Lecture 8: Structure, properties, and applications of ceramics

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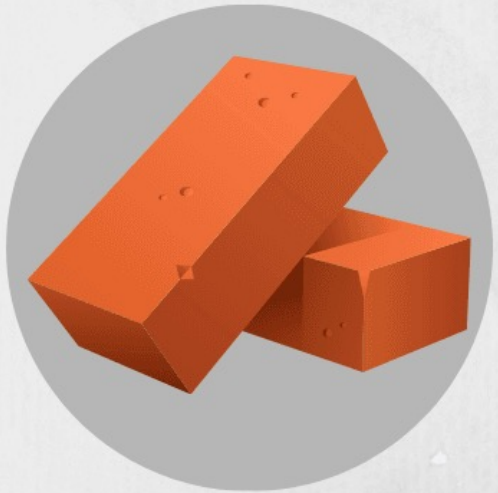
What Is a Ceramic?

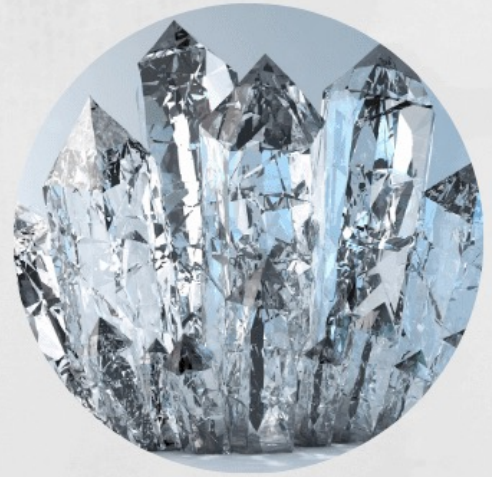
A ceramic is a crystalline non-metallic inorganic material.

Most ceramics are hard, brittle, and corrosion-resistant.

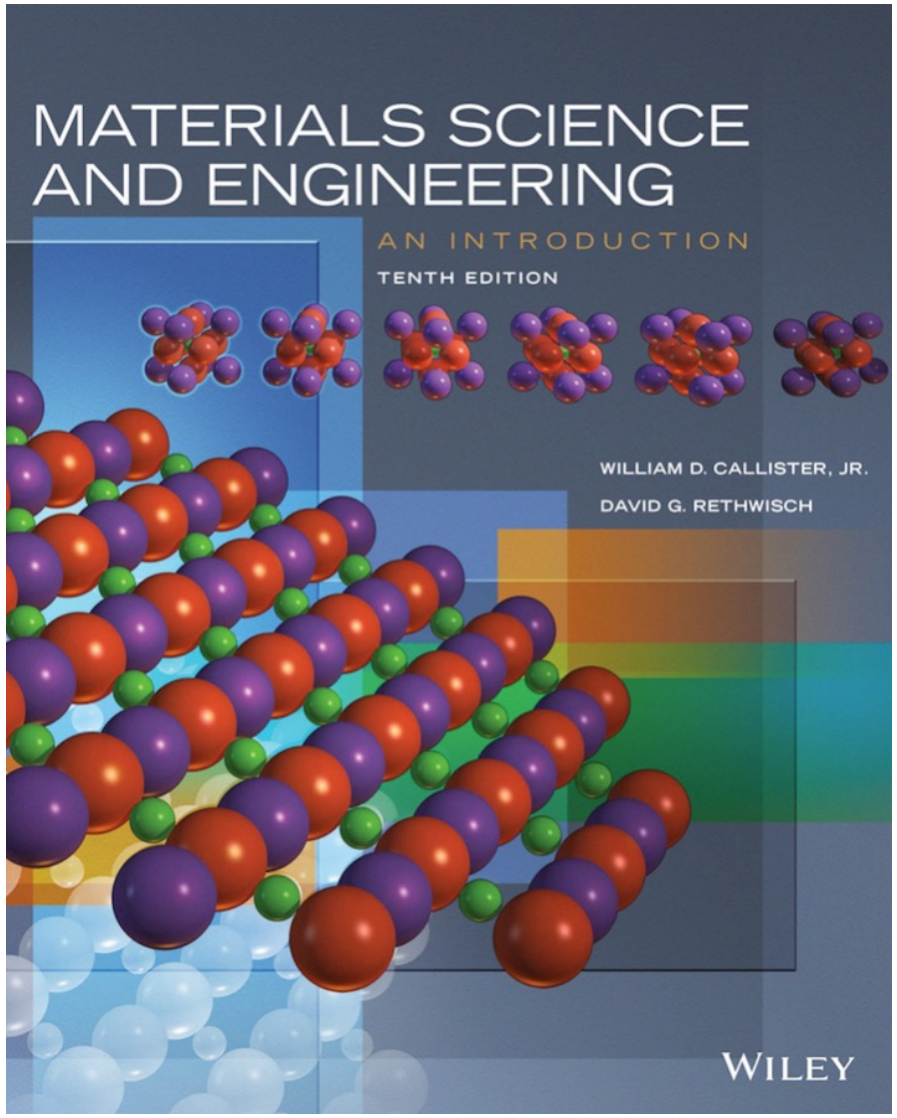






Reading for this subject



Chapter 12 Structures and Properties of Ceramics

This discussion will closely follow **Chapter 12** of Callister, **pages 406-438** of the 10th edition.

