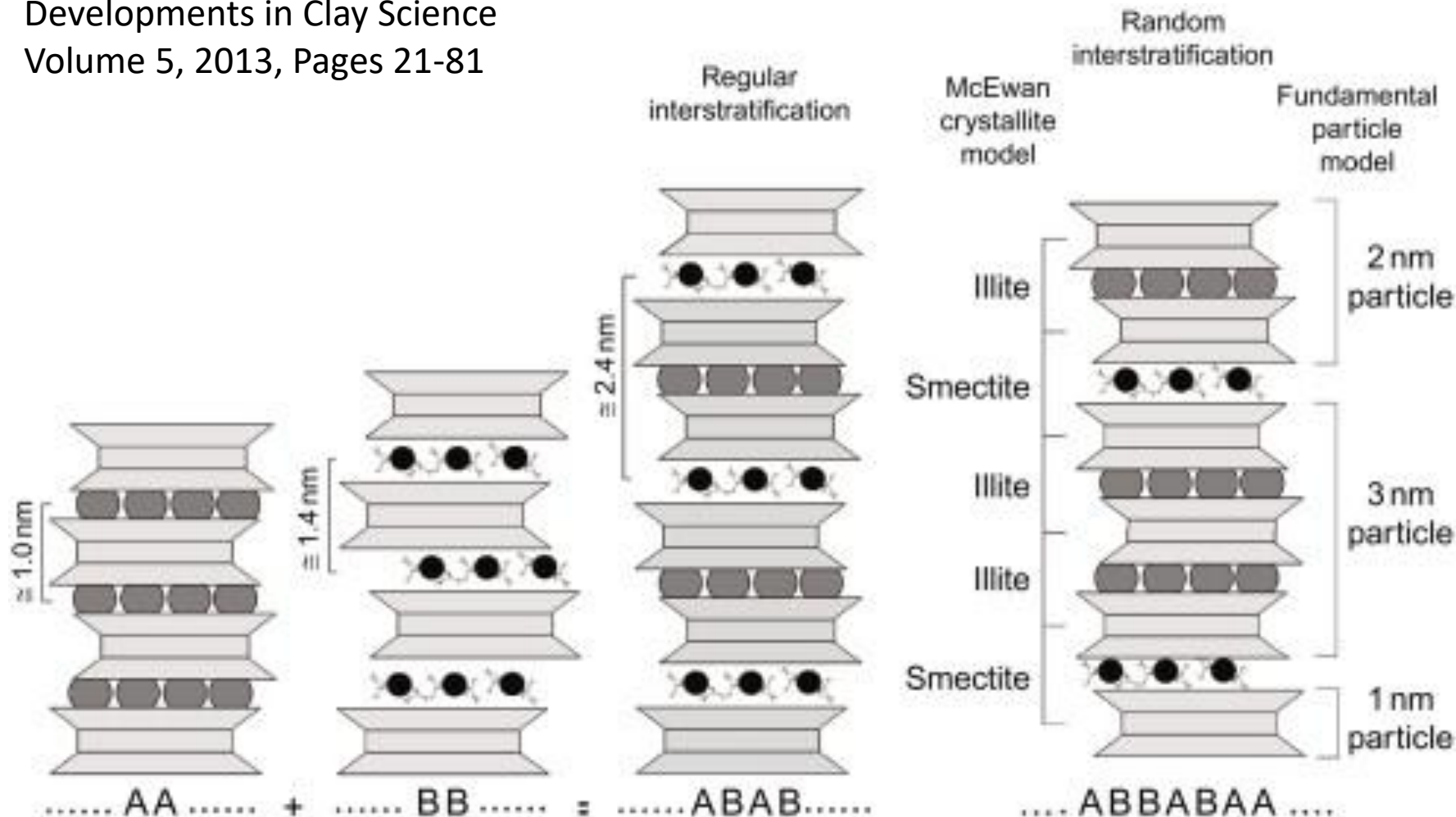
[https://pubs.usgs.gov/info/clays/#:~:text=Most%20clay%20minerals%20form%20where,b%20magma%20\(molten%20rock\).](https://pubs.usgs.gov/info/clays/#:~:text=Most%20clay%20minerals%20form%20where,b%20magma%20(molten%20rock).)

