



MSE2952

Ceramics

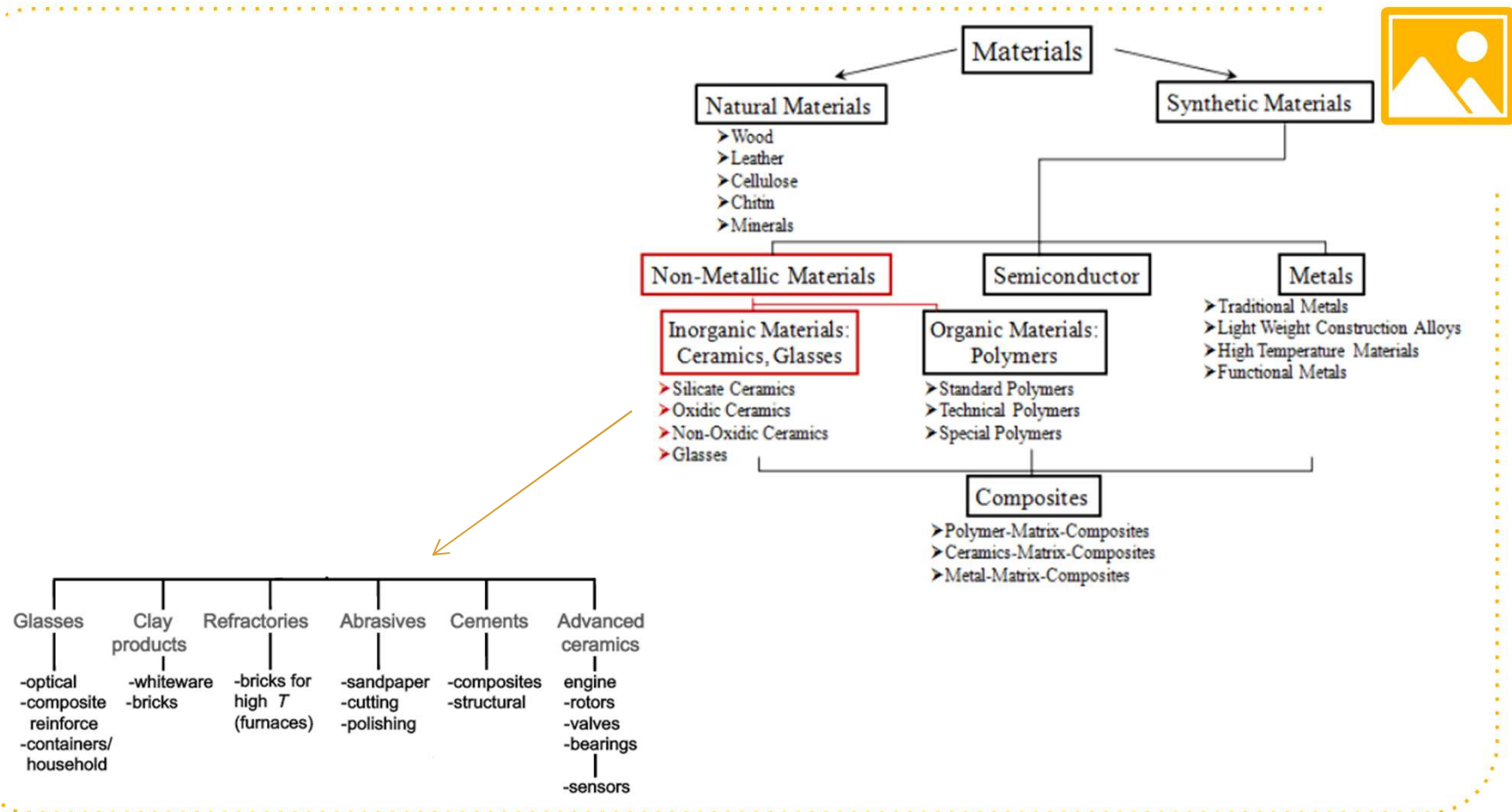
Syllabus



1. Introduction
2. Classification of ceramic products, uses and Turkey Introducing the Ceramic Industry
3. Bonds and Crystal Structures in Ceramic Materials
4. Properties of ceramic materials (Physical and mechanical Properties)
5. Ceramic Phase Diagram
6. Ceramic Raw Materials and their properties
7. Test methods to ceramic raw materials
8. 1st Midterm
9. Molding methods of ceramic materials
10. Drying and Sintering Methods
11. Mechanical test applied to ceramic materials and methods of determination of density, porosity, specific gravity, drying and cooking shrinkage methods
12. Classification of ceramic glazes
13. Properties and applications of engineering ceramics
14. Cement and Refractories

Introduction

Comparasion of Traditional Ceramic Materials and Advanced Ceramic Materials, General Properties of Ceramics



- Ceramics can be found in products like watches (quartz tuning forks-the time keeping devices in watches), snow skis (piezoelectric-ceramics that stress when a voltage is applied to them), automobiles (sparkplugs and ceramic engine parts found in racecars), and phone lines. They can also be found on space shuttles, appliances (enamel coatings), and airplanes (nose cones). Depending on their method of formation, ceramics can be dense or lightweight.
- They demonstrate excellent strength and hardness properties; however, they are often brittle in nature. Ceramics can also be formed to serve as electrically conductive materials, objects allowing electricity to pass through their mass, or insulators, materials preventing the flow of electricity. Some ceramics, like superconductors, also display magnetic properties.

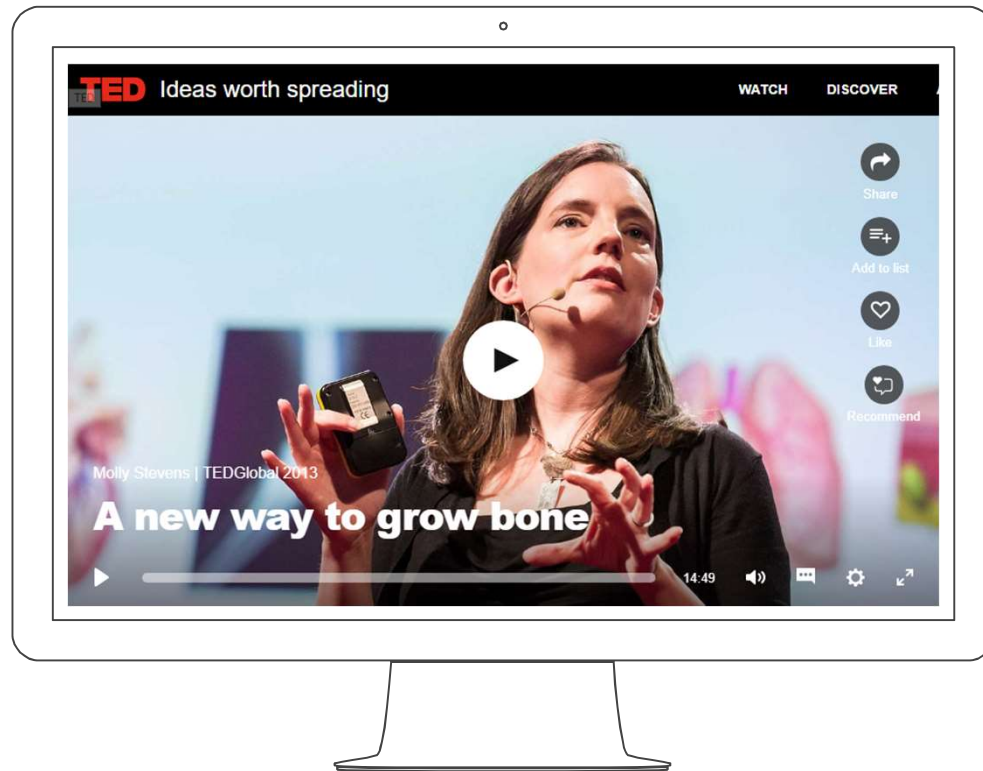


- In addition to clay based materials, today ceramics include a multitude of products with a small fraction of clay or none at all. Ceramics can be glazed or unglazed, porous or vitrified.
- Firing of ceramic bodies induces time-temperature transformation of the constituent minerals, usually into a mixture of new minerals and glassy phases. Characteristic properties of ceramic products include high strength, wear resistance, long service life, chemical inertness and nontoxicity, resistance to heat and fire, (usually) electrical resistance and sometimes also a specific porosity.





https://www.ted.com/talks/boaz_almog_levitates_a_superconductor



http://www.ted.com/talks/molly_stevens_a_new_way_to_grow_bone

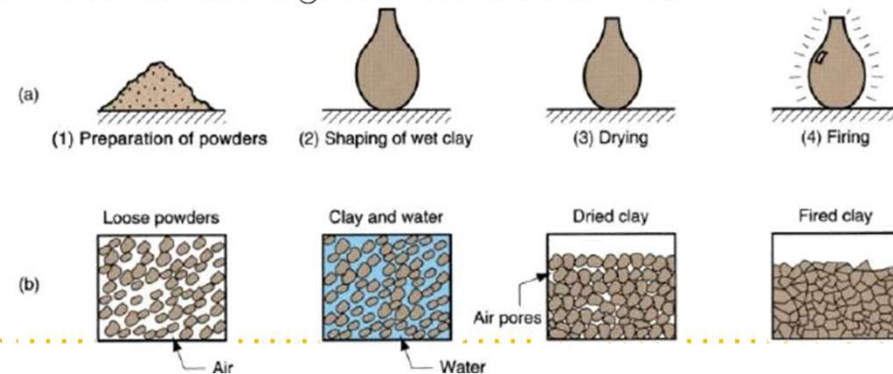
Industrial Ceramics are generally made by taking mixtures of clay, earthen elements, powders, and water and shaping them into desired forms. Once the ceramic has been shaped, it is fired in a high temperature oven known as a kiln. Often, ceramics are covered in decorative, waterproof, paint-like substances known as glazes.



History of Ceramics



- Archeologists have uncovered human-made ceramics that date back to at least 24,000 BC.
- These ceramics were found in Czechoslovakia and were in the form of animal and human figurines, slabs, and balls.
- These ceramics were made of animal fat and bone mixed with bone ash and a fine claylike material. After forming, the ceramics were fired at temperatures between 500-800°C in domed and horseshoe shaped kilns partially dug into the ground with loess walls.
- While it is not clear what these ceramics were used for, it is not thought to have been a utilitarian one. The first use of functional pottery vessels is thought to be in 9,000 BC. These vessels were most likely used to hold and store grain and other foods.



It is thought that ancient glass manufacture is closely related to pottery making, which flourished in Upper Egypt about 8,000 BC. While firing pottery, the presence of calcium oxide (CaO) containing sand combined with soda and the overheating of the pottery kiln may have resulted in a colored glaze on the ceramic pot. Experts believe that it was not until 1,500 BC that glass was produced independently of ceramics and fashioned into separate items.



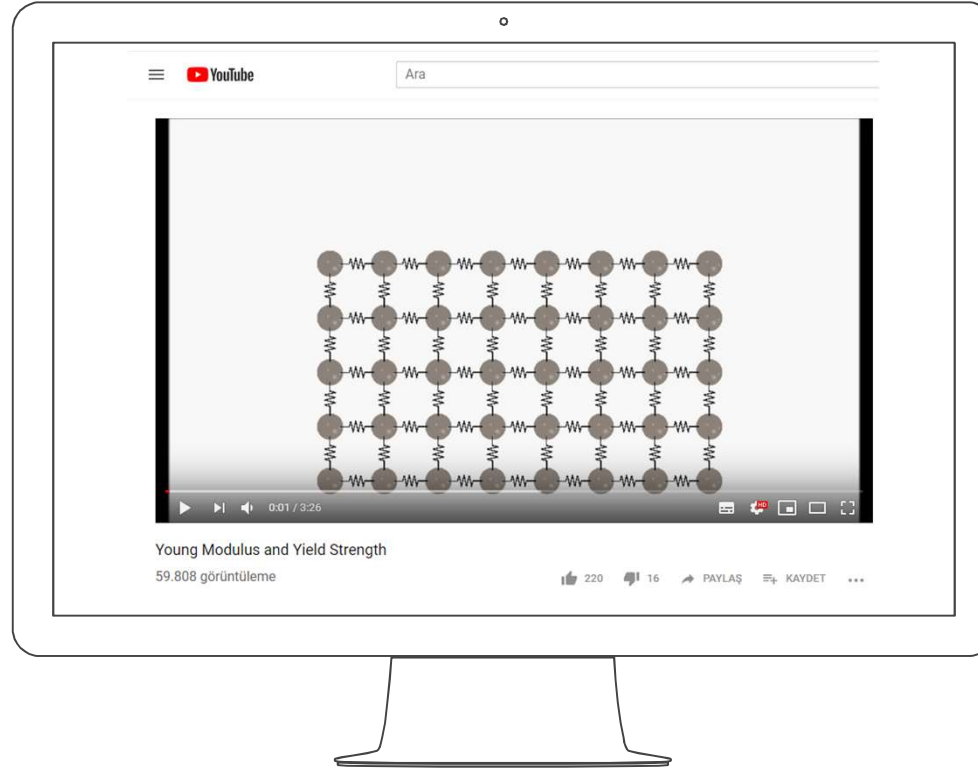
Homework 1:

Please make a brief research on ceramics production and raw materials in ancient times, with references



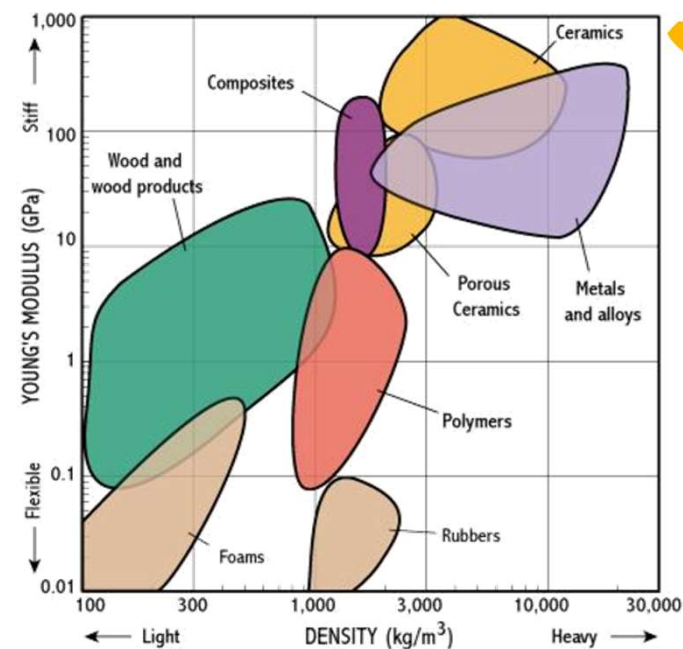
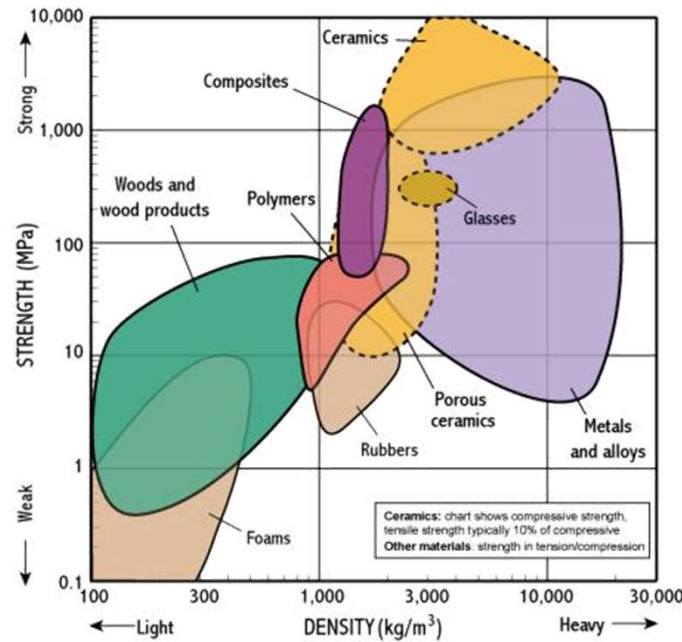
General Properties of Ceramics





Before lesson:

<https://www.youtube.com/watch?v=n7LXYyohmgg>



- Young's **modulus** (E) describes tensile **elasticity**, or the tendency of an object to deform along an axis when opposing forces are applied along that axis; it is defined as the ratio of tensile stress to tensile strain. It is often referred to simply as **the elastic modulus**.
- Relation between stress and strain

Strain $\Delta L/L$

Stress F/A

Young's modulus

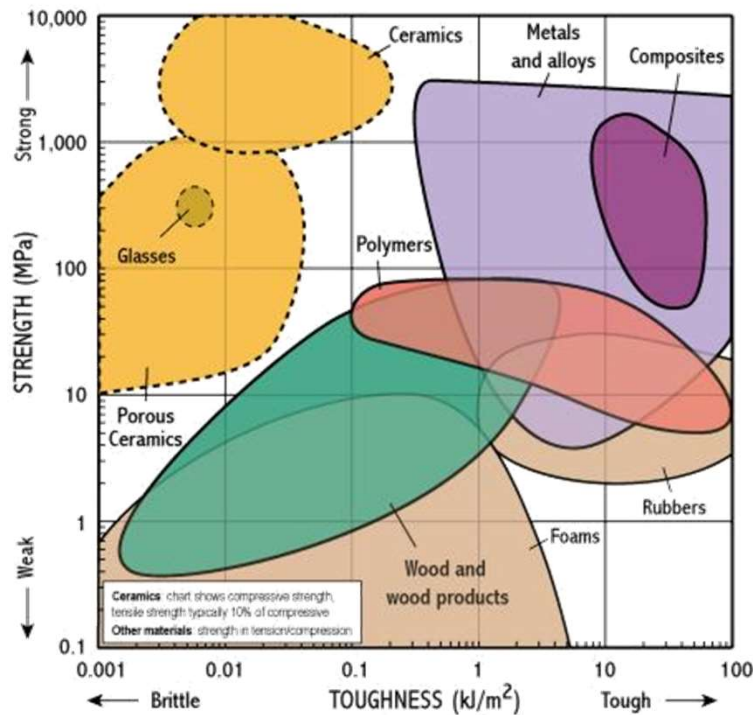
$$E = \frac{\text{Stress}}{\text{Strain}} = \frac{F/A}{\Delta L/L}$$

The diagram shows a cylindrical specimen of length L and cross-sectional area A . A force F is applied at both ends, causing an elongation ΔL . The stress is labeled as F/A and the strain as $\Delta L/L$.

Since oars need to be light and stiff, why not use ceramics?



! Because they would probably break or crack! A strength chart often needs to be used as well as a stiffness chart to make a good selection.



General Information

- Strength measures the resistance of a material to failure, given by the applied stress (or load per unit area)
- The chart shows yield strength in tension for all materials, except for ceramics for which compressive strength is shown (their tensile strength being much lower)
- Toughness measures the energy required to crack a material; it is important for things which suffer impact (*The max energy material can absorb*)
- There are many cases where strength is no good without toughness, e.g. a car engine, a hammer
- Increasing strength usually leads to decreased toughness
- Tempered steel is tougher but less strong than after quenching.



Physical Insights

- Put a pin-prick in a balloon and begin to blow it up - it will burst when the elastic energy cannot be absorbed by the growing crack
- The tensile strengths of brittle materials are very sensitive to the presence of flaws
- Tough materials absorb a lot of energy as a crack grows through them
- Metals are tough because they deform plastically while they crack, absorbing energy
- Cast iron is often brittle because it contains graphite flakes which behave like little cracks within the metal

Example Uses

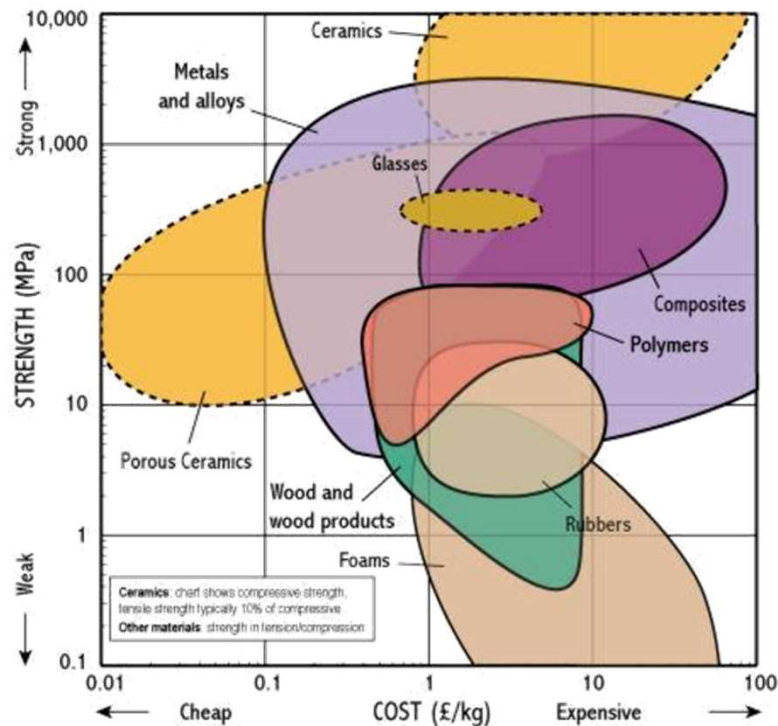
- Steel is often used to absorb energy in car impacts because it is tough and strong
- Saw blades and hammer heads are quench and tempered steel to get moderately high strength with good toughness

Simple Questions

- Select materials for a child's cup or spoon.
- Select materials for a plug casing for an electronic device
- Select materials for a bullet/knife proof vest. Tricky!



A **yield strength** or **yield point** is the material property defined as the **stress** at which a material begins to deform plastically. * *will be seen in detail!*



General Information

- Strength measures the resistance of a material to failure, given by the applied stress (or load per unit area)
- The chart shows yield strength in tension for all materials, except for ceramics for which compressive strength is shown (their tensile strength being much lower)
- Many applications require strong materials, e.g. screw drivers, safety belts – these lie at the top of the chart
- Unfortunately there are few cheap high strength materials (top left)



Physical Insights

- Ceramics and glasses have directional covalent bonds. They are weak in tension because they are sensitive to small cracks or flaws.
- Metals do not have directional bonds and have similar tensile and compressive properties
- Cellulose microfibrils make wood strong in tension along the grain
- Alloys are much stronger than pure metals
- Metals can be strengthened by heat treating to change the microstructure

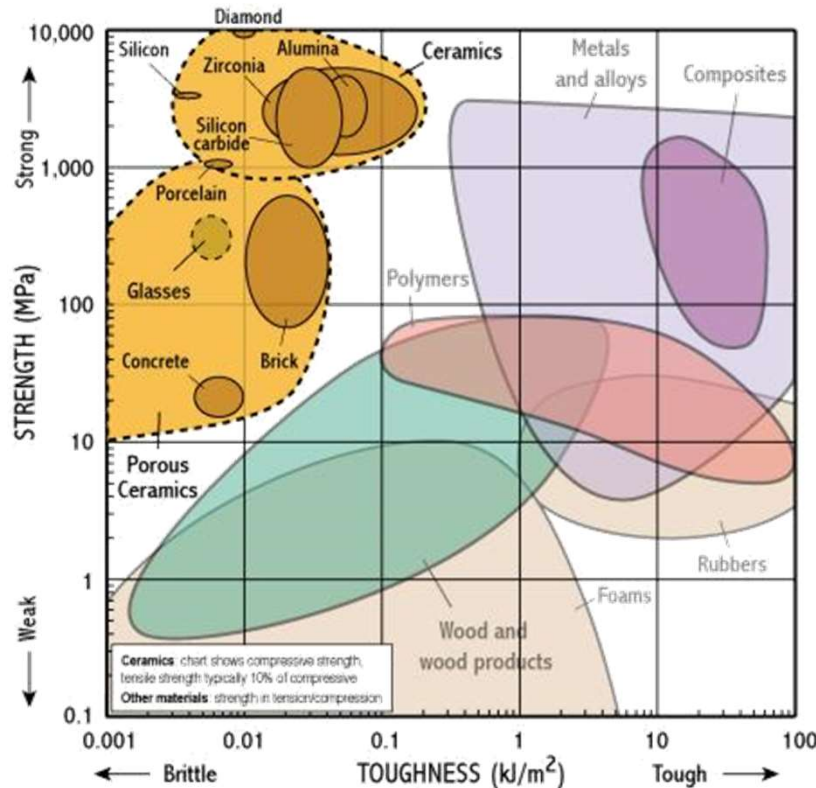
Example Uses

- Teflon as a non stick surface for frying pans
- Ceramic for fire bricks and for coatings for jet engine blades
- Tungsten for light bulb filaments

Simple Questions

- Why is wood used for beams rather than stone, when stone has a higher strength?
- Why is pottery weak?
- Why is steel the most commonly used 'strong' material?
- Select materials for a screwdriver.
- Select materials for a glass-cutting tool.





General Information

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- Toughness measures the energy required to crack a material; it is important for things which suffer impact
- There are many cases where strength is no good without toughness, e.g. a car engine, a hammer
- Increasing strength usually leads to decreased toughness
- Tempered steel is tougher but less strong than after quenching.





Physical Insights

- Put a pin-prick in a balloon and begin to blow it up - it will burst when the elastic energy cannot be absorbed by the growing crack
- The tensile strengths of brittle materials are very sensitive to the presence of flaws
- Quenching carbon steel makes it very hard but brittle.
- Tough materials absorb a lot of energy as a crack grows through them
- Metals are tough because they deform plastically while they crack, absorbing energy
- Cast iron is often brittle because it contains graphite flakes which behave like little cracks within the metal

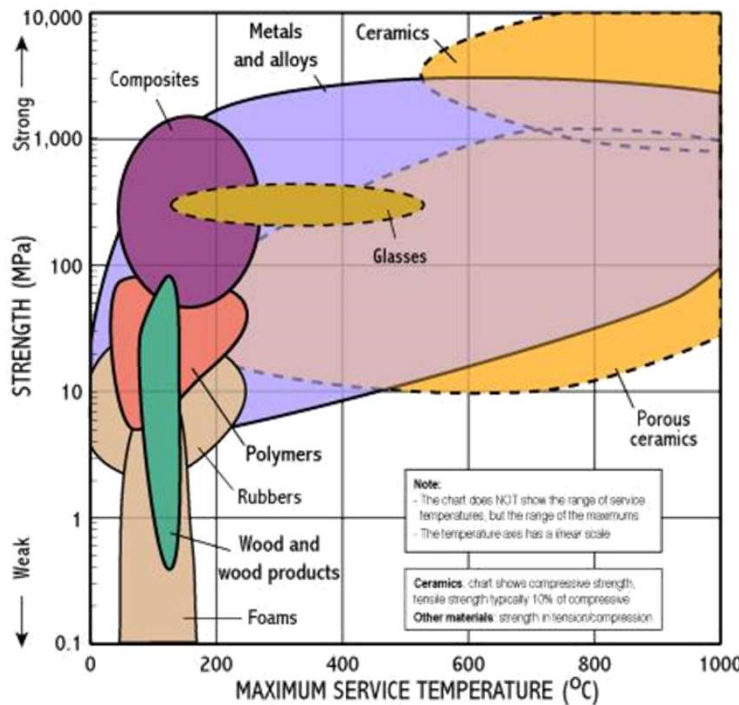
Example Uses

- Steel is often used to absorb energy in car impacts because it is tough and strong
- Saw blades and hammer heads are quenched and tempered steel to get moderately high strength with good toughness

Simple Questions

- Why does prestressed concrete have high tensile strength?
- Select materials for a child's cup or spoon.
- Select materials for a 13A plug casing for a vacuum cleaner.
- Select materials for a bullet/knife proof vest.
- Select materials for a bus shelter window.





General Information

- Strength measures the resistance of a material to failure, given by the applied stress (or load per unit area)
- The chart shows yield strength in tension for all materials, except for ceramics for which compressive strength is shown (their tensile strength being much lower)
- Maximum service temperature indicates the maximum temperature at which a material can be used in engineering – above this its strength rapidly decreases
- This chart is useful for identifying materials for components which operate at temperatures above room temperature, e.g. cooking utensils, car engines and Exhausts
- Polymers are limited to low temperatures, metals to intermediate temperatures, and only ceramics can withstand very high temperatures.





Physical Insights

- Thermoplastic polymers operate at lower temperatures than thermosets because only weak Van der Waals forces hold the chains together
- Ceramics can operate at high temperature because covalent bonds are very stable
- Polystyrene has a maximum use temperature below 100°C - which explains why
- polystyrene coffee cups go out of shape

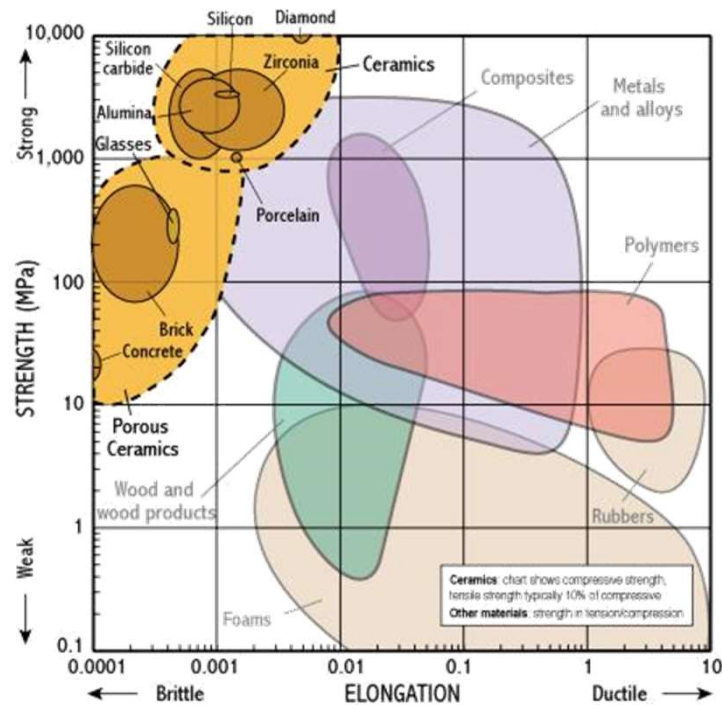
Example Uses

- Teflon as a non stick surface for frying pans
- Ceramic for fire bricks and for coatings for jet engine blades
- Tungsten for light bulb filaments

Simple Questions

- Why is lead-tin used for solder?
- Select materials for a saucepan.
- Select materials for a mould for casting aluminium parts (melting temp 660oC)
- Select materials for a mould for casting steel parts (melting temp 1540oC)





General Information

- Strength measures the resistance of a material to failure, given by the applied stress (or load per unit area)
- The chart shows yield strength in tension for all materials, except for ceramics for which compressive strength is shown (their tensile strength being much lower)
- Elongation measures the percentage change in length before fracture
- Elongation to failure is a measure of ductility



Physical Insights

- Ceramics have very low elongations ($<1\%$) because they can not plastically deform
- Metals have moderate elongation to failure (1-50%) with deformation occurring by plastic flow
- Thermoplastics have large elongations ($>100\%$) because the molecules can stretch out and slide over one another
- Rubbers have long elastic elongations because the chains can coil/uncoil elastically
- Thermosets have low elongations ($<5\%$) because the molecules are bonded together into a network so that they cannot slide over one another
- One way to strengthen a metal is to make plastic flow difficult – this reduces the ductility and elongation

Example Uses

- Few components are designed to elongate significantly - examples are impact protection like crash barriers.
- The chart helps identify materials which can be easily deformed into new shapes during manufacturing
- Designers like to use metals with significant elongations to failure because they are more forgiving of harsh treatment, e.g.
- car chassis, nails

Simple Questions

- What is the difference between elastic and plastic deformation?
- Why is lead used on old roofs and roof flashings?
- Select materials for a car bumper.
- Select materials for a bungee rope.
- Select materials for drawing pins.





*Reading Assessment:
Material and Process Selection charts
Cambridge University Press*

http://www.grantadesign.com/download/pdf/teaching_resource_books/2-Materials-Charts-2010.pdf



Homework 2:

- Why can polymers operate only at low temperatures when their polymer chains contain covalent bonds like ceramics?
- What is the operating temperature of a light bulb filament?
- Thermal toughening of glass places the surfaces in compression the interior in tension - why does this increase the strength?
- Is rubber tough or brittle?
- Why can polymers operate only at low temperatures when their polymer chains contain covalent bonds like ceramics?
- What is the operating temperature of a light bulb filament?

Classification of Ceramic Products

Uses and Turkey Introducing the Ceramic Industry



- The history of Turkish ceramics can be traced back several thousand years. The first notable ceramics from Turkish land were the tiles and bricks covered with coloured glazes made in Anatolia for architectural purposes in the 13th century.
- The Turkish classic ceramic art of "Çini" is famous throughout the world. Early Turkish tribes who lived in Central Asia made the first examples of this ceramic art for their kitchen and household use.
- Later, with the Seljuk movement this art came to Anatolia and became a decorative art piece which was mostly used in the decoration of mosques, public libraries and Turkish baths.



- The first commercial production of ceramics started in 1965 with the foundation of the first plant. At present, there are more than 60 establishments in ceramic production.
- Turkey is rich in ceramic raw materials such as feldspar, clay, kaolin and quartz, and Turkish ceramic raw material reserves are large enough to satisfy the demand.
- Most Turkish firms have installed their own raw material preparation facilities within their facilities.
- Ceramic industry is one of the fastest growing sectors of building materials industry in Turkey. Production of ceramic tiles (175 million square meters in 2012) and sanitaryware (112,2 thousand tons in 2012) meets the domestic demand and provides a significant export capacity.



Top 10 Exporting Countries (2013)

Country	2013 (Sq.m Mill.)	% on 2013 World Export
CHINA	1148	42.9
SPAIN	318	11.9
ITALY	303	11.3
IRAN	114	4.3
TURKEY	88	3.3
MEXICO	80	3.0
BRAZIL	63	2.4
UAE	51	1.9
VIETNAM	50	1.9
POLAND	48	1.8

Source: Ceramic World Review

Top 10 Manufacturing Countries (2013)

Country	2013 (Sq.m Mill.)	% on 2013 World Production
CHINA	5700	47.8
BRAZIL	871	7.3
INDIA	750	6.3
IRAN	500	4.2
SPAIN	420	3.5
INDONESIA	390	3.3
ITALY	363	3.0
TURKEY	340	2.9
VIETNAM	300	2.5
MEXICO	228	1.9

3

Bonds and Crystal Structure in Ceramic Materials



- Ceramic bonds are mixed, **ionic** and **covalent**, with a proportion that depends on the particular ceramics.
- The ionic character is given by the difference of electronegativity between the cations (+) and anions (-). Covalent bonds involve sharing of valence electrons.
- Very ionic crystals usually involve cations which are alkalis or alkaline-earths (first two columns of the periodic table) and oxygen or halogens as anions.

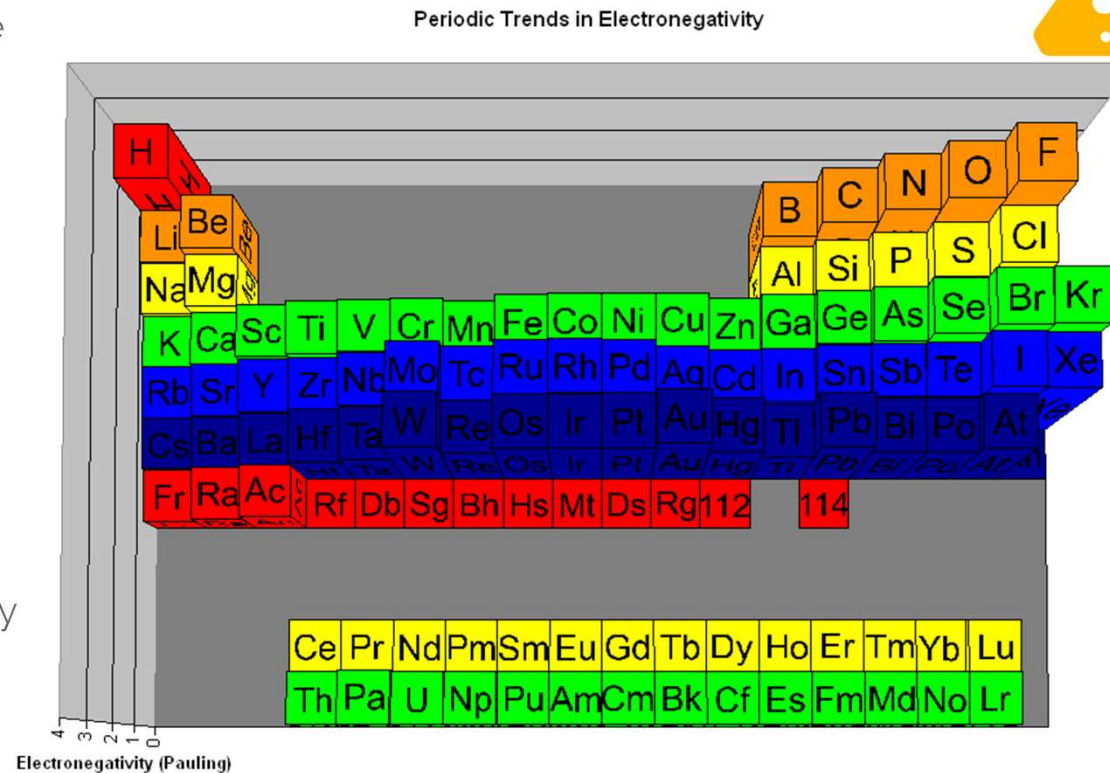
Periodic Table of the Elements

Legend:

- Alkali Metals (Pink)
- Alkaline Earth Metals (Light Blue)
- Transition Metals (Yellow)
- Other Metals (Orange)
- Metalloids (Purple)
- Other Non-Metals (Green)
- Halogens (Red)
- Noble Gases (Light Blue)
- Lanthanides & Actinides (White)

<i>Material</i>	<i>Percent Ionic Character</i>
CaF ₂	89
MgO	73
NaCl	67
Al ₂ O ₃	63
SiO ₂	51
Si ₃ N ₄	30
ZnS	18
SiC	12

- Electronegativity - a measure of how willing atoms are to accept electrons (subshells with one electron - low electronegativity; subshells with one missing electron - high electronegativity).
- Electronegativity increases from left to right.
- The atomic bonding in ceramics is mixed, ionic and covalent, the degree of ionic character depends on the difference of electronegativity between the cations (+) and anions (-)



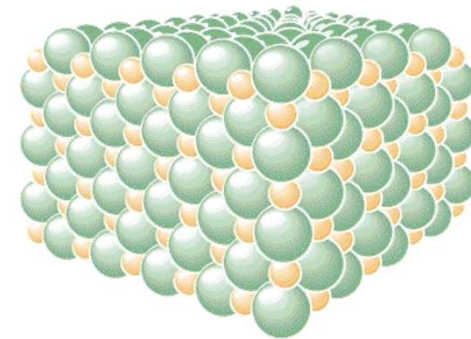
Types of Chemical bonds

- There are six major types: ionic, covalent, metallic, polar, hydrogen and van der Waals.