So far, we've been largely focused on metals

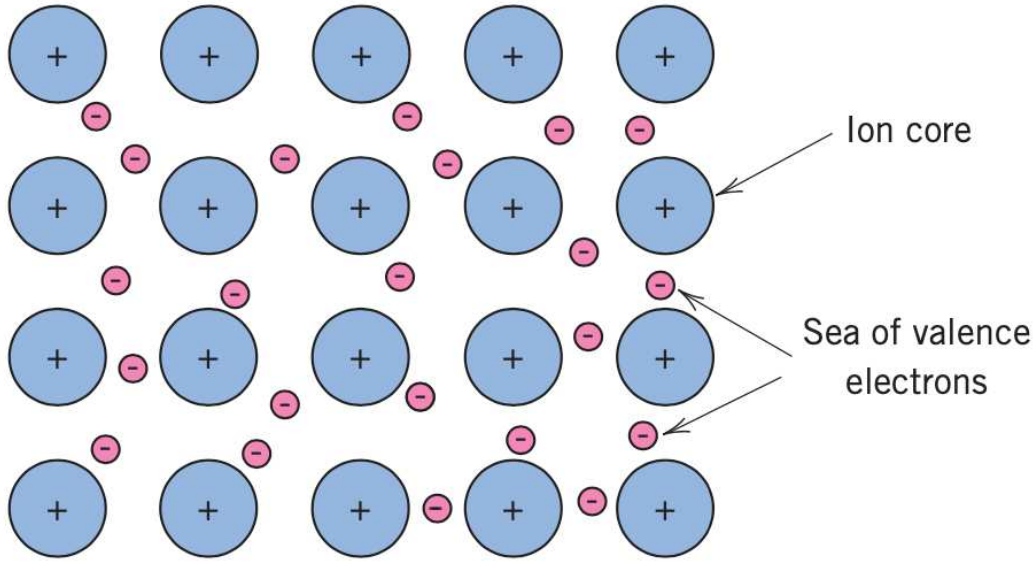


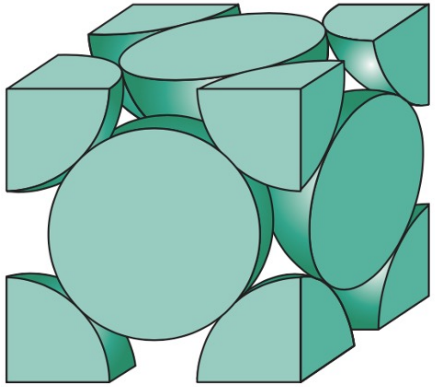


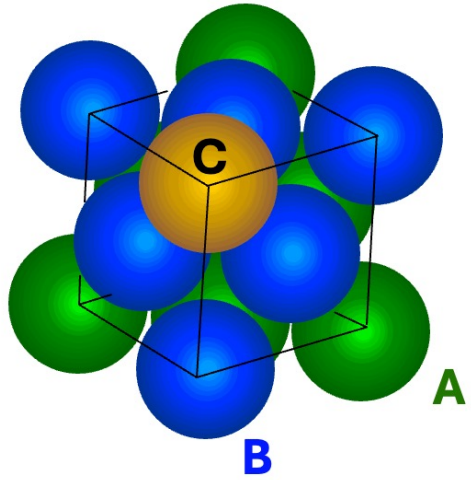
1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	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 Caesium	56 Ba Barium	57 La* Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89 Ac** Actinium	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessine	118 Og Oganesson

Metals

*	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
**	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium





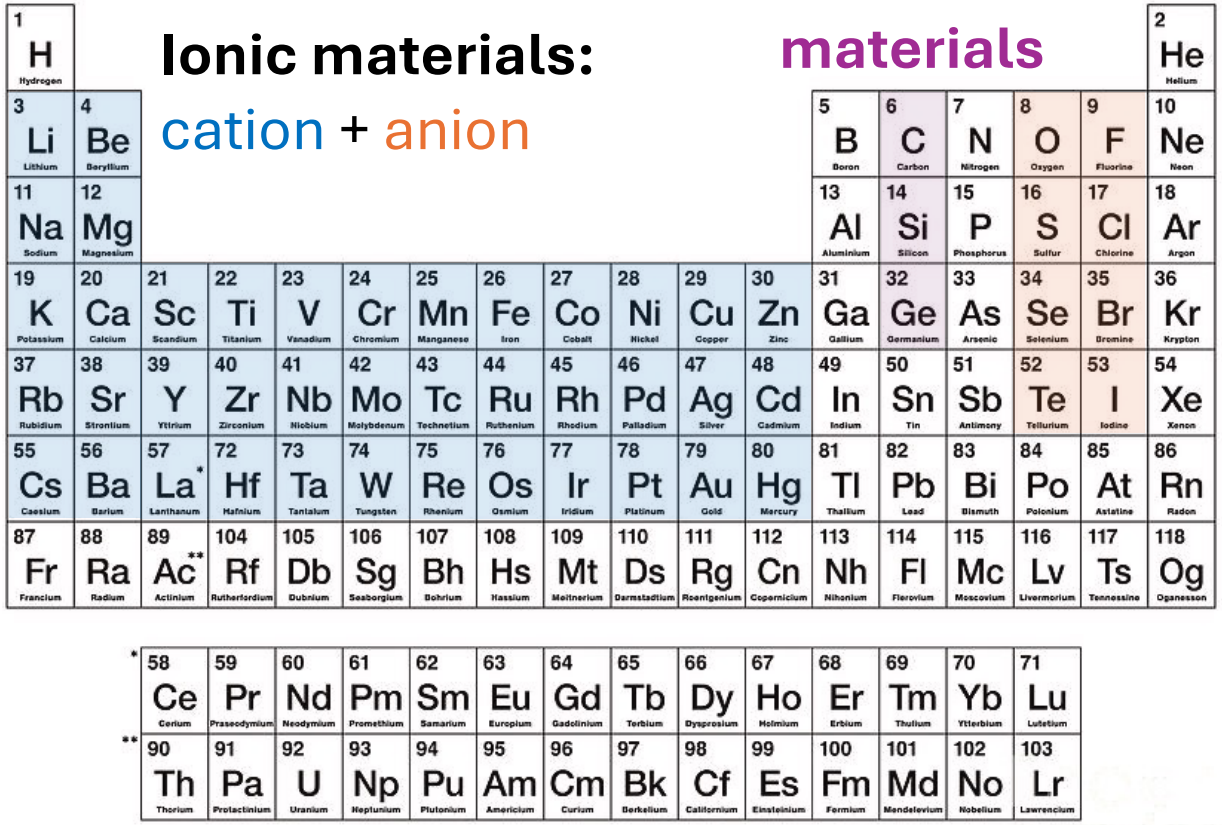


- Metals adopt **close-packed structures**
- They are **often ductile** because these dense planes can slip past one another

Let's transition to ceramics – how do these differ?