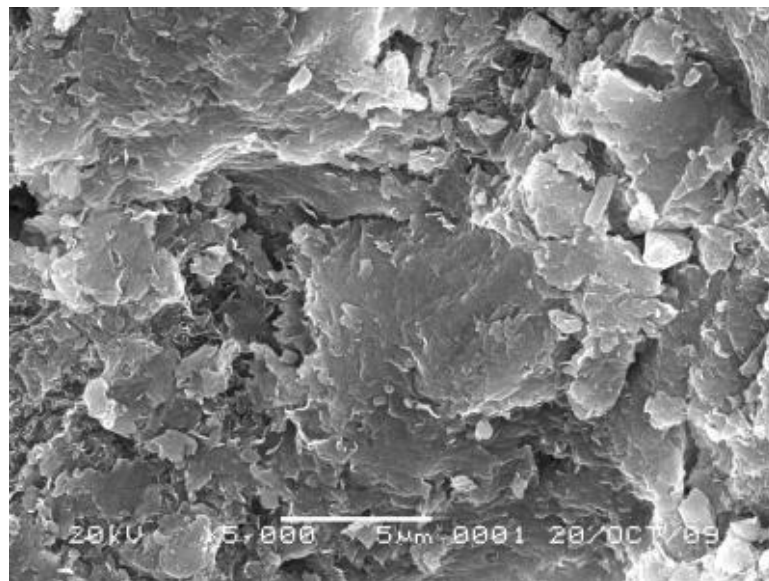
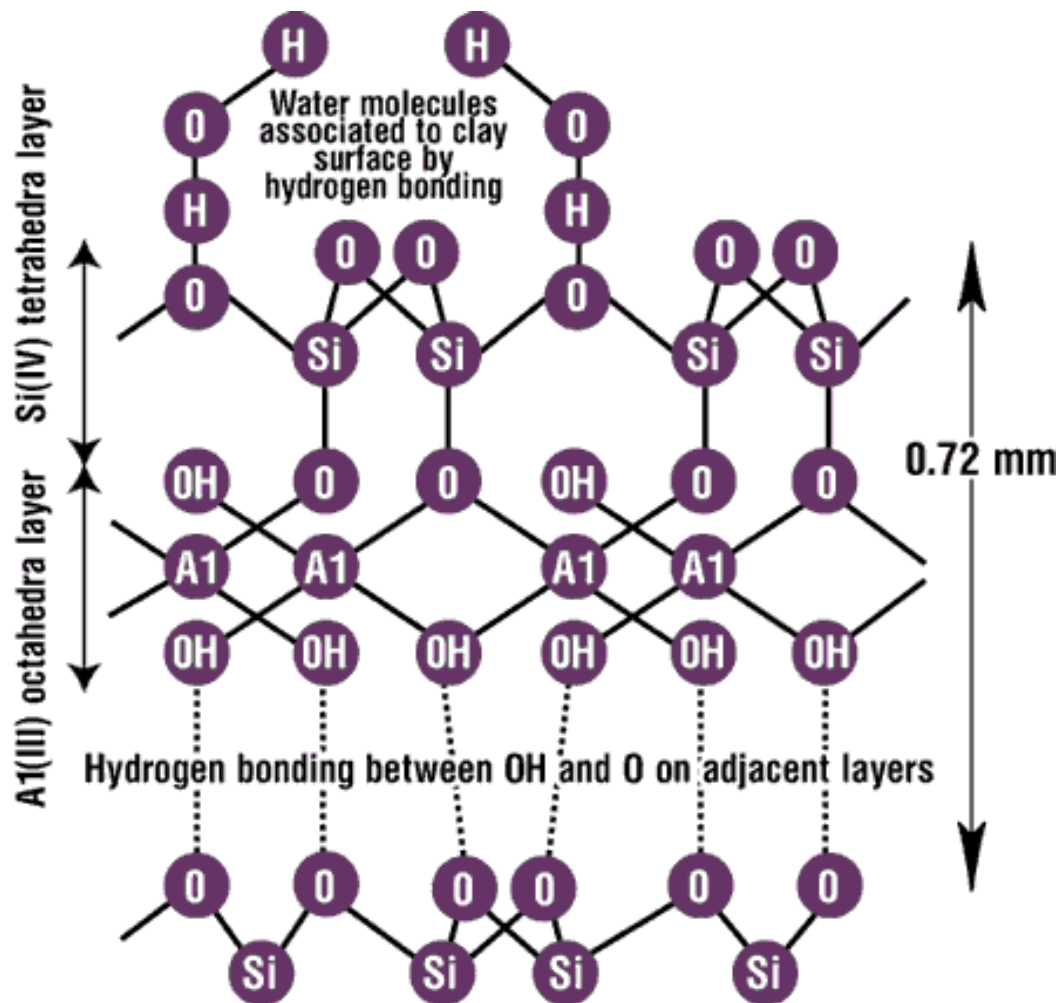
Structure of clays.