In ceramics

a. Ionic Bonding

- Ionic bonding occurs between a pair of atoms when one of the atoms gives up its valence electrons to the other. The result is that both atoms have filled shells. Both atoms also end up with a charge, one negative, and the other positive. We call the positive charged atom a *cation*, and the negatively charged one, an *anion*.

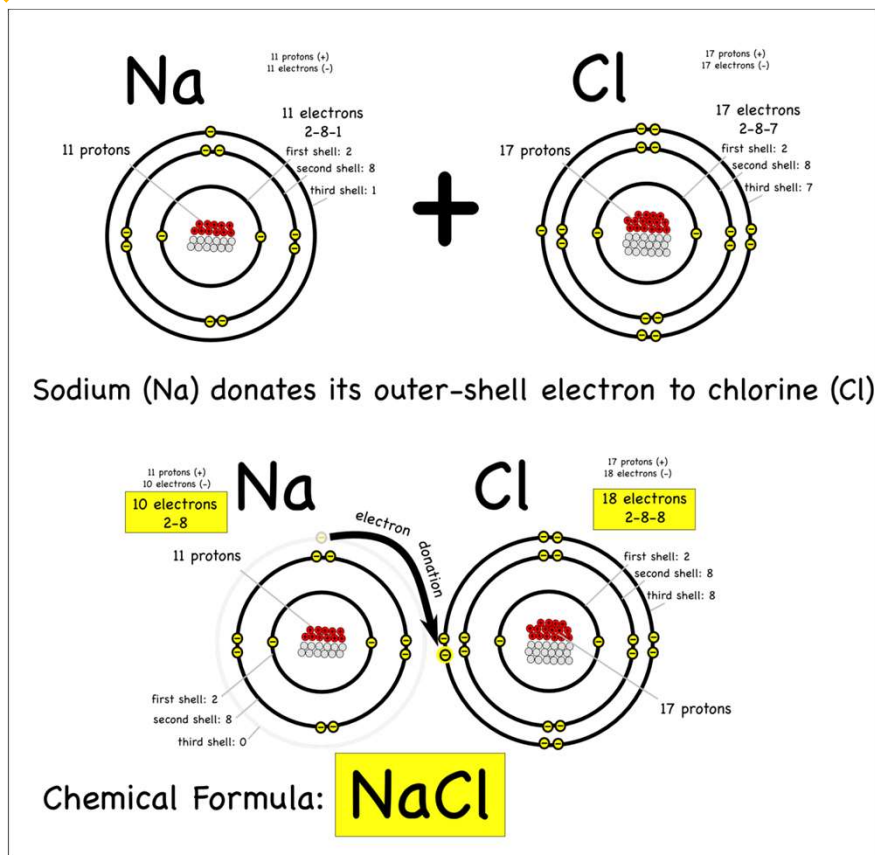


Sodium ion (Na^+)



Chloride ion (Cl^-)

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A classic example of ionic bonding is between Na and Cl.



MgO, FeO, NiO, CaO also have rock salt structure

- Na is a silvery metal. It has 1 valence electron.
- Cl is a yellow-green gas, and it needs 1 electron to fill its valence shell.
- If you put the gas and the metal together, then they will burn as electrons are exchanged.
- The metal dissolves and the gas disappears.
- The ions now have opposite charges and are attracted to each other by electrostatic forces.
- They form a crystal with the rock salt structure.

- In Periodic table, Ionic bonds commonly form between atoms of the 1st column and the 7th, and between the 2nd column and the 6th. E.g. NaCl, MgO
- Materials composed of ionic bonds have distinctive properties. They are strong when pushed together, but weak if cleaved or sheared.
- Once the bond breaks it is not easy to put back together. For instance, with NaCl. The Na is left 1 electron short, the Cl with one extra. They have no need to come close enough together to exchange electrons.
- Ionic crystals also dissolve easily in water, yet they have high melting points.
- So if you break a crystal apart, you can put it back together by dissolving it, or by heating it enough to excite the valence electrons off of the atoms.

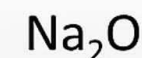


Ionic Compounds

The Periodic Table of the Elements

MetalsMetalloidsNon-Metals

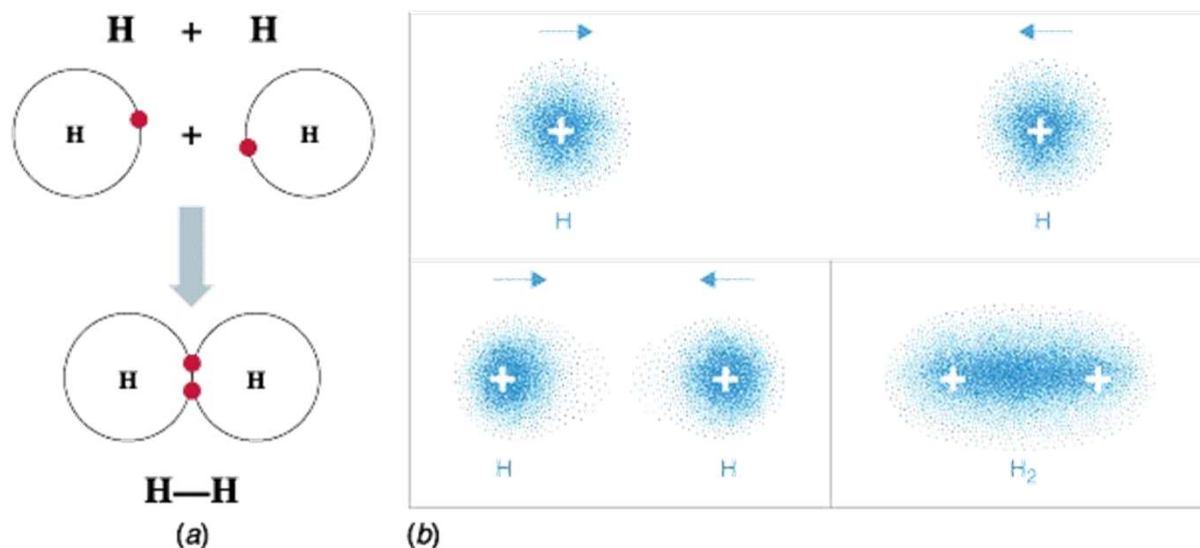
1 H Hydrogen																	2 He Helium						
3 Li Lithium	4 Be Beryllium																	5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium																	13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton						
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon						
55 Cs Cesium	56 Ba Barium	57 La Lanthanum	58 Hf Hafnium	59 Ta Tantalum	60 Ta Tungsten	61 Re Rhenium	62 Os Osmium	63 Ir Iridium	64 Pt Platinum	65 Au Gold	66 Hg Mercury	67 Tl Thallium	68 Pb Lead	69 Bi Bismuth	70 Po Polonium	71 At Astatine	72 Rn Radon						
73 Fr Francium	74 Ra Radium	75 Ac Actinium	76 Rf Rutherfordium	77 Db Dubnium	78 Sg Seaborgium	79 Bh Berkelium	80 Hs Hassium	81 Mt Moscovium	110	111	112	113	114										





b. Covalent Bonding

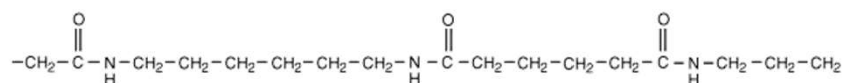
- Covalent bonds often form between atoms with too many electrons in their valence shells to give away, but not enough to easily fill. Thus they *share electrons* with their neighbors, in such a way that including the shared electrons the shells are full.



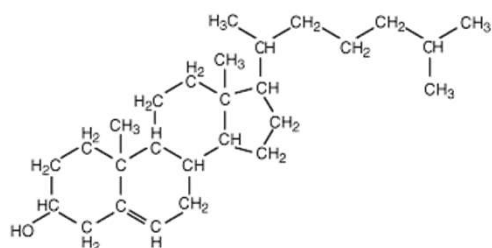
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- E.g. H_2 , N_2 , O_2 , diamond.
- These are stronger bonds than either of the other two types. This is because the electrons are shared.
- The carbon bond usually forms covalent bonds. The possible arrangements are many. Life is based upon carbon-carbon bonding. The branch of science called *organic chemistry* is the study of carbon-based molecules.



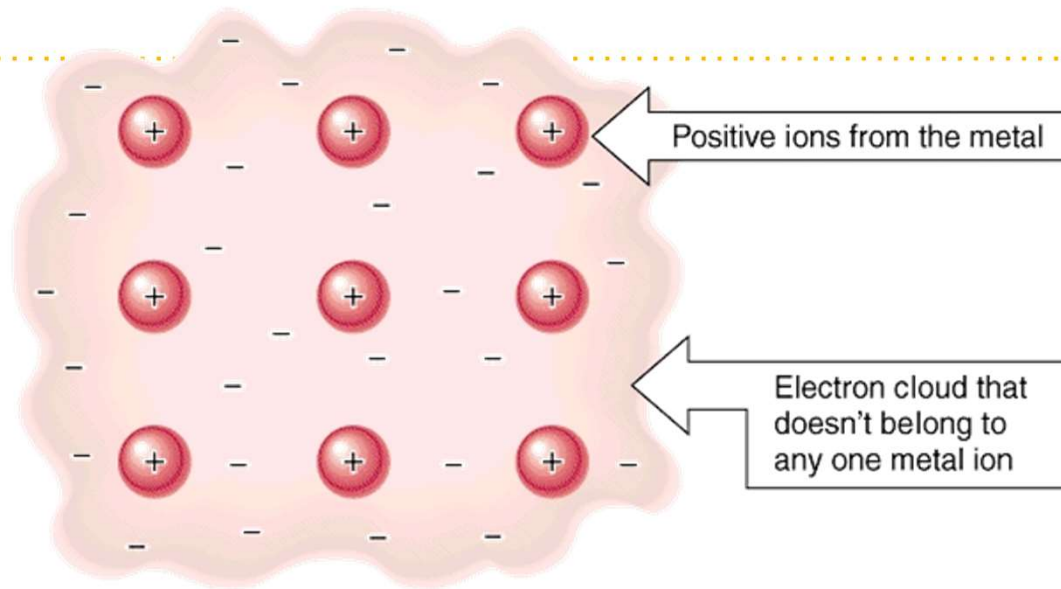
(a)



(b)

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- Your body is based upon carbon bonding. So the covalent bond is considered the most important bond with regards to life.
- Interestingly, Si, just above C in the periodic table, with its covalent bonding, is the basis for the computer industry.



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An extra bonding for ceramists, Metallic Bonding

Metallic bonding occurs between atoms that have a small number of electrons in their valence shells. They give the electrons up, not just to one other atom, but to the complete group of atoms. We think of the electrons as becoming loose. Positively charged atoms sitting in a sea of electrons. We often call it *electron-gas*. E.g. sodium.

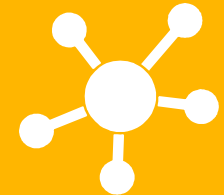
This arrangement provides metals with many of their characteristic physical properties;



- The shiny luster is because with so many free electrons.
- The electrons easily absorb light and re-emit it right back again, with no loss or gain of energy. This is the origin of the metallic luster.
- Metals can conduct electrons easily because the electrons are not localized in the crystal.
- Metals are malleable*. This is because the atoms can easily rearrange themselves in the sea of electrons.

** Can be shaped by pressure, e.g;hammer*

Remember the atomic bondings? – now its time use them!
Introducing the crystal structures...



Types of Chemical bonds

•There are six major types: ionic, covalent, metallic, polar, hydrogen, and van der Waals.

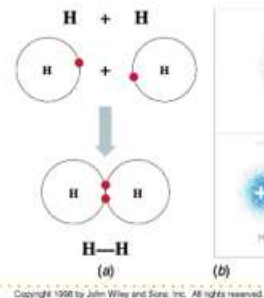
In ceramics

a. Ionic Bonding

•Ionic bonding occurs between atoms that give up their valence electrons. The result is that both atoms end up with a charge. We call the positive one a cation and the negatively charged one an anion.

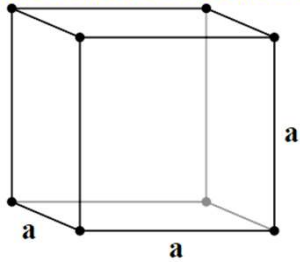
b. Covalent Bonding

•Covalent bonds often form between atoms that share their valence electrons in such a way that including the shared electrons in their outer shell.

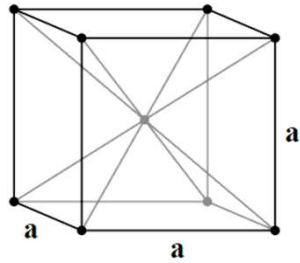


An extra bonding for ceramists, Metallic Bonding

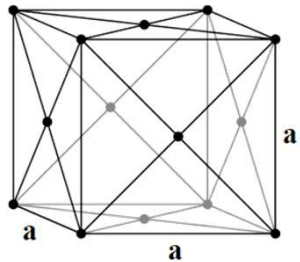
Metallic bonding occurs between atoms that have a small number of electrons in their valence shells. They give the electrons up, not just to one other atom, but to the complete group of atoms. We think of the electrons as becoming loose. Positively charged atoms sitting in a sea of electrons. We often call it *electron-gas*. E.g. sodium.



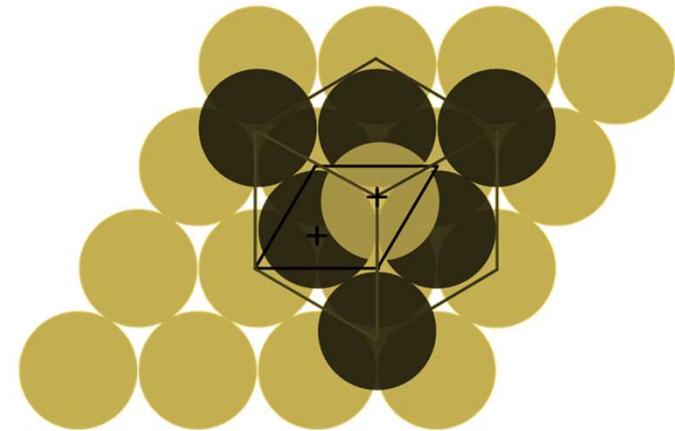
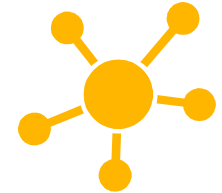
SC= Simple Cubic (primitive cubic)



BCC = Body Centered Cubic



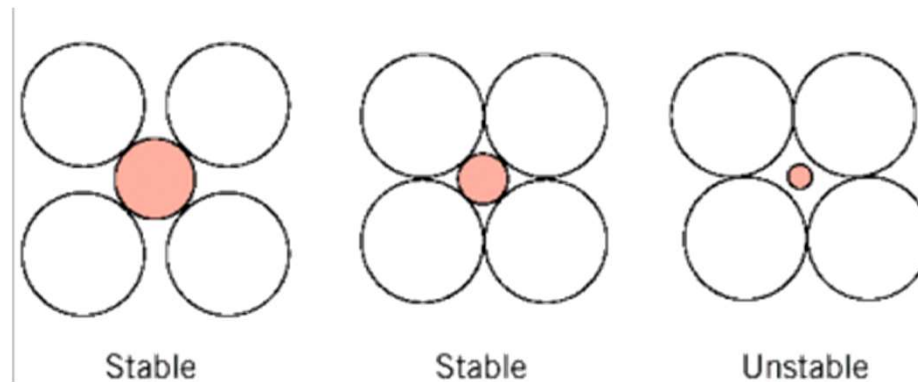
FCC= Face Centered Cubic



Crystal structure is defined by;

Magnitude of the electrical charge on each ion. Charge balance dictates chemical formula (Ca^{2+} and F^- form CaF_2).

Relative sizes of the cations and anions. Cations want maximum possible number of anion nearest neighbors and vice-versa. Crystal Structures in Ceramics with predominantly ionic bonding
Stable ceramic crystal structures: anions surrounding a cation are all in contact with that cation. For a specific coordination number there is a critical or minimum cation/anion radius ratio r_C/r_A for which this contact can be maintained.





Ceramic Crystal Structures

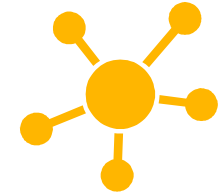
- Broader range of chemical composition than metals with more complicated structures - Contains at least 2 and often 3 or more atoms. - Usually compounds between metallic ions (e.g. Fe, Ni, Al) - called cations - and non-metallic ions (e.g. O, N, Cl) - called anions - Bonding will usually have some covalent character but is usually mostly ionic

Still based on 14 Bravais lattices

- Cation: Metal, positively charged, usually smaller
- Anion: Usually O, C, or N, negative charge, usually larger.

How do Cations and Anions arrange themselves in space?

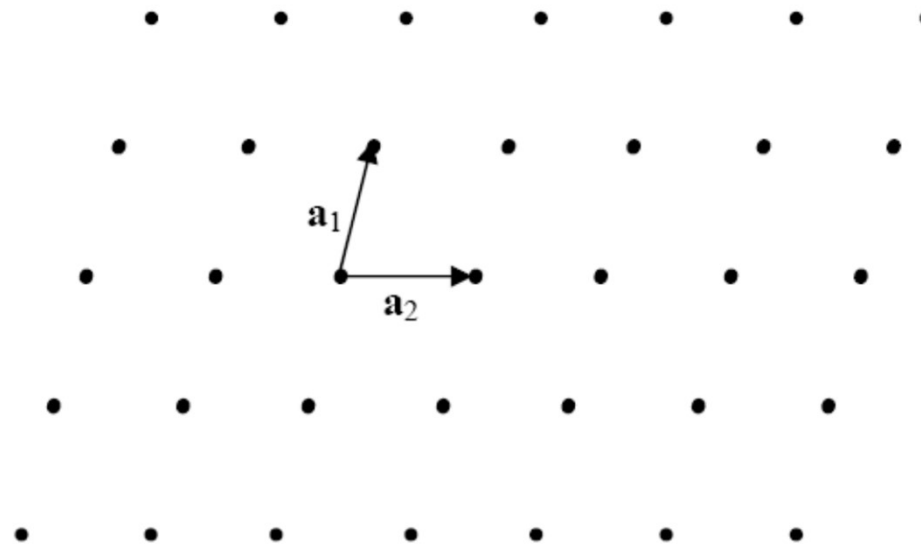
- Structure is determined by two characteristics: 1. Electrical charge - Crystal (unit cell) must remain electrically neutral - Sum of cation and anion charges in cell is 0 2. Relative size of the ions.
- The ratio of ionic radii ($r_{\text{cation}} / r_{\text{anion}}$) dictates the coordination number of anions around each cation. - As the ratio gets larger (i.e. as $r_{\text{cation}} / r_{\text{anion}} > 1$) the coordination number gets larger and larger.

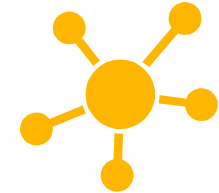


Crystal structure = lattice + basis

- A lattice is a set of regular and periodic geometrical points in space
- A basis is a collection of atoms or molecules at a lattice point

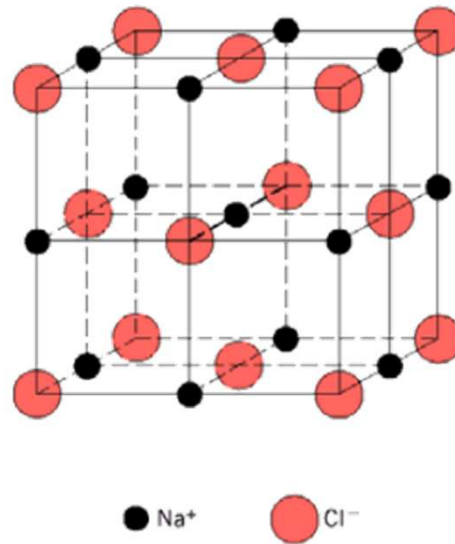
A crystal is a collection of atoms or molecules arranged at all the lattice points.





Crystal Structures in Ceramics Example: Rock Salt Structure

- NaCl structure: $r_C = r_{Na} = 0.102 \text{ nm}$, $r_A = r_{Cl} = 0.181 \text{ nm} \Rightarrow r_C/r_A = 0.56$
- From the table for stable geometries we see that C.N. = 6 Crystal Structures in Ceramics



Example: Rock Salt Structure Two interpenetrating FCC lattices NaCl, MgO, LiF, FeO have this crystal structure

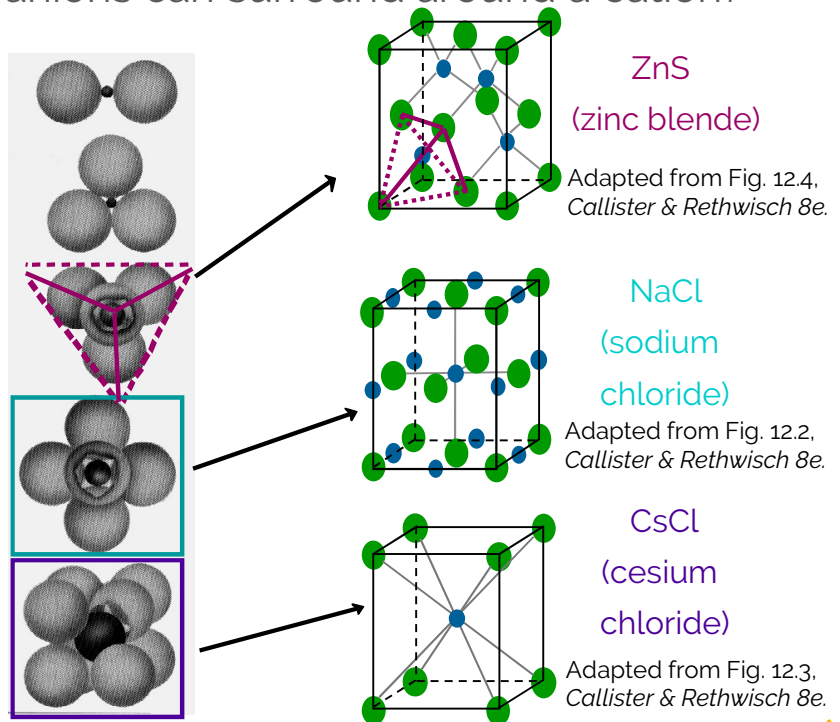
- Coordination # increases with

$$\frac{r_{\text{cation}}}{r_{\text{anion}}}$$

UNIT CELL- ATOM RATIO

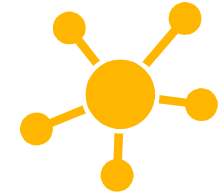
- To form a stable structure, how many anions can surround around a cation?

$r_{\text{cation}}/r_{\text{anion}}$	Coord #	Ion Locations
< 0.155	2	Linear
0.155 - 0.225	3	Triangular
0.225 - 0.414	4	Tetrahedral
0.414 - 0.732	6	Octahedral
0.732 - 1.0	8	Cubic



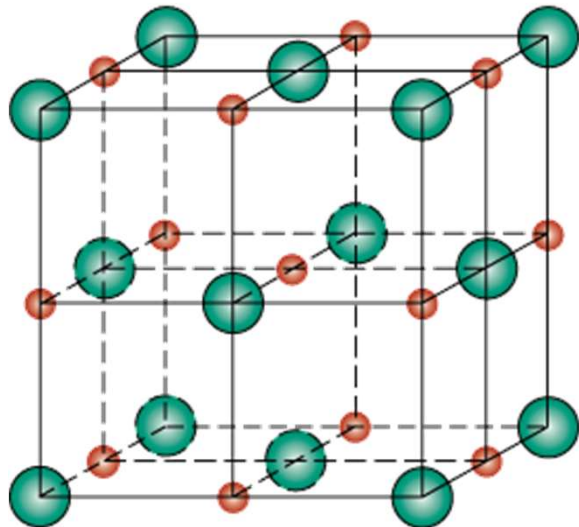
Adapted from Table 12.2, Callister & Rethwisch 8e.





Rock Salt Structure

- Same concepts can be applied to ionic solids in general.
- Example: NaCl (rock salt) structure



● Na^+ $r_{\text{Na}} = 0.102 \text{ nm}$

● Cl^- $r_{\text{Cl}} = 0.181 \text{ nm}$

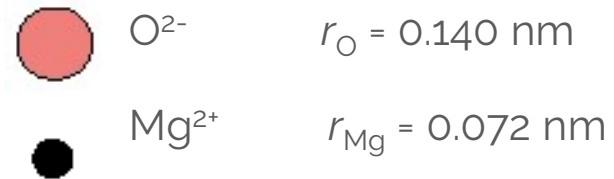
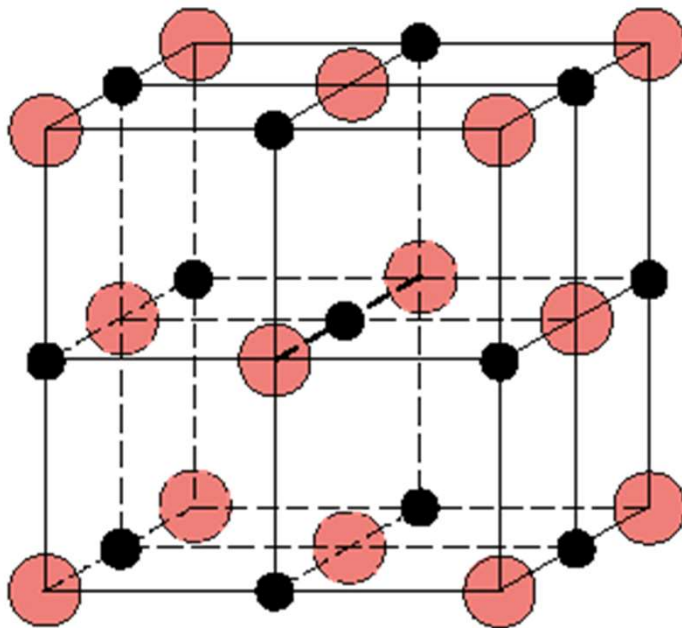
$$r_{\text{Na}}/r_{\text{Cl}} = 0.564$$

$\therefore$ cations (Na^+) prefer octahedral sites

Adapted from Fig. 12.2, *Callister & Rethwisch 8e*.

MgO and FeO

- MgO and FeO also have the NaCl structure

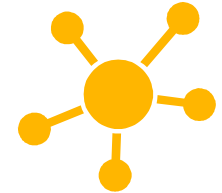


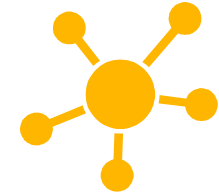
$$r_{\text{Mg}}/r_{\text{O}} = 0.514$$

∴ cations prefer octahedral sites

- So each Mg²⁺ (or Fe²⁺) has 6 neighbor oxygen atoms

Adapted from Fig. 12.2, Callister & Rethwisch 8e.

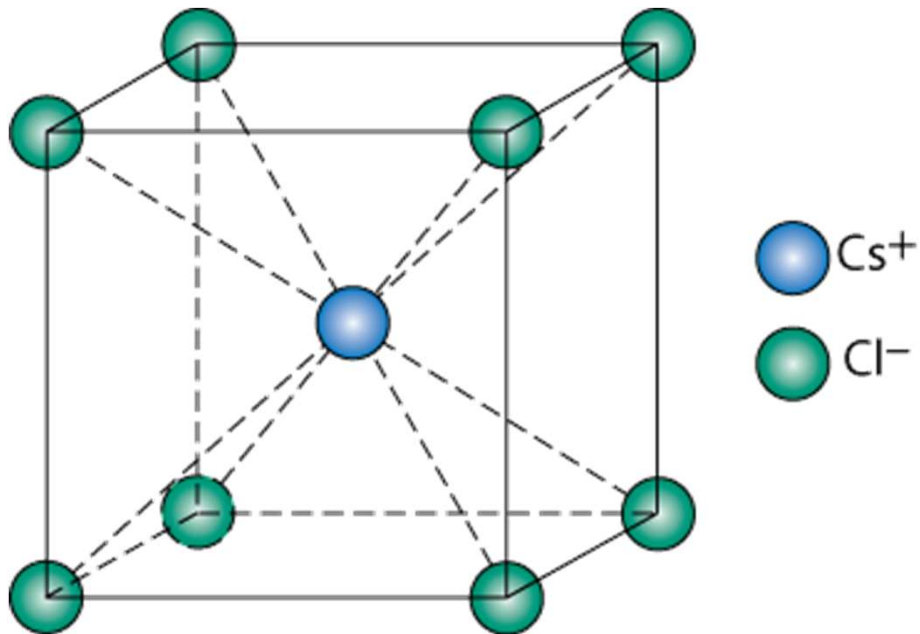




AX Crystal Structures

- AX-Type Crystal Structures include NaCl, CsCl, and zinc blende

Cesium Chloride structure:



$$\frac{r_{\text{Cs}^+}}{r_{\text{Cl}^-}} = \frac{0.170}{0.181} = 0.939$$

∴ Since $0.732 < 0.939 < 1.0$,
cubic sites preferred

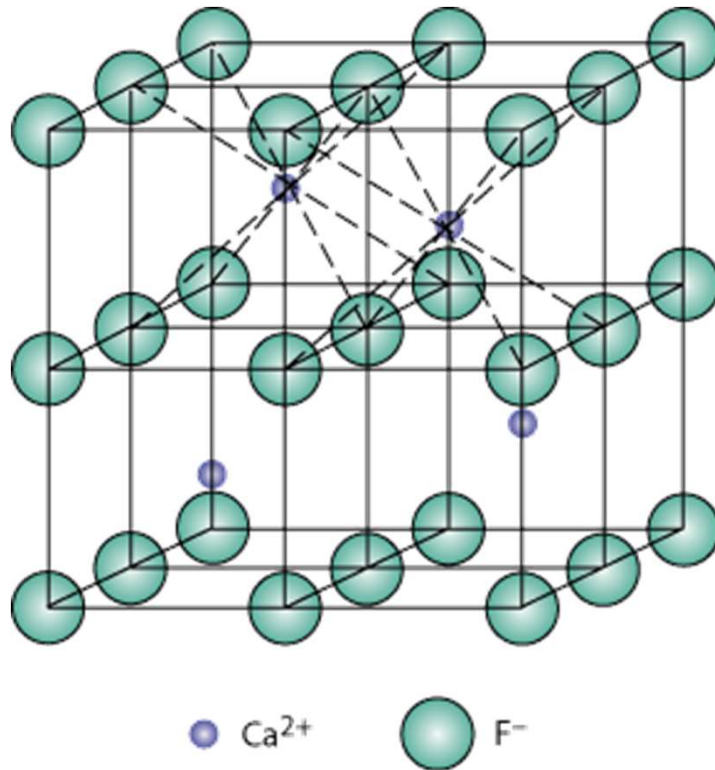
So each Cs⁺ has 8 neighbor Cl⁻

Adapted from Fig. 12.3, Callister & Rethwisch 8e.

AX₂ Crystal Structures

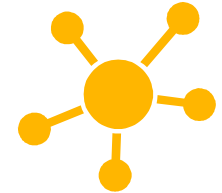
Fluorite structure structure:

UNIT CELL – TWO DIAGONALS

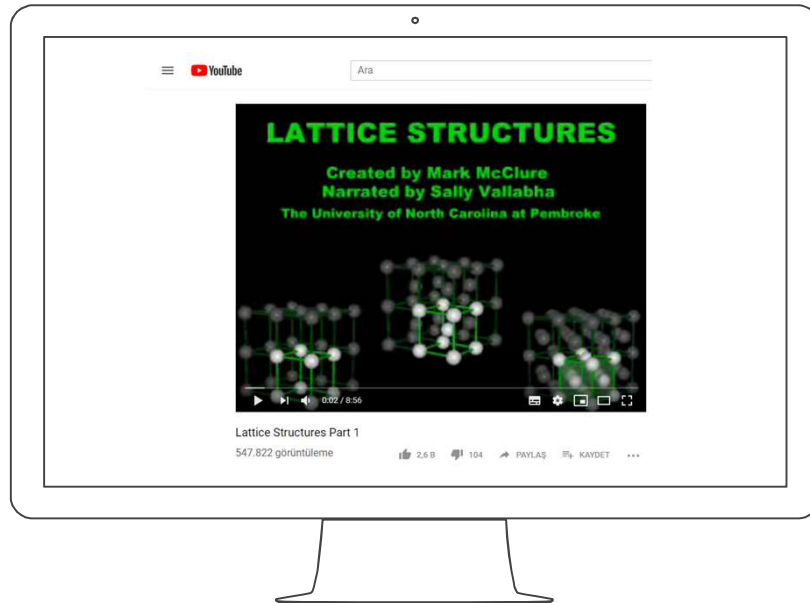


- Calcium Fluorite (CaF₂)
- Cations in cubic sites
- UO₂, ThO₂, ZrO₂, CeO₂
- Antifluorite structure – positions of cations and anions reversed

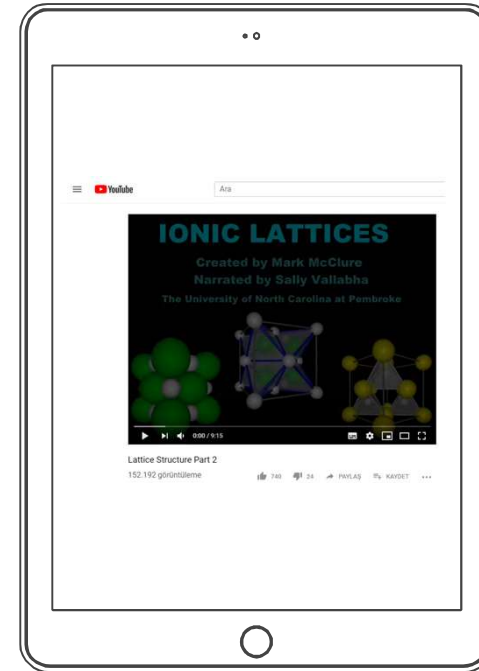
Adapted from Fig. 12.5, Callister & Rethwisch 8e.



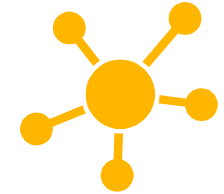
Lattice Structures Animations



<https://www.youtube.com/watch?v=Rm-i1c7zr6Q>



<https://www.youtube.com/watch?v=F4Du4zl4GJo>

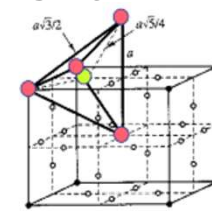


How do Cations and Anions arrange themselves in space?

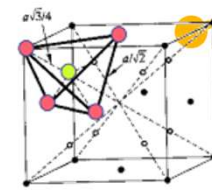
- Structure is determined by two characteristics:
 1. Electrical charge - Crystal (unit cell) must remain electrically neutral - Sum of cation and anion charges in cell is 0
 2. Relative size of the ions
- The ratio of ionic radii ($r_{\text{cation}} / r_{\text{anion}}$) dictates the coordination number of anions around each cation. - As the ratio gets larger (i.e. as $r_{\text{cation}} / r_{\text{anion}} > 1$)
- The coordination number gets larger and larger

Where do Cations and Anions fit ?