Ionic materials:
cation + anion

Covalent materials



Most ceramics have a mix of ionic and covalent bonding

Material	*Percent Ionic Character*	
CaF_2	89	Very ionic
MgO	73	
$NaCl$	67	
Al_2O_3	63	
SiO_2	51	
Si_3N_4	30	
ZnS	18	Very covalent
SiC	12	

The distinct nature of bonding leads to **very different structures from metals**

Crystal structure of ceramic materials

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
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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
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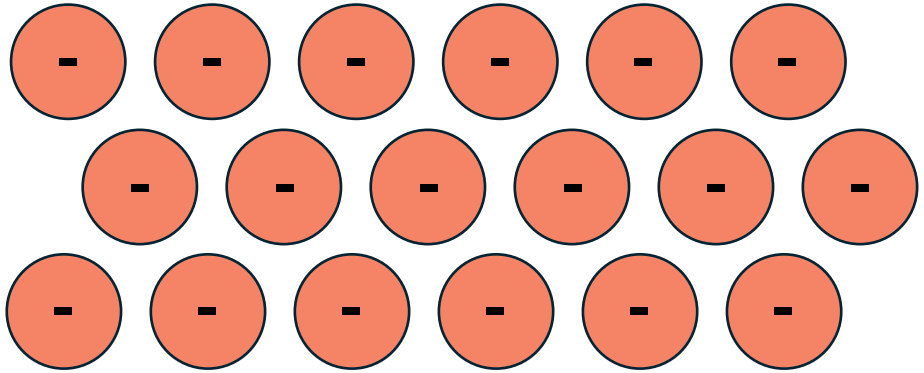
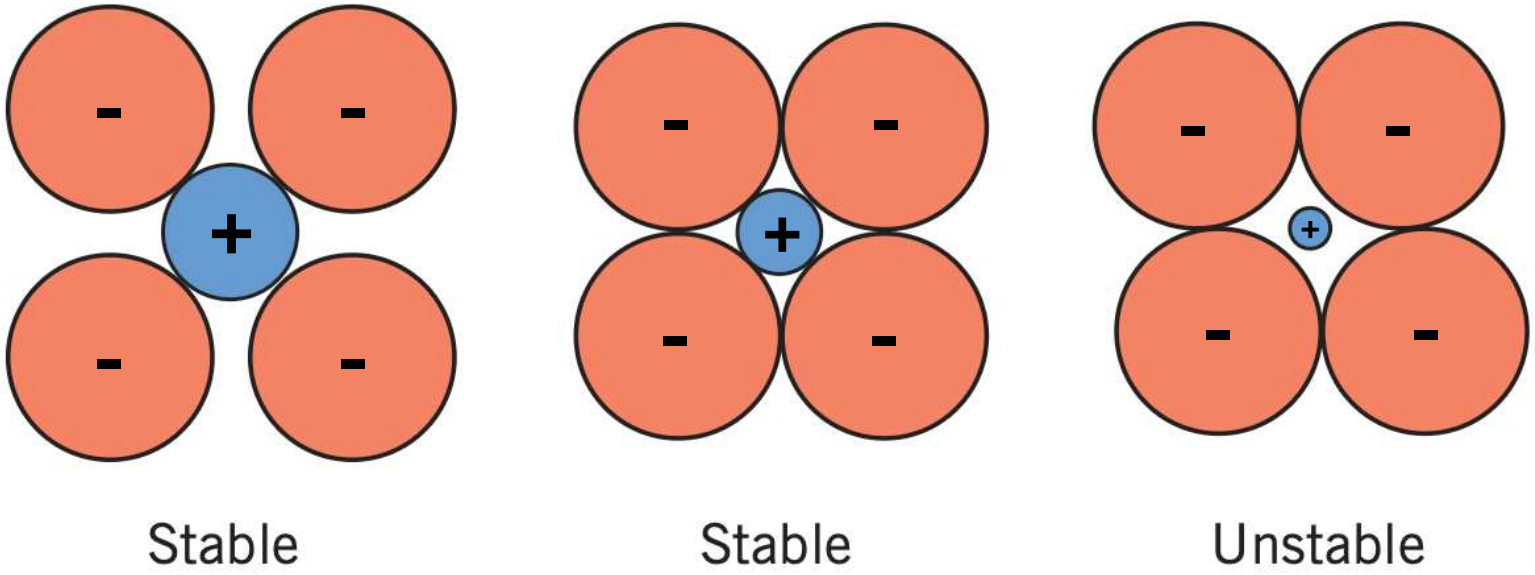
Let's start by thinking of the **anions** as a sublattice. Keep in mind: these are **big** and **negatively charged.**



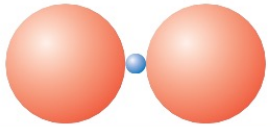
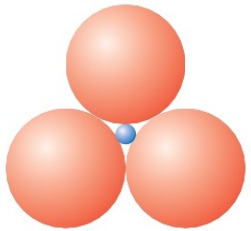
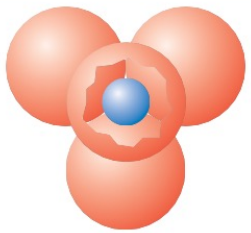
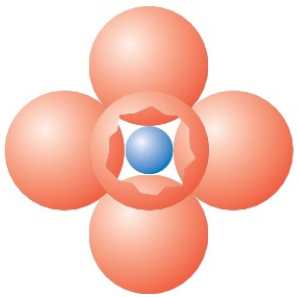
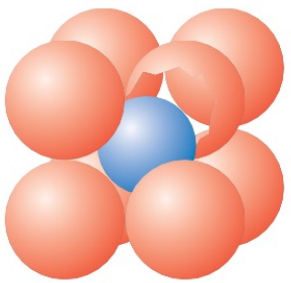
As we add **positively charged cations**, they will fill the voids in such a way to **minimize the electrostatic energy**.

How do anions arrange around this?

Crystal structure of ceramic materials



- It is most favorable to maximize the number of cation-anion neighbors, while minimizing the like-ion overlap (*e.g.*, anions should not touch)
- This leads to **Pauling's rules** for bond coordination based on the ratios of cation radii (r_C) to anion radii (r_A)

Coordination Number	*Cation–Anion Radius Ratio*	*Coordination Geometry*
2	<0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	

