Chapters 15

Ceramics

Dr. Zhe Cheng

Ceramics

- https://en.wikipedia.org/wiki/Ceramic
  "A ceramic is an **inorganic**, **nonmetallic** solid material comprising metal, nonmetal or metalloid atoms primarily held in ionic and covalent bonds"
- W. D. Kingery et al., *Introduction to Ceramics* (1976), p. 3
  "We define ceramics as the art and science of making and using solid articles which have as their essential components, and are composed in large part of, **inorganic** **nonmetallic** materials"
- In short
  Solid, **inorganic** material containing **at least one non-metallic element**

Traditional Ceramics & Glasses

Examples

Stone/Mineral


http://www.granitecountertops.net/

http://www.gettyimages.com/detail/photo/stone-statue-of-the-people-republic-of-high-res-stock-photography/128039733

http://www.neobits.com/vwr_89037_496_caseof5_vwr_mortars_and_pestles_p4152098.html?atc=gbp&gclid=CNKn6vq89MYCFdUUHwodTzEDkg

Pottery or Porcelain



http://mfg.regionaldirectory.us/pottery/

https://en.wikipedia.org/wiki/Porcelain

http://www.linea-aqua.com/shop/LineaAqua-Caraway-One-Piece-Siphonic-Toilet-28-x-15-x-30-Luxury-White-Porcelain-Toilet-with-S-Trap-and-Soft-Closing-Seat-pr-17486.html

Glass (bulk)



http://www.theculturemap.com/colourful-buildings-street-art-reykjavik-iceland/stained-glass-window-church-reykjavik/
https://talkingarchitecture.files.wordpress.com/2012/03/glass-building.jpg

Glaze/Enamel (glass layer)

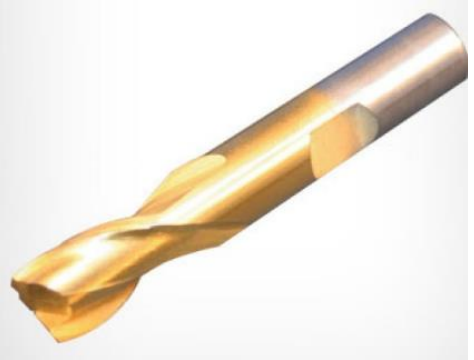

https://www.qualitylogoproducts.com/custom-mugs/enamel-ceramic-mug-17-oz-superextralarge-383936.jpg

http://www.ganoksin.com/borisat/nenam/ajm-metals_under_fire.htm

Structural Ceramics - Mechanical

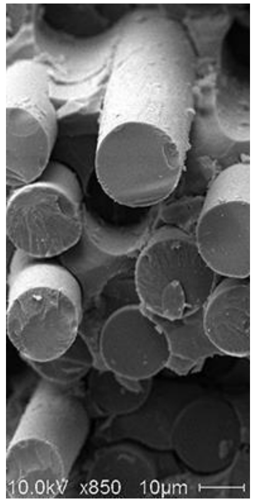
Mechanical Properties & Applications	Examples
High hardness - cutting, grinding, polishing, armor…	c-BN, B_4C, SiC, Si_3N_4, WC…
Low hardness - lubrication, fillers	Talc, MoS_2, Graphite…
Low toughness (Brittle)	Glass, Most ceramics…
Higher toughness – bearings, engine parts	MAX phase (Ti_3SiC_2), Si_3N_4, toughened ZrO_2
High modulus	C or SiC fibers

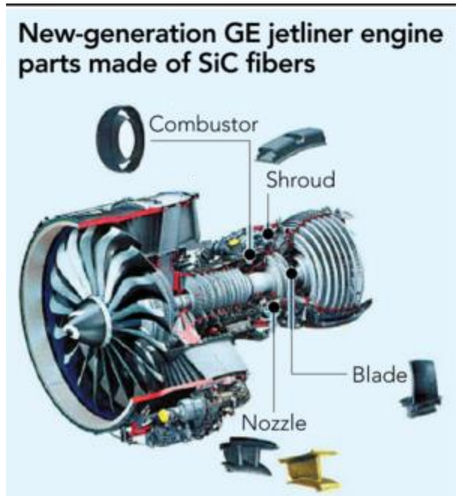












http://vercomaterialsllc.com/gallery/

https://www.ngkntk.co.jp/english/product/cutting_tools/cubic_boron_nitride.html

http://www.intelcoatings.com/product/titanium-nitride/

http://www.chemodex.co.uk/product/mos2-molybdenum-disulphide-dry-film-lubricant/

https://www.gcferrules.com/ecommerce/product/164/

ceramics.org/wp-content/uploads/2013/03/bulletin042013_maxphases.pdf

ceramics.org/wp-content/uploads/2013/03/bulletin042013_maxphases.pdf

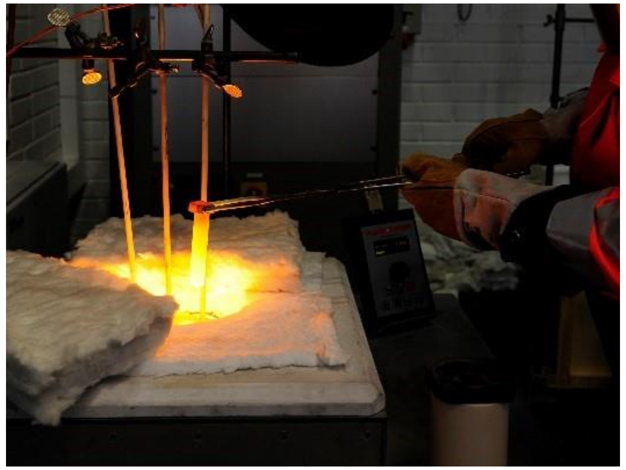
https://www.lily-bearing.com/ceramic-bearings/zirconia-bearings/

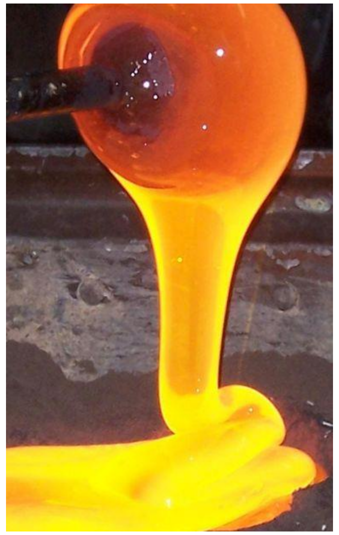
https://asia.nikkei.com/Business/SiC-fibers-find-their-way-into-aircraft-engines

https://www.compositesworld.com/articles/ceramic-matrix-composites-heat-up

Structural Ceramics - Thermal

Thermal Properties & Applications	Examples
Low thermal conductivity - Thermal barrier or insulation material	Al_2O_3, SiO_2, ZrO_2, …
High thermal conductivity - Heat sink for electronics	AlN; diamond…
High melting point - Refractories	Al_2O_3, SiO_2, SiC, ZrB_2, HfC…
Low melting point	Glass (frit); Salts…

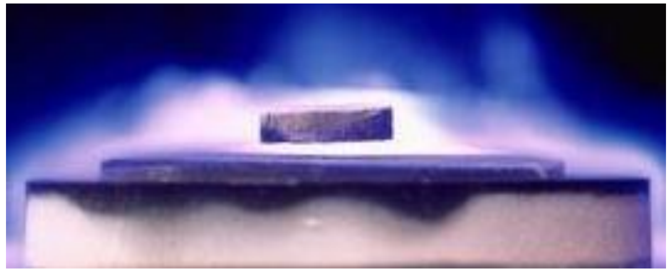


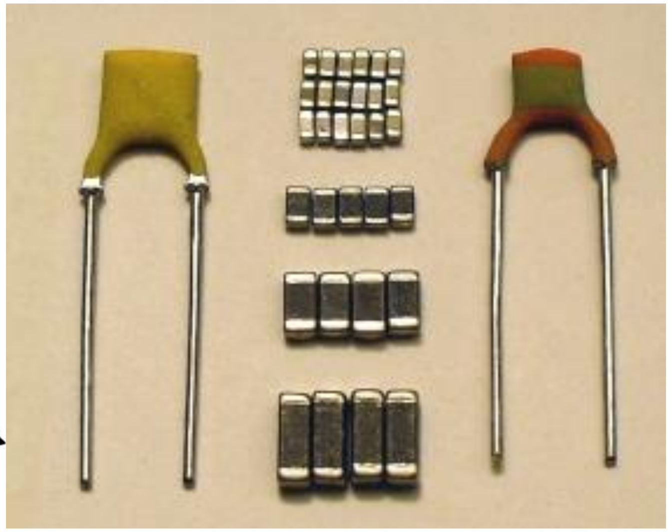


http://www.trymaxgroup.com/enquiry-form-10019.htm?product_slno=1343015
https://www.outotec.com/company/newsletters/smelting-newsletter/smelting-issue-2--2016/refractory-lining-materials-testing/
https://www.ceramtec.com/ceramcool/design/
https://www.pinterest.com/pin/294845106829758796

Functional Ceramics - Electronic

Electrical Property & Applications	Examples
Superconductor – NMR analysis, power generation	$YBa_2Cu_4O_{7-x}$, MgB_2…
Metallic conductor – Thick film conductor	TiC, ZrB_2, Ti_3SiC_2, RuO_2, $SrVO_3$, …
Semiconductor – Solar cell, transparent conductor	GaAs, $CuIn_{1-x}Ga_xSe_2$ (CIGS), CdTe, ZnO…
Ionic conductor - Sensors; fuel cells	Y_2O_3-stabilized ZrO_2, AgI…
Mixed conductor (electrodes; catalysts)	$La_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_3$, $Ce_{1-x}Gd_xO_{2-\delta}$…
Insulator – Electrical insulation	Al_2O_3, SiO_2, MgO…
Piezoelectric/Ferroelectric - capacitor; actuators	$BaTiO_3$, $PbTiO_3$…





Science Photo Library

https://www.solarpowerworldonline.com/2016/05/advantages-flexible-cigs-thin-film-solar-modules/

https://www.likra.nl/index.php?l=_en&id=7&c=58

https://en.wikipedia.org/wiki/Ceramic_capacitor

https://www.tradeindia.com/fp3032293/Electrical-Insulator.html

Functional Ceramics - Others

Function	Property & Application	Examples
Magnetic	Ferromagnetic	Fe_3O_4…
	Parromagnetic	Most other
Nuclear	Fuel	UO_2…
	Shield	B_4C…
Optical	Transparent	Al_2O_3 (sapphire), SiO_2 (quartz), many glasses…
	Black	RuO_2, graphite,
	Colored	Doped Al_2O_3, Cr_2O_3, NiO…
	Isotropic	Glass
	Anisotropic	Single crystals
	Special	Laser applications