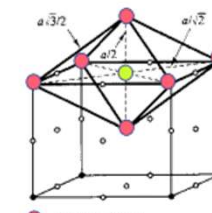
CN	Radius Ratio	Geometry
3	0.155 - 0.225	Triangular
4	0.255 - 0.414	Tetrahedron
6	0.414-0.732	Octahedron
8	0.732 - 1	Cube Center



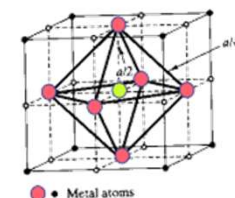
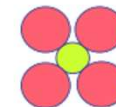
BCC



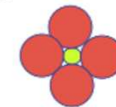
FCC



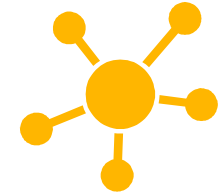
BCC



FCC



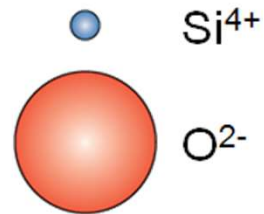
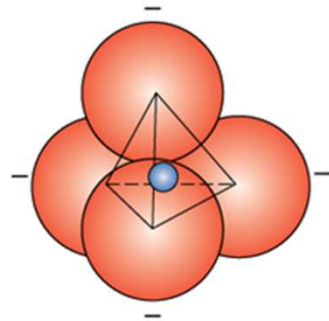
Common Ceramic Structures and Chemical Formulas



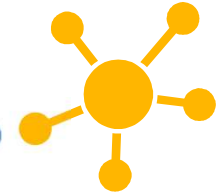
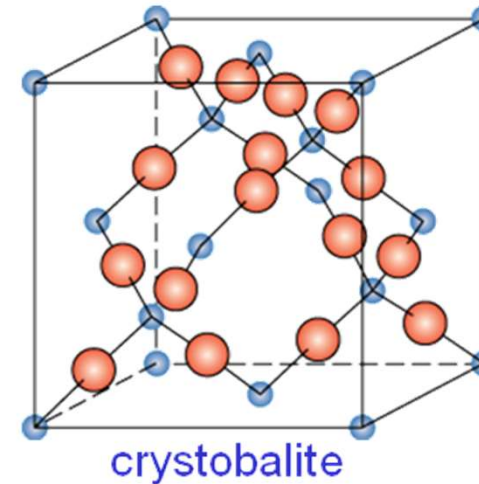
Structure	Lattice	Ch. formula
Cesium Chloride (CsCl)	SC	MX
Rock salt (NaCl)	FCC	MX
Fluorite (CaF ₂)	FCC	MX ₂
Silicates (complex) (SiO ₂)	FCC	MX ₂
Corundum (Al ₂ O ₃)	hexagonal	M ₂ X ₃
Perovskite (CaTiO ₃)	SC	M'M''X ₃
Spinel (MgAlO ₄)	FCC	M'M''X ₄
Diamond	FCC	
Graphite	hexagonal	

Silicate Ceramics

TETRAHEDRON

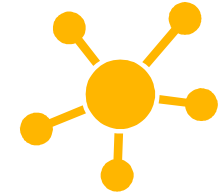


Adapted from Figs.
12.9-10, Callister &
Rethwisch 8e



- SiO₂ (silica) **polymorphic** forms are quartz, cristobalite, & tridymite
- The strong Si-O bonds lead to a high melting temperature (1710°C) for this material

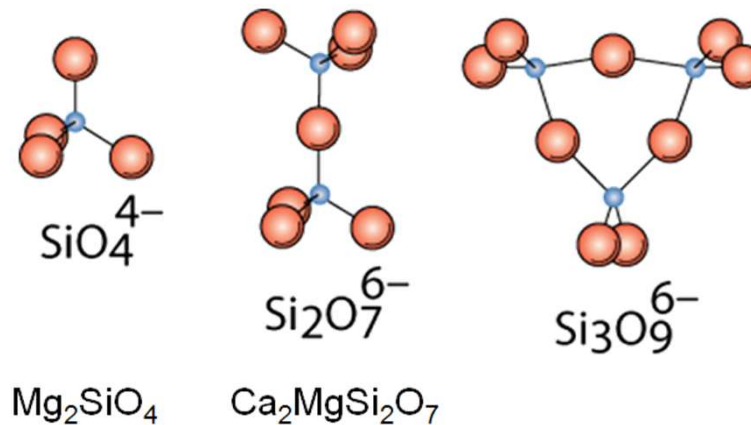
Bonding of adjacent SiO_4^{4-} accomplished by the sharing of common corners, edges, or faces.



Presence of cations such as Ca^{2+} , Mg^{2+} and Al^{3+}

1- Maintain charge neutrality

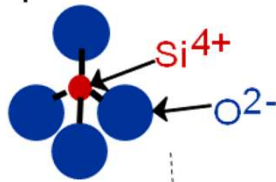
2- ionically bond SiO_4^{4-} to another



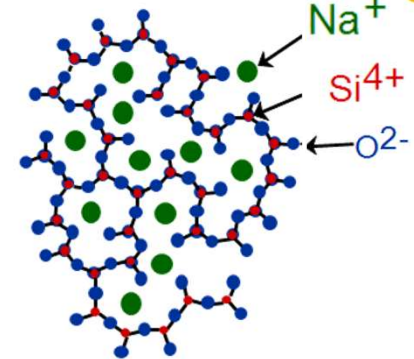
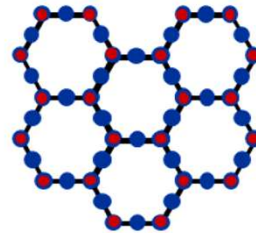
Variations combinations of silicates

Glass Structure (non-crystalline-amorphous)

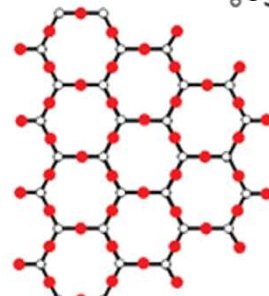
SiO_4^{4-} tetrahedron



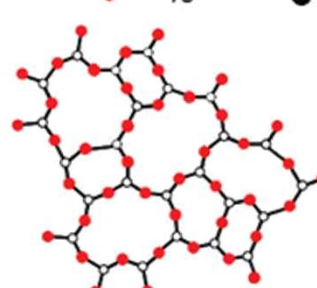
Quartz is **crystalline**
 SiO_2 :



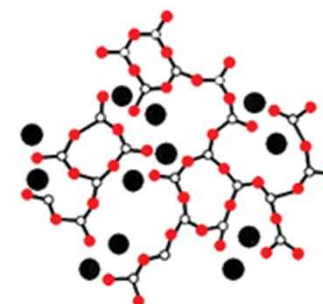
○ - Silicon ● - Oxygen ● - Sodium



SiO_2 Crystal

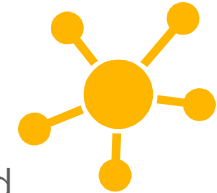


SiO_2 Glass



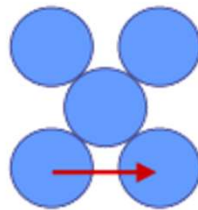
$\text{SiO}_2 - \text{Na}_2\text{O}$ Glass

- Linear Densities fraction of line length in a particular direction that passes through atom centers
- Planar Densities fraction of total crystallographic plane area that is occupied by atoms (plane must pass through center of atom)



Calculate the linear density of the (100) direction for the FCC crystal

- o Calculate the linear density of the (100) direction for the FCC crystal



$$L_D = L_C / L_L \quad \text{linear density}$$

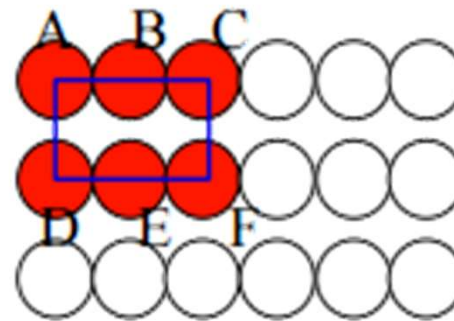
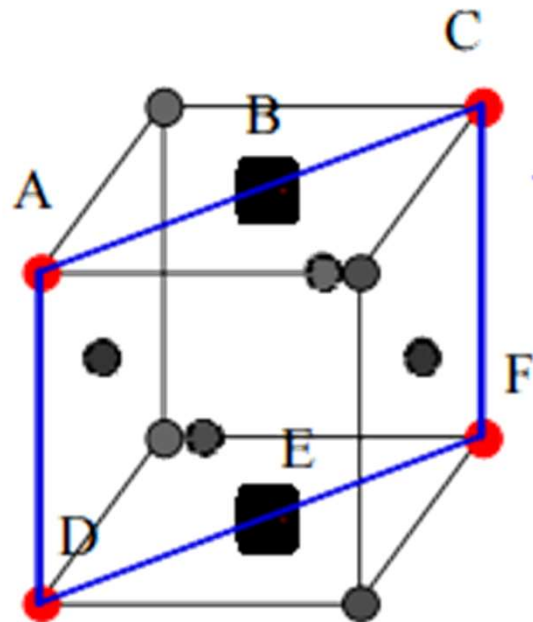
$$L_C = 2R \quad \text{circle length}$$

$$L_L = a \quad \text{line length}$$

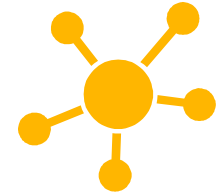
$$\text{For FCC } a = 2R\sqrt{2}$$

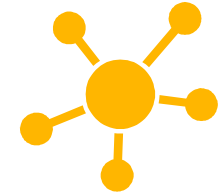
$$L_D = 2R / (2R\sqrt{2}) = 0.71$$

- Calculate the planar density of the (110) plane for the FCC crystal

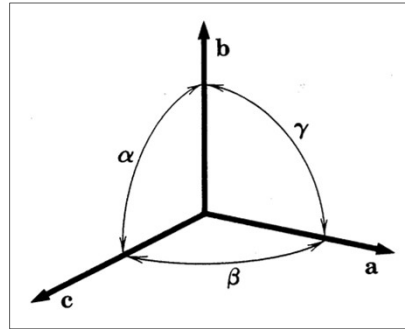


- Compute planar area
- Compute total "circle" area



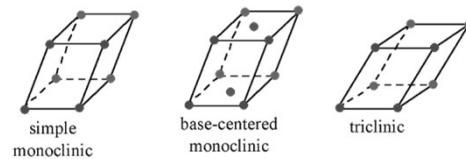
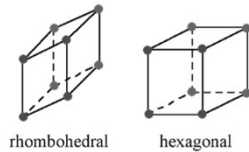
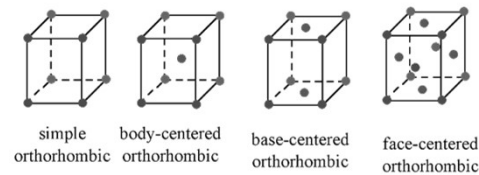
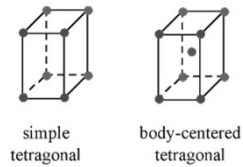
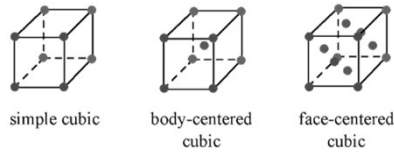


3-D Lattice types



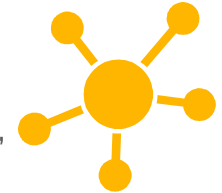
Seven major groups of lattice types

Triclinic	$a_1 \neq a_2 \neq a_3$	$\alpha \neq \beta \neq \gamma$
Monoclinic	$a_1 \neq a_2 \neq a_3$	$\alpha = \gamma = 90^\circ \neq \beta$
Orthorhombic	$a_1 \neq a_2 \neq a_3$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a_1 = a_2 \neq a_3$	$\alpha = \beta = \gamma = 90^\circ$
Cubic	$a_1 = a_2 = a_3$	$\alpha = \beta = \gamma = 90^\circ$
Trigonal	$a_1 = a_2 = a_3$	$\alpha = \beta = \gamma < 120^\circ \neq 90^\circ$
Hexagonal	$a_1 = a_2 \neq a_3$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$

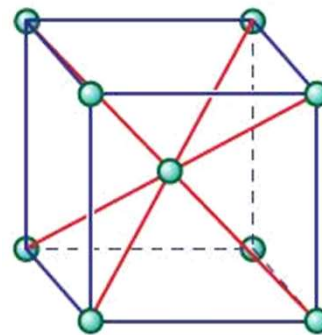


Bravais lattice

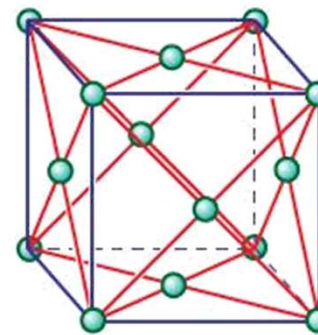
If non-primitive cells (or conventional cell) are allowed, the number will expand to 14.



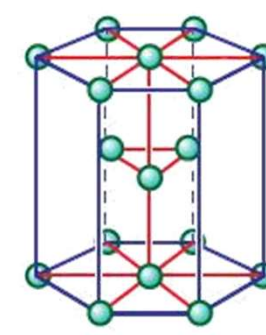
Common metallic crystal structures



body-centred cubic (bcc)



face-centred cubic (fcc)



hexagonal close-packed (hcp)

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Properties of Ceramic Materials

Physical and Mechanical Properties



General Properties (summary)

- Keramikos - burnt stuff in Greek - desirable properties of ceramics are normally achieved through a hightemperature heat treatment process (firing).
- Usually a compound between metallic and nonmetallic elements
- Always composed of more than one element (e.g., Al_2O_3 , NaCl , SiC , SiO_2) $\frac{3}{4}$ Bonds are partially or totally ionic, and can have combination of ionic and covalent bonding
- Generally hard and brittle
- Generally electrical and thermal insulators
- Can be optically opaque, semi-transparent, or transparent Traditional ceramics – based on clay (china, bricks, tiles, porcelain), glasses.
- “New ceramics” for electronic, computer, aerospace industries.

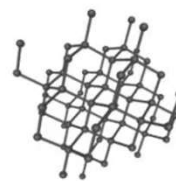
Physical Properties

1. Density

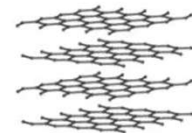
- Ceramics are intermediate (density = ρ = 2.00-6.00 gms/cm³)
- Different for ALLOTROPES (e.g., glass, cristobalite, tridymite, quartz)
- i.e; Non-crystalline materials are less dense than crystalline ones. Why?
- Allotrope?? :Each of two or more different physical forms in which an element can exist. Chemically similar physically different
- Graphite, charcoal, and diamond are all allotropes of carbon.

Density influencing factors:

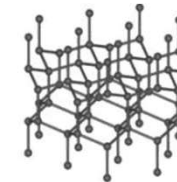
- Atomic weight
- Packaging behaviour of the atoms (atomic structures)
- Porosity within the microstructure



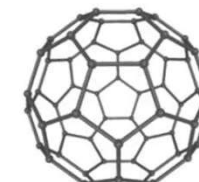
Diamond



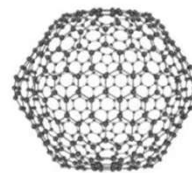
Graphite



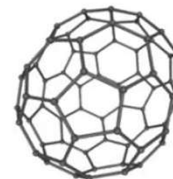
Lonsdaleite



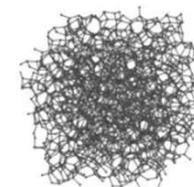
**C60
buckminsterfullerene**



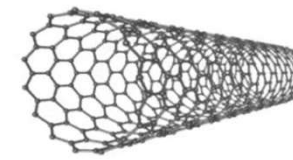
C540, Fullerite



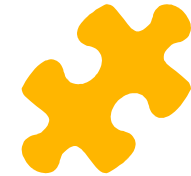
C70



Amorphous carbon



**single-walled
carbon nanotube**





The **crystallographic density** (aka molar density) is;

Number of formula units/unit cell

$$\rho = \frac{n'(\Sigma A_C + \Sigma A_A)}{V_C N_A}$$

Volume of unit cell

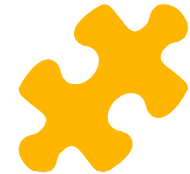
Avogadro's number

ΣA_C = sum of atomic weights of all cations in formula unit

ΣA_A = sum of atomic weights of all anions in formula unit

In macro density calculations $d = M/V$ («Theoric densitiy» without porosity) can be applied as;

$$\text{Density} = \frac{M}{V + V_{\text{porosity}}}$$



2. Thermal Properties

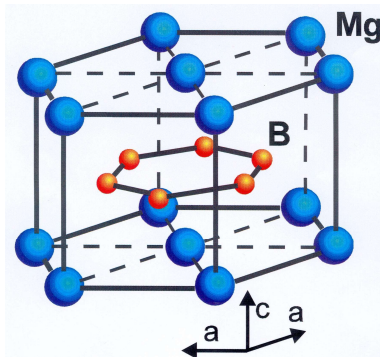
- Bonding is highly important - stronger bonds (covalent/ #Valance e-)
- increases the melting temprature.
- Melting points high (600-4000C) Thermal conductivities are low (insulators)
- Thermal expansion values are low (1-15 ppm/C)
- Because most ceramics have crystal structures that are not cubic ones, they tend to be **ANISOTROPIC**. This means they will have different properties in different directions.

Ceramic	α (LCTE) =	Tm =
CsCl	54 ppm/C	646 C
NaCl	40	800
PbS	20	1120
CaF ₂	20	1330
Fe ₂ O ₃	9	1560
SiO ₂ (Crist.)	12	1710
TiO ₂	7	1840
ZnO	6	1975
Al ₂ O ₃	8	2050
ZrO ₂	10	2700
MgO	9	2800
TiC	7	3190

Anisotropy is the property of being directionally dependent, which implies different properties in different directions, as opposed to isotropy.

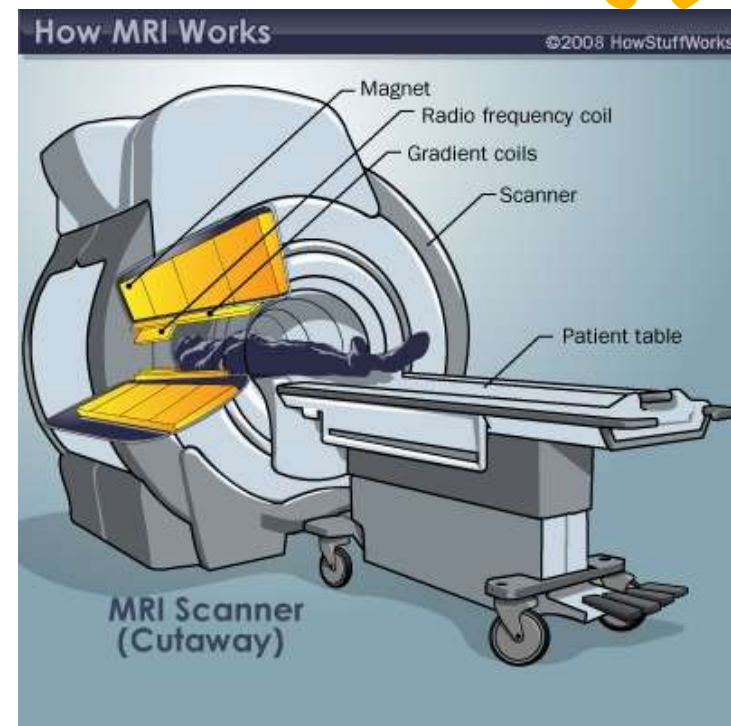
3. Electrical Properties

- Electrical conductivity (insulator or semi-conductor) and recently low/high temperature superconductors.



i.e: MgB_2 used in MRI machines, under 235°C released their ability to resist and MgB_2 turns into a superconductor.

- Generally ceramics are electrical insulators under most circumstances. Hydroxyapatite crystals are insulating. Dentin enamel is 89 volume percent hydroxyapatite. Dentin is 50 volume percent hydroxyapatite crystals. Tooth structure therefore is insulating.

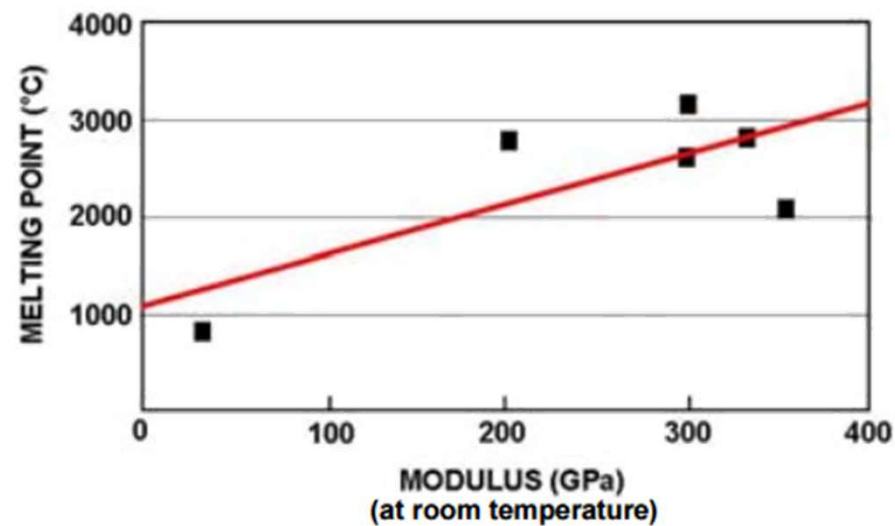


4. Mechanical Properties (The Behaviour of materials under a certain load)

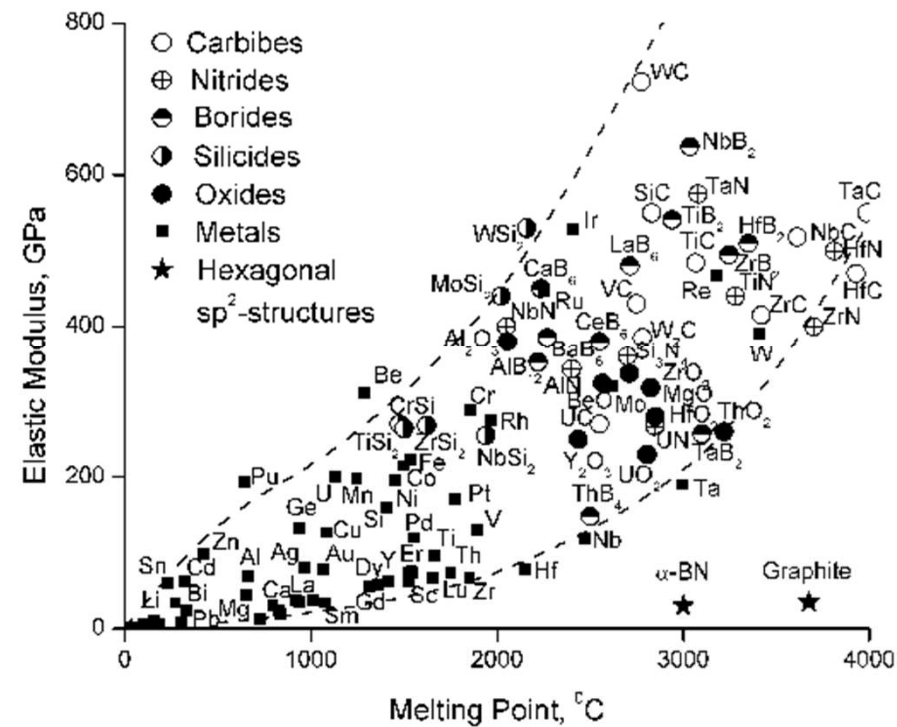
- Ceramics tend to be rigid and brittle (i.e., not capable of much plastic deformation).
- However, their properties depend both on temperature and on the amount of Crystallinity (atomic structure). Lower temperatures and higher crystallinity content tend to increase the modulus and the brittleness.



Ceramic:	E (GPa) =	Tm (C) =
Al ₂ O ₃	310	2050
SiC	345	>2800
TiC	207	3180
BeO	310	2585
MgO	366	2800
NaCl	34	801

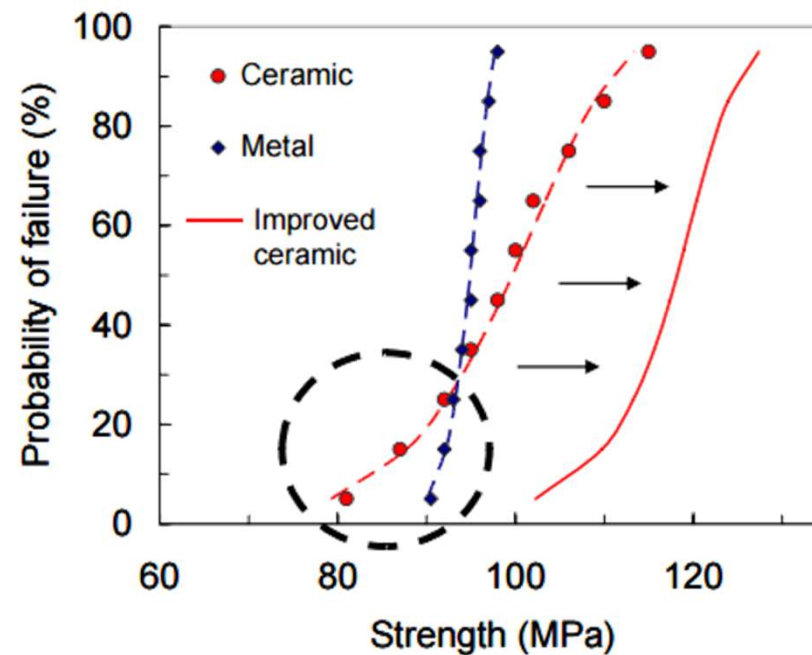


Mechanical properties versus melting temperature: Generally strength and modulus go up and down together. Modulus (E) at 25C linearly related to melting temperature (T_m). (Ceramics = 30-350 GPa, Metals = 50-200 GPa, Polymers =< 50GPa)

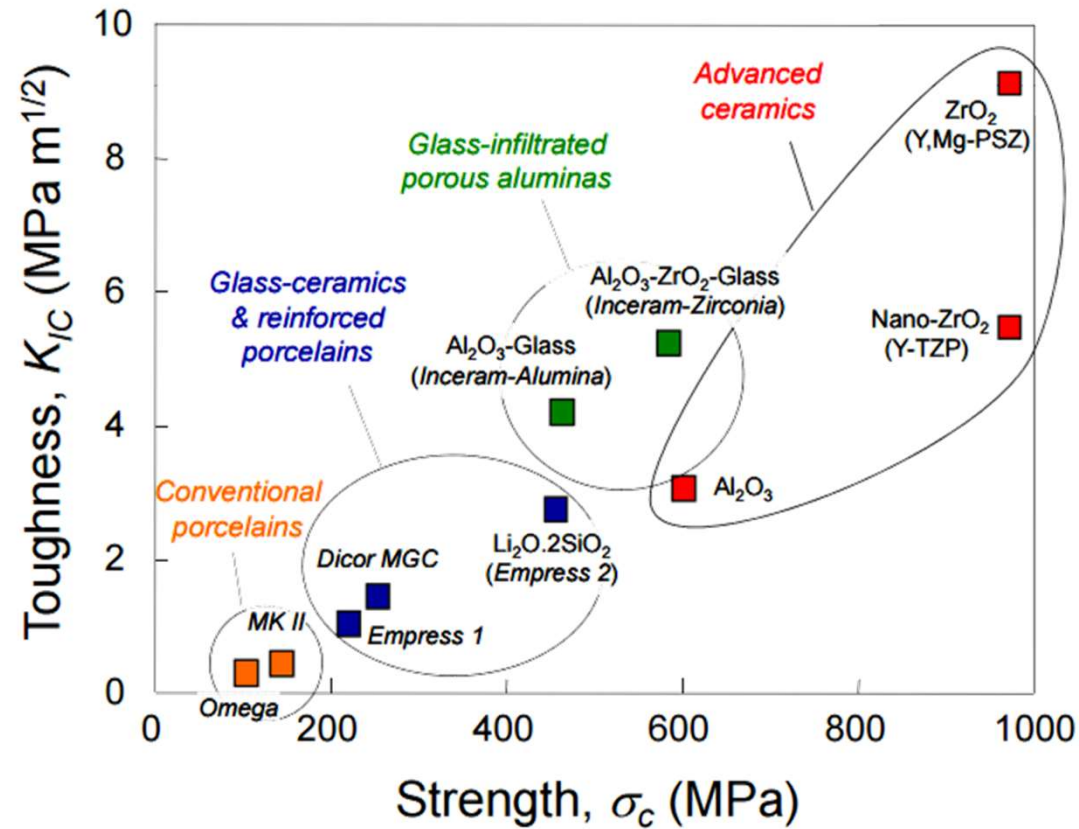


Mechanical properties versus degree of crystallinity:

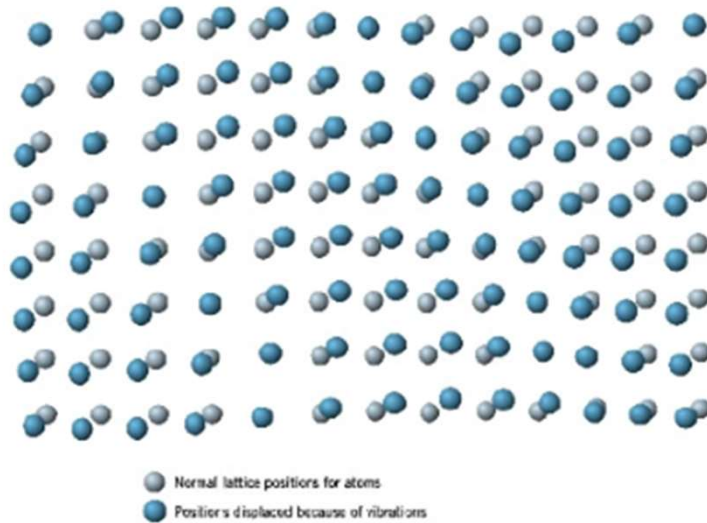
- Crystalline phases are stronger.
- At low T's, crystalline and non-crystalline phases are brittle. At high T's approaching T_m , non-crystalline phases are ductile.



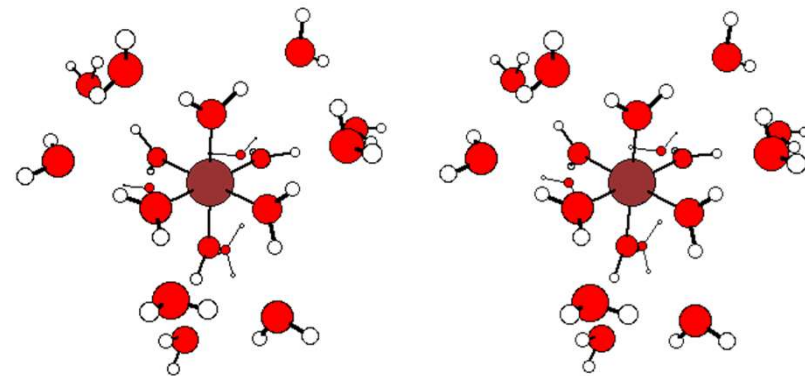
Advanced Ceramics and the Mechanical Properties



Thermal Shock Resistance



- Heat causes atoms to vibrate
- Vibrating in synch is often a low energy configuration (preferred)
 - Generates waves of atomic motion
 - Often called phonons, similar to photos but atomic motion instead of optical quanta

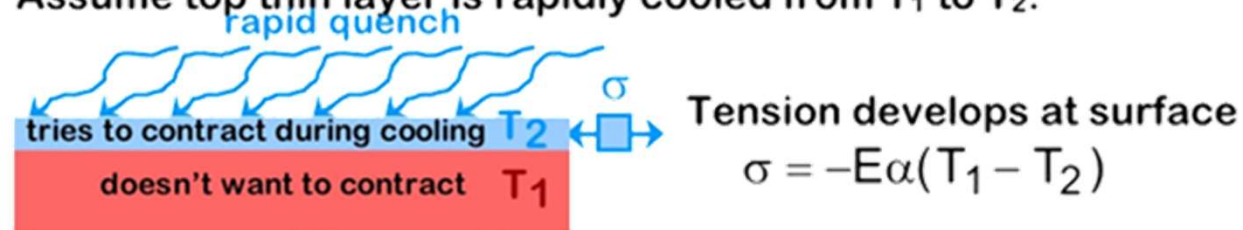


Thermal Shock Resistance

- Thermal shock is fracture of brittle ceramics due to asymmetric thermal expansion
- Occurs due to: Uneven heating/cooling
- The change in T with position leads to built in strain and thus stress



- Ex: Assume top thin layer is rapidly cooled from T_1 to T_2 :

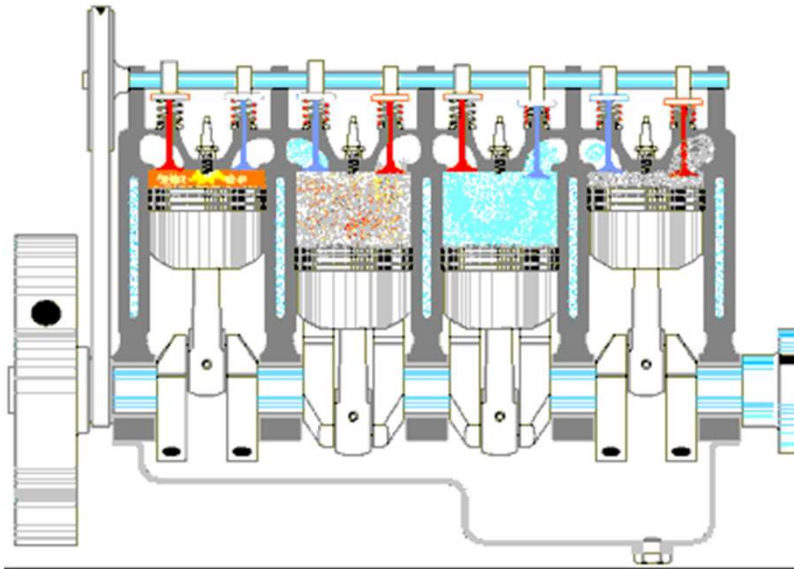


Where E is the Young's modulus, α is the coefficient of expansion and σ_{TS} is tensile strength. ΔT represents the ceramic's thermal shock resistance

Thermal Expansion Comparison of Materials



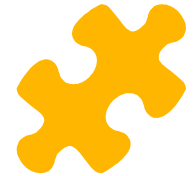
- Thermal expansion mismatch is a major problem for design of everything from semiconductors to bridge
- Particularly an issue in applications where temperature changes greatly (esp. engines)



↑ increasing α

Material	α ($10^{-6}/K$) at room T
• Polymers	
Polypropylene	145-180
Polyethylene	106-198
Polystyrene	90-150
Teflon	126-216
• Metals	
Aluminum	23.6
Steel	12
Tungsten	4.5
Gold	14.2
• Ceramics	
Magnesia (MgO)	13.5
Alumina (Al ₂ O ₃)	7.6
Soda-lime glass	9
Silica (cryst. SiO ₂)	0.4

Thermal Expansion Comparison of Materials



Fine Ceramics
(Alumina)



Metals
(Stainless Steel)



5

Ceramic Phase Diagram

“

Reading Assessment:

Teach Yourself:

Phase Diagrams and Phase Transformations

Cambridge University Press

https://downloadfiles.grantadesign.com/pdf/booklets/Teach_Yourself_Phase_Diagrams_and_Phase_Transformations.pdf

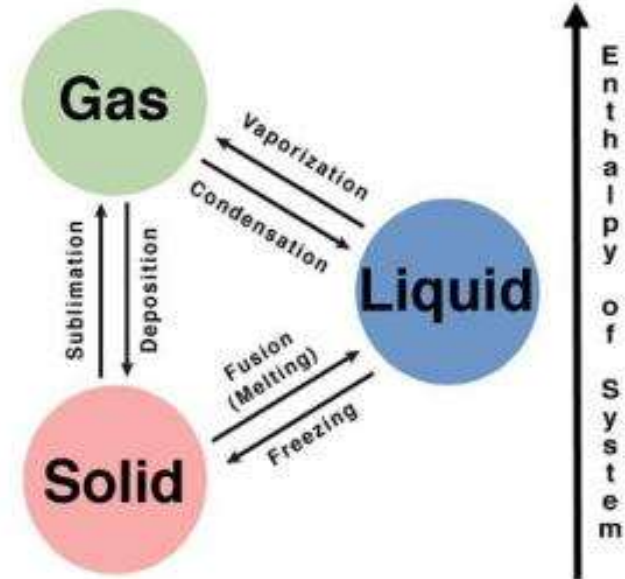
Phase Diagram

A phase is defined as any homogeneous and physically distinct part of a system bounded by a surface and is mechanically separable from other parts of the system.

A phase may be gaseous, liquid or solid. It is perfectly homogeneous and distinct from every other phase that is present in the system. There must be a definite boundary between any two phases. This boundary is known as the interface.

Air constitutes a single phase only as it contains a mixture of nitrogen, oxygen, carbon dioxide, water vapour etc.,. A system consisting of only one phase is said to be homogeneous.

A mixture of two immiscible liquids such as water and benzene, will exist in two distinct liquid phases and in addition there will be a vapour phase. Thus there will be three phases each separated from the other by a well-defined bounding surface.