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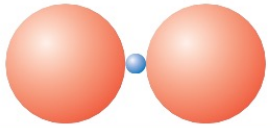
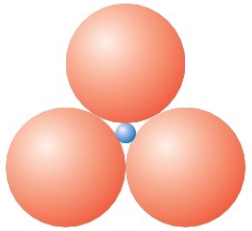
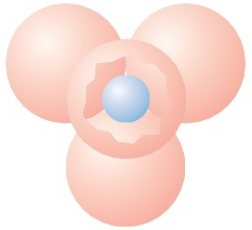
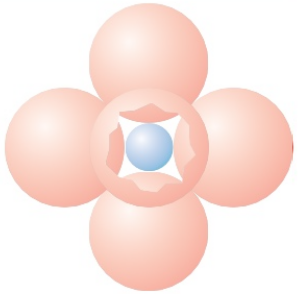
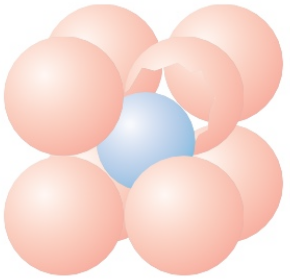
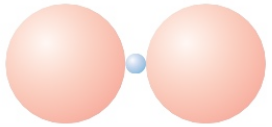
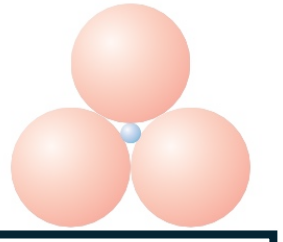
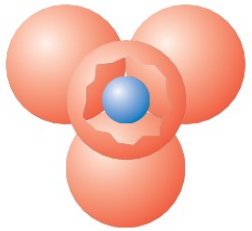
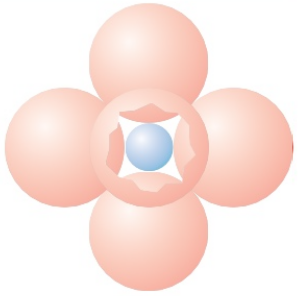
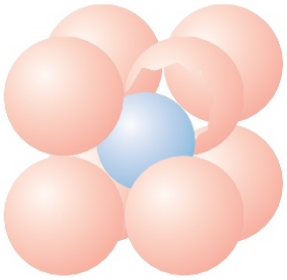
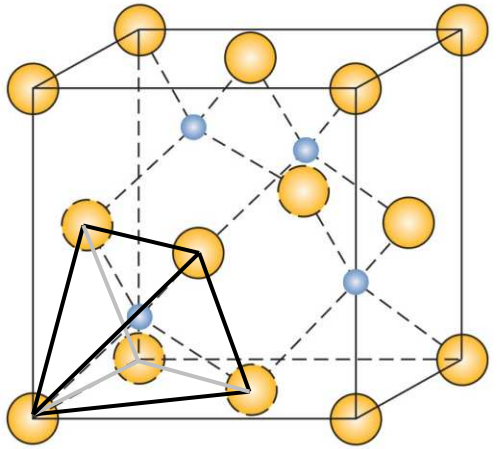
2	<0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	

Large mismatch in ionic radii
→ a **linear** or **trigonal** coordination is adopted to maximize the separation between anions

This is relatively rare…

Coordination Number	Cation–Anion Radius Ratio	Coordination Geometry
2	<0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	



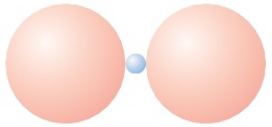
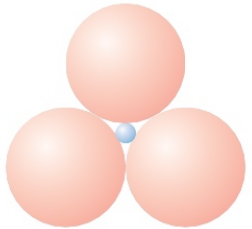
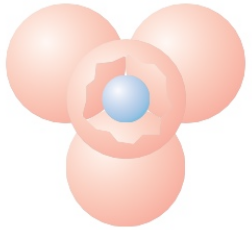
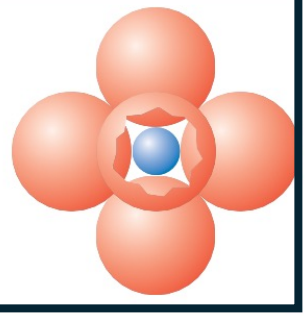
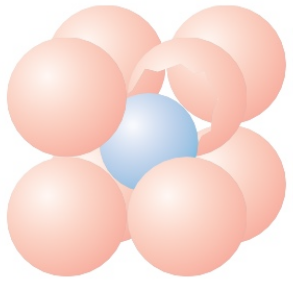
Example: **ZnS**

Zn S

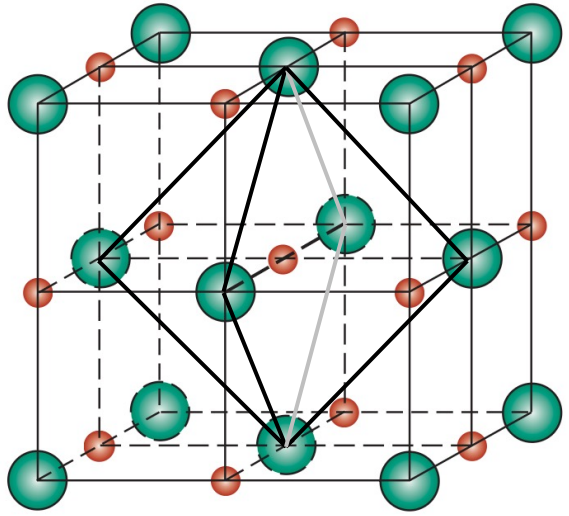
Moderate mismatch in ionic radii → a **tetragonal** coordination is adopted. This is quite common!

Notice: this structure (**zincblende**) is just an FCC arrangements of anions (S) with half the tetrahedral voids filled in with cations (Zn)



Coordination Number	Cation–Anion Radius Ratio	Coordination Geometry
2	<0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	



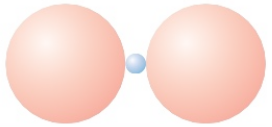
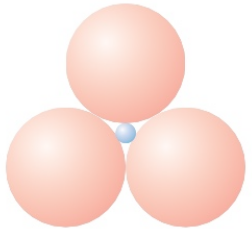
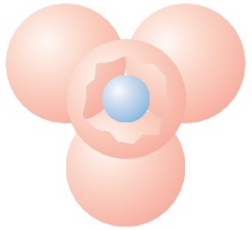
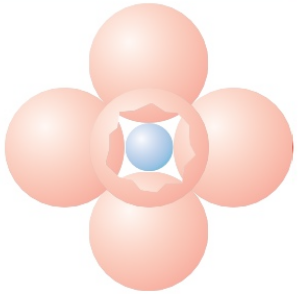
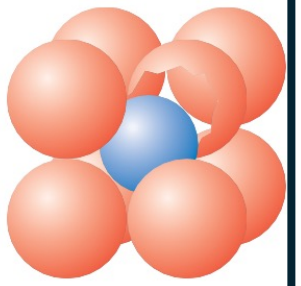


Example: **NaCl**

Na^+ Cl^-

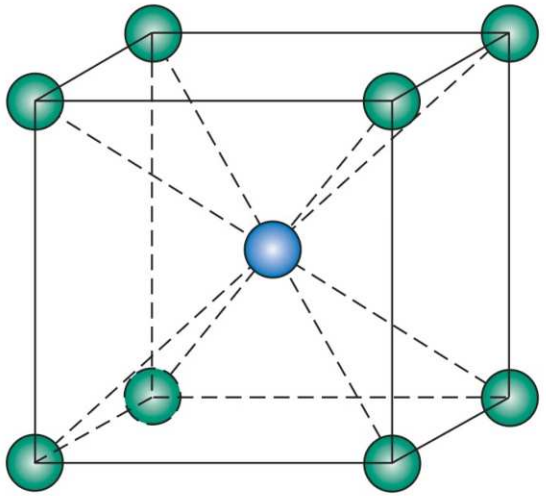
Small mismatch in ionic radii → an **octahedral** coordination is adopted. Even more common!