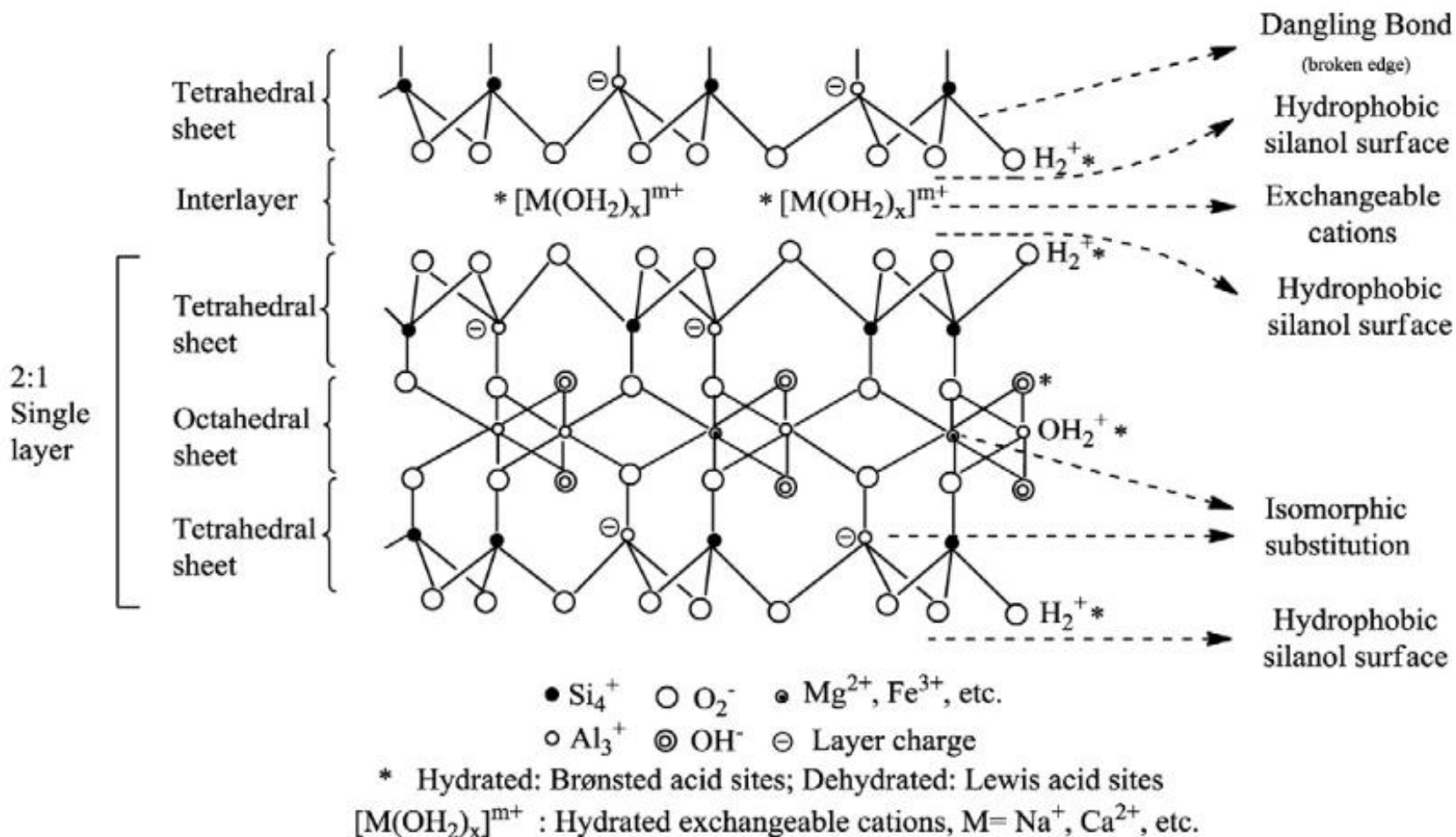
Source of picture:
Oleiwi, Hussein &
Abdulmajeed,
Basma. (2014).
Treatment and Reuse
of Produced Water
from Al-Ahdab Iraqi
Oilfields IN PARTIAL
FULFILLMENT OF
THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF
PHILOSOPHY IN
CHEMICAL
ENGINEERING.