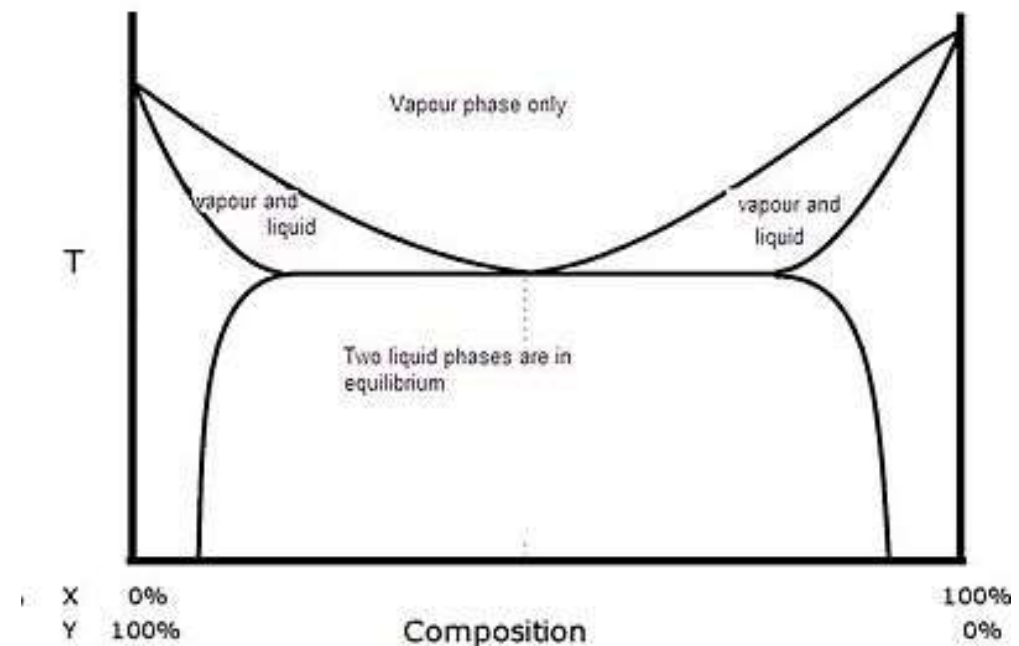


http://www.vssut.ac.in/lecture_notes/lecture1543821158.pdf

https://www.researchgate.net/publication/265602607_Phase_Rule CHAPTER-6 PHASE RULE



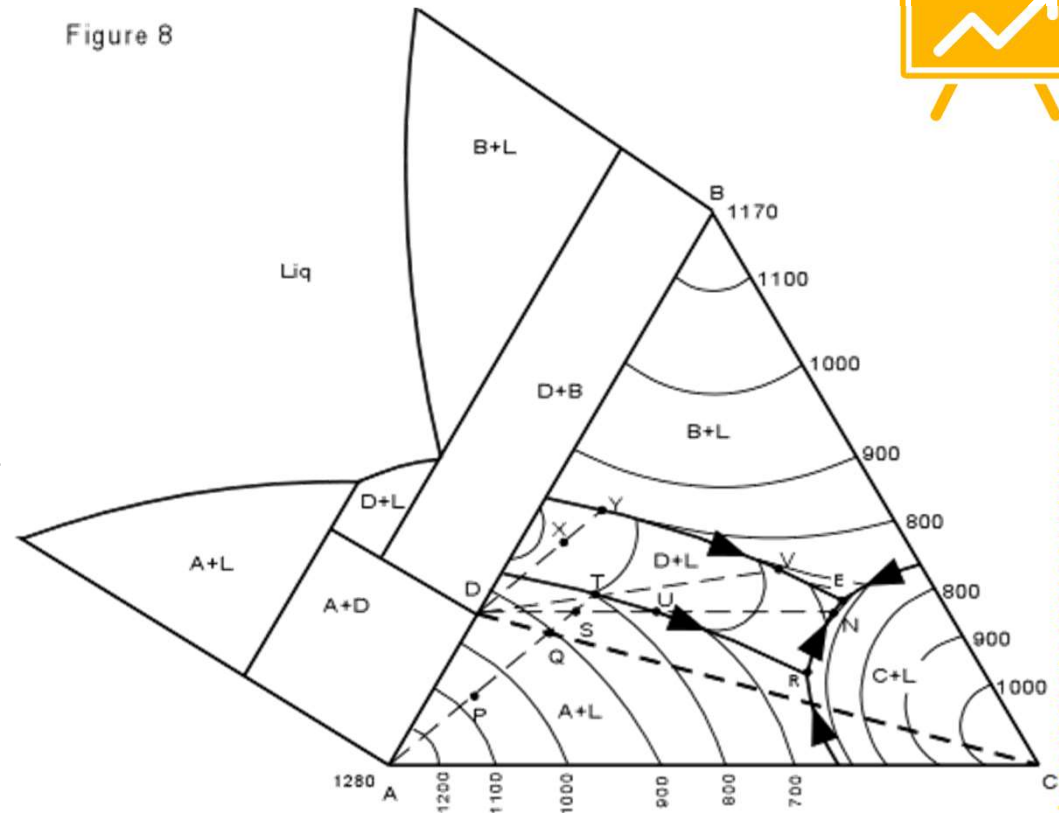
A system consisting of more than one phase is said to be heterogeneous. When various phases are in equilibrium with one another in a heterogeneous system, there can be no transfer of energy or mass from one phase to another. This means that at equilibrium, the various phases must have the same temperature and pressure and their respective compositions must remain constant all along.



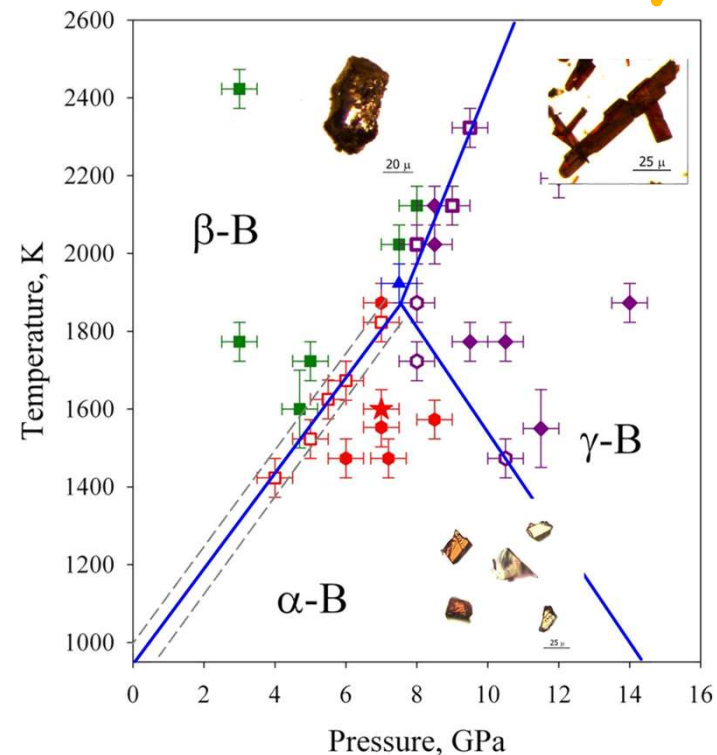
Phase Diagram:

Standard phase diagrams are graphical representations of the equilibrium relationships between minerals (or other phases). These relationships are governed by the laws of thermodynamics. Standard phase diagrams show how phases or phase assemblages change as a function of temperature, pressure, phase composition, or combinations of these variables.

Figure 8



- There are three independent variables that can affect the states of singular or multiphase ceramic. These are **pressure**, **temperature** and **composition**. For most practical situations the pressure can be taken as constant.
- Phase Diagrams provide useful information on the following topics:
 - Phases in equilibrium conditions
 - Chemical composition of phases at specific temperature
 - The total ratio of each phase
 - The melting temperature of the compounds (Usually the amount of each ceramic compound)
 - Presence and solubility of a compound in one another
 - The presence of polymorphic transformations and their transformation temperatures



- Phase diagrams can be prepared using experimental data or thermodynamic calculations. Experimental methods include methods such as thermal analysis, microstructural investigation and X-ray diffraction(XRD)

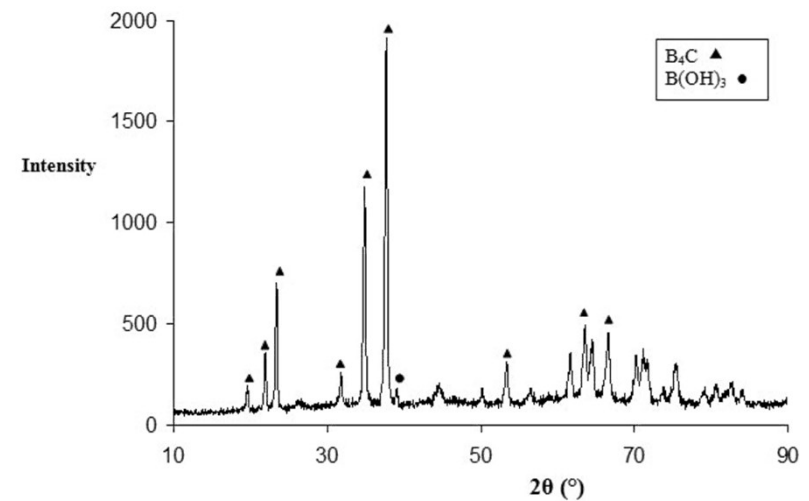
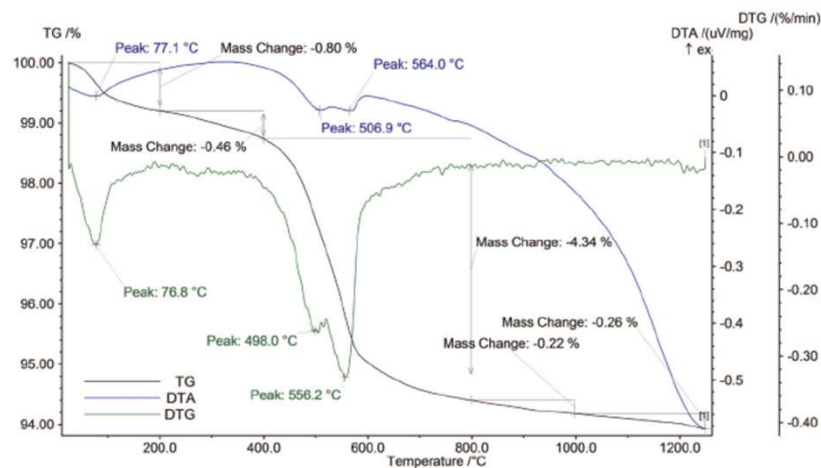


Figure 3: XRD pattern of the mixture of TTIP, B₄C and isopropanol after milling at about 430K.

Gibbs Phase Rule



An important equation describing the degree of freedom of a system in equilibrium is the Gibbs phase rule.

$$F = C - P + 2$$

F= the degree of freedom

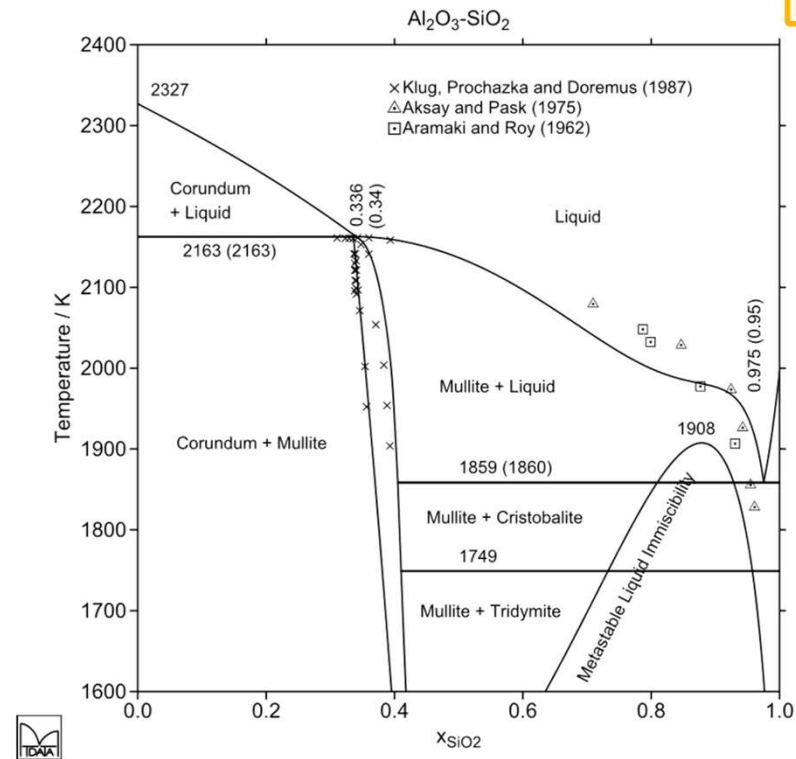
C= the number of components

P= the number of phases in equilibrium

Degrees of freedom number or level indicates that the number of variables that must be determined to fully identify an equilibrium state. (temperature, pressure and compound)

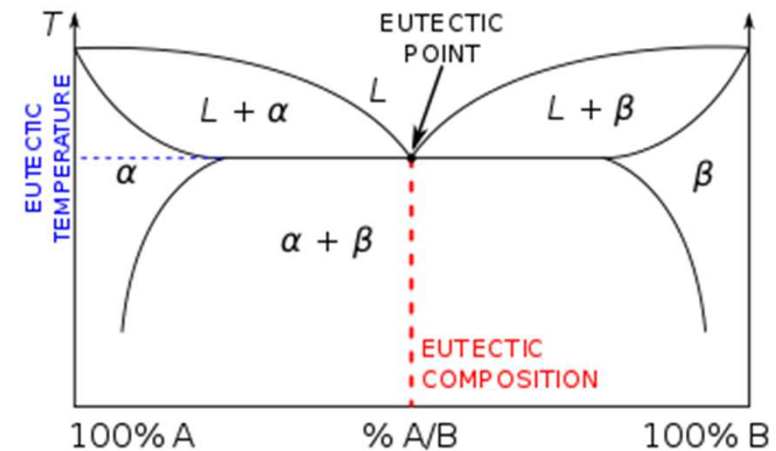
Some of the information that can be read directly from the diagram are given below:

- Melting temperature of each pure compound
- The degree of reduction in melting temperature as two or more compounds are mixed
- The interaction of two compounds (such as SiO_2 plus Al_2O_3) to form a third compound ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, mullite)
- The presence and degree of solid solution
- The effect of temperature on the degree of solid solution





- The temperature at which a compound goes from one crystal structure to another (polymorphic phase transformation)
- The amount and composition of liquid and solid phases at a specific temperature and bulk composition
- The presence at high temperature of immiscible liquids (liquids that are not soluble in each other)
- Depending on the amount of components of the mixture, the lowest melting temperature (Eutectic), the highest temperatures at which solidification starts with cooling (Liquidus), minimum temperatures at which solidification is completed (Solidus), Resolution limits (Solvus)



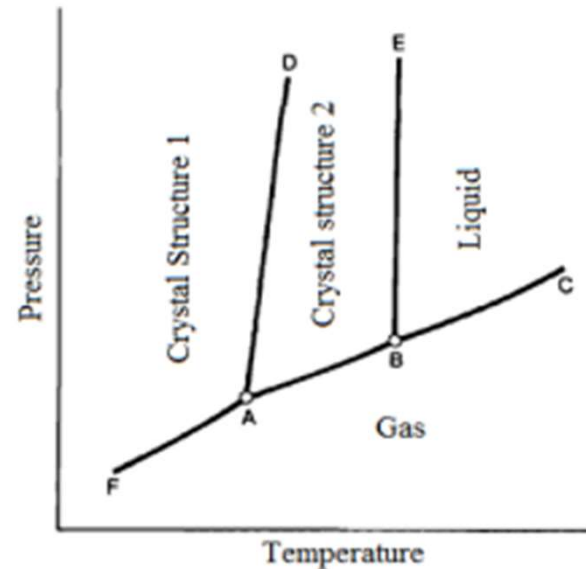


Single Phase Diagram

In a single component system, a chemical compound (H_2O , Al_2O_3 , SiO_2), one molecule (H_2) or an element (C) are homogeneously distributed throughout each phase of the system.

$$C=1 > P + F = 3$$

- At point A the crystal structure 1, crystal structure 2 and gas phases are in equilibrium.
- The crystal structure 2, liquid and gas phases are
- equilibrium at point B as well.
- At these points ; $F=0$ (invariant point)





Single Phase Diagram

- In single component systems, solid phases can exist in more than one crystal structure (allotropy, polymorphism)
- In the case of silica at equilibrium, three different solid (quartz, tridymite, cristobalite), liquid and gas phases are existed. Because the change between the phases is very slow, the metastable phases are found in the material.

Equilibrium
diagram for
SiO

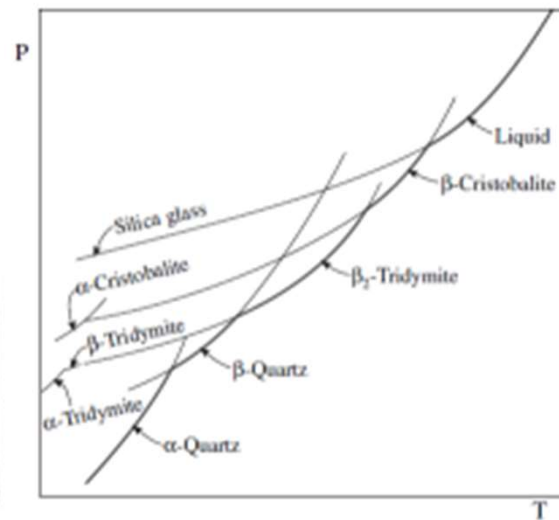
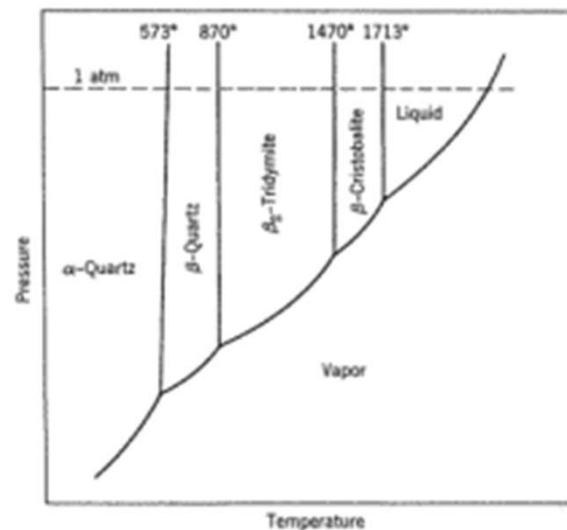
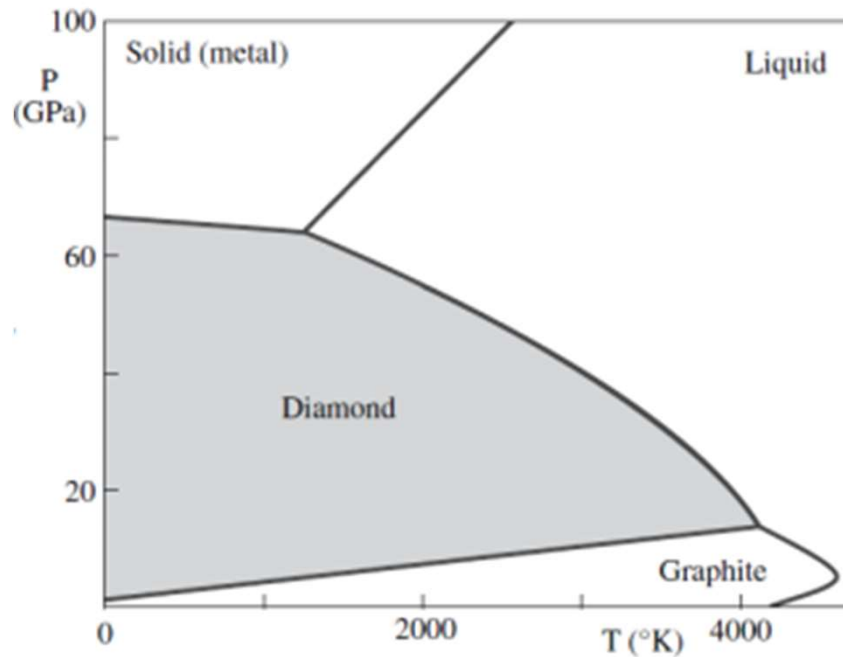


Diagram
including
metastable
phases
occurring in
the system
SiO₂

Kingery, W.D. et. al., *Introduction to Ceramics*, 2nd ed., Wiley, New York, 1976

Single Phase Diagram



Carter, C.B.; Norton, M.G.; "Ceramic Materials: Science and Engineering", Springer, 2007

- Synthetic diamond from graphite production constitutes an important component of the implementation of a phase diagram.
- As the figure shows, very high temperatures and pressures are required for diamond transformation; Liquid metal catalysis such as nickel is needed to accelerate the reaction in addition to these conditions.

Binary Phase Diagram

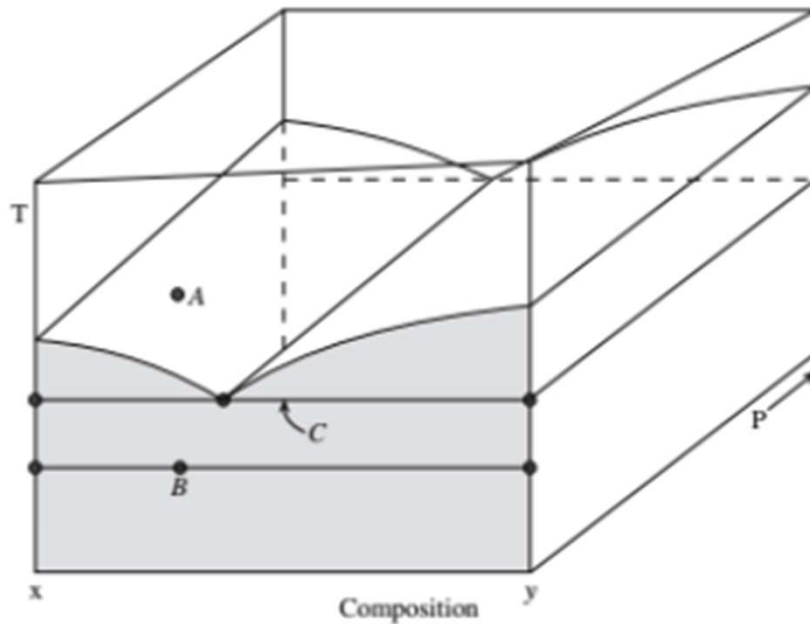


FIGURE 8.9 A model binary phase diagram showing T , P , and composition as variables.

Carter, C.B.; Norton, M.G.; "Ceramic Materials: Science and Engineering", Springer, 2007

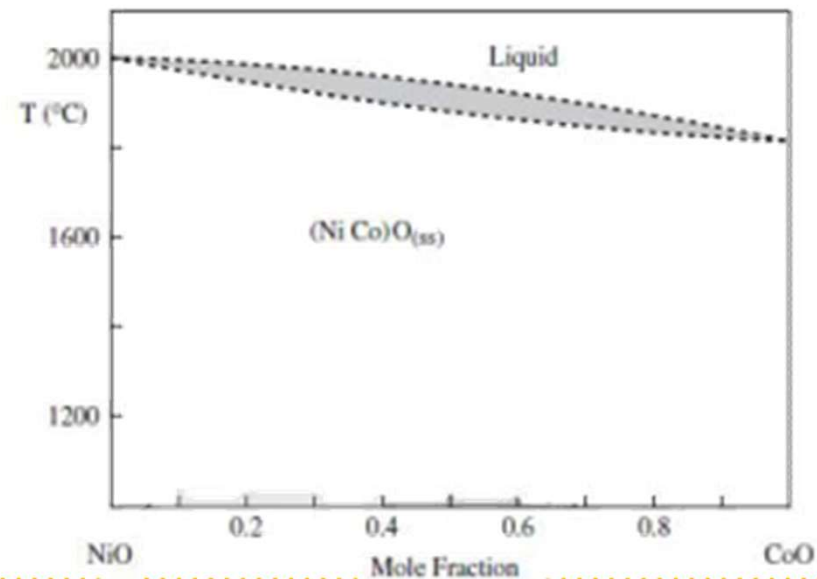
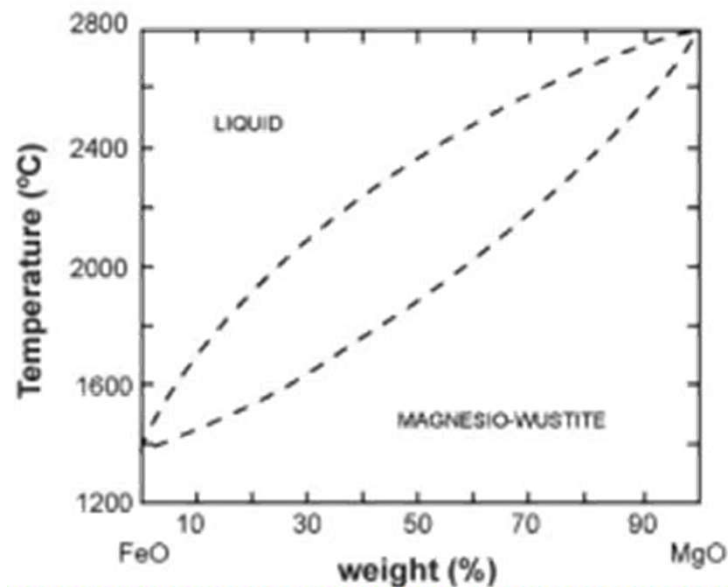
Binary phase diagrams are very important for ceramics. The two most important cases for ceramics are

- the combination of a metal plus oxygen
- the combination of two oxides.



Binary Phase Diagram

- In these systems two different compounds or atoms are dissolved in lattice structure of each other to form a single phase or different phases separated into certain boundaries macroscopically.
- FeO-MgO and NiO-CoO alloys are dissolved in each other and present as a single phase in solid solution below the liquidus line.

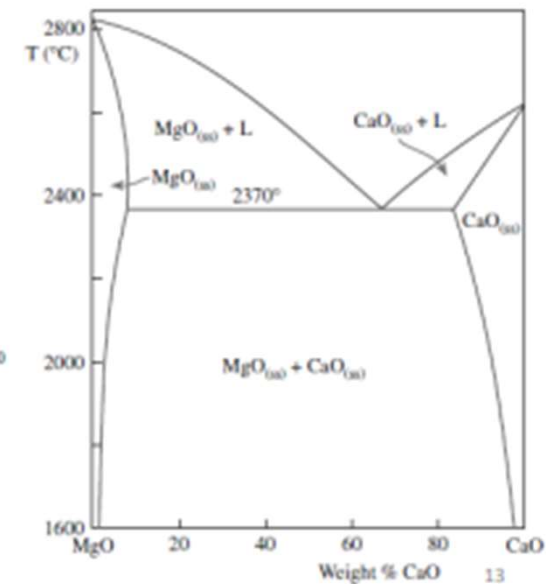
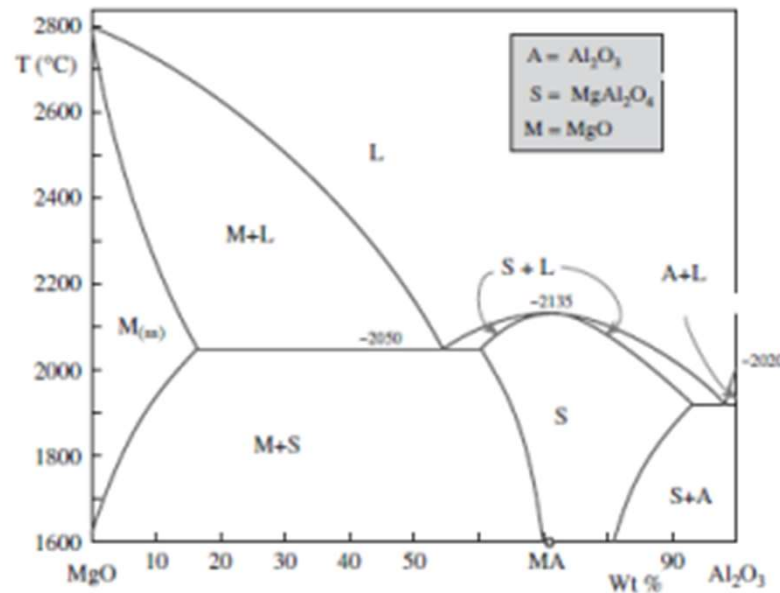




Binary Phase Diagram

- In contrast to previous alloys, there is limited solid solubility in the MgO-Al₂O₃ and MgO-CaO binary systems (solid melt zone) and at the temperature-composition region where dissolution does not occur the two component solid phase are present as an eutectic structure

Carter, C.B.; Norton, M.G.; "Ceramic Materials: Science and Engineering", Springer, 2007





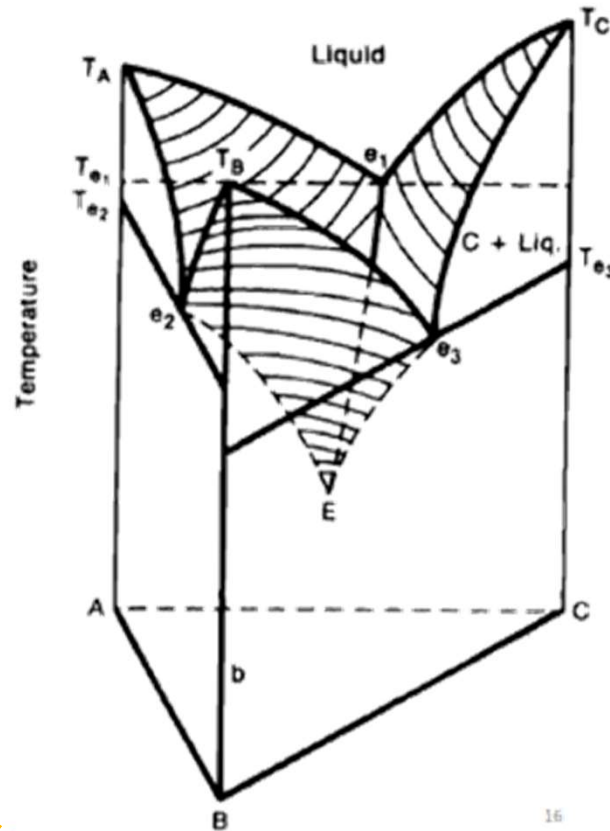
Binary Phase Diagram

Reaction Name	Equation	Appearance in the diagram
Monotectic	$L_1 \longleftrightarrow L_2 + \text{Solid}$	$\frac{L_1}{L_2 + K}$
Eutectic	$L \longleftrightarrow K_1 + K_2$	$\frac{L}{K_1 + K_2}$
Eutectoid	$K_1 \longleftrightarrow K_2 + K_3$	$\frac{K_1}{K_2 + K_3}$
Peritectic	$L + K_1 \longleftrightarrow K_2$	$\frac{L + K_1}{K_2}$
Peritectoid	$K_1 + K_2 \longleftrightarrow K_3$	$\frac{K_1 + K_2}{K_3}$
Synthetic	$L_1 + L_2 \longleftrightarrow K$	$\frac{L_1 + L_2}{K}$

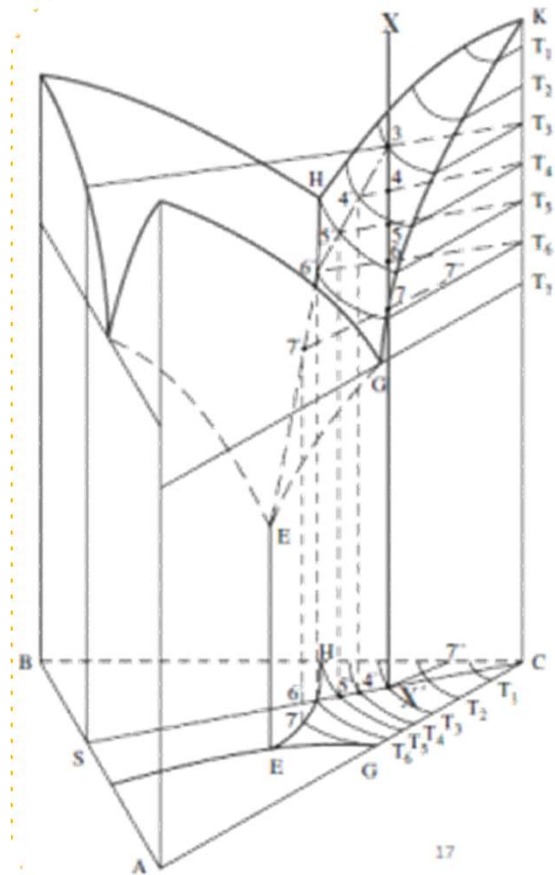
Transformations in two component systems.



Ternary Phase Diagram



- Ternary phase diagrams are the most important part of ceramic systems.
- In many of the industrial applications the phase diagrams composed of more than two components are the most encountered.
- To draw ternary phase diagrams (ternary system $C=3$) are pretty difficult because of $F+X=5$.
- If the pressure is held constant, there are 4 variables.
- There is a need for an axis for each variable and temperature. Therefore components are placed on the corners of the triangle and temperature is placed on the axis which is perpendicular to them.



Ternary Phase Diagram

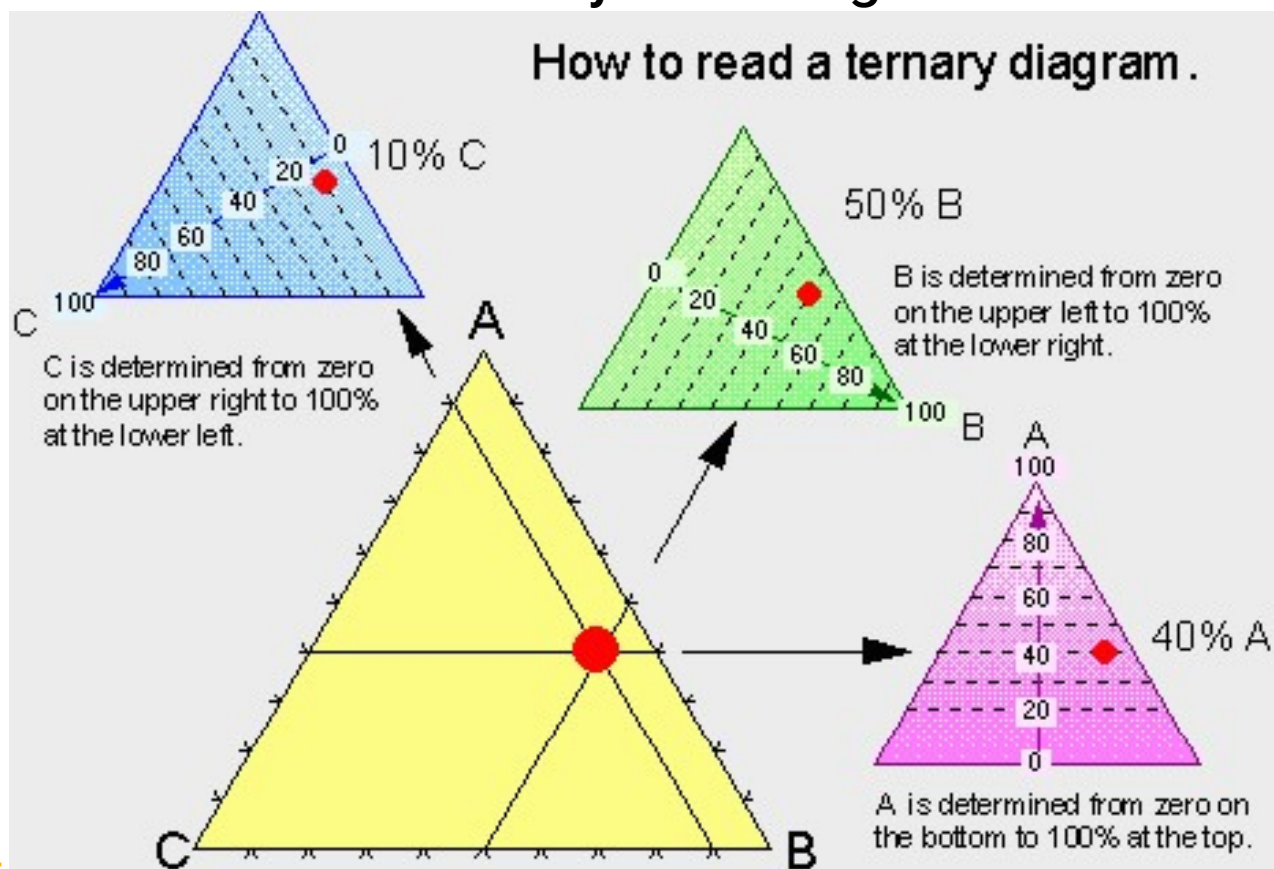


When the projection of the equilateral triangle is taken, there is a two dimensional image of the ternary equilibrium diagram.