Notice: this structure (**rocksalt**) is just an FCC arrangements of anions (Cl) with all the octahedral voids filled in with cations (Na)

Coordination Number	Cation–Anion Radius Ratio	Coordination Geometry
2	<0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	



Notice: this structure (**CsCl**) is just a simple cubic arrangement of anions (Cl) with all the square (8-coord) voids filled in with cations (Cs)



Example: **CsCl**



Little to no mismatch in ionic radii
→ a **square** coordination is adopted.

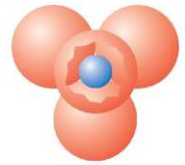
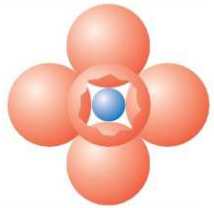
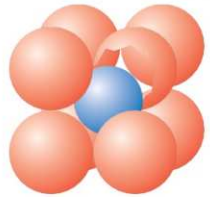
Example problem: predicting structure

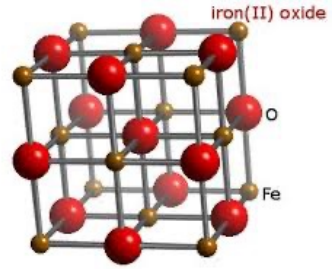
On the basis of ionic radii, **what crystal structure would you predict for FeO?**

Cation	Ionic radius (nm)
Al^{3+}	0.053
Fe^{2+}	0.077
Fe^{3+}	0.069
Ca^{2+}	0.100

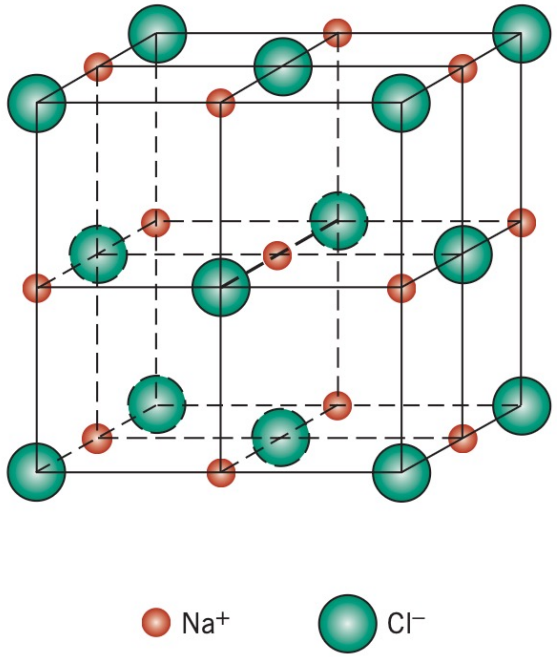
Anion	Ionic radius (nm)
O^{2-}	0.140
Cl^{-}	0.181
F^{-}	0.133

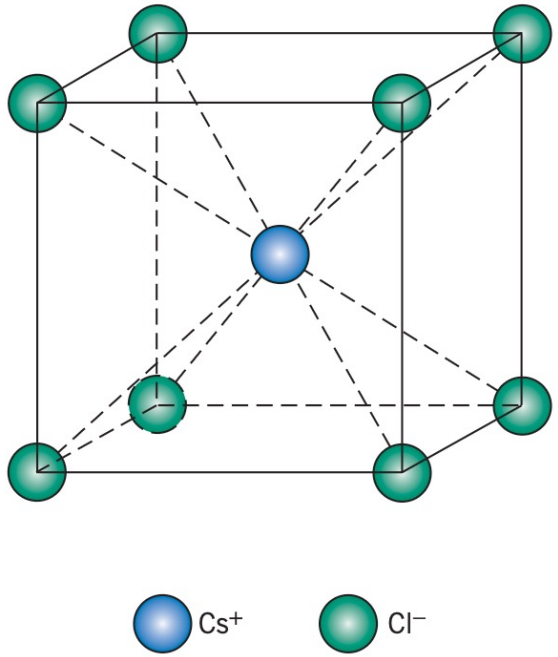
$$\frac{r_C}{r_A} = \frac{0.077}{0.140} \approx 0.55 \longrightarrow$$ **Rocksalt (NaCl)!**

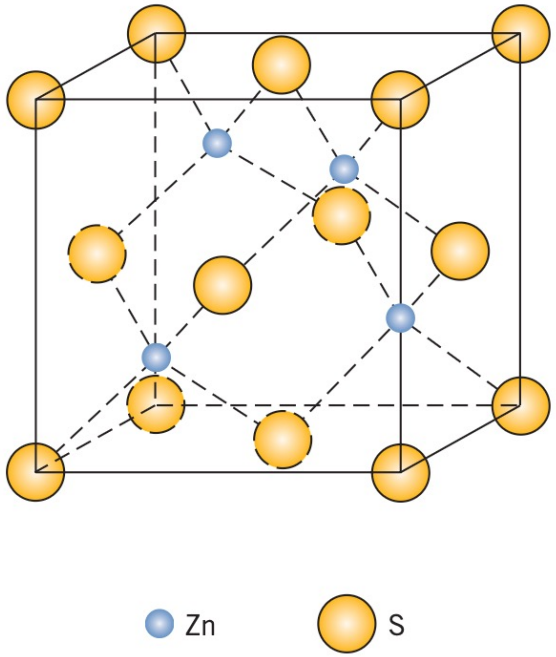
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	