Source of figure:
Developments in Clay Science
Volume 5, 2013, Pages 21-81







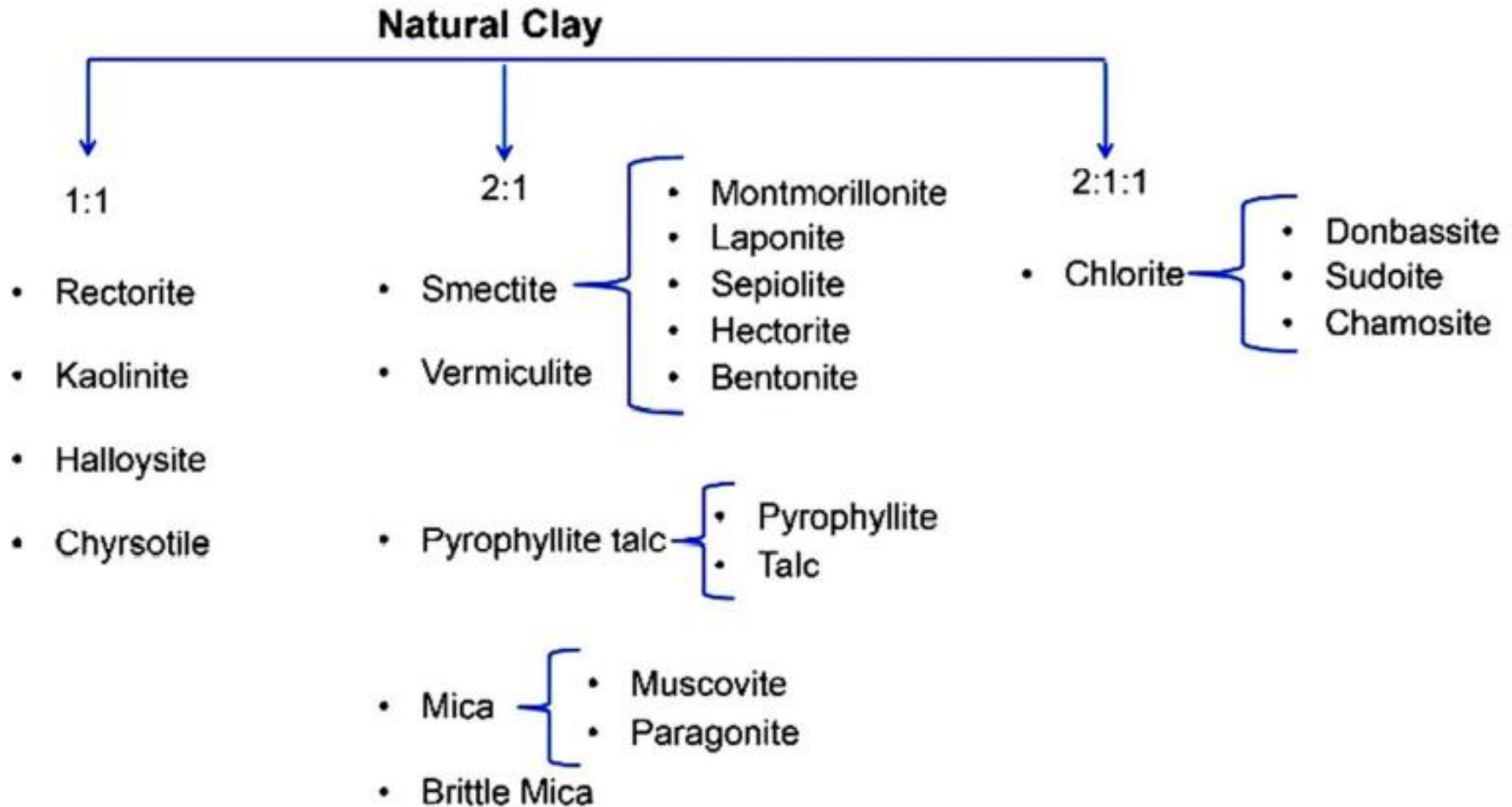
The ability to **exchange ions**, related to the charged surface of clay minerals is an important property of the clay mineral. Various ions can be attracted to the surface of a clay particle or taken up within the structure of these minerals.

Clay type	Chemical formula
Montmorillonite	$\text{Al}_2(\text{OH})_2\text{Si}_4\text{O}_{10}$
Illite	$\text{K}_{0-2}\text{Al}_4(\text{Si}_{8-6}\text{Al}_{0-2})\text{O}_{20}(\text{OH})_4$
Kaolinite	$\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$
Nontronite	$\text{Fe}_2(\text{OH})_2\text{Si}_4\text{O}_{10}$
Hydrous Mica	$\text{KAl}_2(\text{OH})_2(\text{AlSi})_3\text{O}_{10}$

Classifications are mainly made based on the **type of combinations of the tetrahedral and octahedral silicate sheets** and the way they stack.