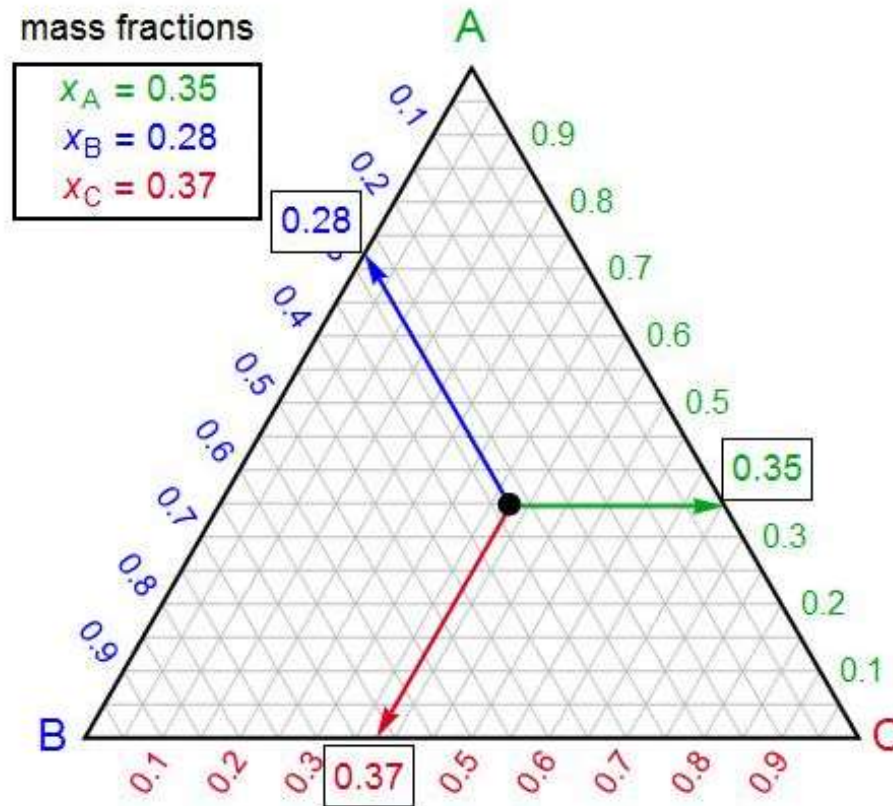


Ternary Phase Diagram

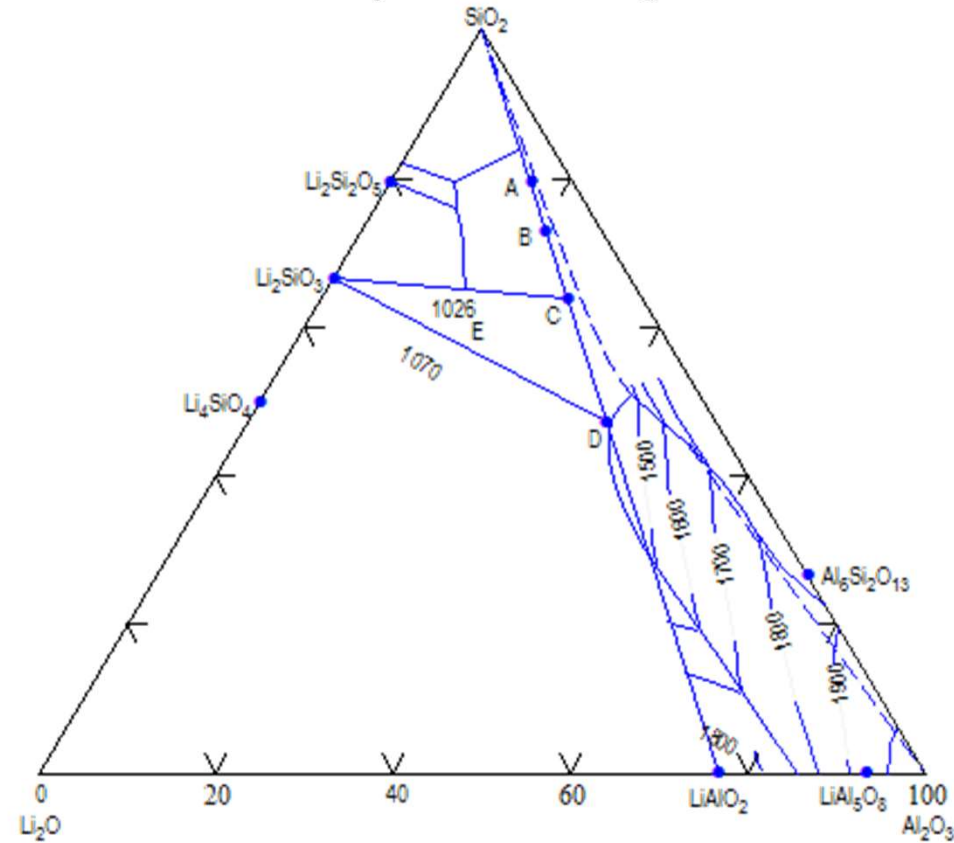
How to read a ternary diagram.

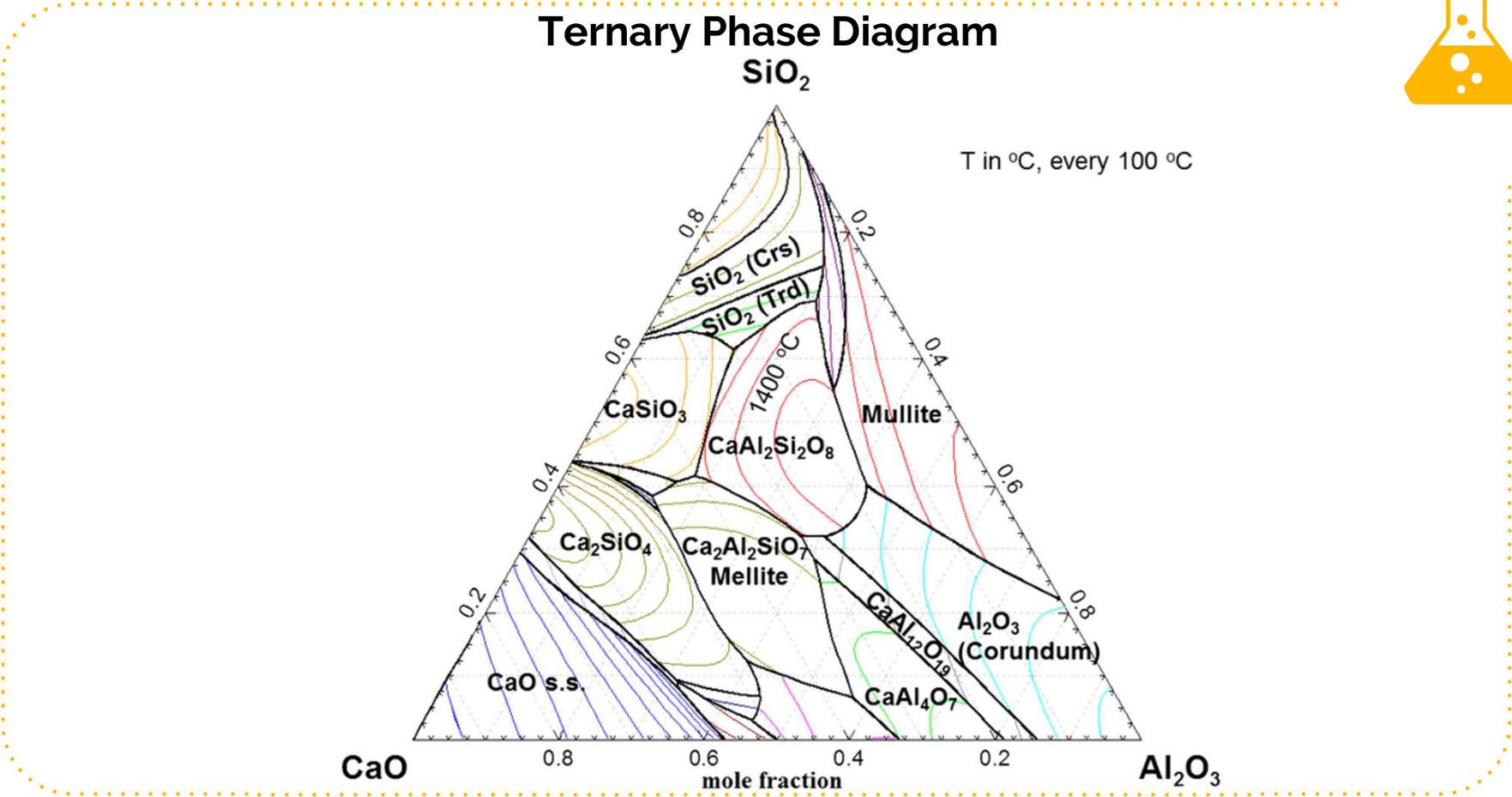


Ternary Phase Diagram



Ternary Phase Diagram

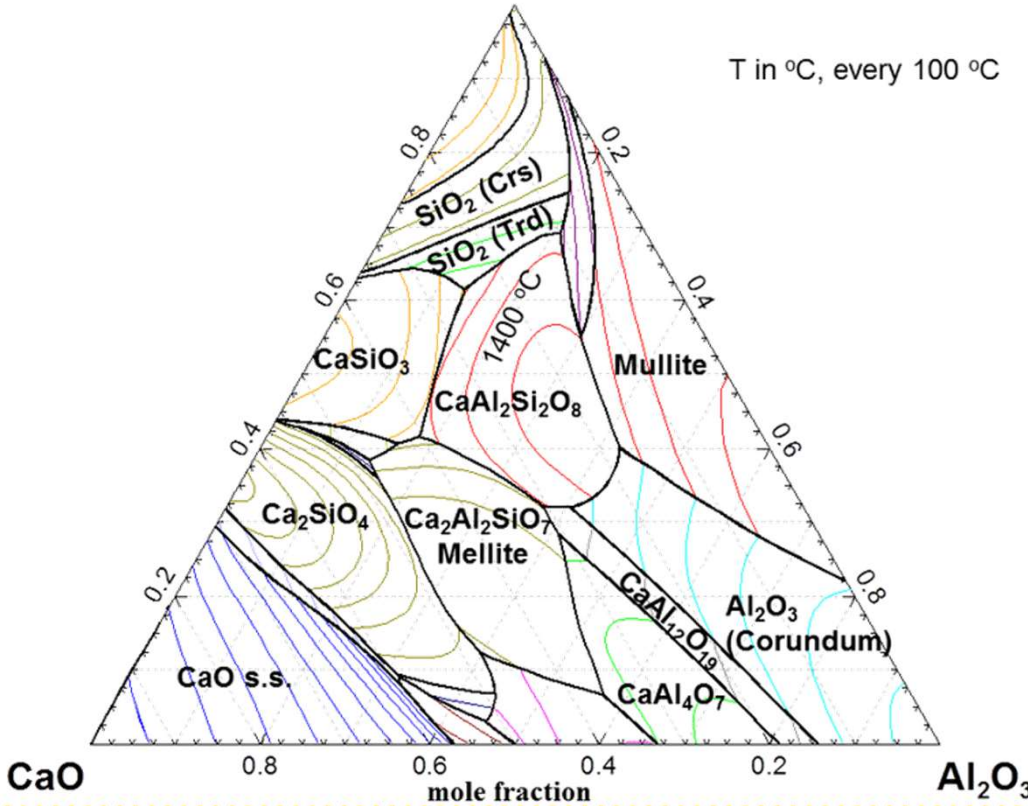




Ternary Phase Diagram

 SiO_2

T in °C, every 100 °C

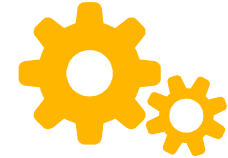


mole fraction

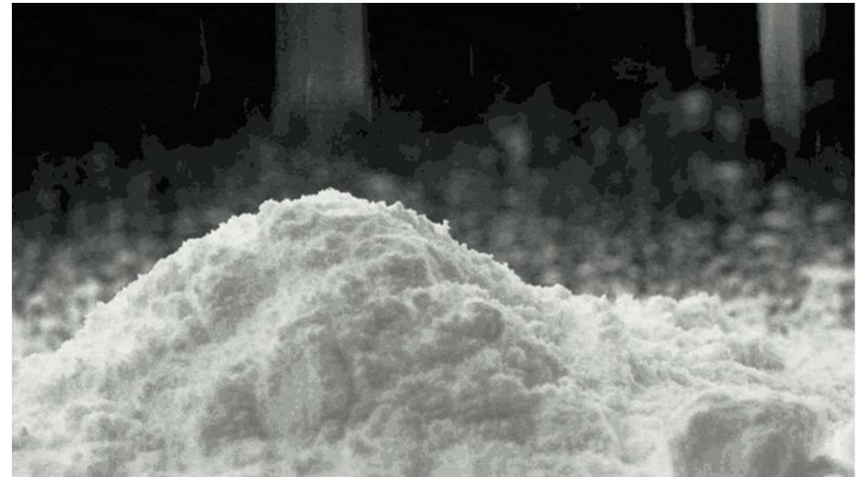
Ceramic Raw Materials and Their Properties

- Quartz, feldspar, talc, limestone, SiC, B₄C, Al₂O₃,
- Clay, kaolen, formations and thermal behaviors

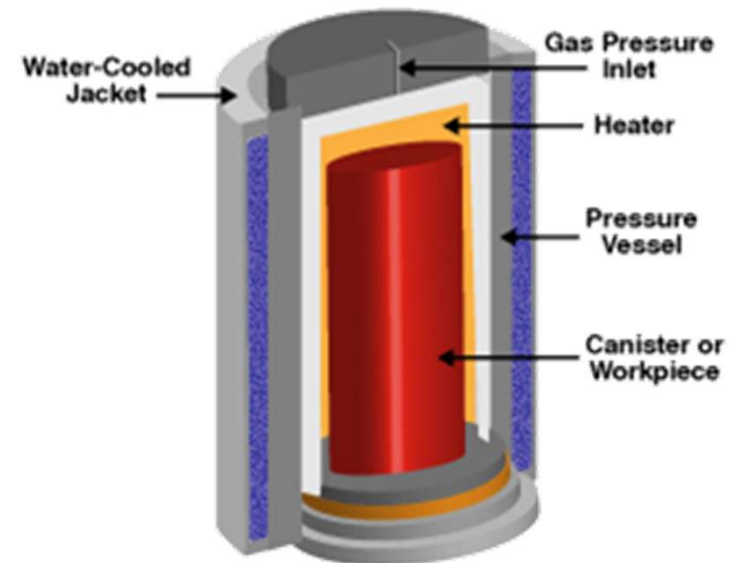
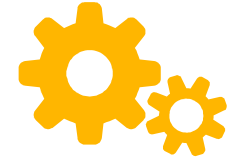
Powder Compaction



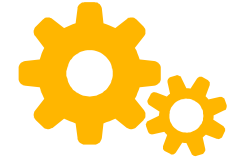
- Powder compaction is simply the pressing of a free flowing powder.
- The powder may be dry pressed (i.e., without the addition of a binder) or pressed with the addition of a small amount of a suitable binder.
- The pressure is applied either uniaxially or isostatically. The choice of pressing method depends on the shape of the final product.
- We make simple shapes by applying the pressure uniaxially; more complex shapes require isostatic pressing



- Mechanical compaction of dry or semidry powders in a die is one of the most widely used forming operations in the ceramic industry.
- In general the applied pressure is not transmitted uniformly because of friction between the particles and the die walls as well as between the particles themselves.
- The stress variations lead to density variations in the green body, thereby placing considerable limits on the degree of packing uniformity that can be achieved.
- Although the density variations can be reduced significantly by isostatic pressing, mechanical compaction provides far less control in the manipulation of the green body microstructure than the casting methods.

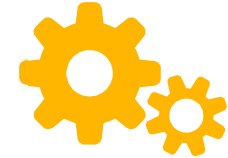


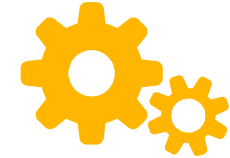
- The aim of the process is to transform loose powders into a green compact with a desired shape and a maximal overall density.
- Close geometrical tolerances, minimal variations of density, packing homogeneity, and sufficient strengths and integrity to withstand the stresses occurring during the subsequent handling, debinding and sintering treatment are further properties required of the green compact.
- These properties are determined by the behavior of the powders during the pressing process. The unit operations of this process are filling of the die or mold, compaction of the powder under a particular state of stress and, in the case of uniaxial die pressing, ejection of the green compact from the die.



memeguy.com

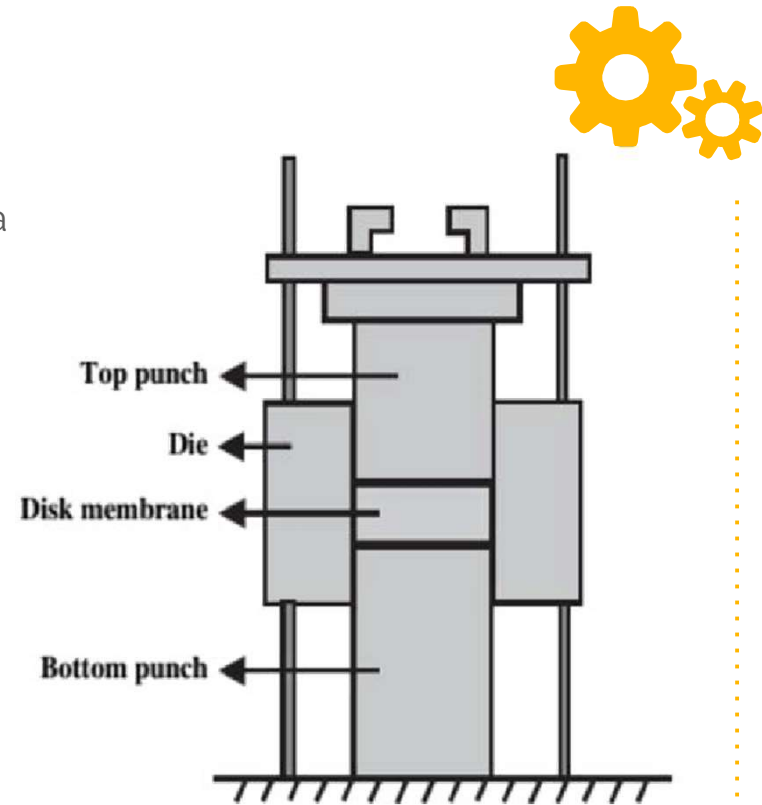
- Powder compaction by dry pressing is widely used in industry for shaping of ceramic products.
- This can be explained by the high efficiency of the process, which has two variants: uniaxial die pressing; and isostatic pressing.
- Both methods can be automated to a high degree and are used in the mass production of parts such as ceramic cutting tools (via uniaxial pressing) or spark plug insulators (via isostatic pressing).



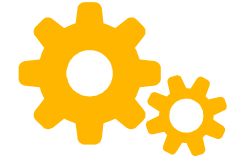


- Powders used in the industrial production of ceramics very rarely have spherical particles.
- The surfaces of the particles are also rarely smooth. Particles with rough surface textures or shapes suffer from agglomeration because of increased interparticle friction, and the packing density decreases as the particle shape departs from that of a sphere.
- Spherical particles are normally desirable when a high packing density is required. However, the use of non-spherical particles does not always lead to a reduction in the packing density if the particles have a regular geometry. The highest packing density and most isotropic structures are obtained with spheres and with particles having simple, equiaxial shapes (e.g., cubes).
- Anisotropic particles can be packed to high packing density if they are ordered, but in random packing, the packing density can be quite low.

- Uniaxial die pressing produces shapes with accurate dimensions in large quantities, in the shortest cycle times.
- Compared to injection molding, dry pressing requires a relatively small amount of additives (~2%), and thus allows for less expensive additive removal operations.
- Fine powders lack the flowability required for the process, in general they must be transformed into a free-flowing press granulate, by employing a granulation process.
- A second problem results from the nonuniform pressure transmission, leading to nonuniform particle arrangements and density variations in the compacts, which is a well-known source of nonuniform grain growth and other sintering defects.

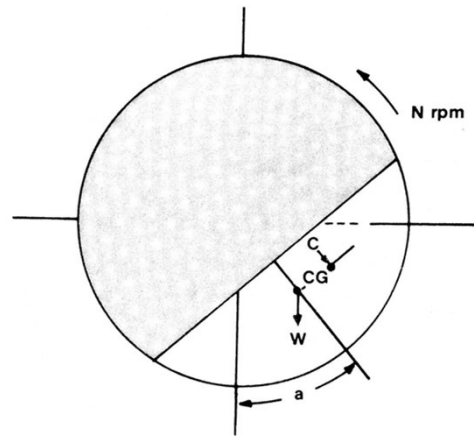


Dry Milling of Ceramic Raw Materials

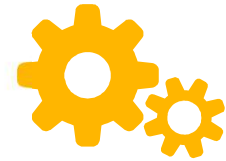
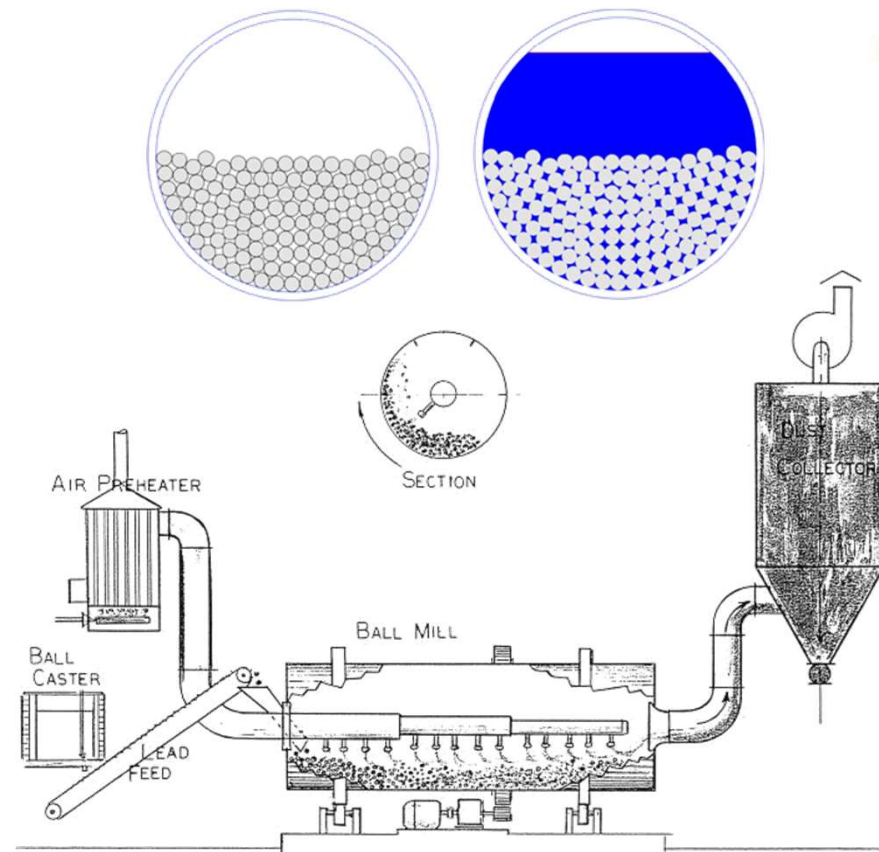
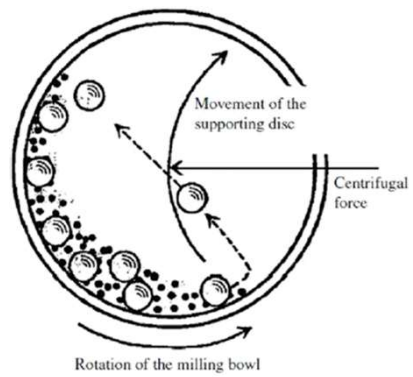


- Drying of raw materials with humidity content above 20%
- Feeding & batching of mixture components
- Primary milling
- Final milling-drying-particle size grading
- Check screening & iron removal
- Homogenizing, agglomerator, humidity control
- Storage and press feeding rotating screen mixer
- Supervision and Intelligent electronic managment og the plant

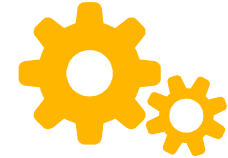




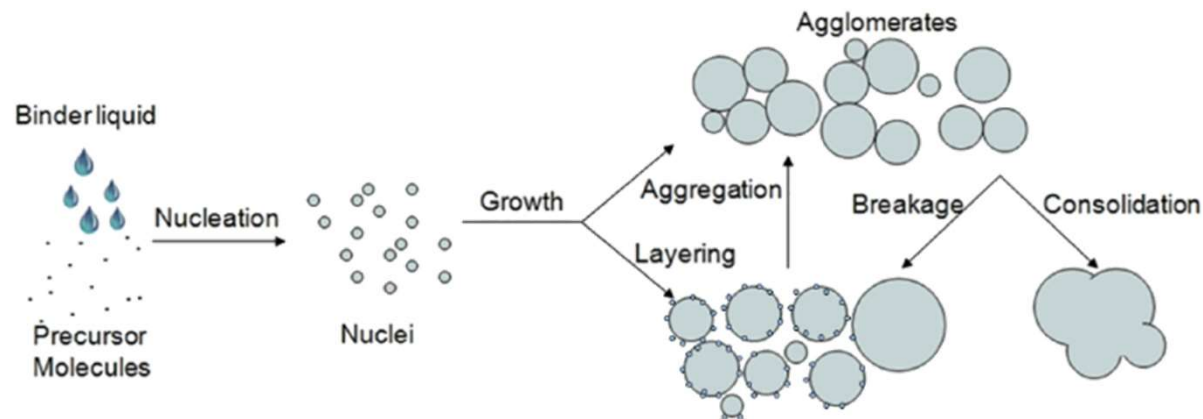
Horizontal section



Granulation



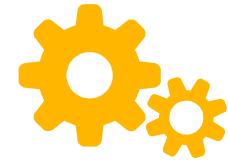
- For the production of technical ceramics, the poor flowability of the micron or submicron powders makes it necessary to form press granulates by the controlled agglomeration of the primary particles.
- Granulation methods can be divided into agitation, pressure, or spray techniques.
- Agitation methods use moist particles, bringing them into contact by mixing or tumbling so that the particle bonding forces can cause agglomeration.



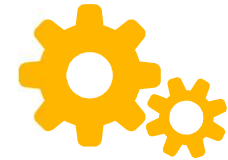
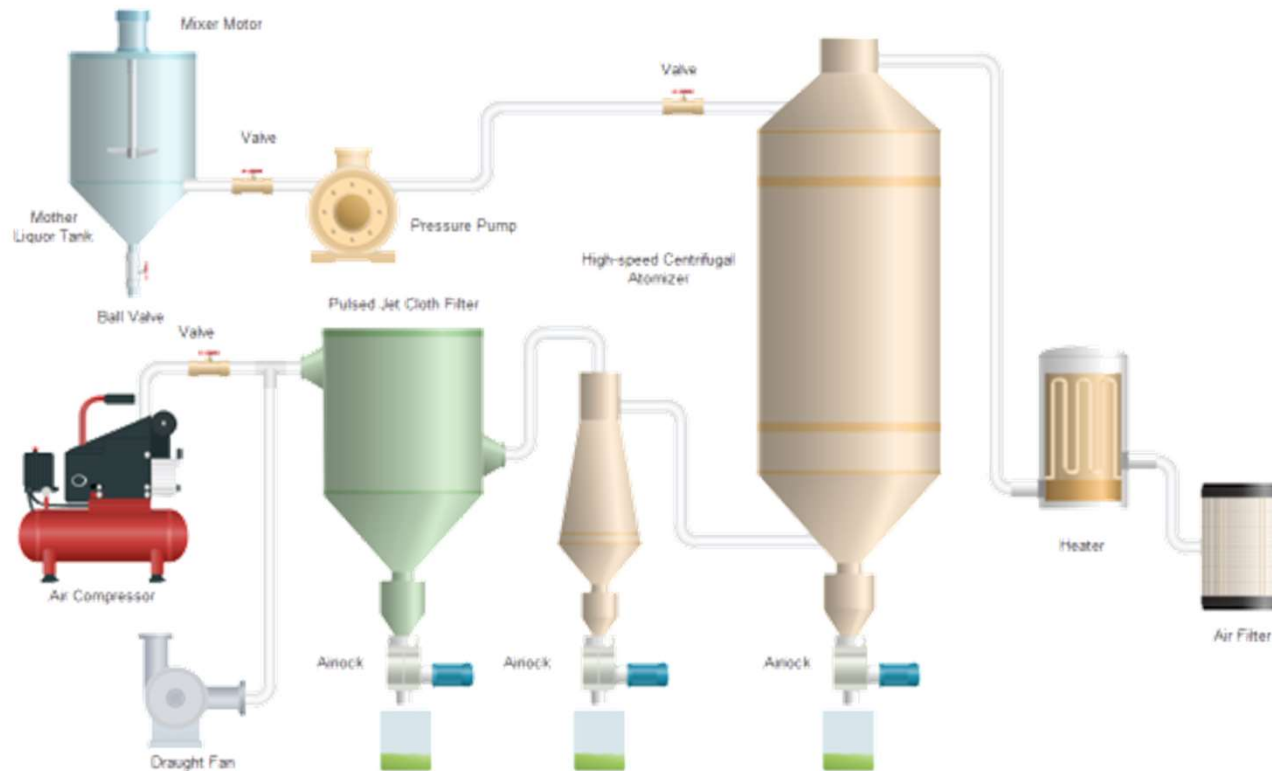
- Main method of granulation is spray drying: produce spherical particles ($\sim 20\text{ }\mu\text{m}$), high productivity (e.g. $\sim 10\text{--}100\text{ kg/h}$); suitable for subsequent pressing process.
- Use hot air to dry flowing solids
- Droplet size $\sim$ product size
- Slurry viscosity: important operation variable, should be shear thinning

Applications of spray granulation

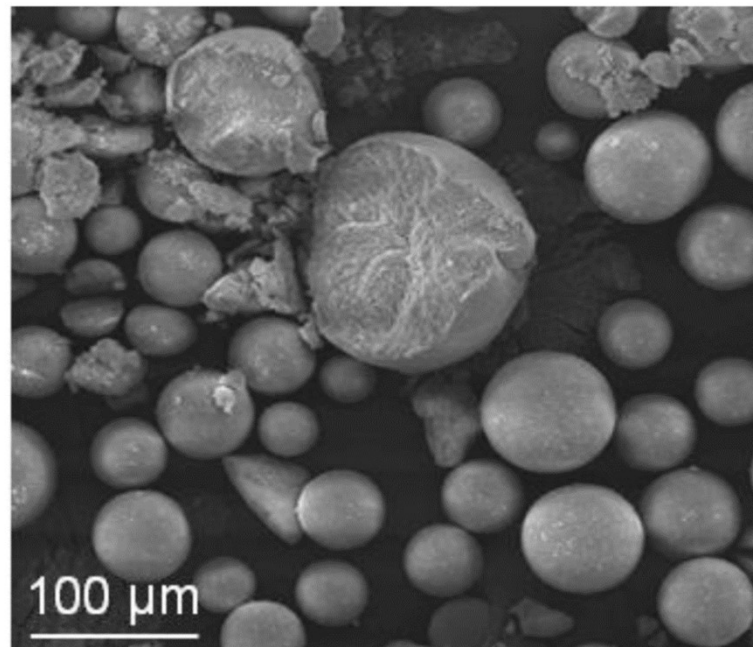
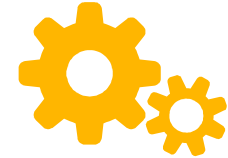
- Traditional ceramics
- Advanced ceramics
- Refractories



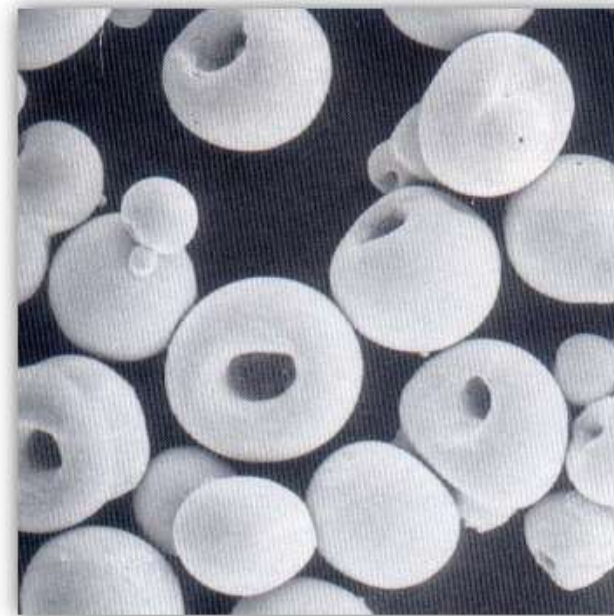
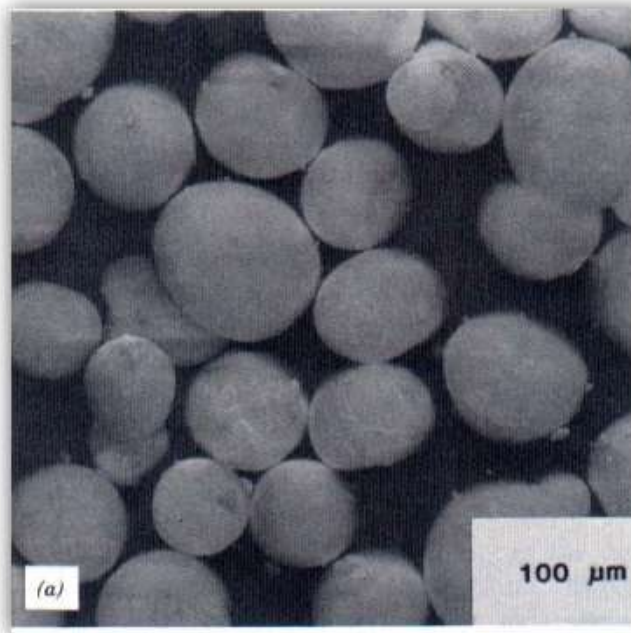
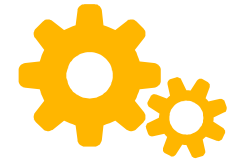
Pressure Spray Dryer Process Flow Diagram

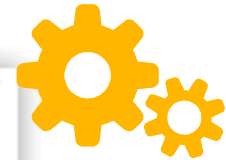
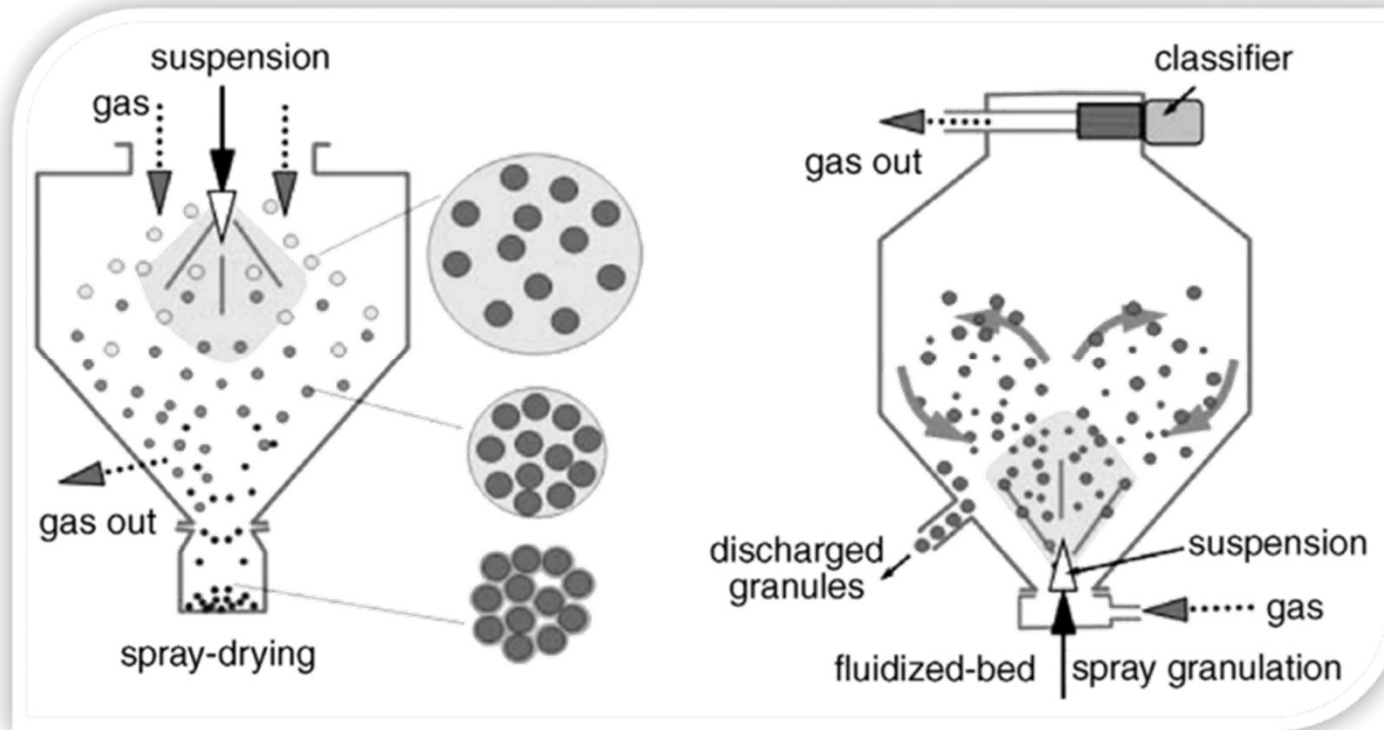


- To transform a concentrate into many small droplets that are then exposed to a fast current of hot air.
- Because of the very large surface area of the droplets, the water evaporates almost instantaneously and the droplets are transformed into powder particles.