Ceramics: AB versus A_xB_y structures





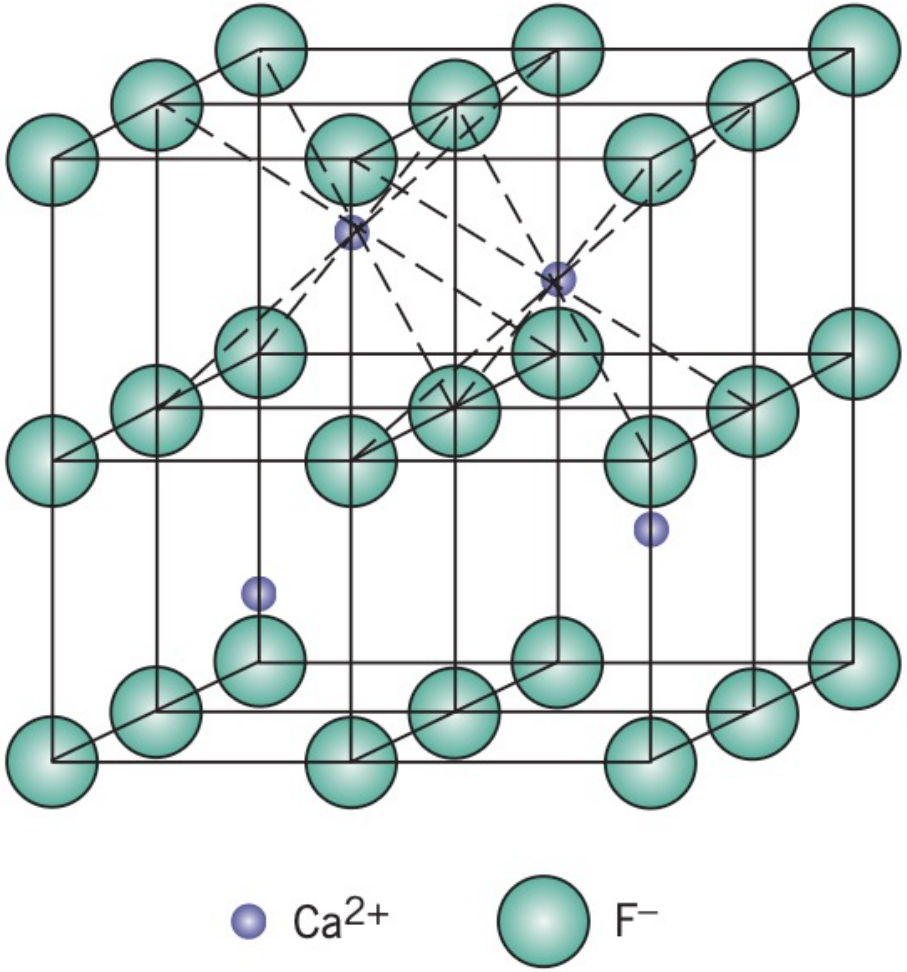


These are all **AB-type** structures with **1:1 ion ratios** (like charges)

Ionic materials ***must*** **maintain electroneutrality!** Stoichiometry adjusts as needed

$$Ca^{2+}F_2^{1-} \qquad Li_2^{1+}O^{2-} \qquad Mn_2^{3+}O_3^{2-}$$

AB_2-type structures

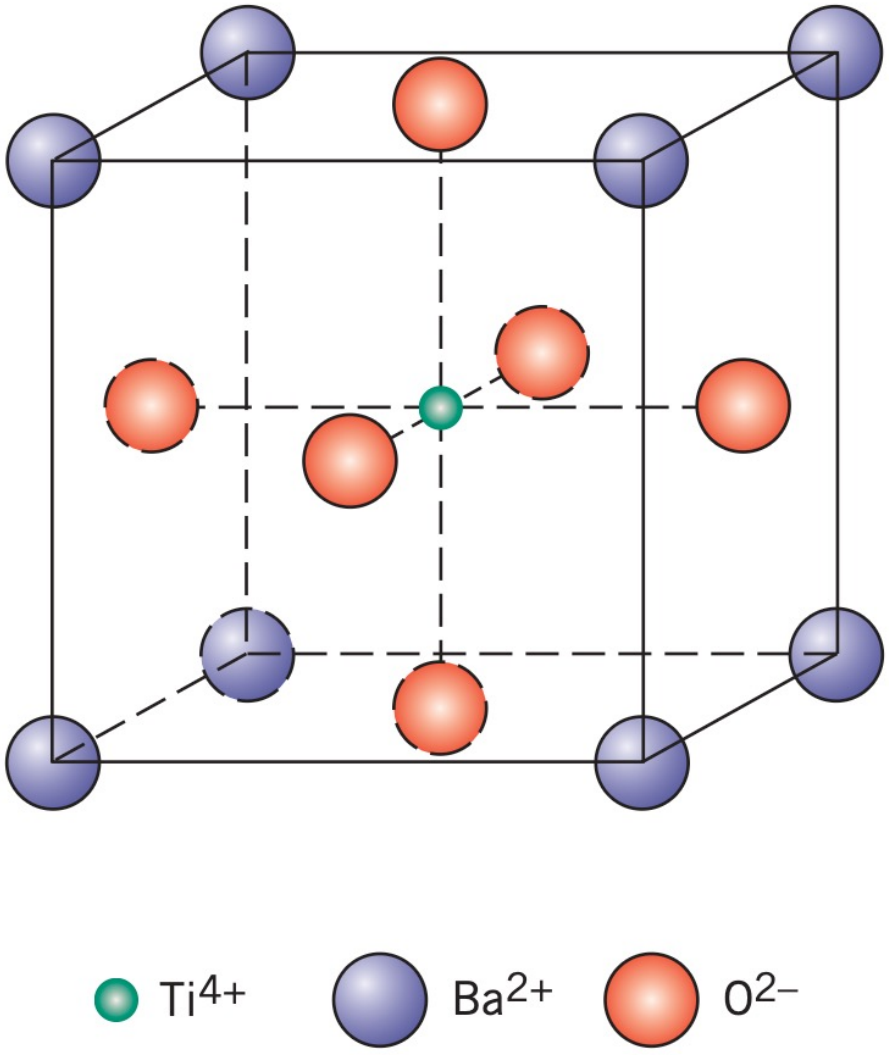


- The **fluorite** structure is most common for AB_2-type compounds
- FCC anion sublattice with only *half* the octahedral sites occupied by cations
- Examples: CaF_2, ZrO_2, CeO_2, UO_2





ABX_3-type structures

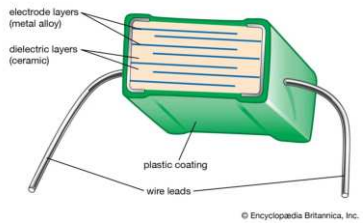


- The **perovskite** structure is most common for ABX_3 compounds
- Think of this as **three sublattices**:
  - B cations form simple cubic lattice
  - A cations occupy body center
  - X anions occupy face centers
- Examples: $BaTiO_3$, $SrZrO_3$, $PbTiO_3$

  → Ferroelectrics!