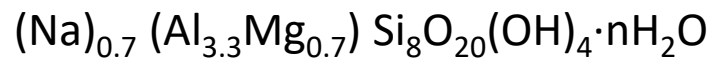
1. kaolinites, where one octahedral sheet is linked with one tetrahedral (1:1 ratio) (e.g., kaolinite, halloysite, and serpentine);
2. nonexpanding clays, where one octahedral sheet intercalates between two tetrahedral sheets (2:1 ratio) (e.g., mica and illite);
3. limited expanding clays (2:1 ratio) (e.g., vermiculite);
4. strongly expanding clays (2:1 ratio) (e.g., montmorillonite (Mt));
5. uncharged group (2:1 ratio) (e.g., pyrophyllite and talc);
6. 2:1:1 group with a brucite octahedral layer between a 2:1 mineral (e.g., chlorites); and
7. fibrous silicates (e.g., palygorskite and sepiolite)

Clays classification



Source of figure: Clays and Clay Minerals in the Construction Industry, Minerals 2022, 12, 301

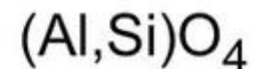
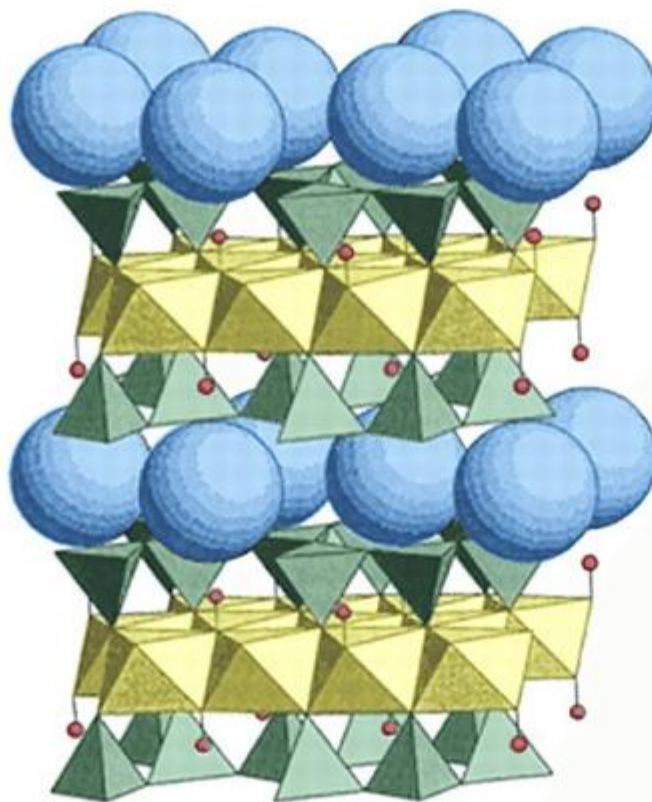
Bentonite



2:1 silicate layer

interlayer

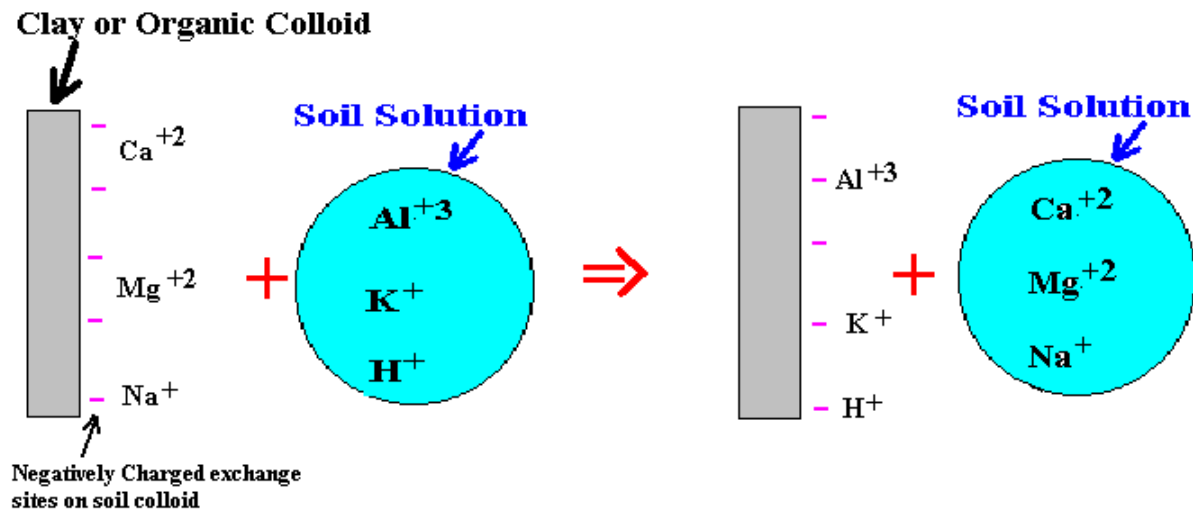
2:1 silicate layer



Two important properties:

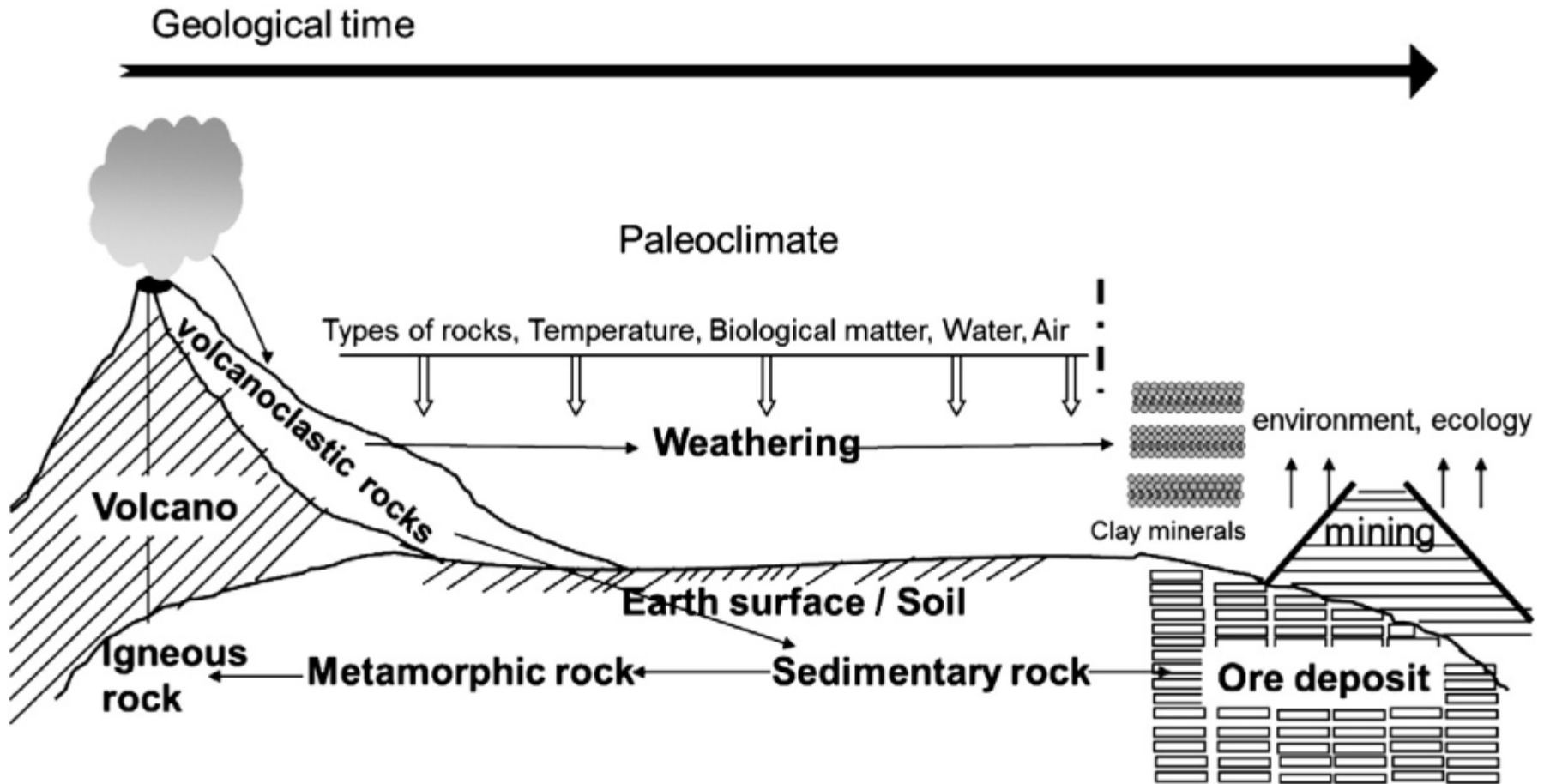
- **cation exchange capacity** (CEC): milliequivalents of cations exchanged per 100 g of dry clay;
- **zero point of charge (ZPC)**: the pH value where the negative surface charge of the clay has been neutralized, and has a value between 0 and 7.