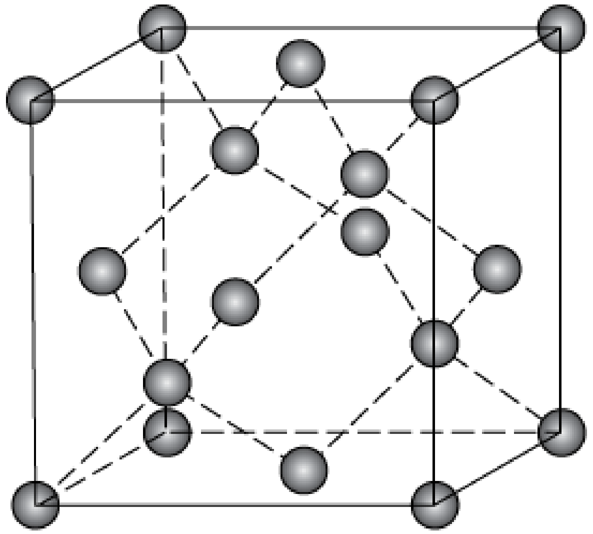
Bonding in Ceramics

- Mostly covalent (sharing of e^-) or ionic bond (complete transfer of e^-)
- Often mixed nature, i.e., covalent + ionic
- May even have metallic bonding: e.g., MAX phase Ti_2AlC (can be viewed as TiC + TiAl)

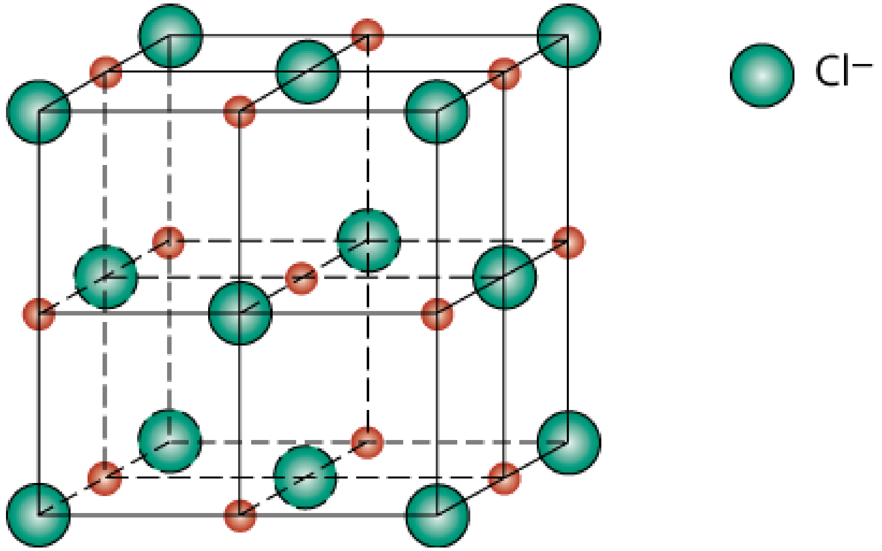
Covalent	**Mixed**	**Ionic**
B_4C	GaN	NaF
Diamond	CdTe	MgO
Si	Ti_2AlC	Li_3N
SiC	TiC	

Examples of Crystal Structures in Ceramics

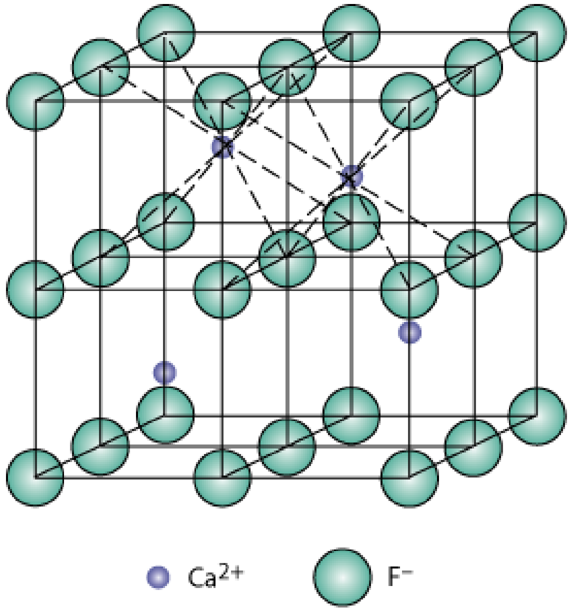
Diamond type



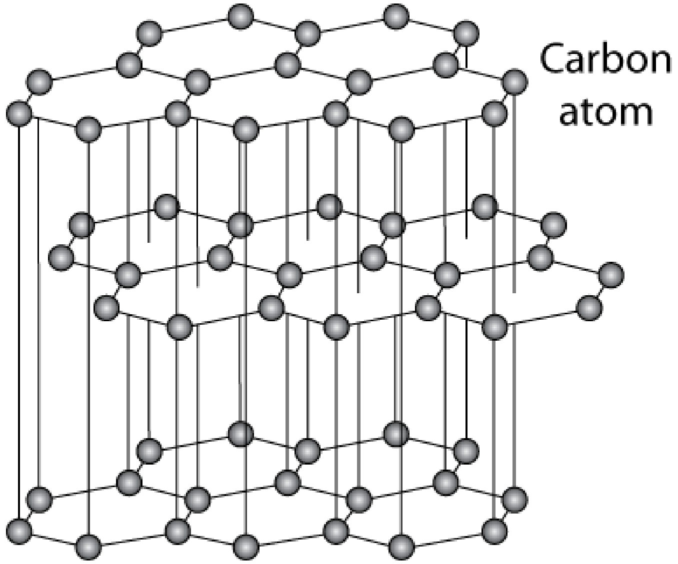
NaCl type



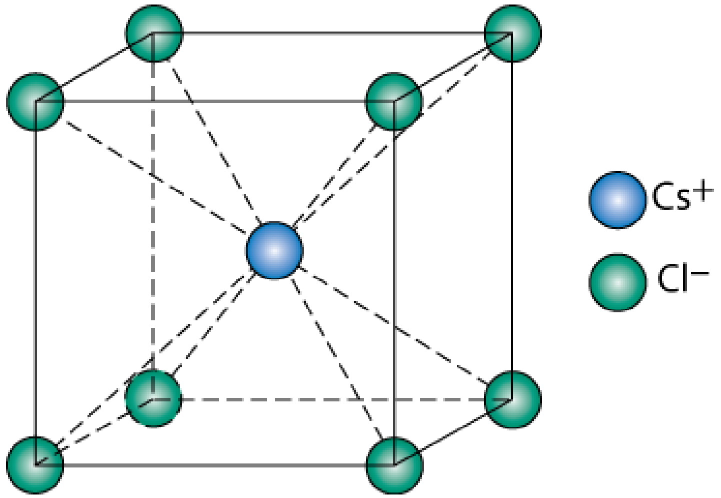
CaF_2 type



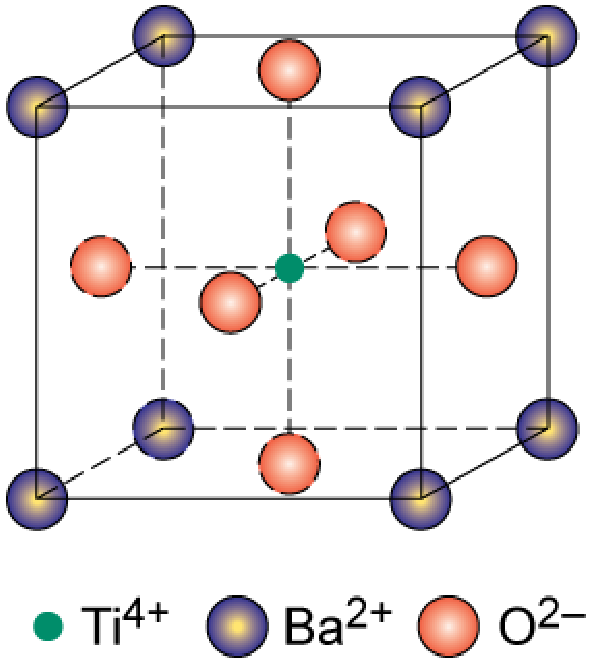
Graphite type



CsCl type



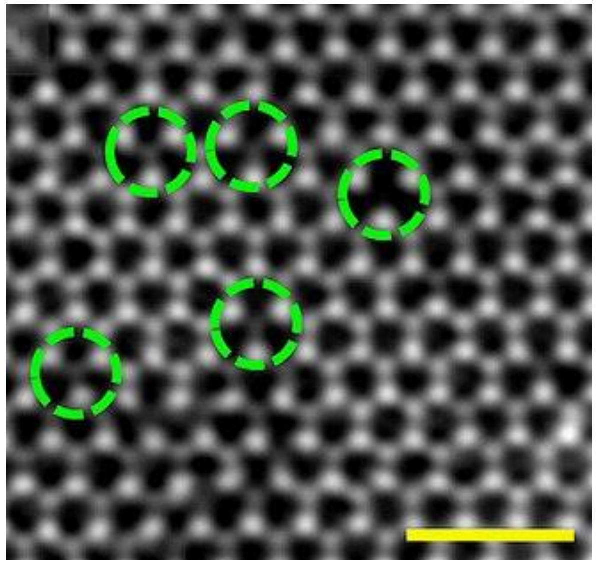
$BaTiO_3$ type



Defects in Ceramics

Point (0D) defects

(e.g., vacancy, interstitials, substitution atom)

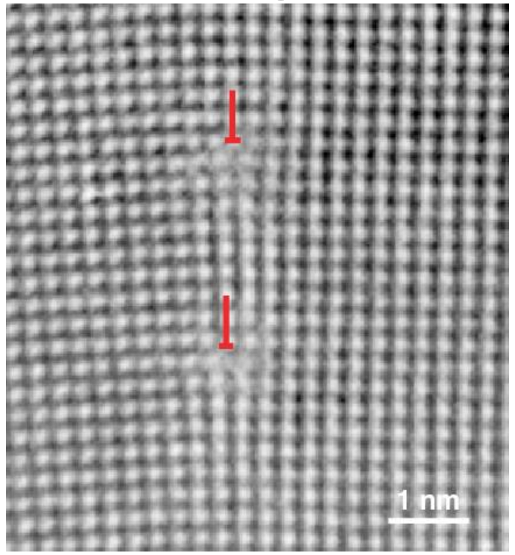


Sulfur vacancy in MoS_2 monolayer

Hong et al., Nature Comm v6, 6293 (2015)