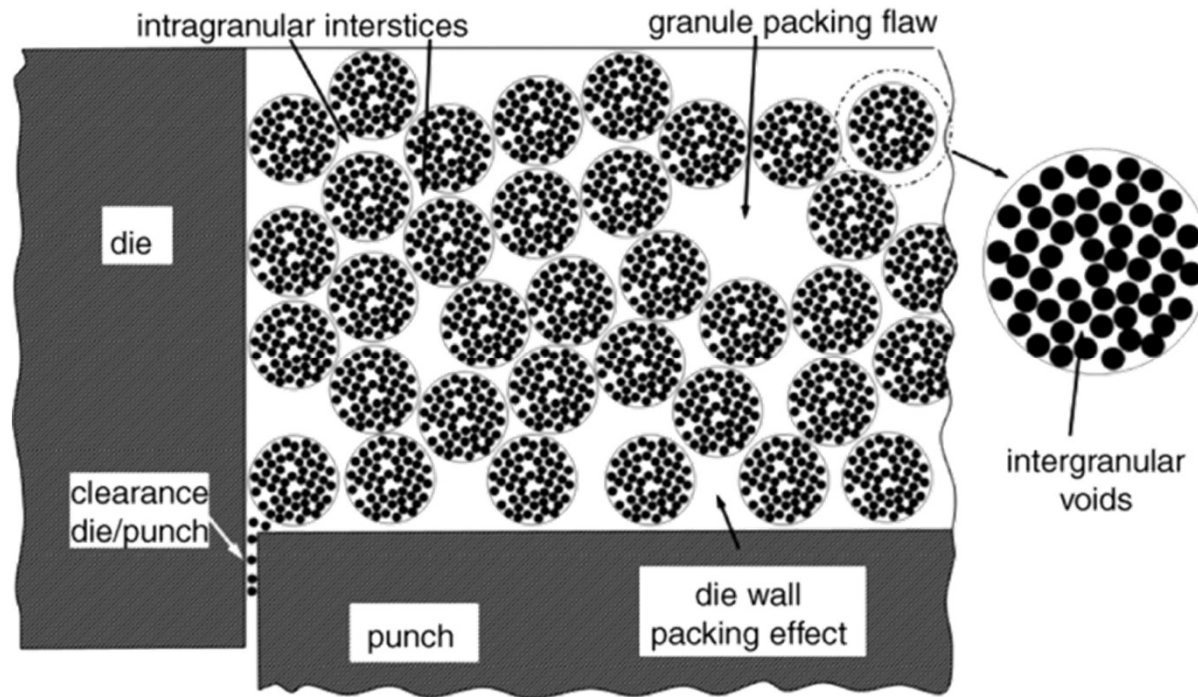
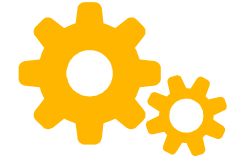


Spray dried samples: Donut particle , temperature rise too fast , surface dried (sealed), vaporization of internal liquid pores (viscous binder fluid may flow toward inside)



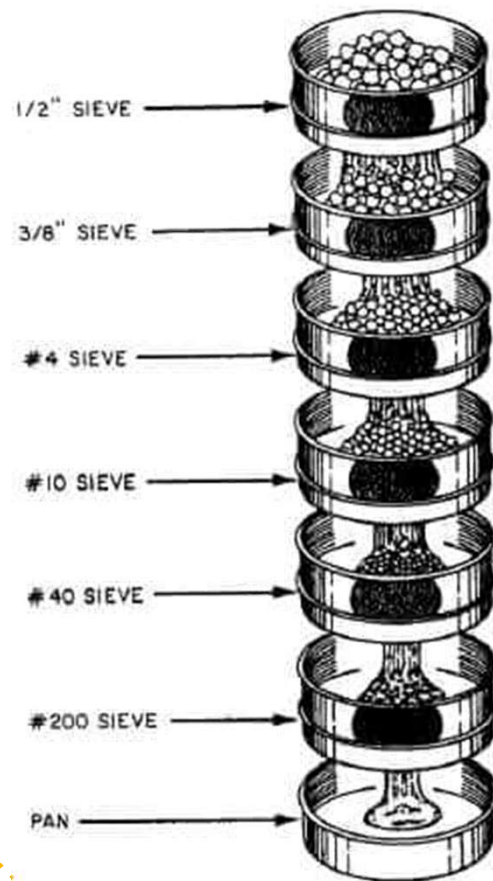


Hierarchic packing structure of a press granulate



Test Methods Applied to Ceramic Raw Materials

- Physical Tests: Sieve analysis, plasticity count, drying and firing shrinkage, flow test, thixotropic property
- Mineralogical Analysis: X-rays, DTA



Retsch Technical Data

Sieve Analysis

- For the characterization of bulk goods of different forms and sizes, the knowledge of their particle size distributions is essential.
- The particle size distribution, i.e. the number of particles of different sizes, is responsible for important physical and chemical properties such as solubility, flowability and surface reaction.
- Advantages of the sieve analysis include easy handling, low investment costs, precise and reproducible results in a comparably short time and the possibility to separate the particle size fractions.
- Therefore, this method is an accepted alternative to analysis methods using laser light or image processing.

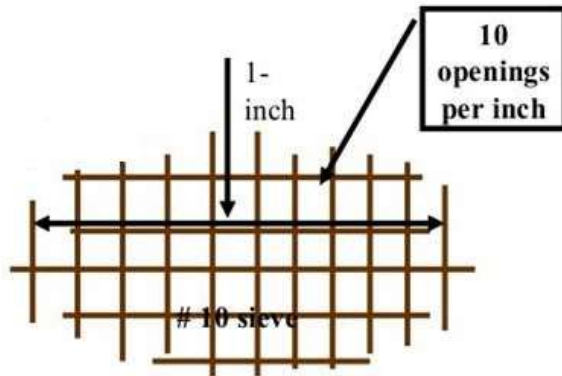


Sieve Analysis Equipments and How to Perform

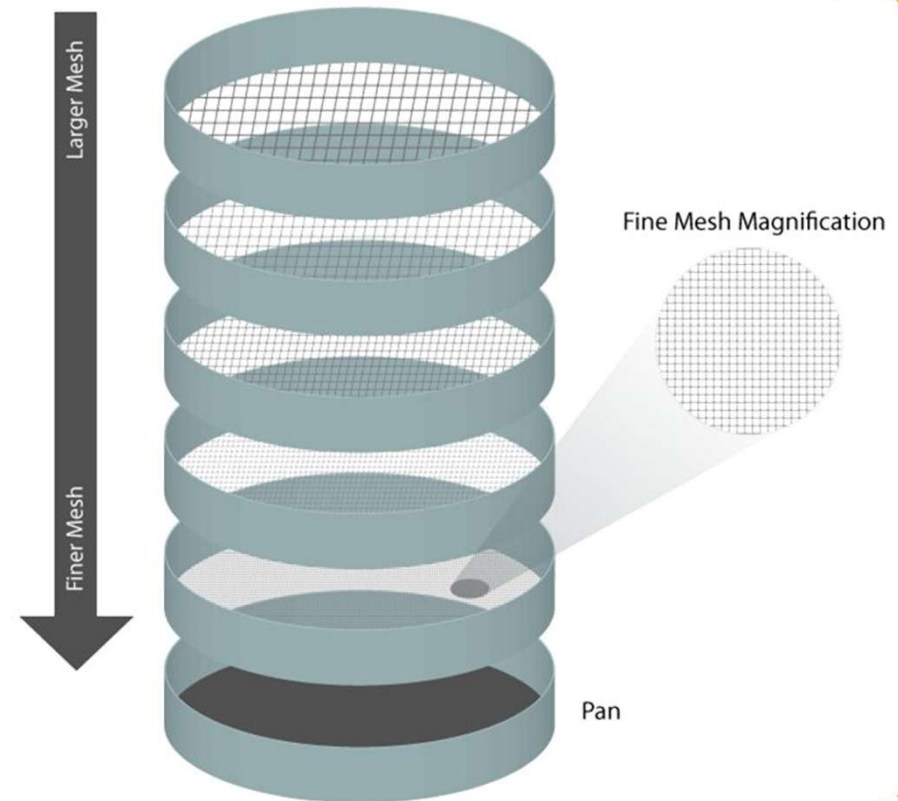


How to perform video

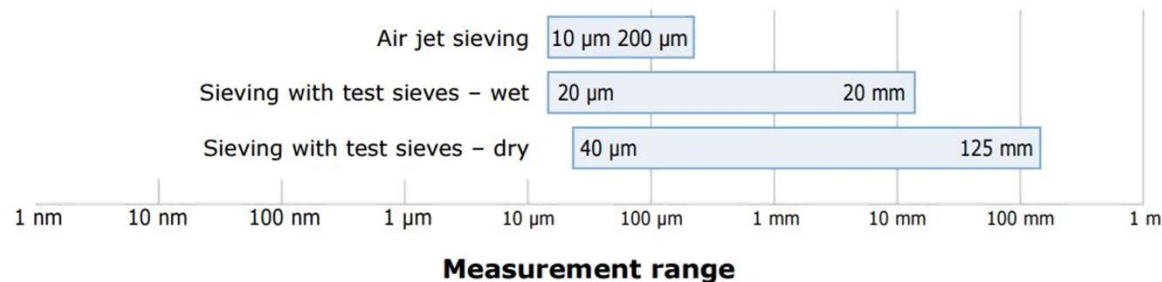
Sieve Number and Size



Mesh	μm	Mesh	μm
4	4760	80	177
6	3360	100	149
8	2380	140	105
12	1680	200	74
16	1190	230	62
20	840	270	53
30	590	325	44
40	420	400	37
50	297	625	20
60	250	1250	10
70	210	2500	5



Sieving Methods of Sieve Analysis



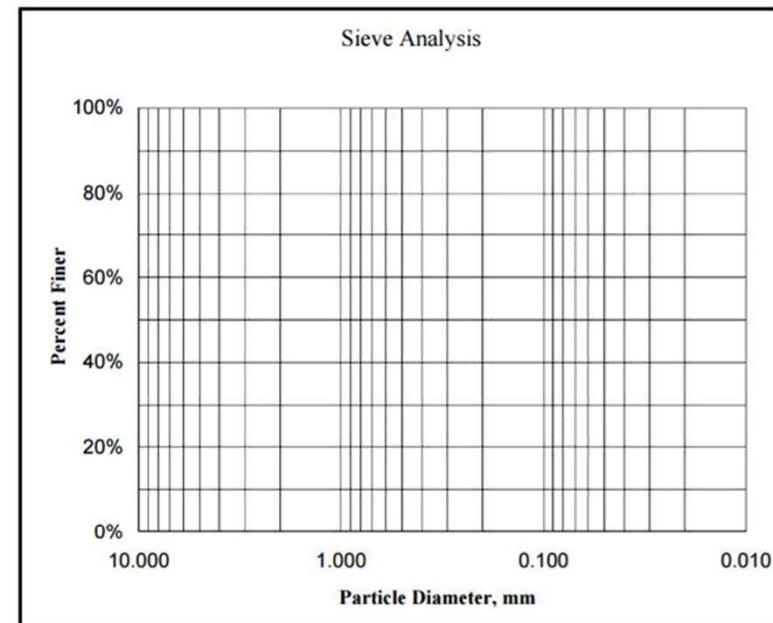
- During sieving the sample is subjected to vertical movement (vibratory sieving) or horizontal motion (horizontal sieving).
- With tap sieve shakers both movements are superimposed. During this process the particles are compared with the apertures of every single sieve.
- The probability of a particle passing through the sieve mesh is determined by the ratio of the particle size to the sieve openings, the orientation of the particle and the number of encounters between the particle and the mesh openings.
- The appropriate sieving method depends on the degree of fineness of the sample material.
- Dry sieving is the preferred method for the size range between 40 μm and 125 mm.
- However, the measurement range is limited by properties of the sample such as a tendency to agglomerate, density or electrostatic charging.

Sieving Methods of Sieve Analysis



SIEVE ANALYSIS						
Soil Description:						
Mass of Pan:		(g)				
Mass of Pan + Dry Soil:		(g)				
Sample Dry Mass:		(g)				
Sieve Size	Sieve Opening (mm)	Retained Soil + Pan (g)	Mass of Dry Soil (g)	% Mass Retained	% Cumulative Retained	% Finer
#4	4.750					
#10	2.000					
#20	0.850					
#40	0.425					
#60	0.250					
#100	0.150					
#200	0.075					
PAN	-					
Total Soil Mass Sieved (g)						
% Loss During Sieve Analysis						
			D ₁₀ :	mm		
			D ₃₀ :	mm		
			D ₆₀ :	mm		
			C _u :			
			C _c :			

Sample Data Sheet - Sieve Analysis



Graphsheet sample

Vibratory Sieving

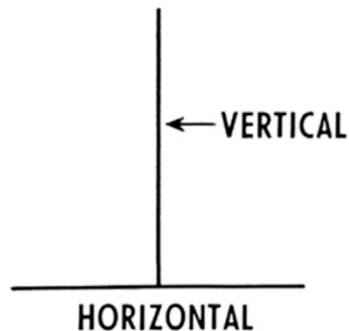


- The sample is thrown upwards by the vibrations of the sieve bottom and falls back down due to gravitation forces. The amplitude indicates the vertical oscillation height of the sieve bottom.
- Due to this combined motion, the sample material is spread uniformly across the whole sieve area. The particles are accelerated in vertical direction, rotate freely and then fall back statistically oriented.
- Also in sieve shakers, an electromagnetic drive sets a spring/mass system in motion and transfers the oscillations to the sieve stack. The amplitude can be adjusted continuously to a few millimeters.



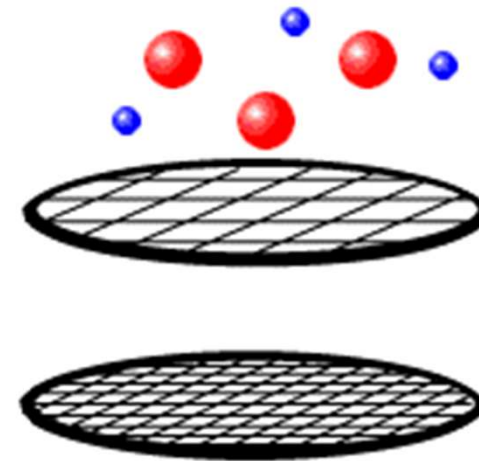
Horizontal Sieving

- In a horizontal sieve shaker the sieves move in horizontal circles in a plane.
- Horizontal sieve shakers are preferably used for needle-shaped, flat, long or fibrous samples.
- Due to the horizontal sieving motion, hardly any particles change their orientation on the sieve.



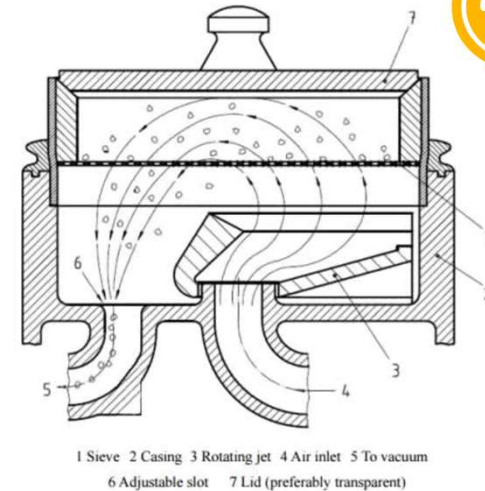
Tap Sieving

- In a tap sieve shaker a horizontal, circular movement is superimposed by a vertical motion generated by a tapping impulse.
- Tap sieve shakers are specified in various standards for particle size analysis.
- The number of comparisons between particles and sieve apertures is substantially lower in tap sieve shakers than in vibratory sieve shakers (2.5 s⁻¹ as compared to ~50 s⁻¹) which results in longer sieving times.
- On the other hand, the tapping motion gives the particles a greater impulse, therefore, with some materials, such as abrasives, the fraction of fine particles is usually higher.
- With light materials such as talcum or flour however, the fraction of fine particles is lower.



Air Jet Sieving

- The air jet sieve is a sieving machine for single sieving, i.e. for each sieving process only one sieve is used. The sieve itself is not moved during the process.
- The material on the sieve is moved by a rotating jet of air:
 - I. A vacuum cleaner which is connected to the sieving machine generates a vacuum inside the sieving chamber and sucks in fresh air through a rotating slit nozzle.
 - II. When passing the narrow slit of the nozzle the air stream is accelerated and blown against the sieve mesh, dispersing the particles.
 - III. Above the mesh, the air jet is distributed over the complete sieve surface and is sucked in with low speed through the sieve mesh.
 - IV. Thus the finer particles are transported through the mesh openings into the vacuum cleaner or, optionally, into a cyclone.



Air Jet Sieving Animation

Touch screen with graphical user interface for intuitive operation provides:

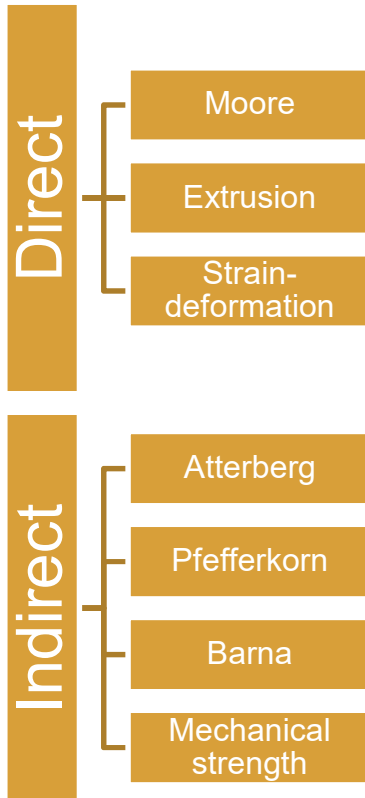
- Analysis guide
- Language selection
- Country-specific units of measurement
- User administration
- Password protection
- comparative analyses
- SOP management
- Archiving and export of the analysis results



ALPINE Air Jet Sieve



Plasticity Count



- Plasticity is the characteristic behaviour of a ceramic material to become permanently deformed after the application of an external force.
- This property is the most characteristic one in clays, and there are some factors that influence the plasticity and they should be considered in plasticity measurements:
 - I. Water physical characteristics like, viscosity, surface tension...
 - II. Particle size distribution of the solid sample and its specific surface
 - III. Chemical and mineralogical composition of samples
 - IV. Effect of the additives added to the clay/water system
 - V. Sample temperature
 - VI. The way to prepare the sample, particularly the energy used to mix and to process clay, water & additives
- Plasticity is defined as the capacity to be deformed without being broken. Many methods available to measure it, and they are classified into two groups: direct and indirect methods.

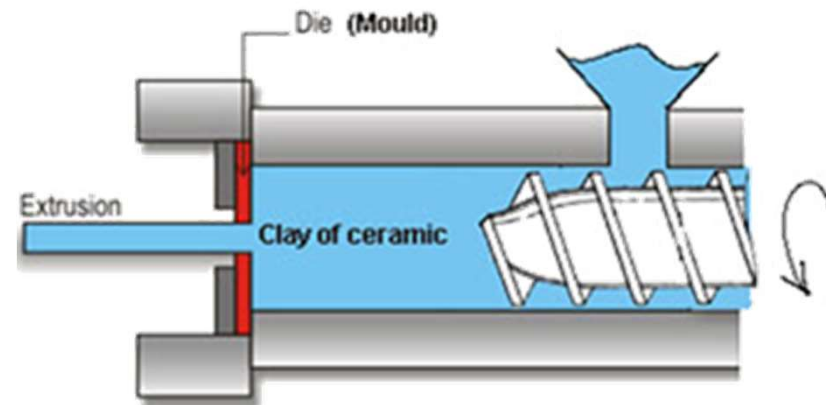
Direct Plasticity Methods



Moore (compression): It provides good results due to its low sensitivity to small speed modification and its independency of moisture content. It is defined as the ratio between pressures to deform a cylindrical probe up to 10% and 50% of its original height.

Extrusion: Real time process at pilot plant scale in which many parameters are recorded like amperage, pressure, throughput, consistency, temperature...

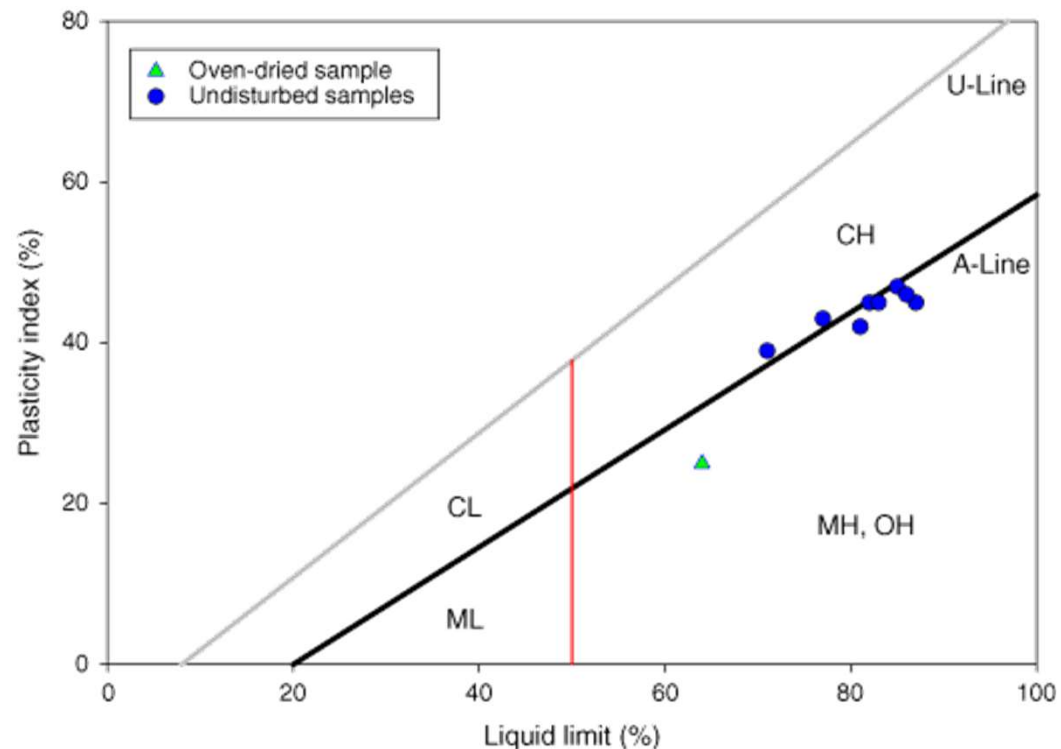
Strain-deformation: Compression, traction, flexion, torsion.



Indirect Plasticity Methods



Atterberg: It determines humidity range in which the samples are workable, and is defined as the difference between liquid and plastic limits. Liquid limit is the maximum moisture that gives some consistency to the clay to be workable, and plastic limit is the minimum moisture for the clay to be mouldable.



CL = low-plasticity clay, CH = high-plasticity clay, ML = low-plasticity silt, MH = high-plasticity silt, OH = high-plasticity organic soil.

Indirect Plasticity Methods



Pfefferkorn:

- It determines the amount of water required to achieve a 30% contraction in relation to the initial height of a test body under the action of a standard mass.
- The results are normally expressed as graphs showing height reduction as a function of moisture content.
- Measuring of plasticity is based on the principle of impact deformation using a sample with a defined diameter and height deformed by a free falling plate with a given mass.

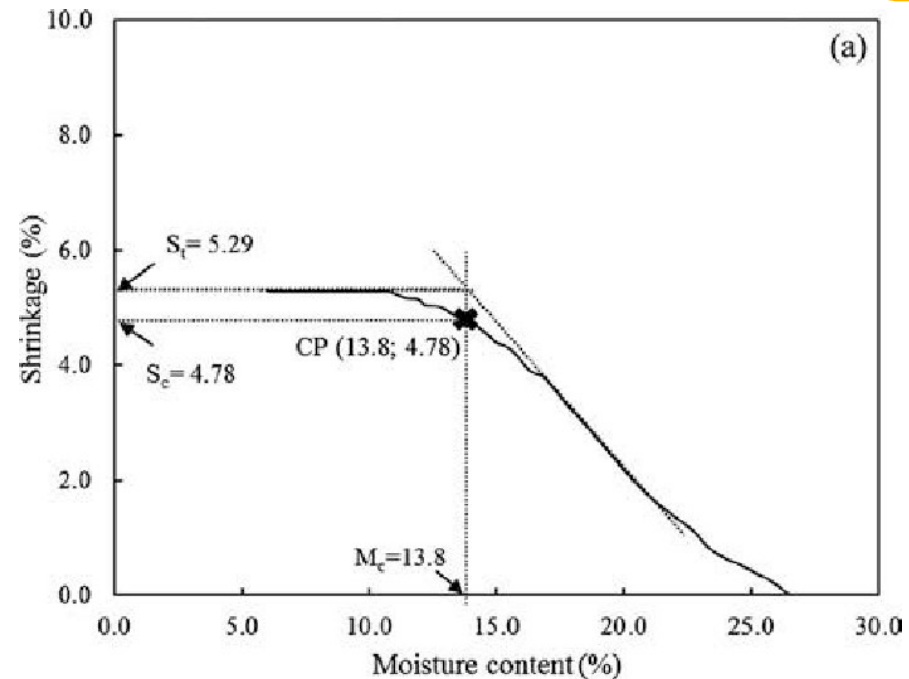


Indirect Plasticity Methods



Barna: It is defined as the ratio between the water responsible of tile contraction and the total water; Bigot curves show this information.

Mechanical Strength:
This method calculates Modules of rupture of a small tile, by breaking it.



Mancuhan, E., Özen, S., Sayan, P., & Sargut, S. T. (2016). Experimental investigation of green brick shrinkage behavior with Bigot's curves. *Drying Technology*, 34(13), 1535–1545

Drying and Firing Shrinkage



11% shrinkage clay spec will look like the above comparing wet clay to finished product (stoneware / cone 6)

- Ceramic shrinks both in drying and in firing.
- Different ceramic bodies shrink at different rates which can be as little as 4%, or as much as 15% for some ceramic bodies.
- Even one percentage point can make a difference in the final product depending on your need for precision.
- Your design, therefore, needs to account for the shrinking for the temperature to which you fire.

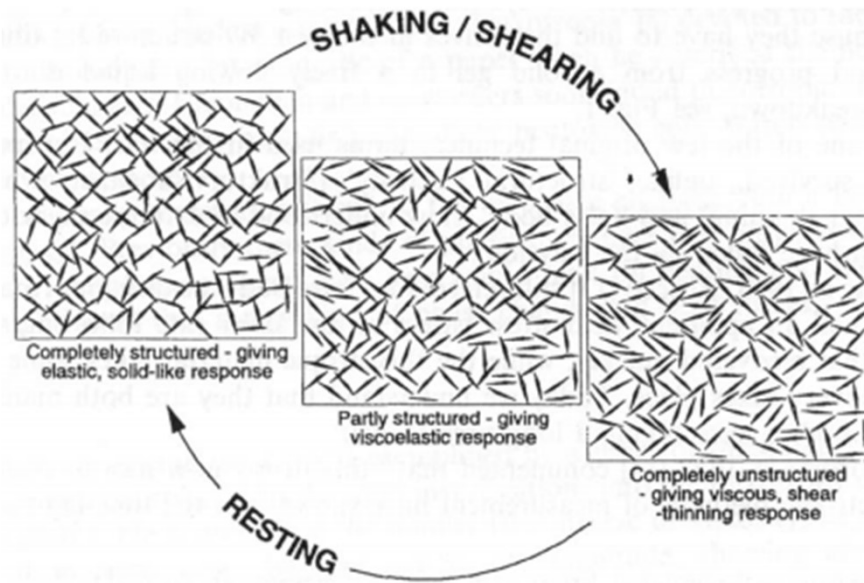
Drying and Firing Shrinkage



Flow Test



Thixotropy Properties



- The term Thixotropy was first used by Peterfi in 1927 from the Greek work thixis (stirring or shaking) and trepo (turning or changing)
- Thixotropy was originally referred to reversible changes from fluid to solid-like elastic gel.
- 'explanation of thixotropy as being due to the secondary minimum so that particles can form a loose association which is easily destroyed by shaking but re-established itself on standing'
- Shear-thinning ('structural viscosity') vs. Thixotropy: 'structural viscosity is seen as a material with nearly zero time of recovery'

Thixotropy- a review by Howard A. Barnes, Hatsopoulos Microfluids Laboratory, Department of Mechanical Engineering, Massachusetts Institute of Technology



Thixotropy Properties

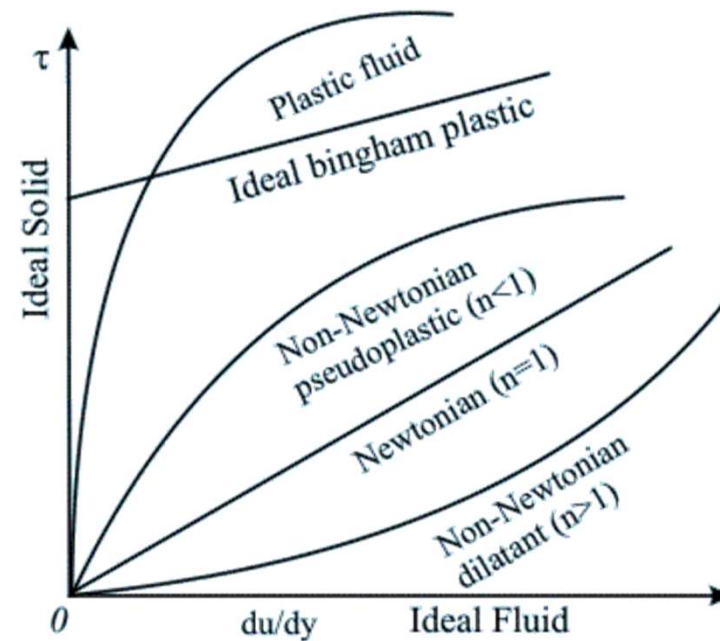
Cone no.	Temperature °C	Formula		
022	600	Na ₂ O 0.5 P ₂ O ₅ 0.5		SiO ₂ 2 B ₂ O ₃ 1
021	650	Na ₂ O 0.5 CaO 0.25	Al ₂ O ₃ 0.02	SiO ₂ 1.04 B ₂ O ₃ 1
020	670	Na ₂ O 0.5 CaO 0.25 MgO 0.25	Al ₂ O ₃ 0.04	SiO ₂ 1.08 B ₂ O ₃ 1
019	690	Na ₂ O 0.5 CaO 0.25	Al ₂ O ₃ 0.08	SiO ₂ 1.16 B ₂ O ₃ 1
018	710	Na ₂ O 0.5 CaO 0.25 MgO 0.25	Al ₂ O ₃ 0.13	SiO ₂ 1.26 B ₂ O ₃ 1
017	730	Na ₂ O 0.5 CaO 0.25 MgO 0.25	Al ₂ O ₃ 0.2	SiO ₂ 1.4 B ₂ O ₃ 1
016	750	Na ₂ O 0.5 CaO 0.25 MgO 0.25	Al ₂ O ₃ 0.31	SiO ₂ 1.61 B ₂ O ₃ 1
015a	790	Na ₂ O 0.432 CaO 0.432 MgO 0.136	Al ₂ O ₃ 0.34	SiO ₂ 2.06 B ₂ O ₃ 1
014a	815	Na ₂ O 0.385 CaO 0.385 MgO 0.230	Al ₂ O ₃ 0.34	SiO ₂ 1.92 B ₂ O ₃ 0.77
013a	835	Na ₂ O 0.343 CaO 0.343 MgO 0.314	Al ₂ O ₃ 0.34	SiO ₂ 1.78 B ₂ O ₃ 0.68
012a	855	Na ₂ O 0.345 CaO 0.341 MgO 0.314	Al ₂ O ₃ 0.365	SiO ₂ 2.04 B ₂ O ₃ 0.68
011a	880	Na ₂ O 0.349 CaO 0.340 MgO 0.311	Al ₂ O ₃ 0.4	SiO ₂ 2.38 B ₂ O ₃ 0.68
010a	900	Na ₂ O 0.338 K ₂ O 0.011 CaO 0.338 MgO 0.313	Al ₂ O ₃ 0.423	SiO ₂ 2.626 B ₂ O ₃ 0.675
09a	920	Na ₂ O 0.336 K ₂ O 0.018 CaO 0.335 MgO 0.311	Al ₂ O ₃ 0.468	SiO ₂ 3.087 B ₂ O ₃ 0.671
08a	940	Na ₂ O 0.279 K ₂ O 0.038 CaO 0.369 MgO 0.314	Al ₂ O ₃ 0.543	SiO ₂ 2.691 B ₂ O ₃ 0.539

- A ceramic slurry includes the ceramic raw materials, water and auxiliary agents such as binders, deflocculants ext.
- In order to prepare an optimum composition, special tables are used which called as Seger Tables or Seger Rates.
- This Seger tables point out the ratios between the oxides which are present in the ceramic raw materials.
- Keeping the ratios constant is necessary while developing new compositions because every oxide has a different effect on rheology.
- Seger tables varies concerning the final product and the desired properties from the final product.

Thixotropy Properties



- Rheology is the science of fluidity. Fluidity can be explained by two main values which are viscosity and thixotropy.
- Viscosity is the value of the fluidity of a material, fluidity and viscosity has an inverse ratio between them.
- Thixotropy is the value of the change in viscosity with time.
- There are two main fluid groups which are Newtonian and Non-newtonian fluids
- Newtonian fluids are just like water, their viscosity don't change with time. But for Non-newtonian fluids, viscosity changes with time.
- Viscosity of the Non-newtonian fluids decrease with the counting time.



Thixotropy Properties



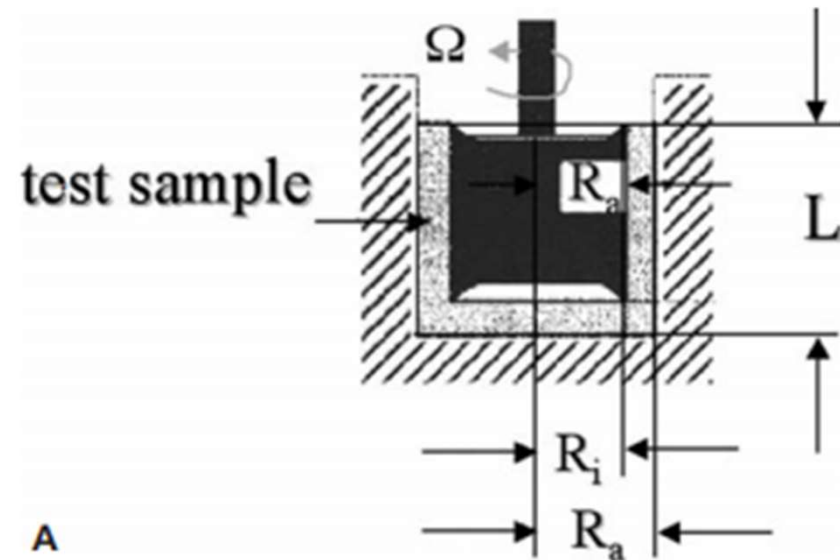
- Ceramic slurry is a Non-newtonian fluid and it shows thixotropy property.
- For the rheological study of a ceramic slurry, terms like flocculation, deflocculation and deflocculant should be explained.
- For ceramics, if the viscosity is too low, the surface quality of the products will be low and there might be cracks on the surface.
- If the viscosity is too high, this will cause pinhole defects and difficulties for the transportation of the slurry (mobility).
- When it comes to thixotropy, it is also as important as viscosity.
- If the thixotropy is too high, drying time of the product will be long and if the thixotropy is too low, this will cause the product to become fragile.



Thixotropy Properties

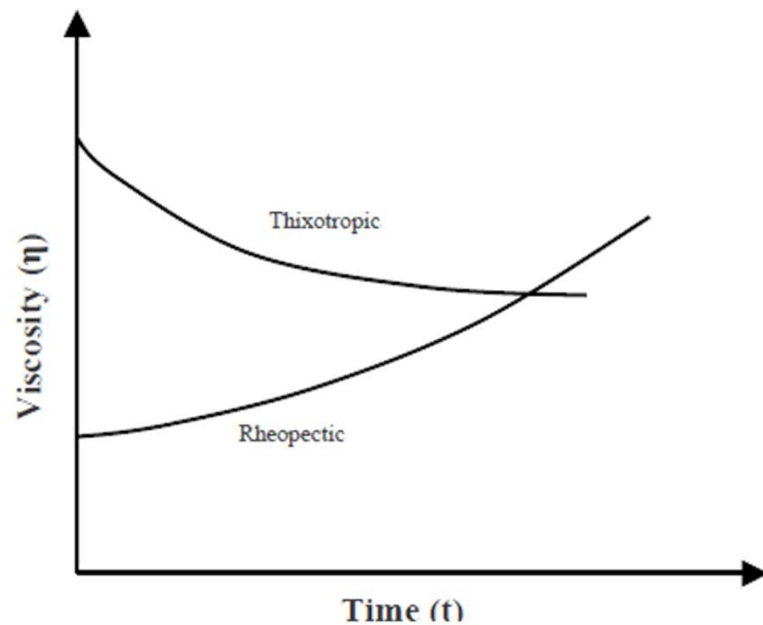
A viscometer or rheometer

In general a viscometer can make only CR measurements – in other words flow and viscosity curves are the main purpose of the instruments. As a result thixotropy loops, and steady shear measurements can also be made with these instruments. A rheometer is capable of much more, including viscoelastic measurements, creep and recovery measurements and so on. CS instruments have an air bearing so that these extra measurements can be made. The air bearing also allows shear and recovery measurements to be made because they can probe the structure of the material without influencing the rate at which it rebuilds.

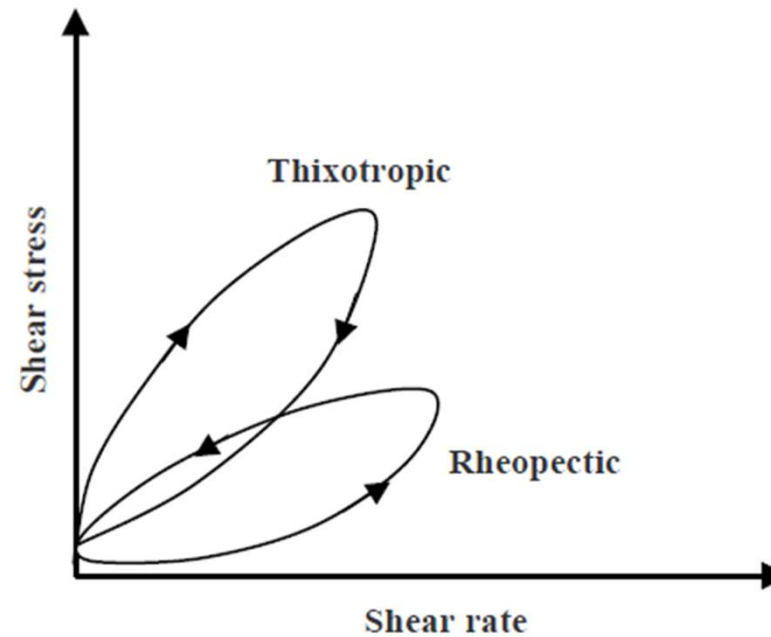


Controlled Rate, CR, (impose a shear rate and measure the shear stress) or in Controlled Stress, CS, (impose a shear stress and measure the resultant shear rate).