Cation Exchange Illustrated



Clay type	Particle size (mm)	CEC (mequiv/100 g)
Montmorillonite	0.01-1.0	80-100
Illite	0.1-2.0	15-40
Kaolinite	0.1-5.0	3-15

Clays formation



Schematic depicting the inter-relationship of clay mineral formation with geology, climate, environment and ecology (ask details to prof. Ardit)

Clays and clay minerals occur under a fairly limited range of geologic conditions. The environments of formation include soil horizons, continental and marine sediments, geothermal fields, volcanic deposits, and weathering rock formations. Most clay minerals form where rocks are in contact with water, air, or steam.

MAIN MECHANISMS FOR CLAY FORMATION

Erosion

The transport and deposition of clays and clay minerals produced by eroding older continental and marine rocks and soils are important parts of the cycle that forms sedimentary rocks.

Diagenesis

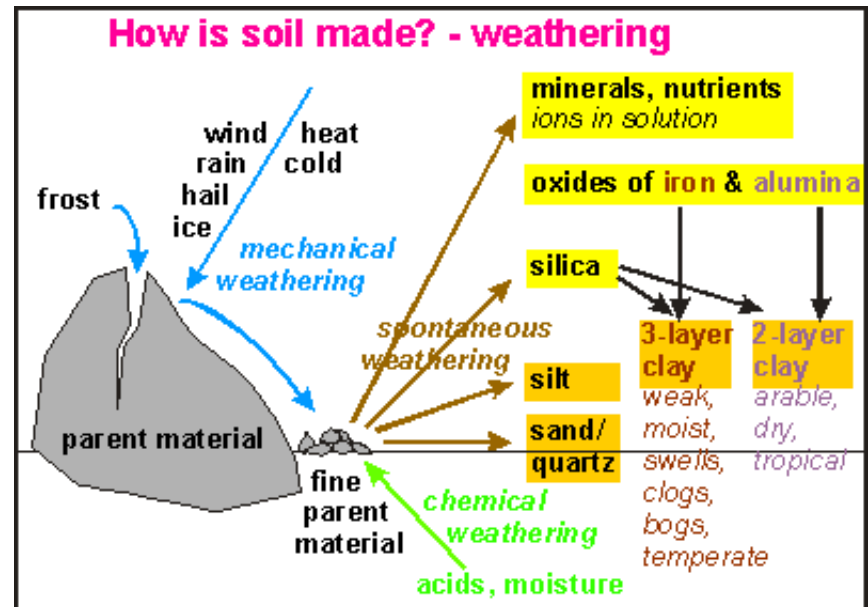
Diagenesis is the in-place alteration of a mineral to more stable forms, excluding surficial alteration (which is weathering); diagenesis occurs, for example, when minerals stable in one depositional environment are exposed to another by burial and compaction.

U.S. Geological Survey

[https://pubs.usgs.gov/info/clays/#:~:text=Most%20clay%20minerals%20form%20where,b%20magma%20\(molten%20rock\).](https://pubs.usgs.gov/info/clays/#:~:text=Most%20clay%20minerals%20form%20where,b%20magma%20(molten%20rock).)

Weathering

Weathering of rocks and soil is the primary way that clays and clay minerals form at the Earth's surface today. The weathering process involves physical disaggregation and chemical decomposition that change original minerals to clay minerals; weathering is uneven, and many stages of breakdown may be found in the same clay sample. Factors governing rock weathering and soil formation include the initial type of rock, the ratio of water to rock, the temperature, the presence of organisms and organic material, and the amount of time. The types of clay minerals found in weathering rocks strongly control how the weathered rock behaves under various climatic conditions (such as humid-tropical, dry-tropical, and temperate conditions).



SPECIFIC PROPERTIES

- (a) very large specific surface area that arises from the layered structure, along with swellability and the potential for delamination;
- (b) small size of the particles in the range of micro- to nano-scale; and
- (c) naturally-charged particles leading to relatively strong electrostatic interactions