Line (1D) defects

(e.g., dislocations)

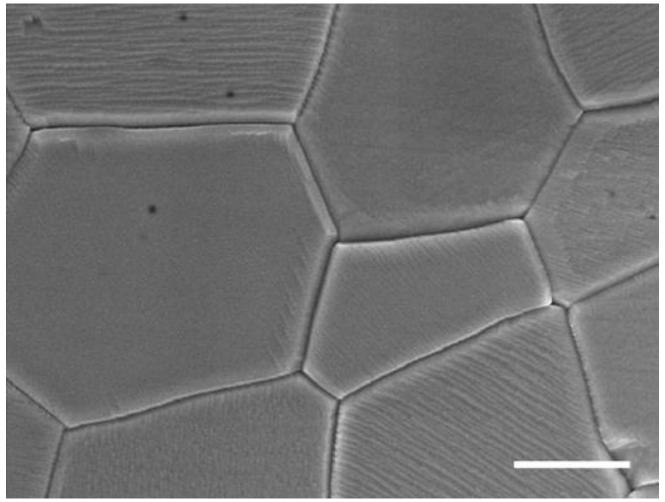


Edge dislocation in $SrTiO_3$

Sigle et al. Philosophical Magazine v86(29-31), 4809, (2006)

Plane (2D) defects

(e.g., surface, grain boundaries, twins)

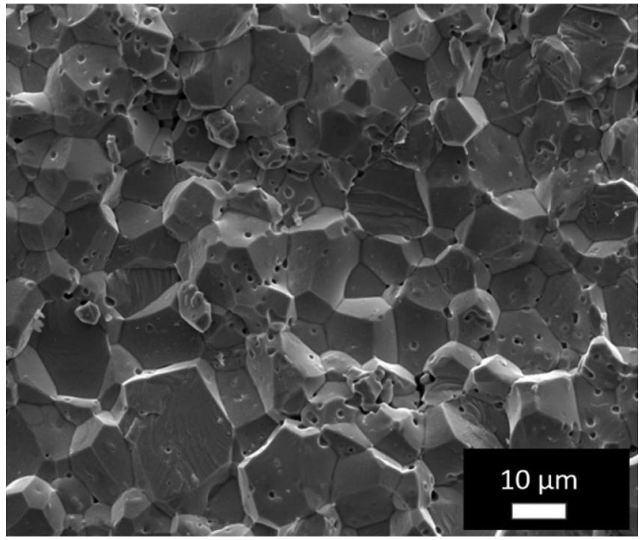


Grain boundaries in Al_2O_3

Sayed et al., Acta Materialia v227, 117685 (2022)

Volume defects

(e.g., impurity phase, pores, cracks)



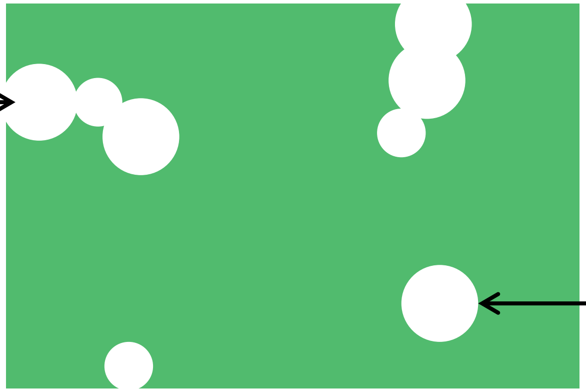
Pores in sintered ZrN

Das et al., J Am Ceram Soc v105, 3925 (2022)

Pores & Porosity in Ceramics

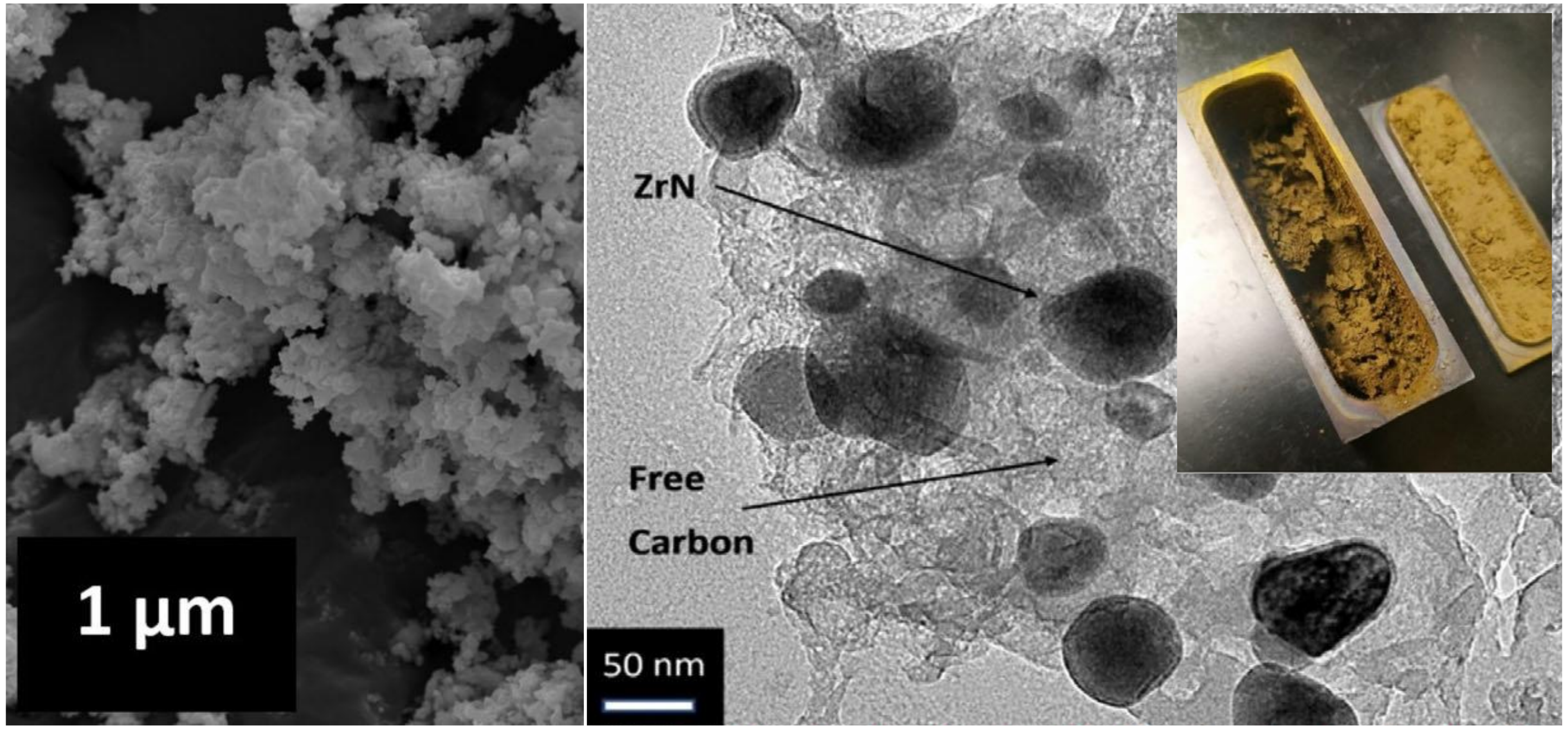
- Ceramics are often “sintered” from powders into bulk materials, w/o melting
- Open and closed pores in ceramics after left, after sintering

Open pores (connected w/ outside)

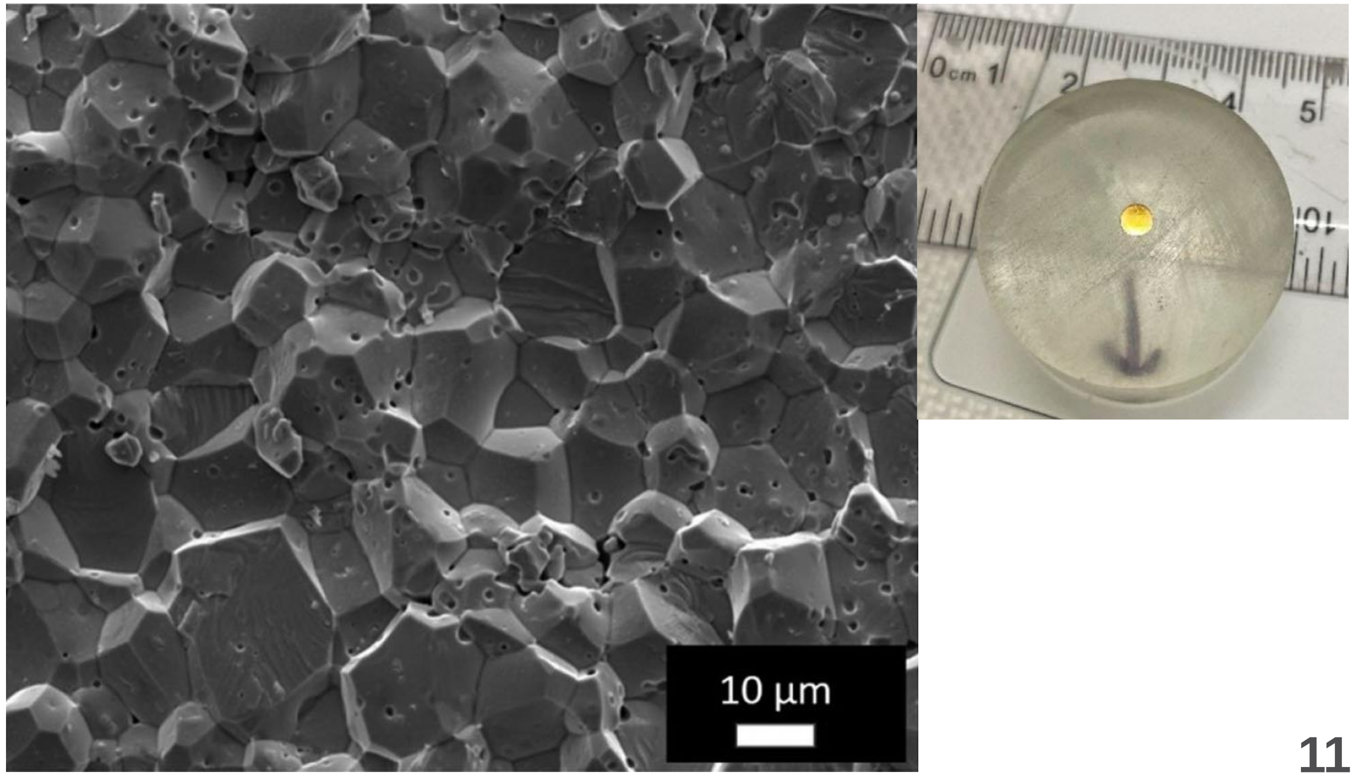


Closed pores (isolated from outside)