Thixotropy Properties

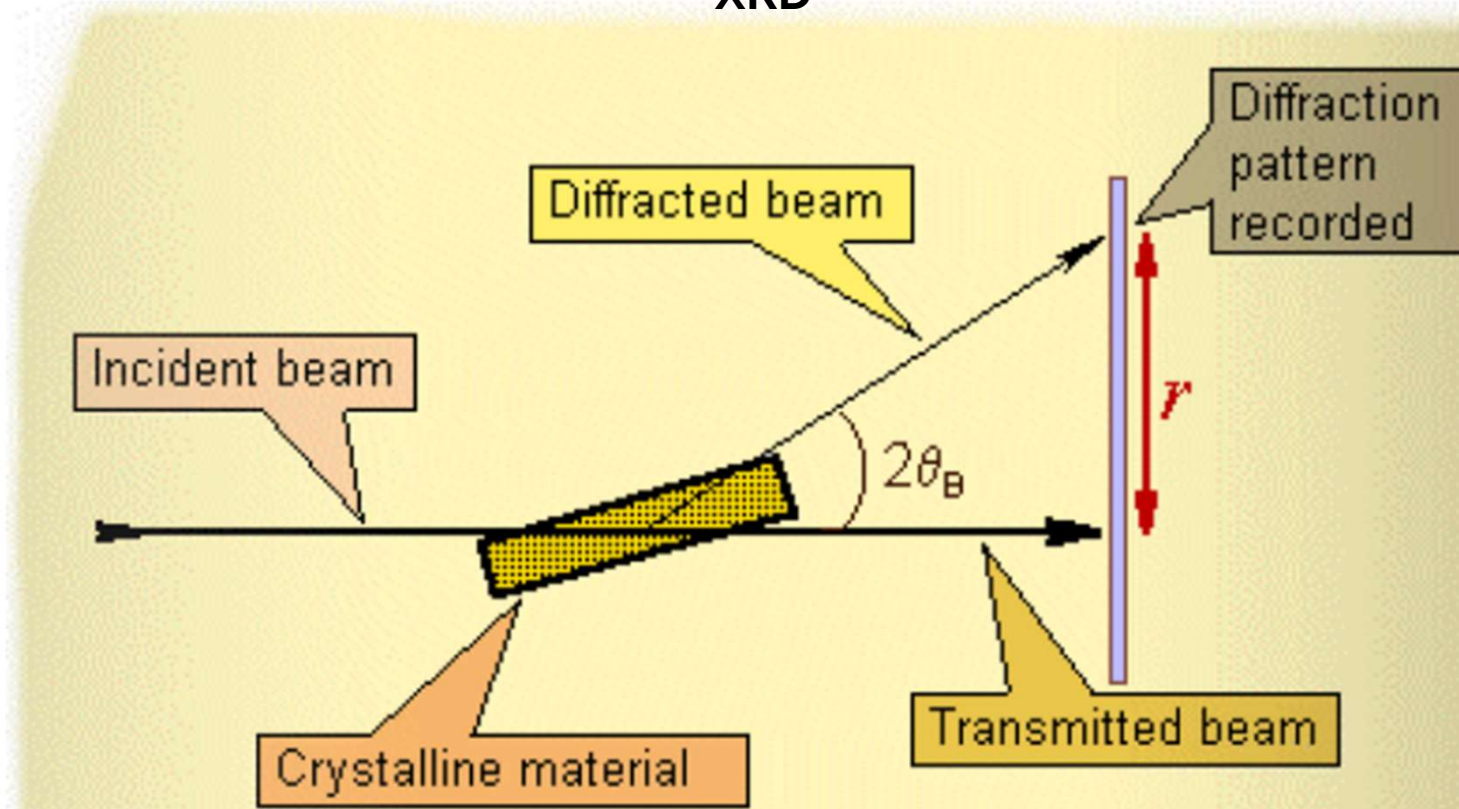


Viscosity versus time curves at a given shear rate for time-dependent nonNewtonian suspensions.



Shear stress versus shear rate curves of time-dependent fluids subjected to varying shear rates.

XRD

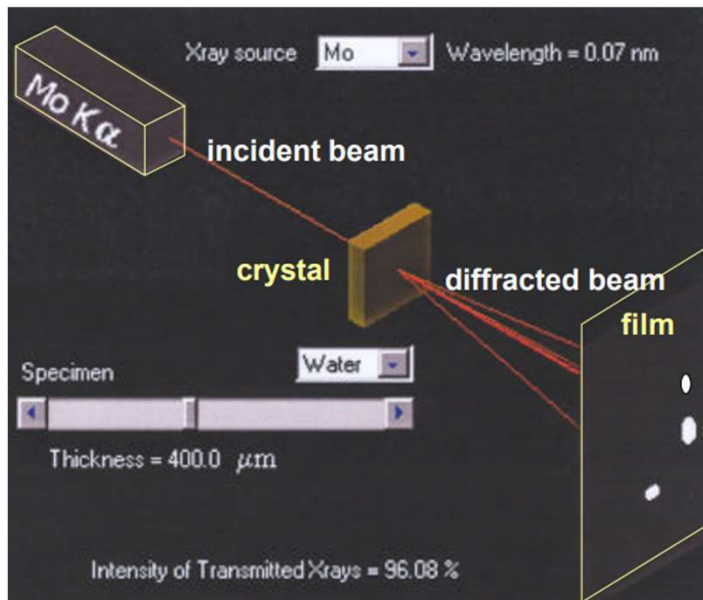


<http://www.micro.magnet.fsu.edu/primer/java/interference/index.html>

XRD

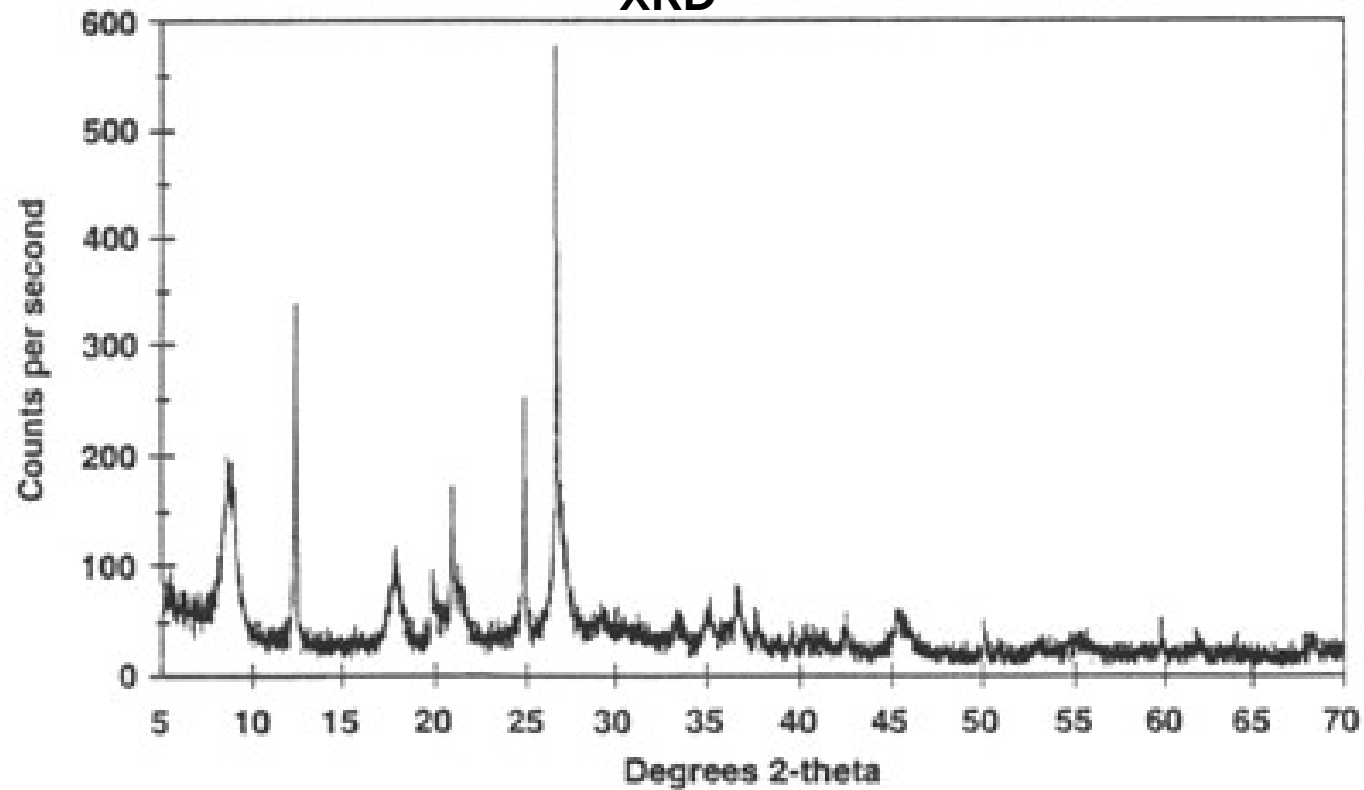


- Measure the average spacings between layers or rows of atoms
- Determine the orientation of a single crystal or grain
- Find the crystal structure of an unknown material
- Measure the size, shape and internal stress of small crystalline regions



The atomic planes of a crystal cause an incident beam of X-rays to interfere with one another as they leave the crystal. The phenomenon is called X-ray diffraction.

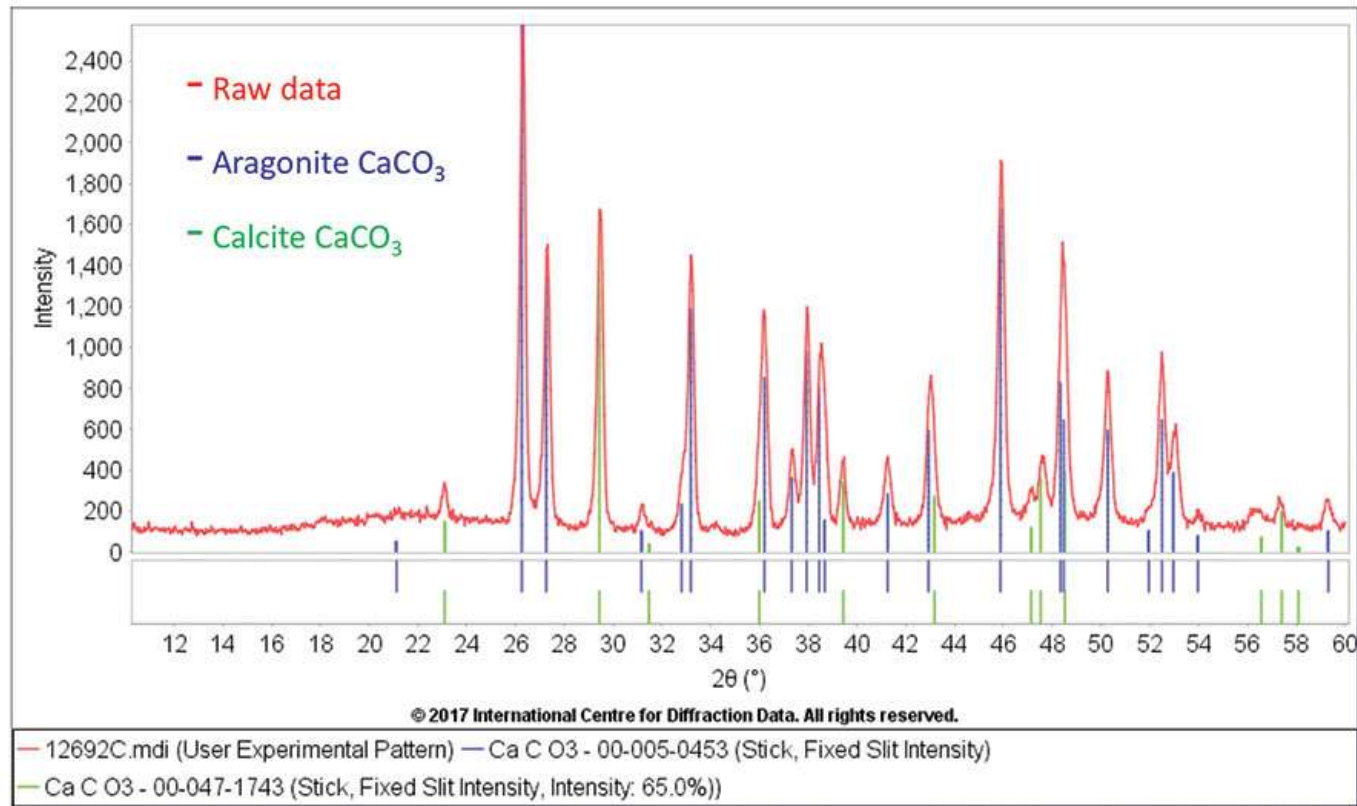
XRD



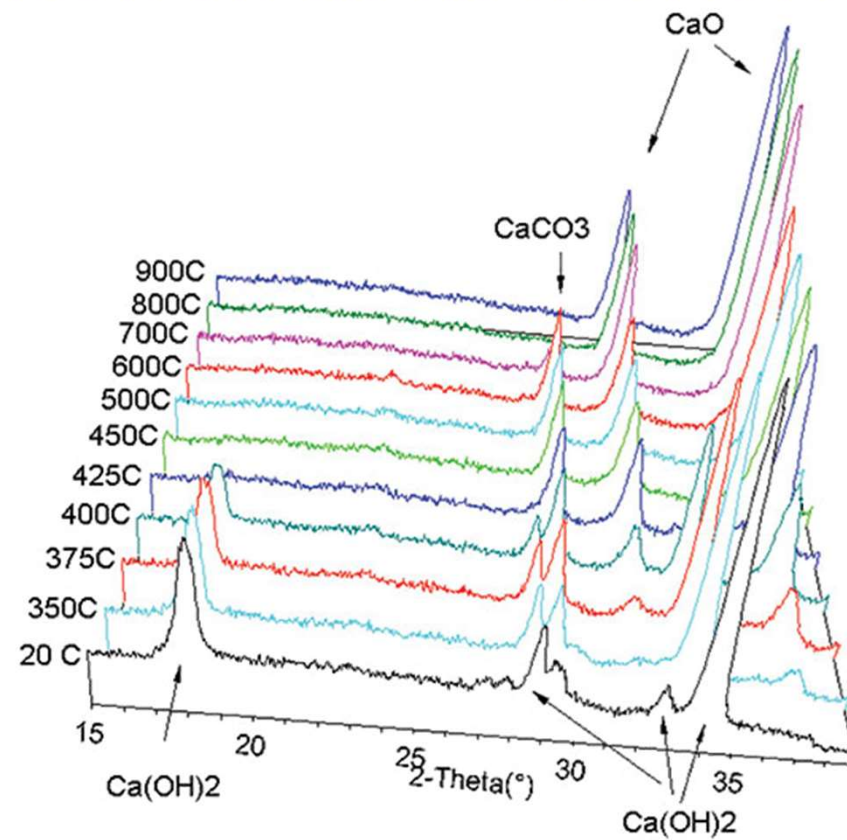
X-ray powder diffractogram. Peak positions occur where the X-ray beam has been diffracted by the crystal lattice. The unique set of d-spacings derived from this pattern can be used to 'fingerprint' the mineral.

<https://serc.carleton.edu/download/images/8418/xrayplot-usgs2.gif>

XRD



<https://www.ceramicindustry.com/articles/96252-ceramic-materials-characterization-using-x-ray-diffraction>



<https://www.ceramicindustry.com/articles/96252-ceramic-materials-characterization-using-x-ray-diffraction>

DTA-TGA



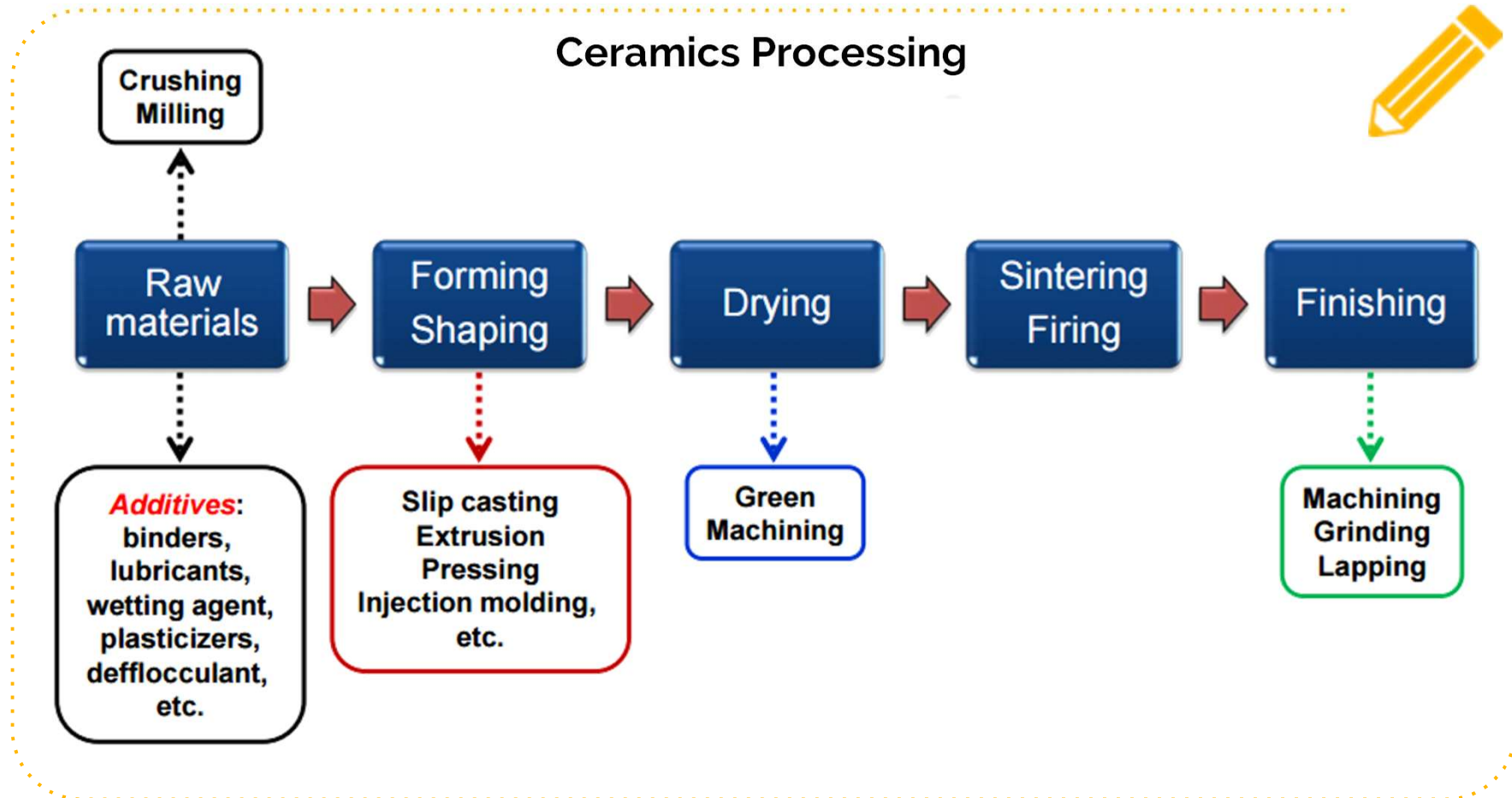
8

Midterm Week

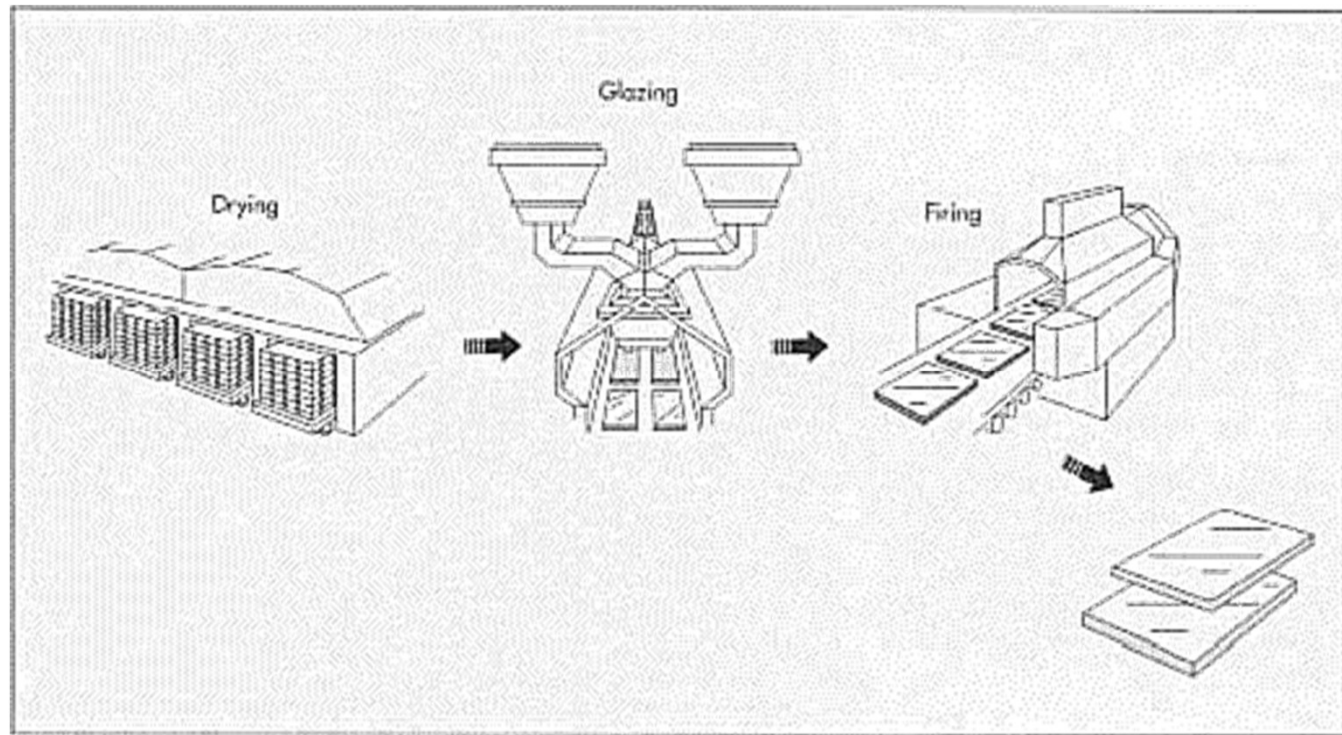
Molding Methods of Ceramic Materials

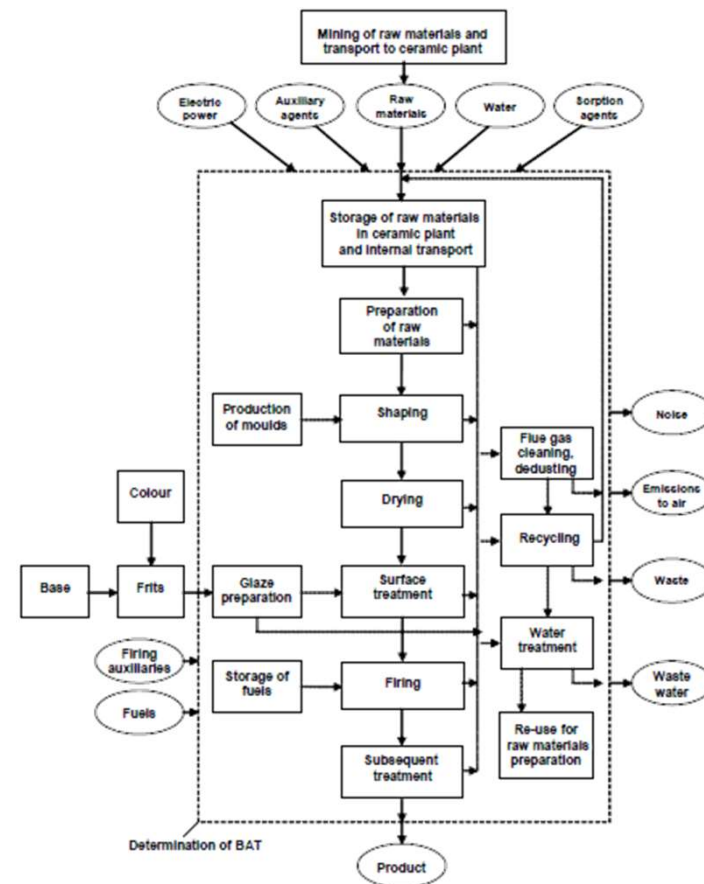
- Casting, forming, on the die press: Cold Press, Cold-Isostatic Press, Hot Press, Hot-Isostatic Press,
- Extrusion, Injection

Ceramics Processing



Simply, Daily Life Ceramics 😊 :

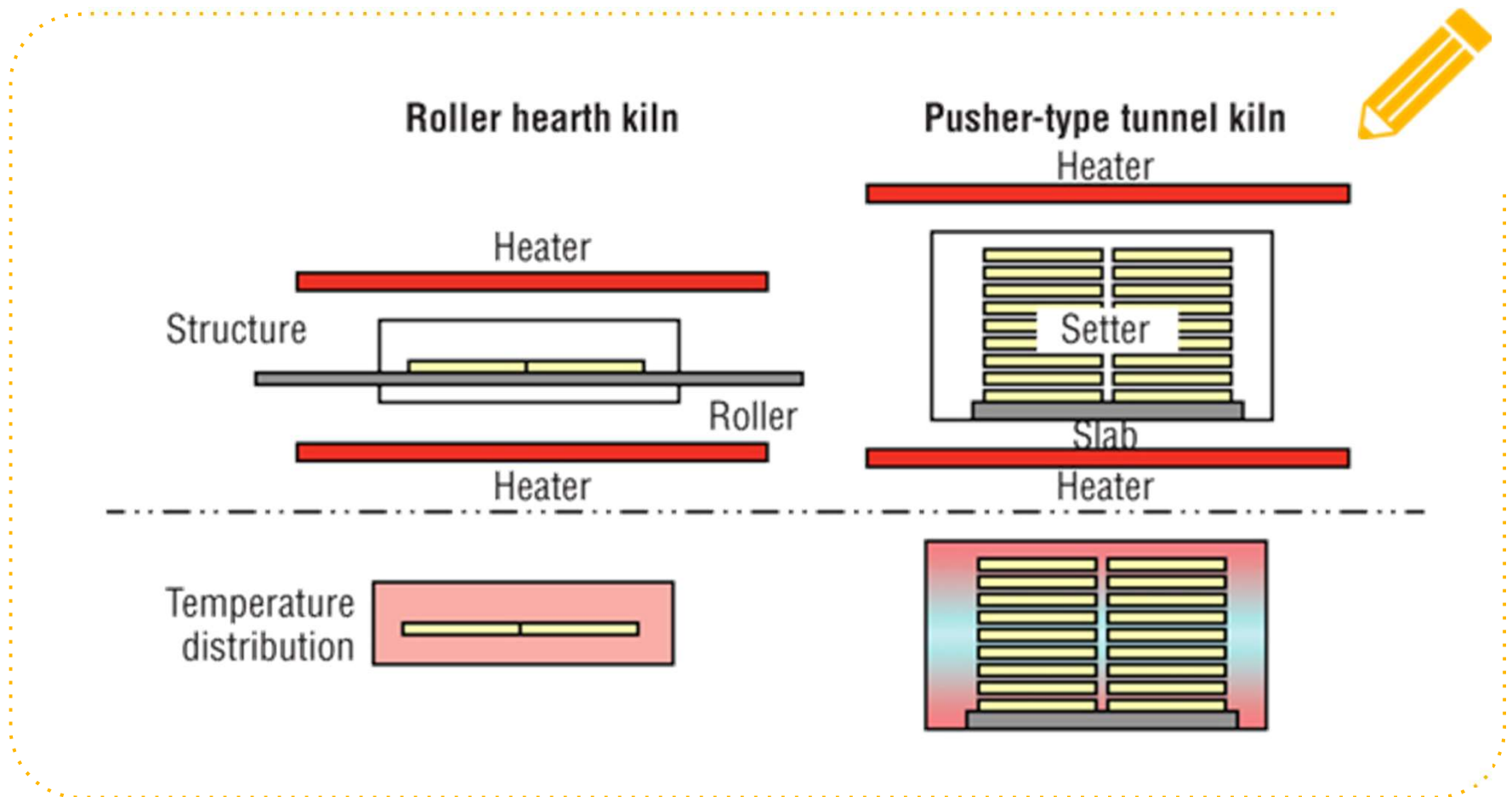


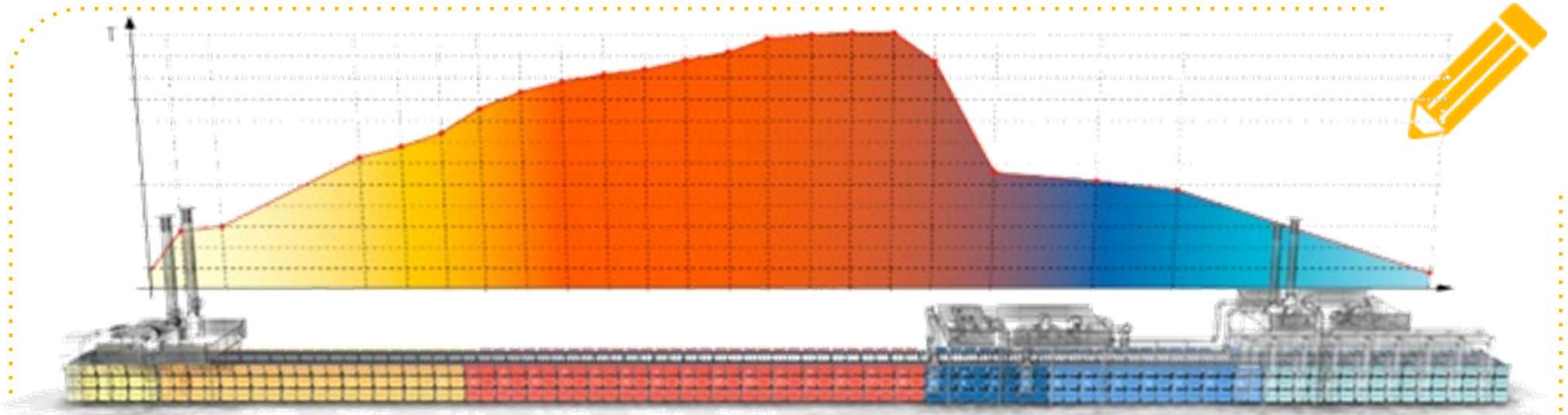




- Ceramic materials cannot be formed by the manufacturing processes known from metallic or organic materials.
- The energy to melt and cast ceramic raw materials would be far too costly. The process used to form ceramic materials is a heat treatment of very fine powders of the raw materials called sintering.
- The brittle nature of ceramic end products demands as little as possible machining after sintering. The ceramic parts have, therefore, to be shaped before sintering.







Alumina roller bars

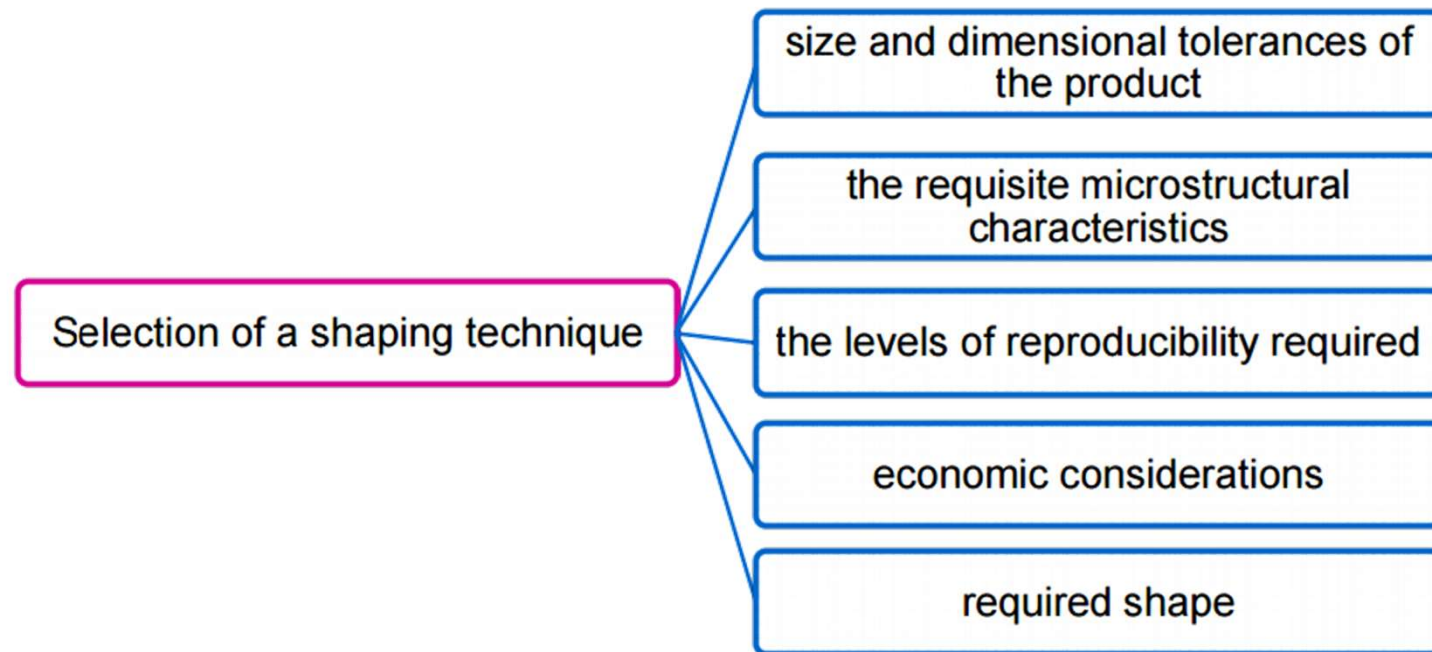


Sanitaryware kilns



Tile Furnaces

Shaping transforms an unconsolidated powder mixture into a coherent, consolidated body having a chosen geometry.

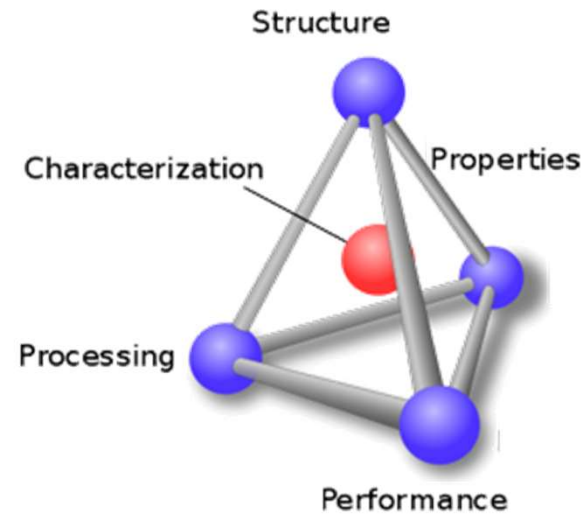


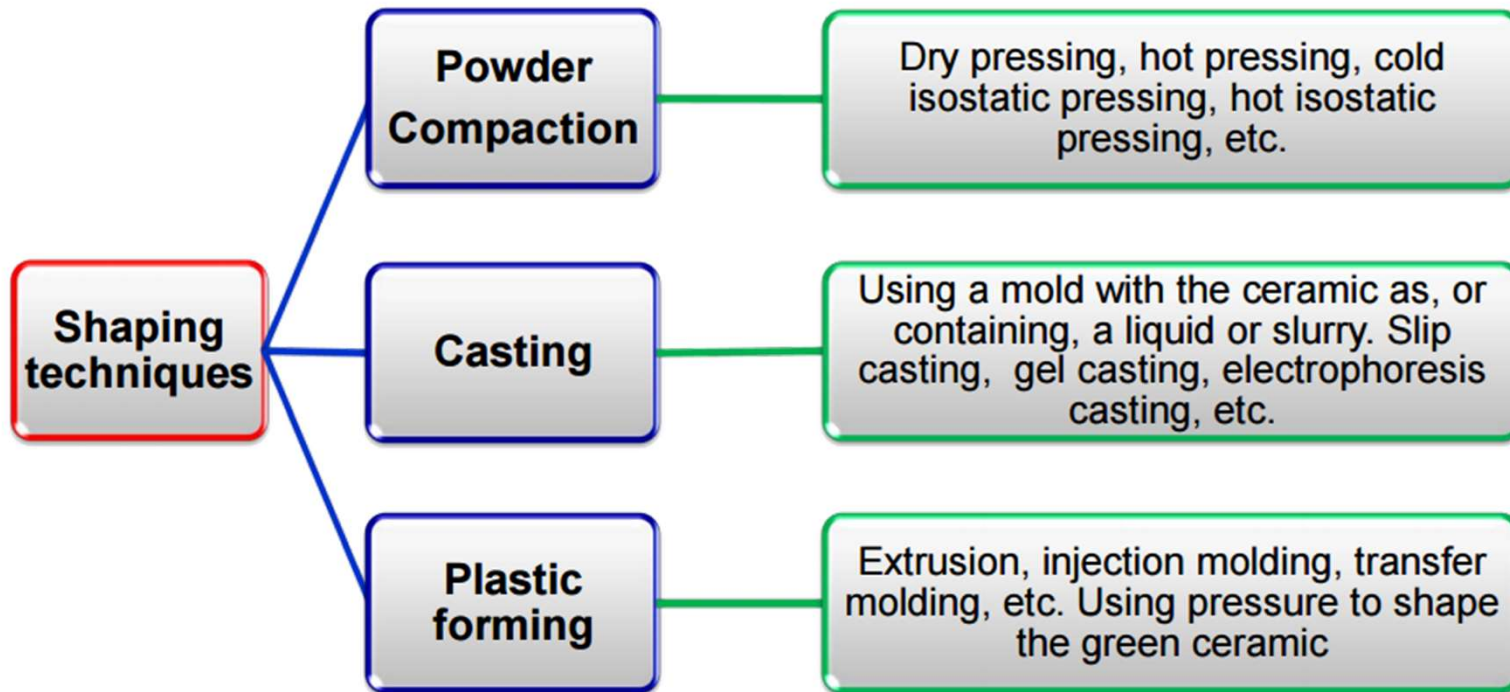
- Many shaping methods are used for ceramic products and these can be grouped into three basic categories, which are not necessarily independent.