SPECIAL ISSUE ARTICLE

To be discussed later

International Journal of
**Applied
Ceramic
TECHNOLOGY**

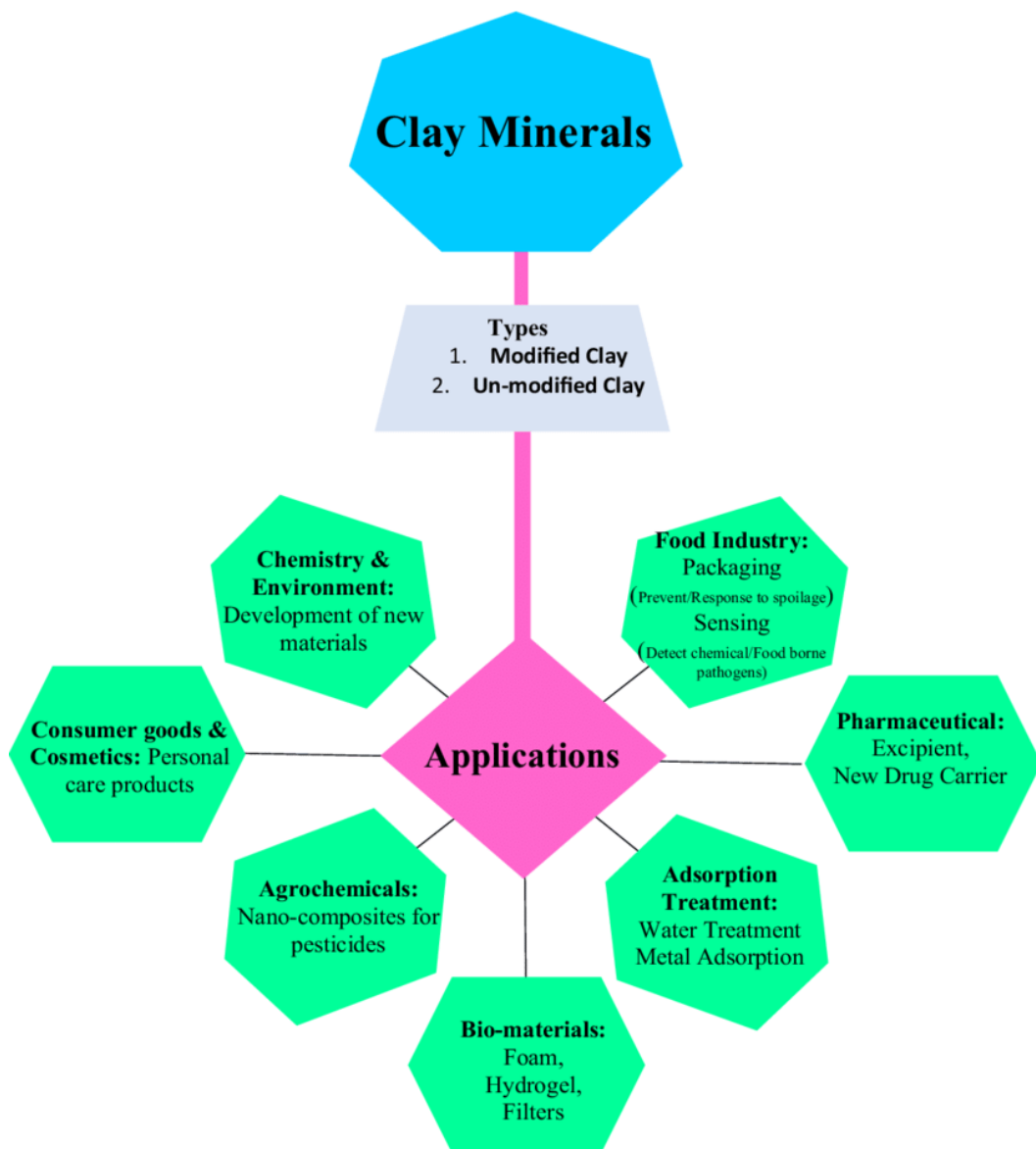
Circular economy in cementitious ceramics: Replacement of hydrated lime with a stoichiometric balanced combination of clay and marble waste

Markssuel T. Marvila¹  | Afonso R. G. de Azevedo^{1,2}  | Jonas Alexandre¹ |
Henry Colorado³  | Maria L. Pereira Antunes⁴ | Carlos M. F. Vieira¹

Industrial relevance of clays

- clay minerals used by the paint industry to promote even dispersion of pigment and to reduce settling.
- A mixture of clay with a little water results in a mud that can be shaped and dried to form a relatively rigid solid body (potters and ceramics industry) to produce plates, cups, bowls, pipes
- The **swelling and drying properties** of montmorillonitic clays make them ideal for such diverse uses as drilling mud, foundry-sand bonding agent, and binder for pelletizing iron ore.
- Environmental industries use the properties of swelling and dispersion to produce homogeneous liners from montmorillonitic clays for containment of waste
- adsorbents for the removal of heavy metal ions from water.
- effective adsorbents/absorbents of oily pollutants and animal waste
- carriers for the controlled release of pesticides and fertilizers.
- Montmorillonite is also used as a liner to restrict the leakage of radioactive elements that may arise from activities of the nuclear power industry
- Heterogeneous catalysis
- fillers for composites
- Precursors for cement/concrete

Industrial relevance of clays



Source of the figure: Awasthi, Anuradha & Jadhao, Pradip & Kumari, Kanchan. (2019). Clay nano-adsorbent: structures, applications and mechanism for water treatment. SN Applied Sciences. 1. 10.1007/s42452-019-0858-9.