ZrN powder

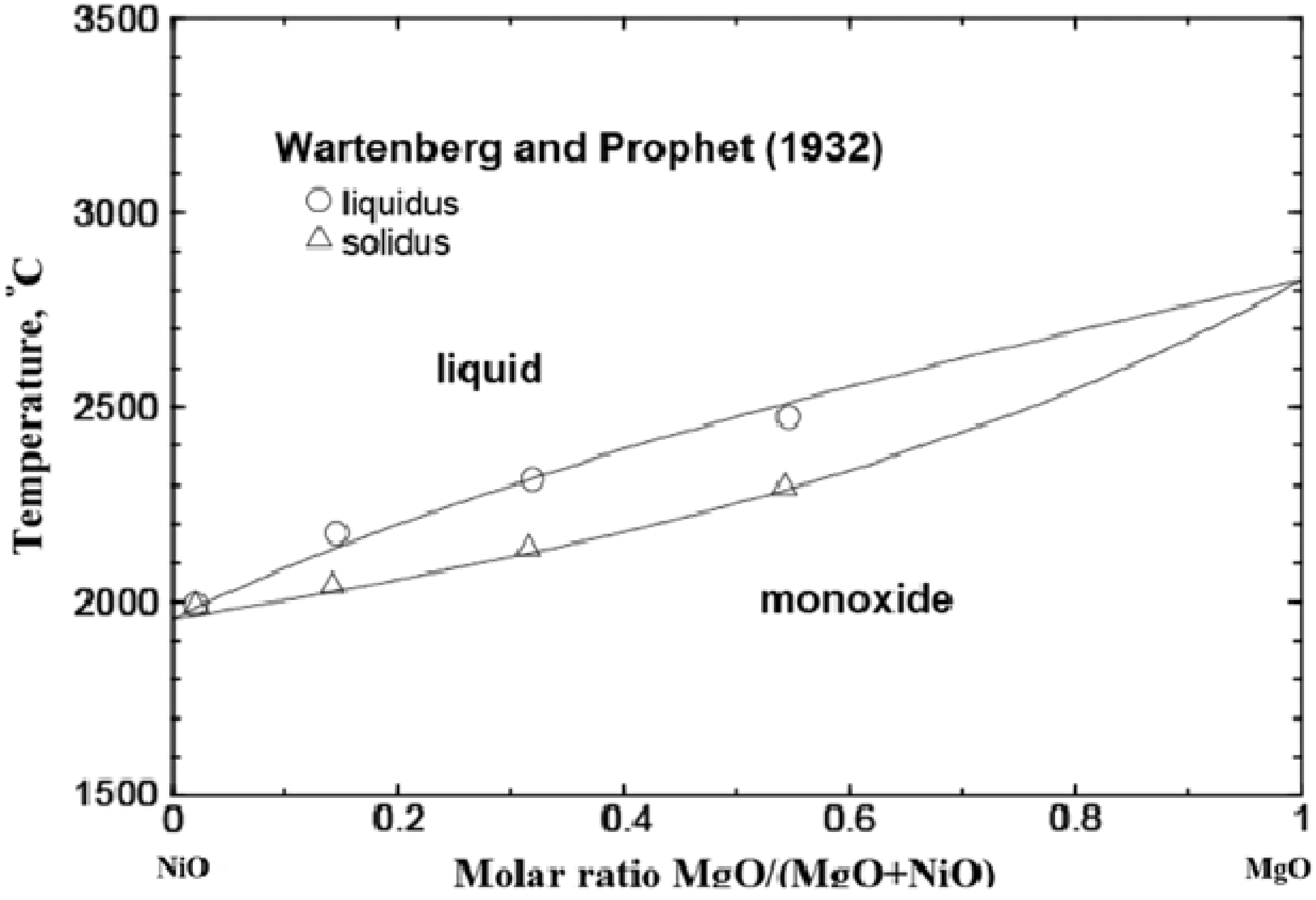


Sintered ZrN showing porosity

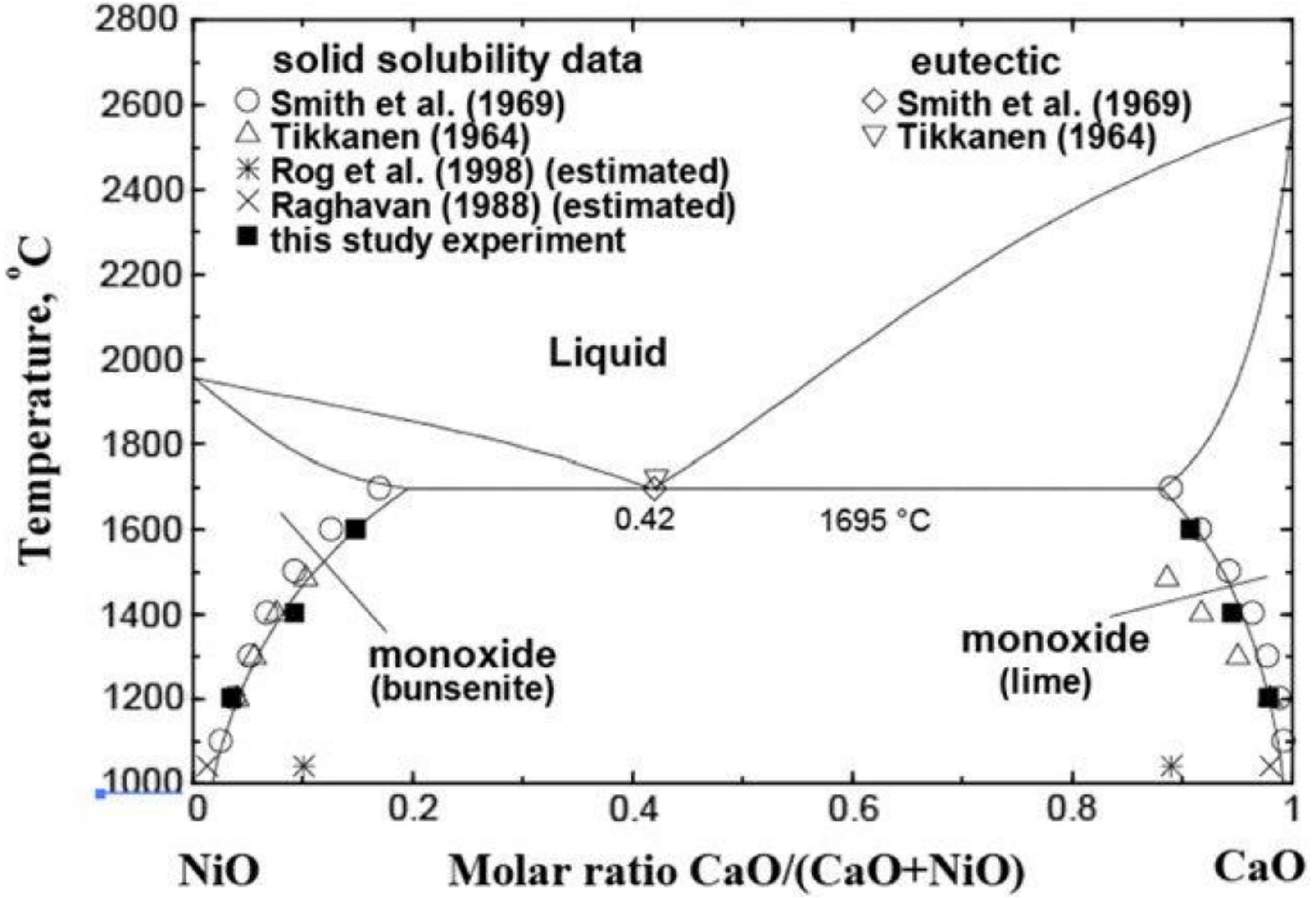


Ceramic Phase Diagram Examples

NiO - MgO



NiO - CaO

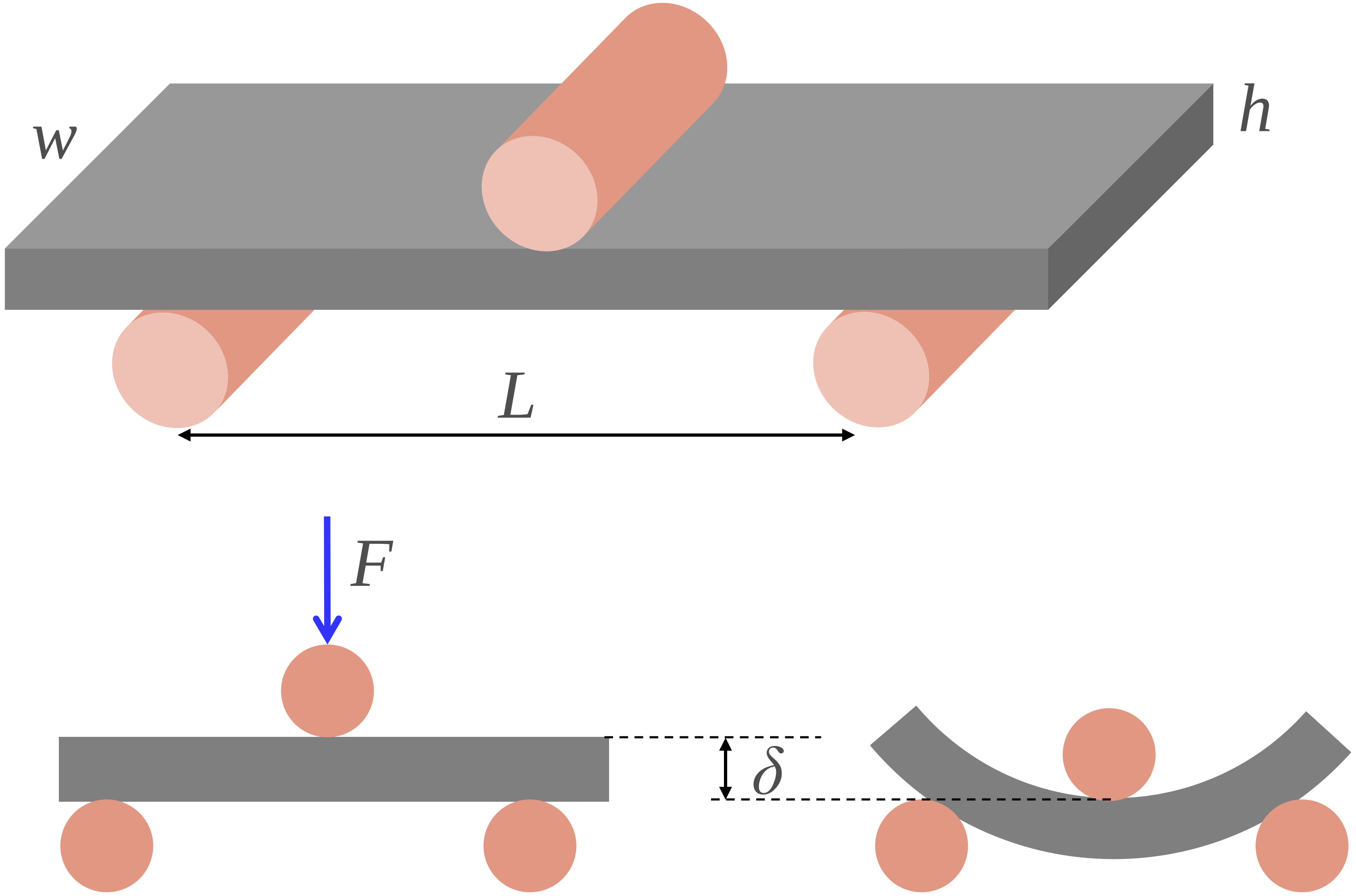


Same principles for:

- Number and identity of phases present
- Compositions (chemistry) of each phase
- Relative amount (i.e., weight or molar fraction) for each phase

Measurement of Mechanical Properties for Ceramics

- Mechanical properties of ceramics measured by bending or flexural tests instead of tensile test due, partly, to difficulty with tight clamping required for tensile tests



Bending modulus

$$E = \frac{L^3 F}{4wh^3 \delta}$$

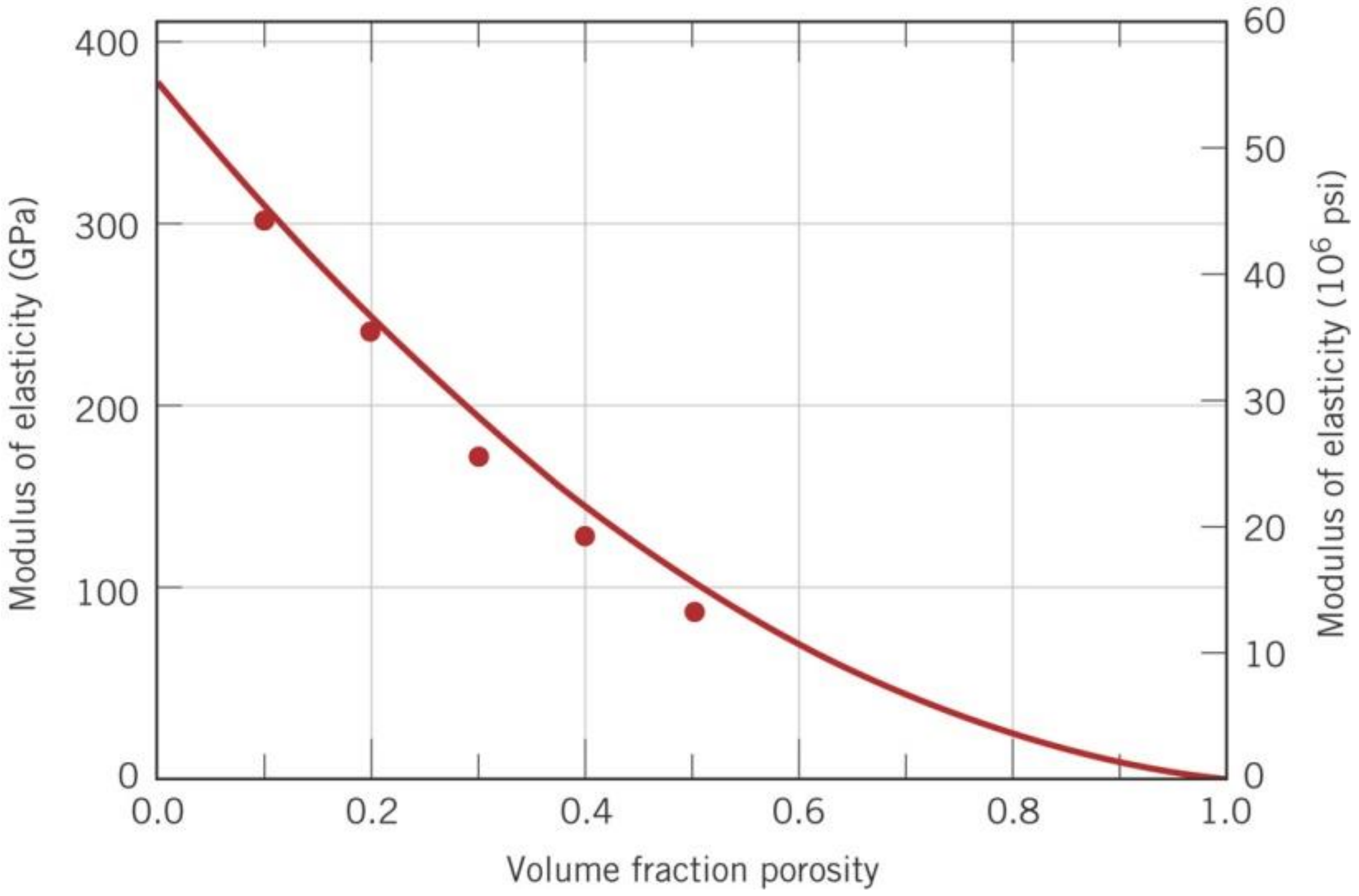
Flexural strength (3-point)

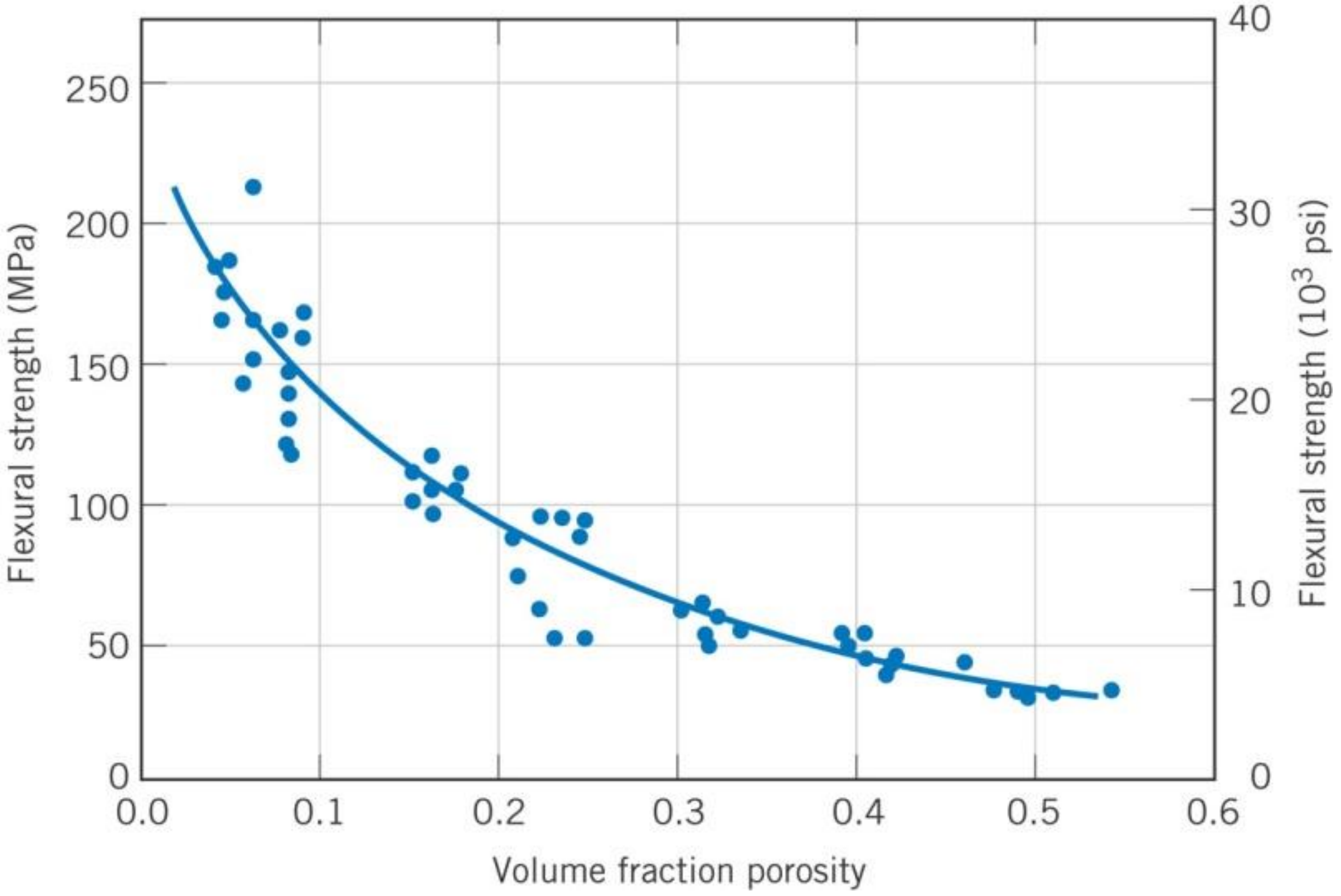
$$\sigma_{flexural\_3} = \frac{3FL}{2wh^2}$$

* 4-point bending suitable for samples containing flaws due constant momentum (pure bending)

Change of Ceramics Mechanical Properties with Porosity

Elastic modulus & flexural strength decrease as porosity/pore volume fraction increases