Questions so far?

There are many structures that ceramics can adopt, but these are by far the most common

Rocksalt, Zincblende, CsCl, Fluorite, Perovskite

A special case: silicates



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 Aluminium	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
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87 Fr Francium	88 Ra Radium	89 Ac** Actinium	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessine	118 Og Oganesson

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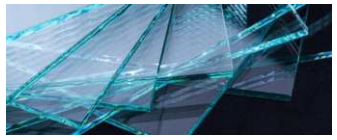
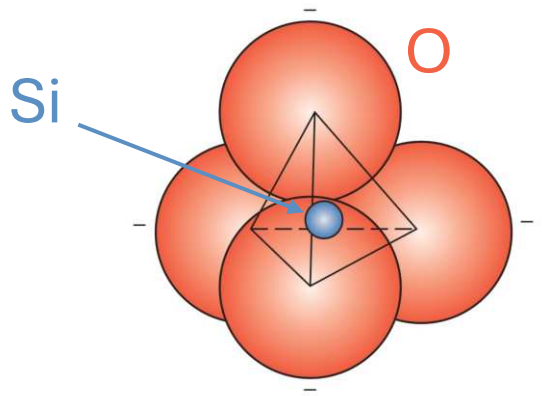






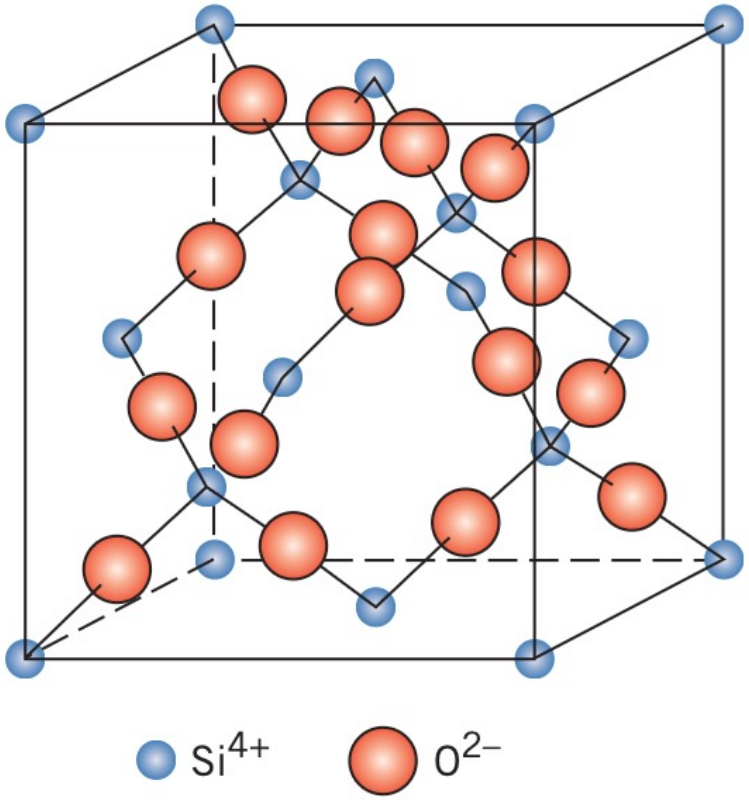
- **Si and O** are the most abundant elements on earth!
- These two elements form very **strong polar covalent bonds**
- When considering silicates – materials containing Si and O – it is convenient to think about building blocks of $\mathbf{SiO_4^{4-}}$ **units**

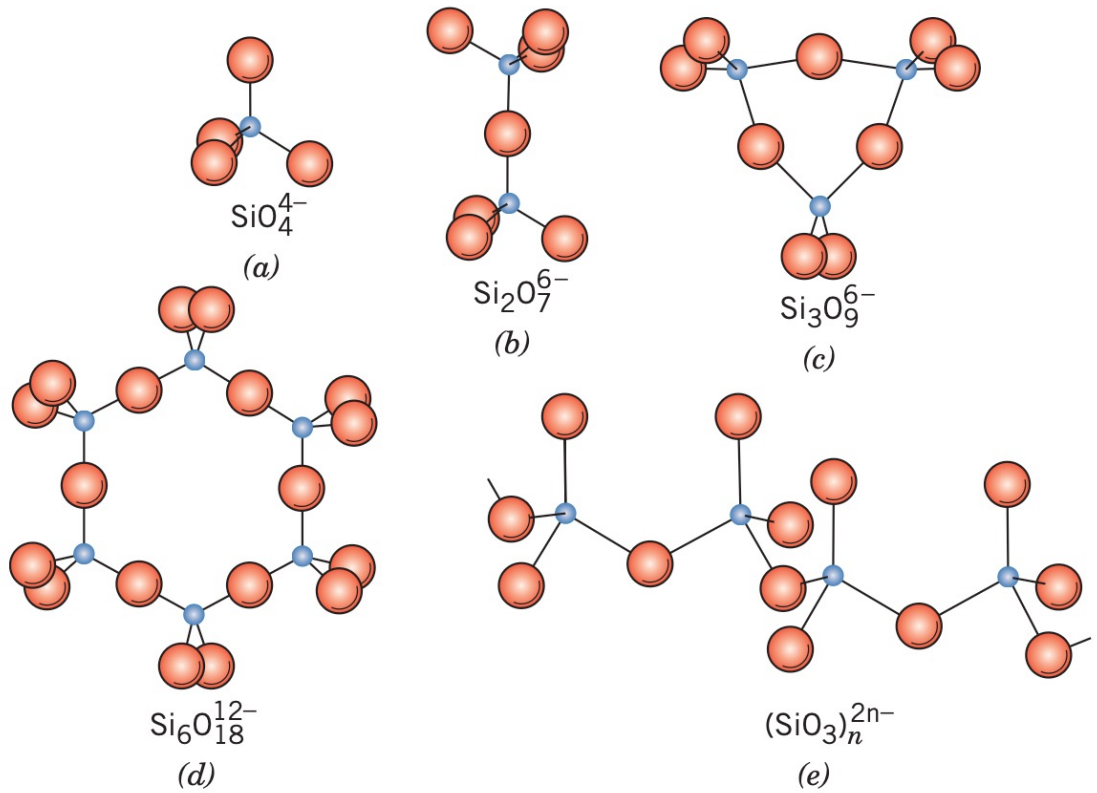




The structure of silica (SiO_2)