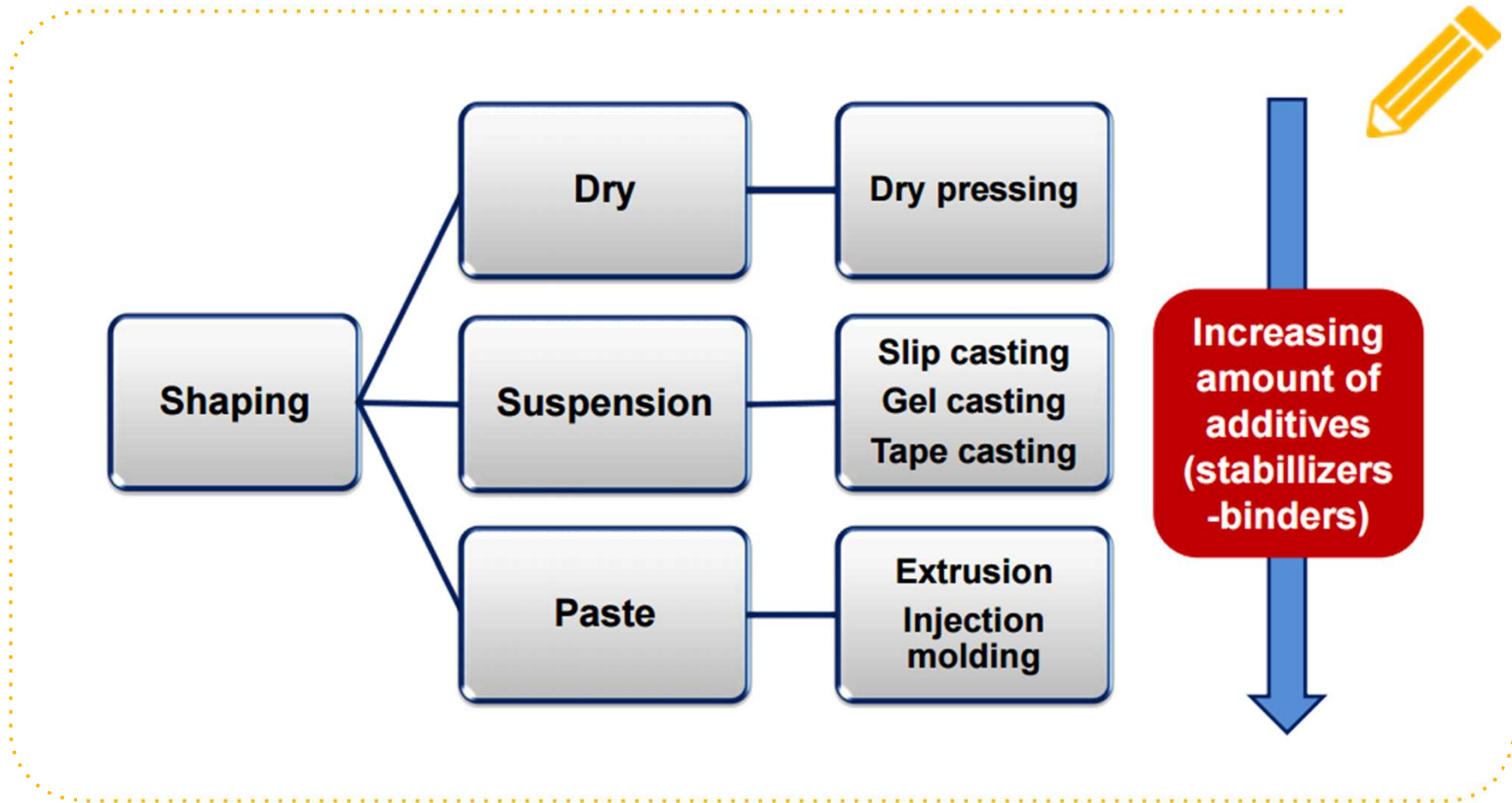


Factors to be considered:

- Complexity of object
- Size
- Quantity (production rate) etc.







Forming method	Feed material	Shape of green body
Dry or semi-dry pressing		
Uniaxial pressing (Die compaction)	Powder or free-flowing granules	Small simple shapes
Isostatic pressing	Powder or fragile granules	Larger, more intricate Shapes
Casting of a slurry		
Slip casting	Free-flowing slurry with low binder content	Thin intricate shapes
Tape casting	Free-flowing slurry with high binder content	Thin sheets
Deformation of a plastic mass		
Extrusion	Moist mixture of powder and binder solution	Elongated shapes with uniform cross section
Injection molding	Granulated mixture of powder and solid binder	Small intricate shapes



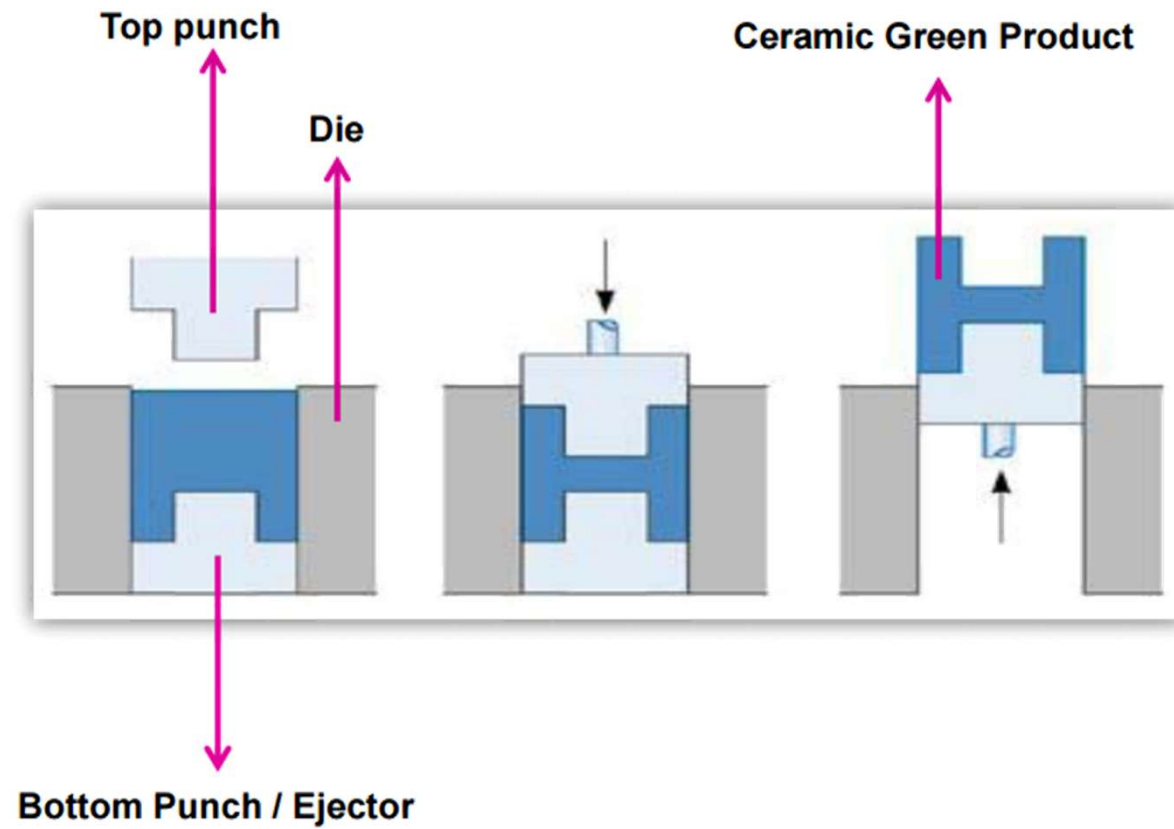


Tight control of dimension
→ superior control of process
through forming and sintering
→ plus final machining
(polishing) – an expensive
step

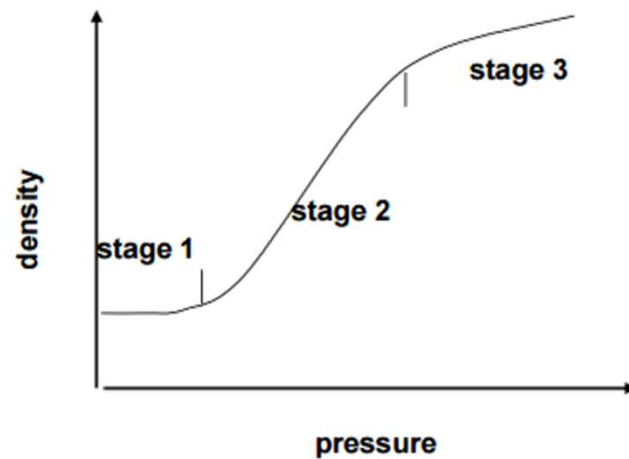
Total volume shrinkage =
(drying stage) + (calcination
stage) + (sintering stage)
Precise control depends on
the control at this three stages

**Dry pressed, injection
molded** → drying stage
shrinkage ~ 0;
extruded and slip casted parts
→ drying stage shrinkage
~ 3-12%

**Shrinkage during
calcination:** high for injection
molding and tape casting

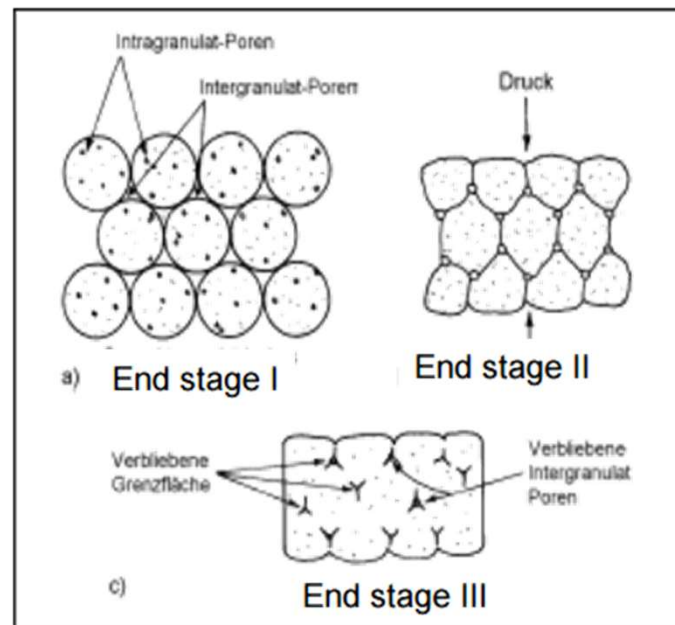


Compaction of granules



Compaction behavior of granulated powders

stage I	granule flow and rearrangement
stage II	granule deformation
stage III	granule densification



Evolution of the green-body microstructure during compaction of granules

Die pressing additives



TABLE 22.3 Additives Used in Industrial Pressing Powders

Product	Binder	Plasticizer	Lubricant
Alumina	Polyvinyl alcohol ^a	Polyethylene glycol ^b	Mg Stearate
96 % alumina substrates	Polyethylene glycol ^c	None	Talc, ^d clay ^d
Alumina spark plug insulation	Microcrystalline wax emulsion	KOH + tannic acid	Wax, talc ^d clay ^d
MnZn Ferrites	Polyvinyl alcohol ^a	Polyethylene glycol ^b	Zn Stearate
Ba Titanate	Polyvinyl alcohol ^a	Polyethylene glycol ^b	
Steatite	Microcrystalline wax, clay	Water	Wax, talc, ^d clay ^d
Ceramic tile	Clay	Water	Talc, ^d clay ^d
Hotel china	Clay, polysaccharide	Water	Clay ^d
Refractories	Ca/Na lignosulfonate	Water	Stearate

^aLow-viscosity grade.

^b400 molecular weight.

^c20,000 molecular weight.

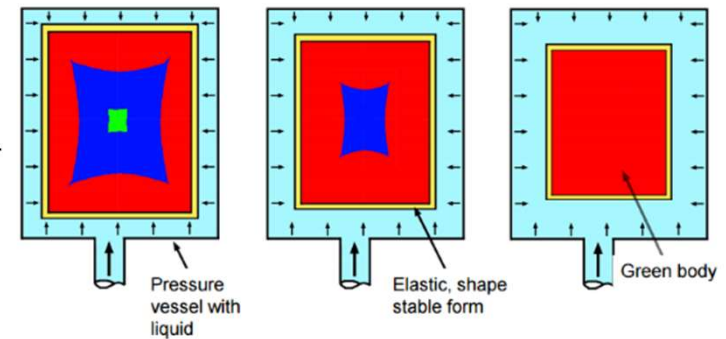
^dColloidal size.

ISOSTATIC PRESSING

Isostatic Pressing: Ceramic powder is loaded into a flexible chamber and pressure is applied outside the chamber with hydraulic fluid. Examples: Spark plug insulators, carbide tools.

Uses hydrostatic pressure to compact the ceramic powders from all directions • Avoids the problem of non-uniform density in the final product that is often observed in conventional uniaxial pressing • Same process used in powder metallurgy

Cold isostatic pressing is a powder-forming process where compaction takes place under isostatic or near-isostatic pressure conditions.



The advantage of isostatic compaction is a more homogeneous density distribution. The complexity of the mold is, however, limited.

- Cold isostatic Pressing (CIP)
 - Powder is placed in a flexible rubber mold
 - Pressurized hydrostatically
 - Uses pressures up to 150 KSI
 - Typical application is automotive cylinder liners

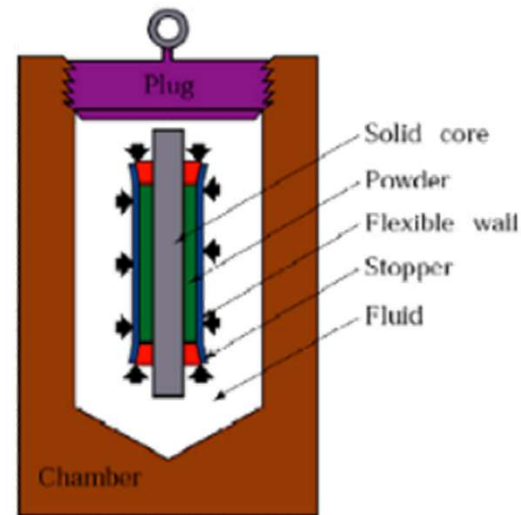


Fig: Schematic diagram, of cold isostatic, as applied to forming a tube. The powder is enclosed in a flexible container around a solid core rod. Pressure is applied iso-statically to the assembly inside a high-pressure chamber.

Casting



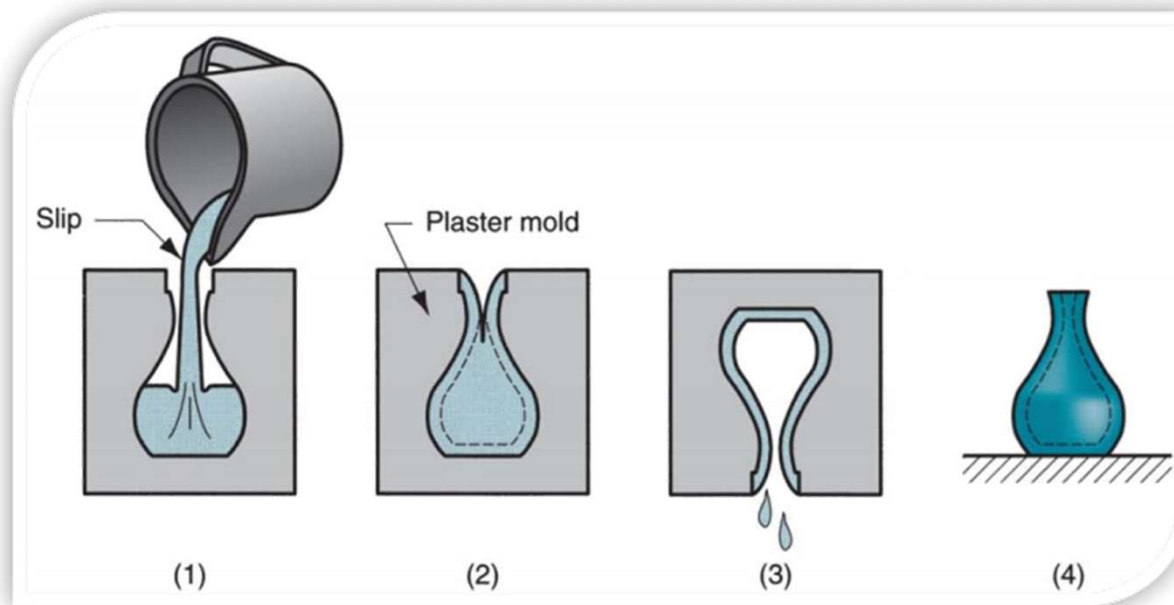
- Casting ceramics is carried out at room temperature and generally requires the ceramic powder particles to be suspended in a liquid to form a slurry; note this process is quite unlike the casting of metals.
- The slurry is then poured into a porous mold that removes the liquid (it diffuses out through the mold) and leaves a particulate compact in the mold. This process is known as slip casting.
- The process has been used to form many traditional ceramic products (e.g., sanitary ware) and more recently has been used in forming advanced ceramic products (e.g., rotor blades for gas turbines).
- The other main casting process for ceramics is tape casting, which, as you would guess, is used to make thick films or sheets.

- This process was introduced into many European porcelain factories in the eighteenth century, and was commonly employed for the casting of terra cotta sculpture in the nineteenth century.
- Today you may find that many common things you have such as: figurines, doll faces, dishes, flower pots, lamp bases, toilets, etc. are made from this technique of mass production.
- A suspension of ceramic powders in water, called a slip, is poured into a porous plaster of paris mold so that water from the mix is absorbed into the plaster to form a firm layer of clay at the mold surface.
- The slip composition is 25% to 40% water.
- Two principal variations: – Drain casting - the mold is inverted to drain excess slip after a semi-solid layer has been formed, thus producing a hollow product. – Solid casting - to produce solid products, adequate time is allowed for entire body to become firm.



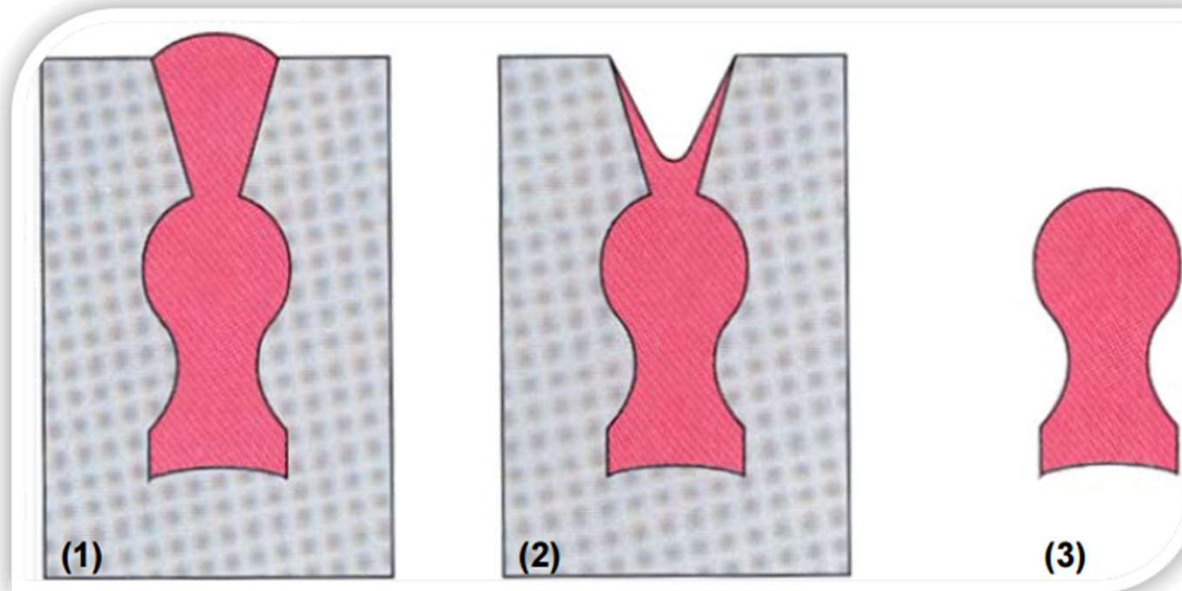
Drain Casting

(1) Slip is poured into plaster of Paris mold cavity, (2) water is absorbed into plaster mold to form a firm layer, (3) excess slip is poured out, and (4) green body is removed from the mold



Solid Casting

(1) Slip is poured into plaster of Paris mold cavity, (2) water is absorbed into plaster mold and (3) green body





- • What happens to LCTE when T_m increases?
- • What produces ionic colors in ceramics?
- • As T_m increases, what happens to E ?
- • What phase is T_g associated with in a semi-crystalline material?
- • What is the ductile-brittle behavior below T_g for mixed phases?
- • How does the LCTE compare for each mixed phase below T_g



- What happens to LCTE when T_m increases? DECREASES
- What produces ionic colors in ceramics? SUBSTITUTIONAL DEFECTS OF METAL IONS
- As T_m increases, what happens to E ? INCREASES
- What phase is T_g associated with in a semi-crystalline material? NON-CRYSTALLINE PHASE
- What is the rule-of-thumb relating T_g to T_m ? $T_g = \frac{1}{2} T_m$ (on the absolute temperature scale)
- What is the ductile-brittle behavior below T_g for mixed phases? BOTH CRYSTALLINE AND NON-CRYSTALLINE ARE BRITTLE
- How does the LCTE compare for each mixed phase below T_g ? LCTE FOR NON-CRYSTALLINE APPROXIMATELY CRYSTALLINE.

Drying and Sintering Methods and Considerations in Ceramic Materials

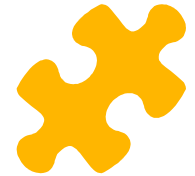
Introduction of Furnaces Used for this purpose

Mechanical test applied to ceramic materials

Methods of determination of density, porosity, specific gravity,
drying and cooking shrinkage methods

Theoretical Strength and Actual Strength are not Equal!

Example:

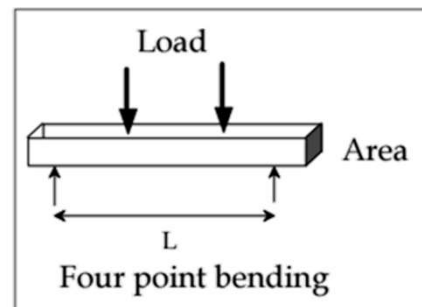
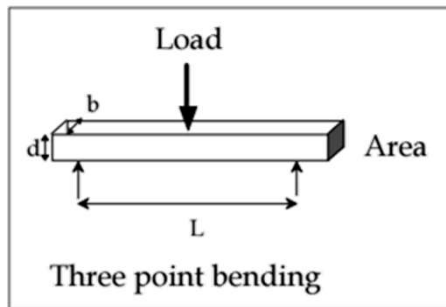
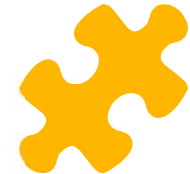
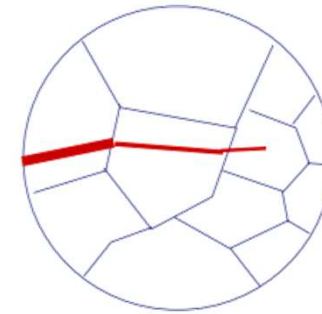


- Consider the fracture strength of ordinary window glass
 - Theoretical Strength = 7000 MPa (if bonds between individual atoms are broken)
 - Actual Strength = 35 MPa
 - That is 200x weaker!
- Why the big difference?
 - Preexisting flaws bigger than stress concentration



Fracture Mechanisms

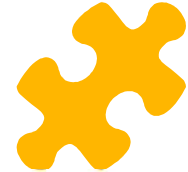
- Fracture is usually transgranular (rather than intergranular)
- Cracks often grow along high density crystallographic planes (cleavage planes)



Brittle ceramic materials are usually tested in bending (not in tension as are most metals), why?

- Sample preparation is easier
- Significant difference in results for testing in tension, compression and bending

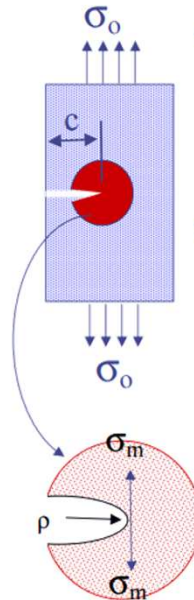
Observed Mechanical Strength and Fracture Mechanisms



Stress magnification by flaws

- ♦ σ_o = external stress
- ♦ ρ = radius of crack tip
- ♦ c = crack length
- half length for internal cracks
- ♦ σ_m = magnified stress at crack tip

$$\sigma_m = 2 \sigma_o \sqrt{\frac{c}{\rho}}$$



- ♦ Suppose you have a crack of length (c) 0.5 mm and radius (r) 1000 angstroms

$$\sigma_m / \sigma_o = 70.7$$

- ♦ For the same crack length suppose the radius is 100 angstroms

$$\sigma_m / \sigma_o = 224$$

Crack length ↓ and radius ↑ matters

Best if spherical defect

For brittle metals, most crystalline ceramics and glasses

Stress Concentration!

$$K_{IC} = Y\sigma_f\sqrt{\pi a}$$

K_{IC} : fracture toughness $\text{MPa}\sqrt{\text{m}}$
 Y : *geometric* constant
 a : crack length



- K is the stress intensity
- Y is a geometry dominated factor known as the stress intensity factor
- σ is the tensile stress opening the crack
- a is the crack length

- Failure occurs when the stress intensity, K, reaches a critical level of intensity known as the fracture toughness. Fracture toughness is a material property. Formulae exist to determine Y, the stress intensity factor for many common geometries.
- So, in order to reduce the risk of brittle fracture, it is necessary to understand the stress distribution caused by loading the component during launch, or during service, AND to understand the size, orientation, and location of existing cracks or defects.

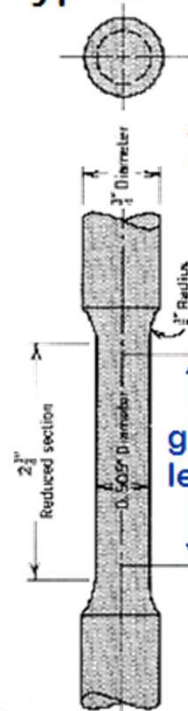


Stress and Strain in Relation and Measurement (Test)

How it is measured? Ceramics and non-ceramics



• Typical tensile specimen



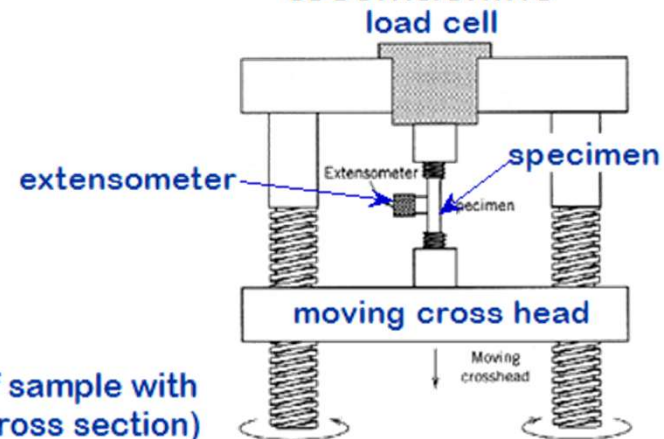
Adapted from Fig. 6.2,
Callister 6e.

gauge = (portion of sample with
length = reduced cross section)

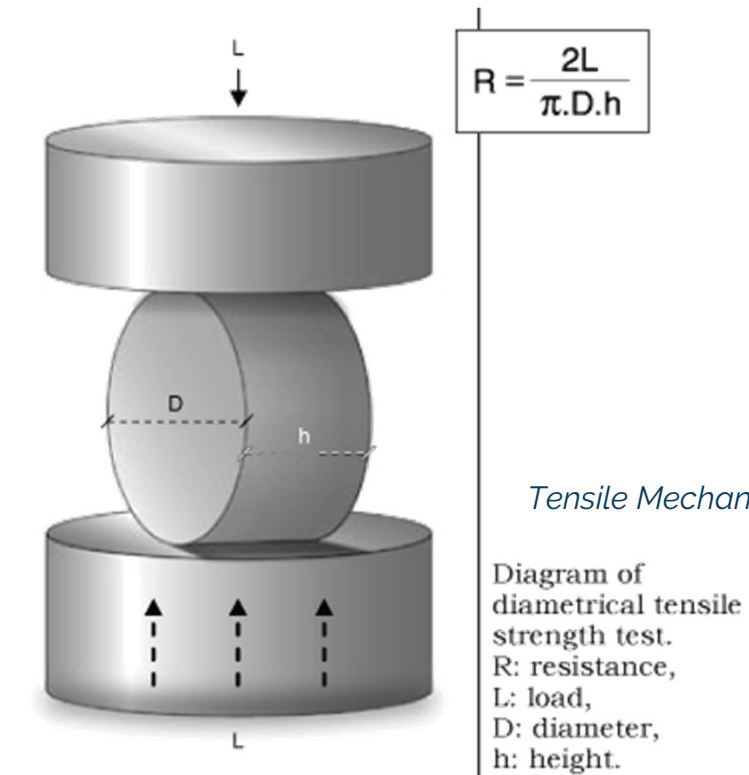
• Other types of tests:

- compression: brittle materials (e.g., concrete)
- torsion: cylindrical tubes, shafts.

• Typical tensile test machine



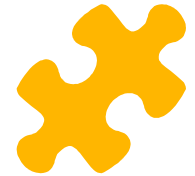
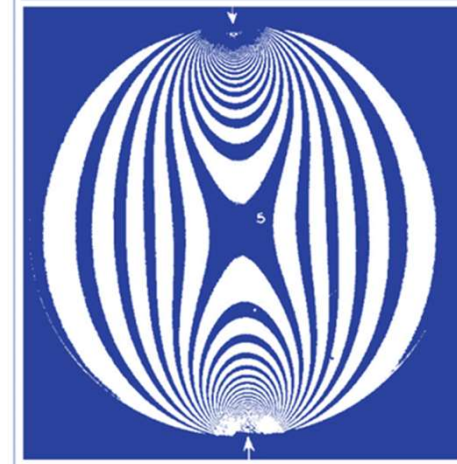
New approaches: Brazilian test method



Tensile Mechanism ←



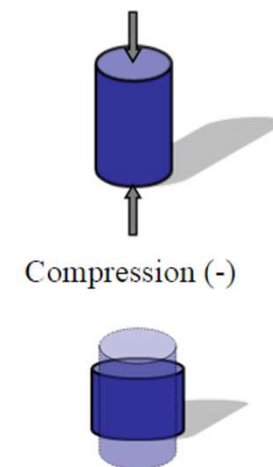
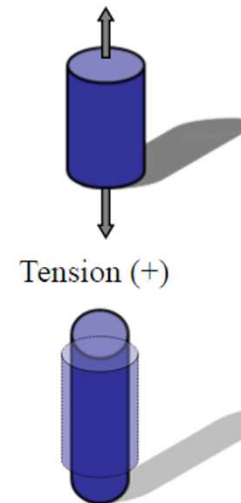
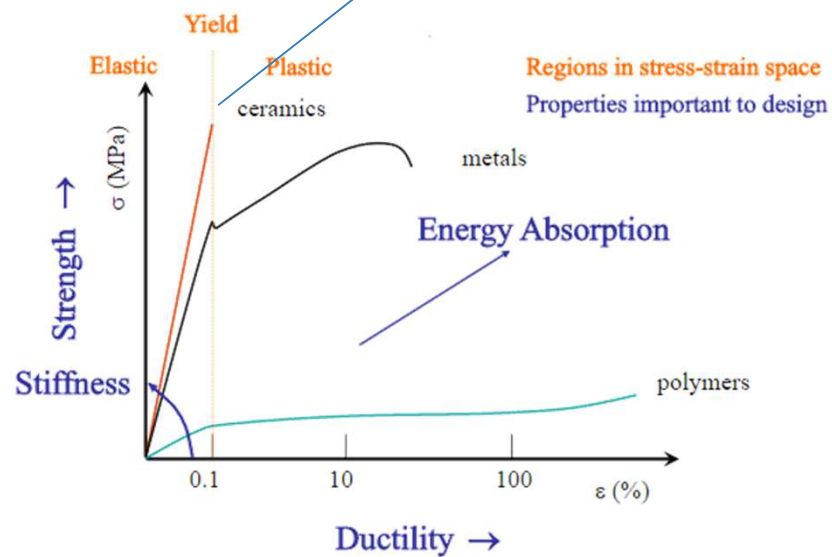
Figure 2 – Isostress fringes at disk under diametral compression (extracted from: Frocht (12))



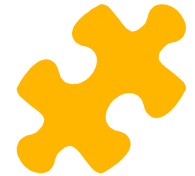
Stress- Strain Curves and Tensile-Compressive strength



Yield point marks the transition from elastic to plastic deformation



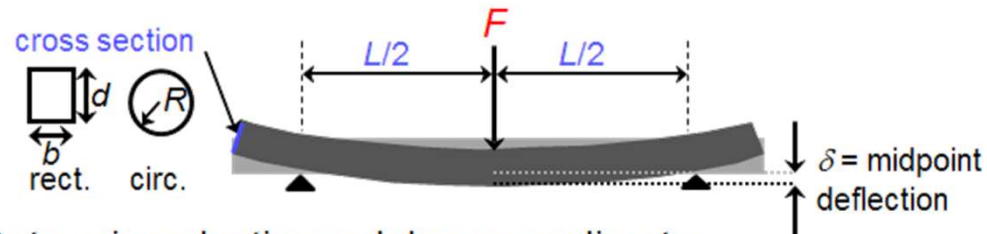
Flexural Tests – Measurement of Elastic Modulus



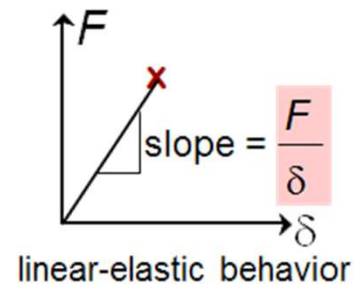
Room T behavior is usually elastic, with brittle failure.

3-Point Bend Testing often used.

-- tensile tests are difficult for brittle materials.



Determine elastic modulus according to:



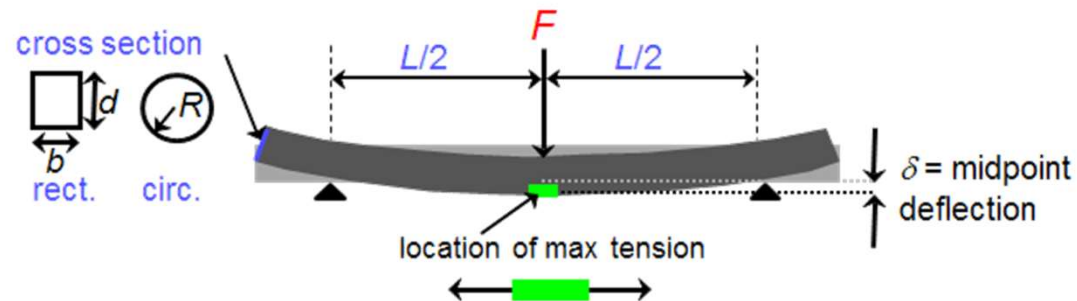
$$E = \frac{F}{\delta} \frac{L^3}{4bd^3} \quad (\text{rect. cross section})$$

$$E = \frac{F}{\delta} \frac{L^3}{12\pi R^4} \quad (\text{circ. cross section})$$

Flexural Tests – Measurement of Elastic Modulus

Flexural testing is the most common method used to measure the uniaxial tensile strength of ceramics and glasses.

3-point bend test to measure room-*T* flexural strength.



Flexural strength:

$$\sigma_{fs} = \frac{3F_f L}{2bd^2} \quad (\text{rect. cross section})$$

$$\sigma_{fs} = \frac{F_f L}{\pi R^3} \quad (\text{circ. cross section})$$

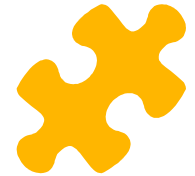
• Typical values:

Material	σ_{fs} (MPa)	E (GPa)
Si nitride	250-1000	304
Si carbide	100-820	345
Al oxide	275-700	393
glass (soda-lime)	69	69

Data from Table 12.5, Callister & Rethwisch 8e.

Flexural Tests – Measurement of Elastic Modulus

Flexural testing is the most common method used to measure the uniaxial tensile strength of ceramics and glasses.



Classification of ceramic glazes

Glaze Raw Materials, Preparation of glazes, experiments applied to glazed structures

Glazing Units



So, whats Frit and whats Glaze?

Properties and applications of engineering ceramics

SiC, B₄C, Al₂O₃

14

Cements and Refractories



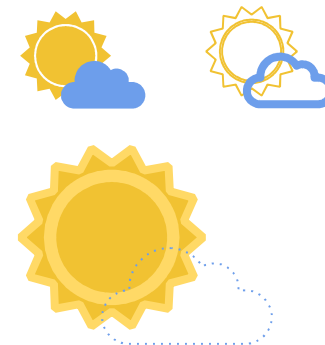
SlidesCarnival icons are editable shapes.

This means that you can:

- Resize them without losing quality.
- Change fill color and opacity.
- Change line color, width and style.

Isn't that nice? :)

Examples:





Now you can use any emoji as an icon!
And of course it resizes without losing quality and you can change the color.

How? Follow Google instructions

<https://twitter.com/googledocs/status/730087240156643328>