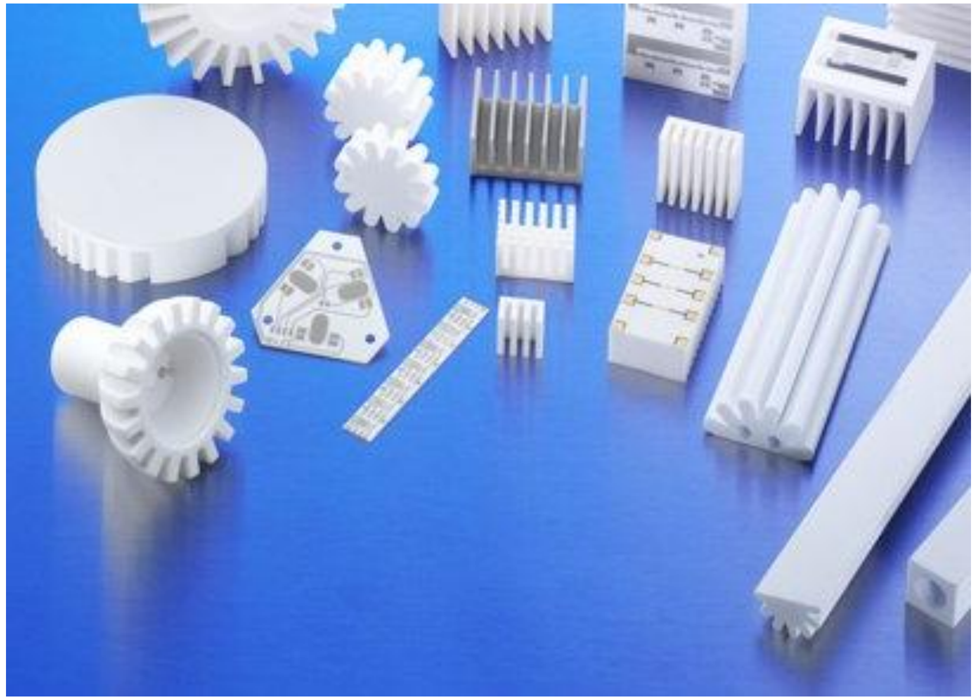


Ceramic Processing from Powders/Particulates

- Due to their generally high melting points, **ceramics**, especially common oxides, carbides, nitrides, are almost **never casted**

Material	Al	Fe	Cast iron	Ti	Al_2O_3	MgO	SiO_2	SiC	WC	TiN
T_m (°C)	660	1538	~1150	1668	2072	2800	1710	2700	2870	2950

- Ceramics are mostly processed from **powders/particulates**, w/ following steps:
  - Green body formation
  - Firing/sintering
    - ✓ Remove organics
    - ✓ Bond powders/particulates together
    - ✓ Eliminate (at least reduce) porosity



Green Body Formation (1) - Mechanical Compaction

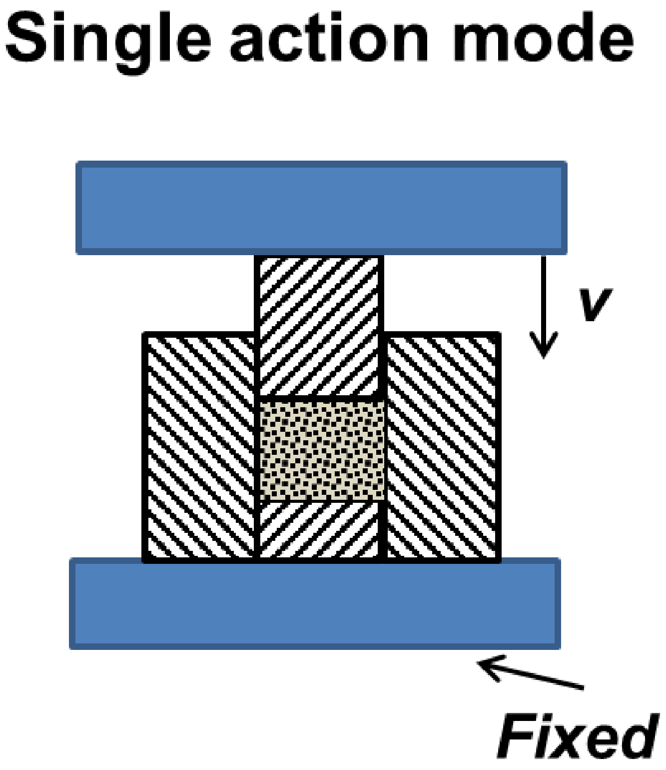
Mechanical compaction

Pressing dry or semi-dry powders in metal dies with mechanical pressure (uniaxial or isostatic)

- Advantages: simplest, fast process
- Disadvantages: limited shape/dimension and microstructure uniformity

Dry-pressing die

Press



http://www.ebay.co.uk/itm/20mm-Diameter-ID-Pellet-Press-Steel-Dry-Pressing-Die-Set-Mold-/200438956668

Green Body Formation (2) - Casting (of Slurry/Suspension)

Casting (of slurry/suspension)

Casting ceramic powder slurry/suspension w/ low enough viscosity that flows under its own weight

- Advantages: form complex shape
- Disadvantage: involves drying of solvent, volume shrinkage might be large

Casting green ceramic ware

http://www.veniceclayartists.com/african-pottery-arts-traditional-contemporary/

Tape-casting green ceramic tape

http://www.cgcri.res.in/page.php?id=43

Green Body Formation (3) - Plastic Forming

Plastic forming

Plastically shaping thick ceramic powder paste/doll by applying mechanical stress

- Advantages: fast, continuous production
- Disadvantages: limited shape/dimension

Extrusion of ceramic honeycomb

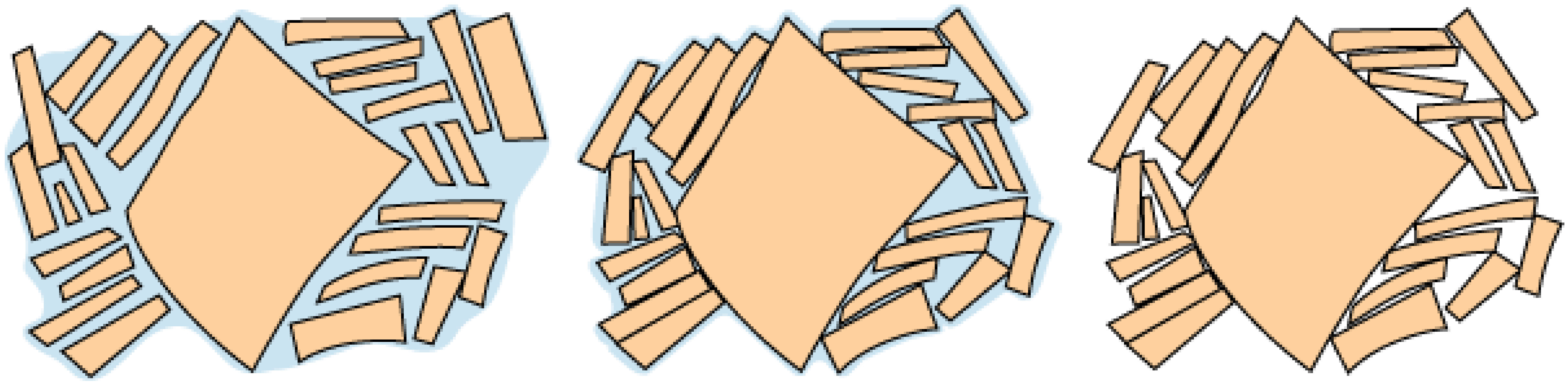
Extruded ceramic parts after sintering

http://www.ikts.fraunhofer.de/en/research_fields/processes_and_components/Shaping/Extrusion.html

Drying

After ceramic green body formation via extrusion, slip casting or tape casting, the products need to go through “drying” to remove solvents (e.g., water or other solvents)

- As solvent (e.g., water) is removed - interparticle spacings decrease, and relative density increase



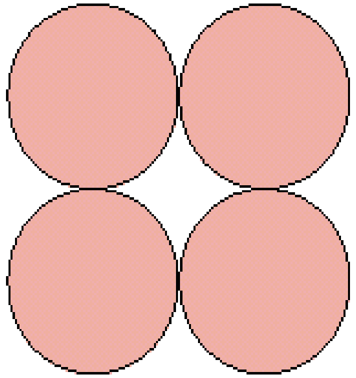
Wet body　　Partially dry　　Completely dry

- Drying too fast causes samples to **<u>warp</u>** or **<u>crack</u> due to non-uniform <u>shrinkage</u>**

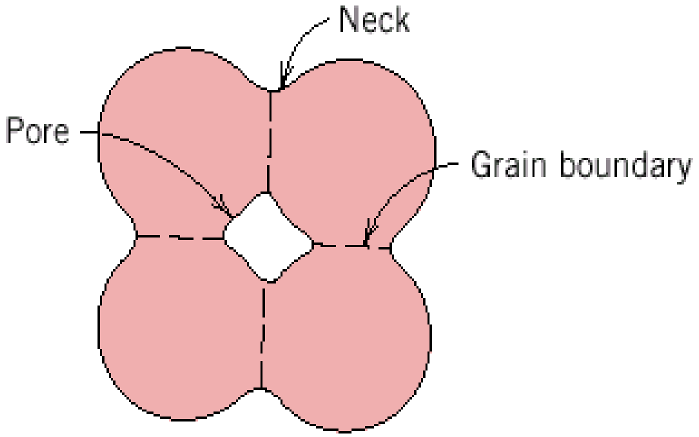
Firing/Sintering

Firing or sintering of green ceramic bodies at high temperature (e.g., >~1200 ^{o}C) have to be carried out to bond the powders together and eliminate (or, at least, reduce) the porosity so that desirable mechanical and other properties are obtained

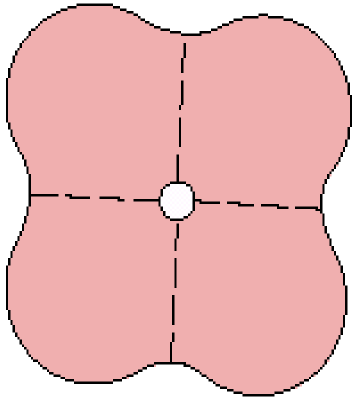
Green body

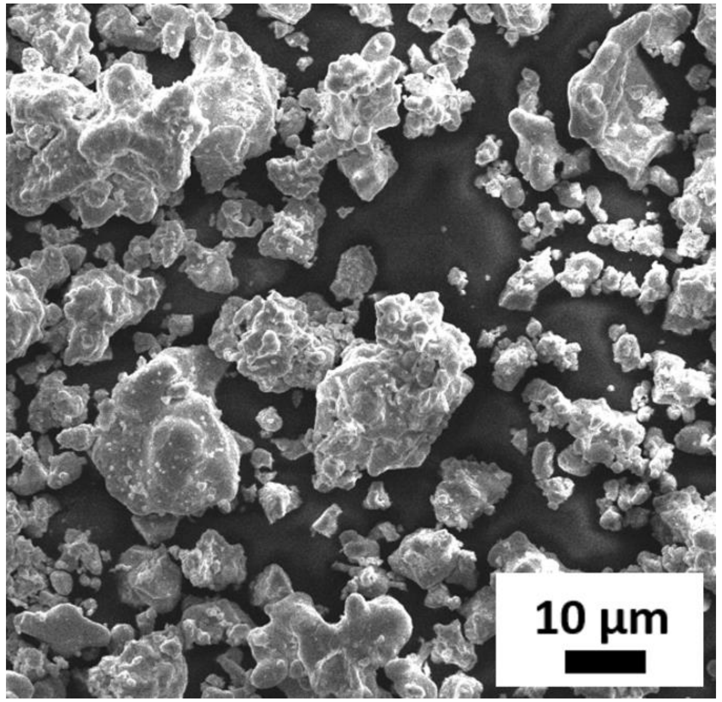


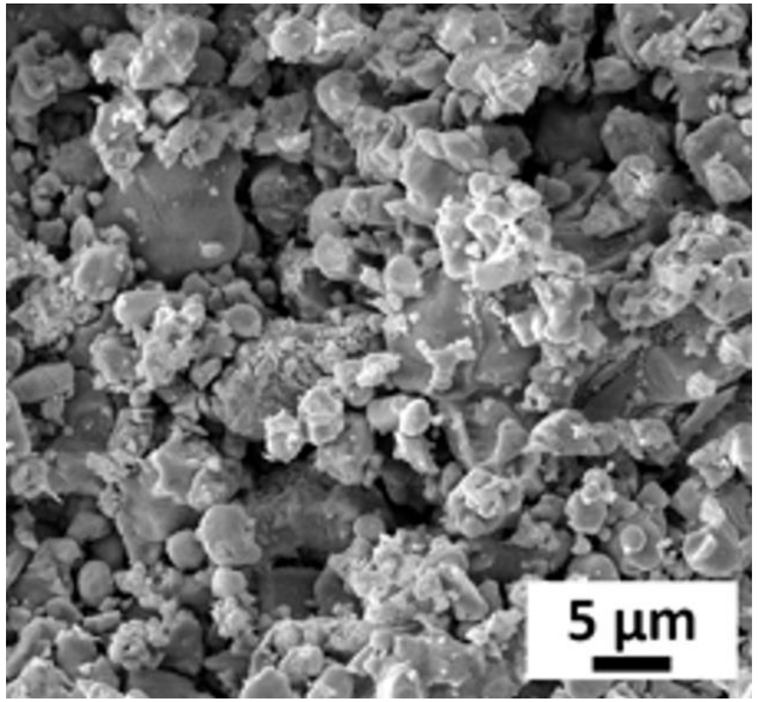
Partially sintered

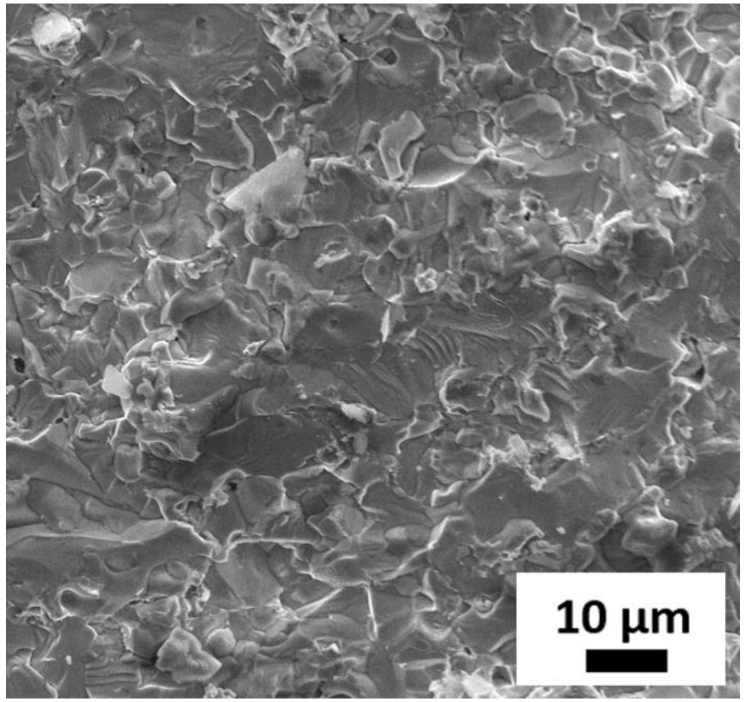


Near fully sintered









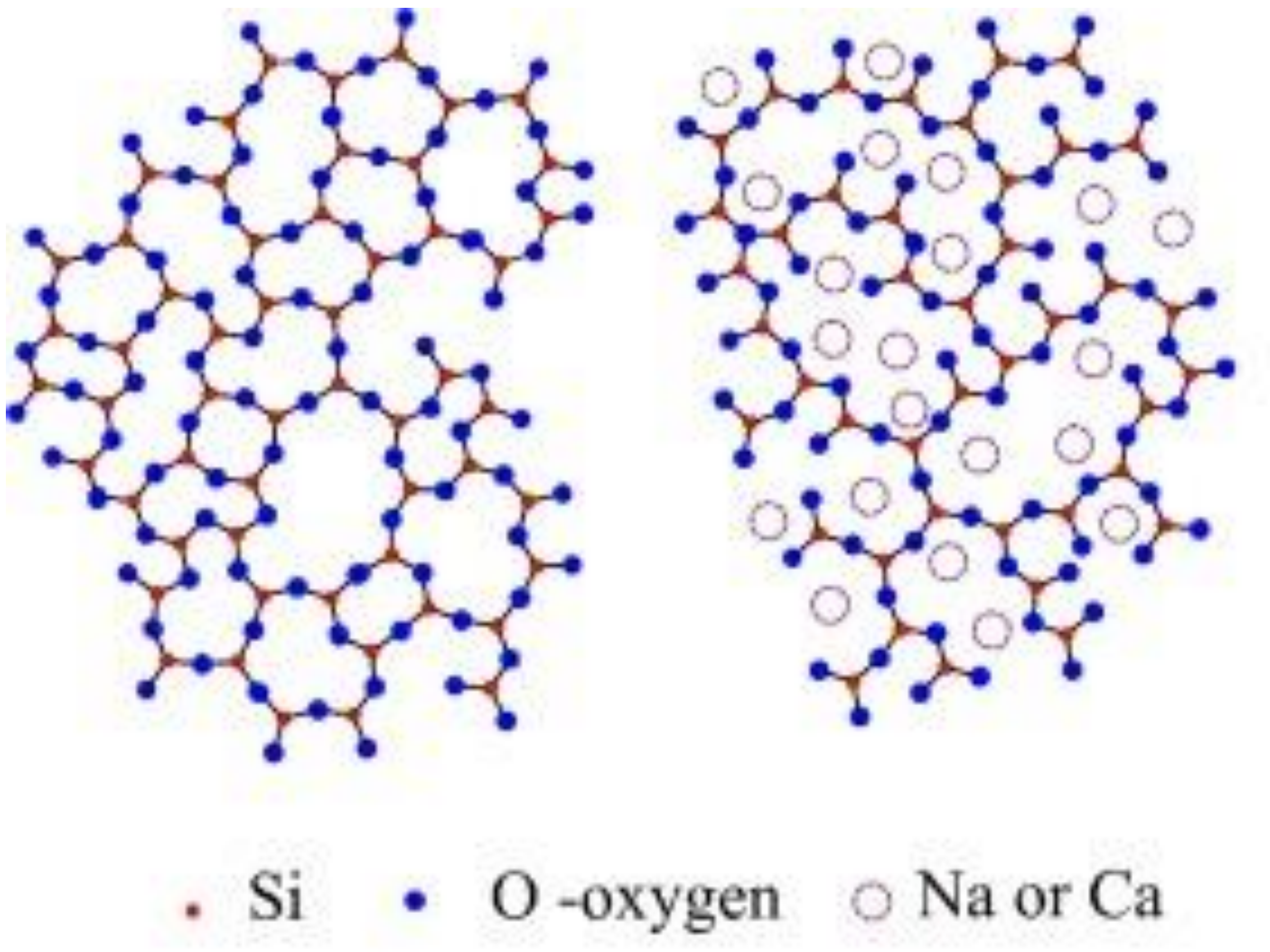
Eskandariyun et al., J Am Ceram Soc v107, p3735 (2024)

Glass

- **Amorphous** or **non-crystalline solid** material

- Under the same condition, often **higher energy** state and **less stable** than the corresponding crystalline state

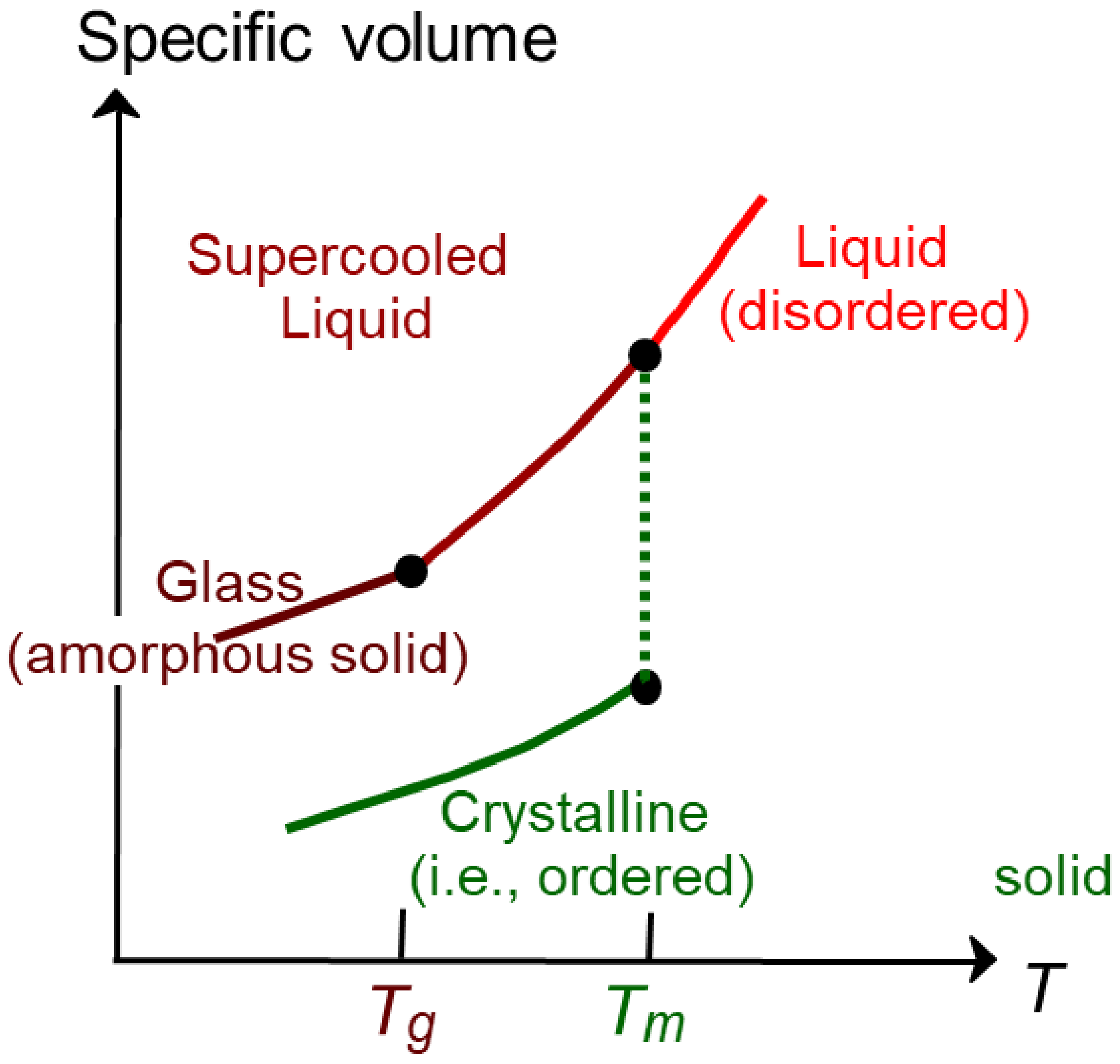
- Formed often in **complex** systems via **rapid cooling**, i.e., not giving enough time to form regular, crystalline structure



(a) Silica Glass (b) Na-Ca Silicate Glass

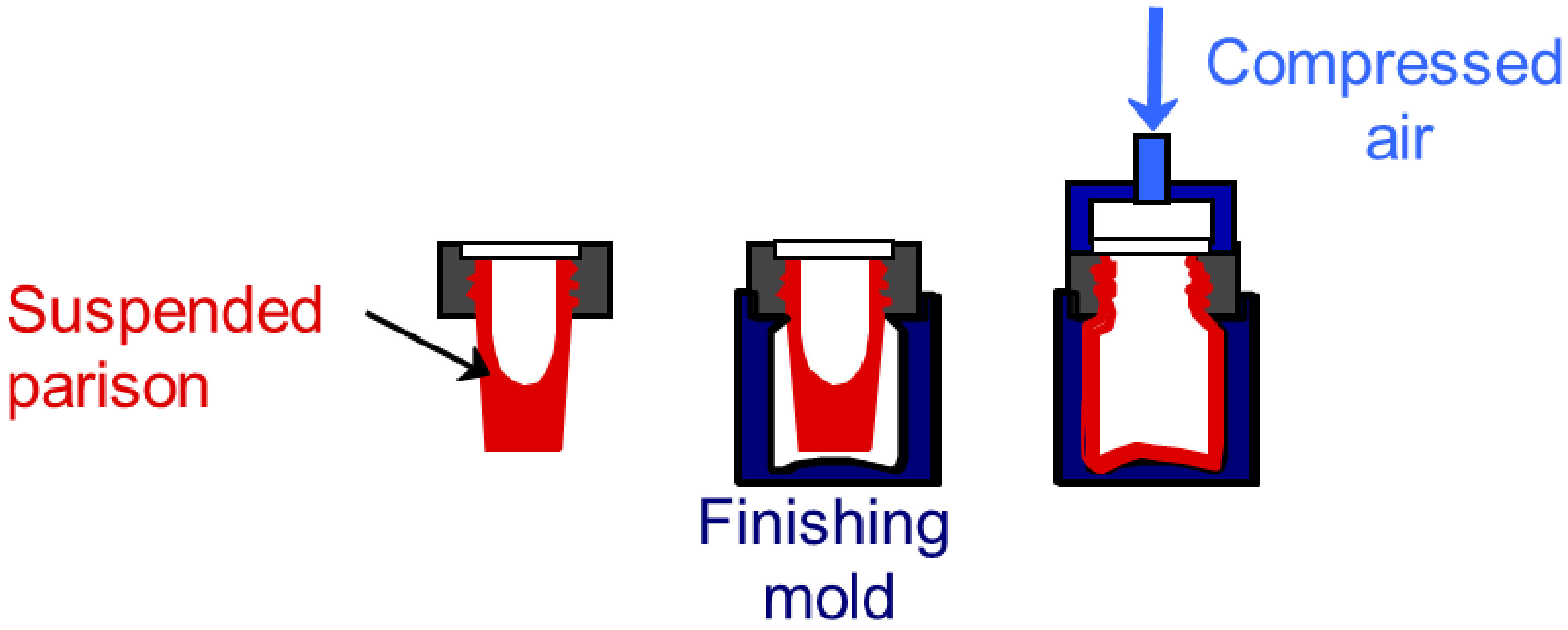
Glass Transition

- Glass can be viewed as super cooled liquid – liquid cooled below equilibrium melting point T_m
- Viscosity for glass/supercooled liquid continue to increase as T drops, until essentially infinity or slope change in physical property such as specific volume, at a critical temperature - glass transition temperature T_g.
- No grain boundaries
- Long time heating of glass at or above T_m lead to transition to crystalline phase(s)

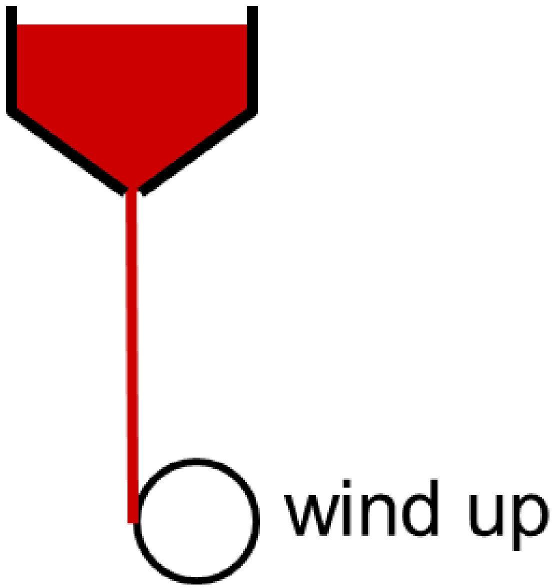


Glass Processing (1)

- Process from melt/liquid
- Plastic formation

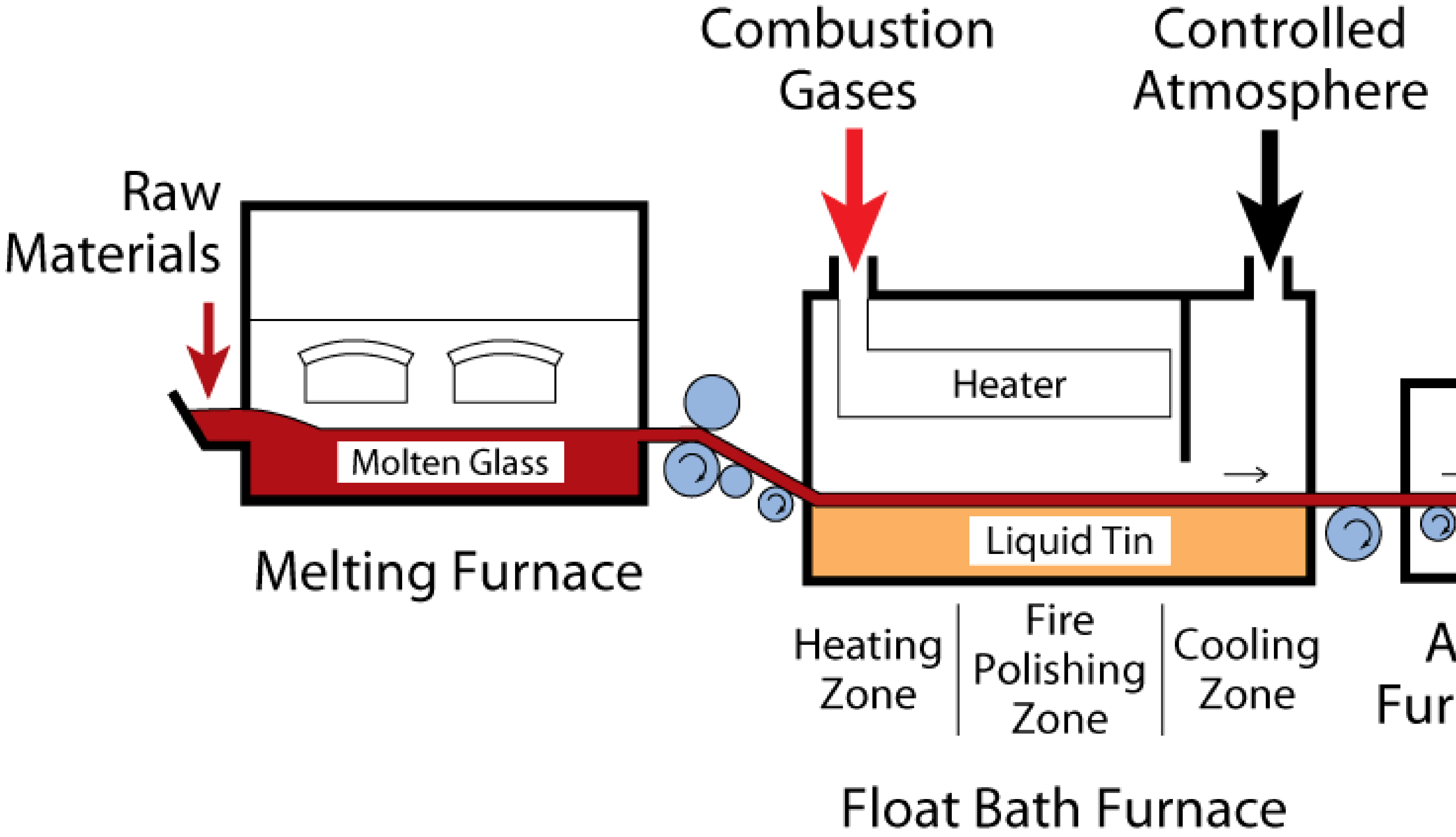


- Fiber drawing:



Glass Processing (1)

Continuous casting: glass sheets formed by floating the molten glass on molten metal



END

Homework 0

Carefully review chapter 15 lecture slides and, if interested, read textbook sections of Askeland 15 and give an honor statement confirming the reading