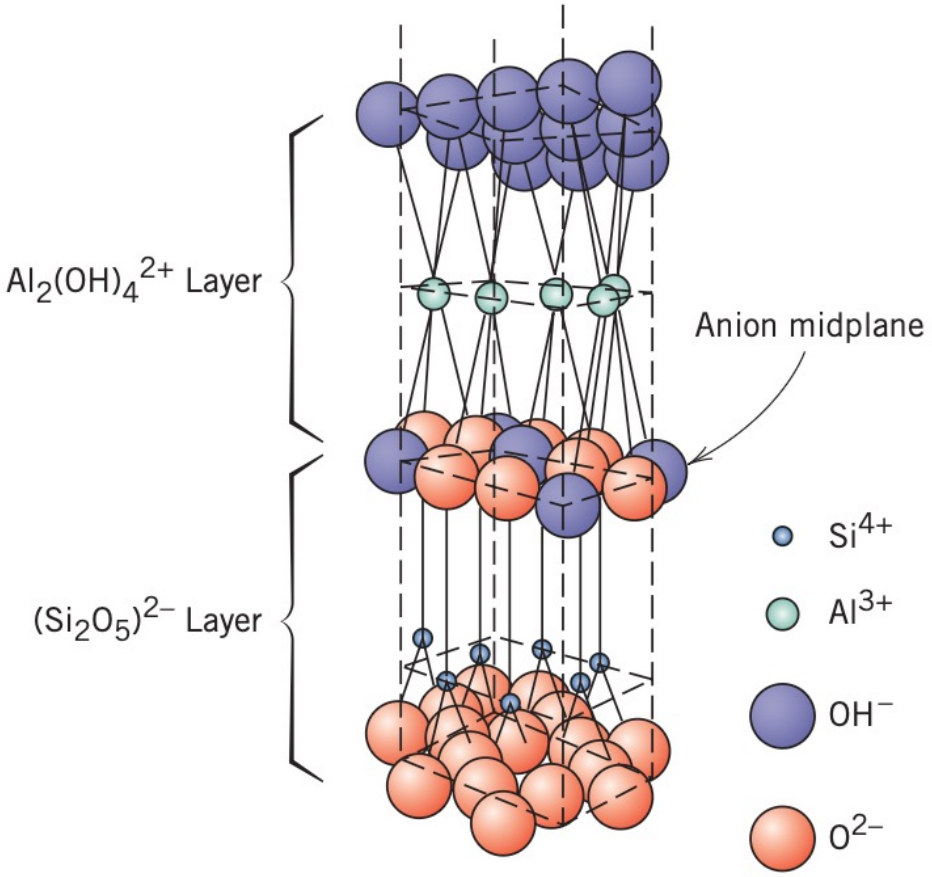
Cristobalite is a common structure for **SiO_2** – but it is *not* the only one. There are *many* possible structures (polymorphs) that can be formed by connecting the SiO_4 tetrahedra in various ways.





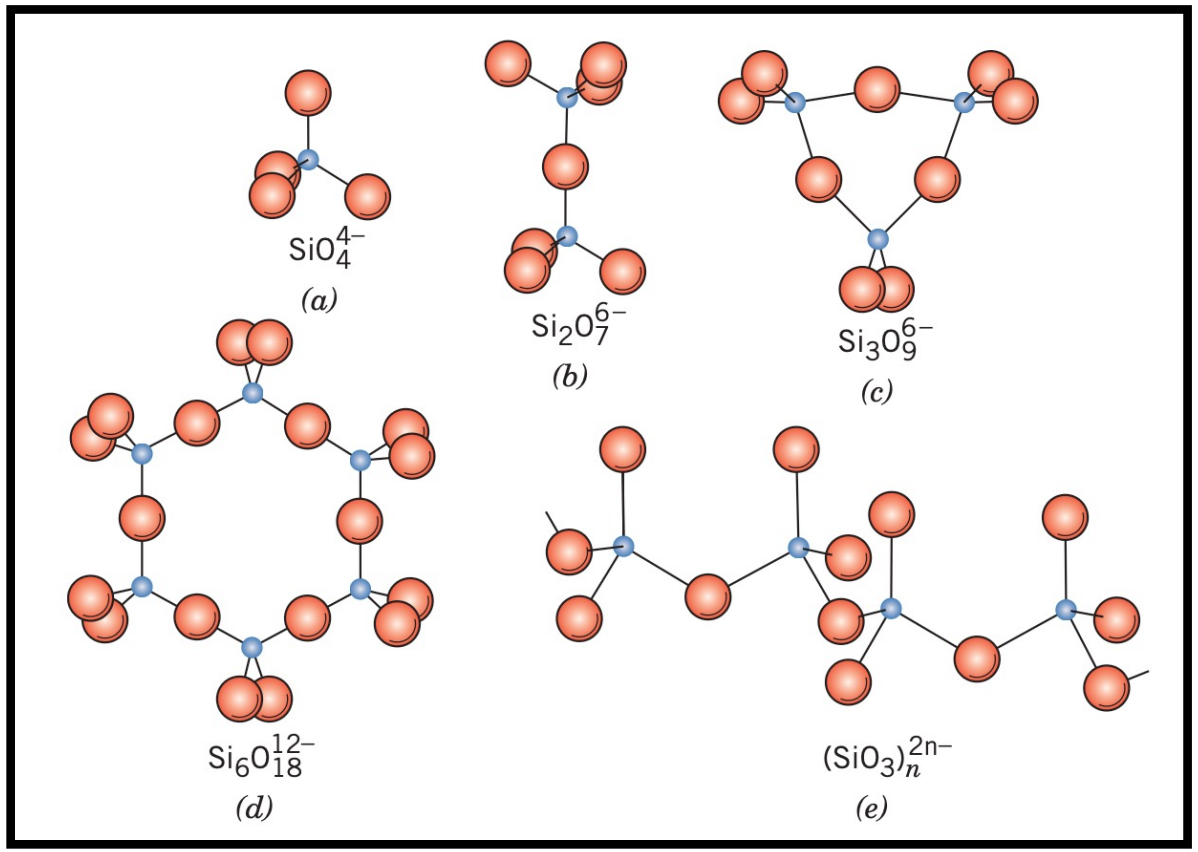


The structure of layered silicates

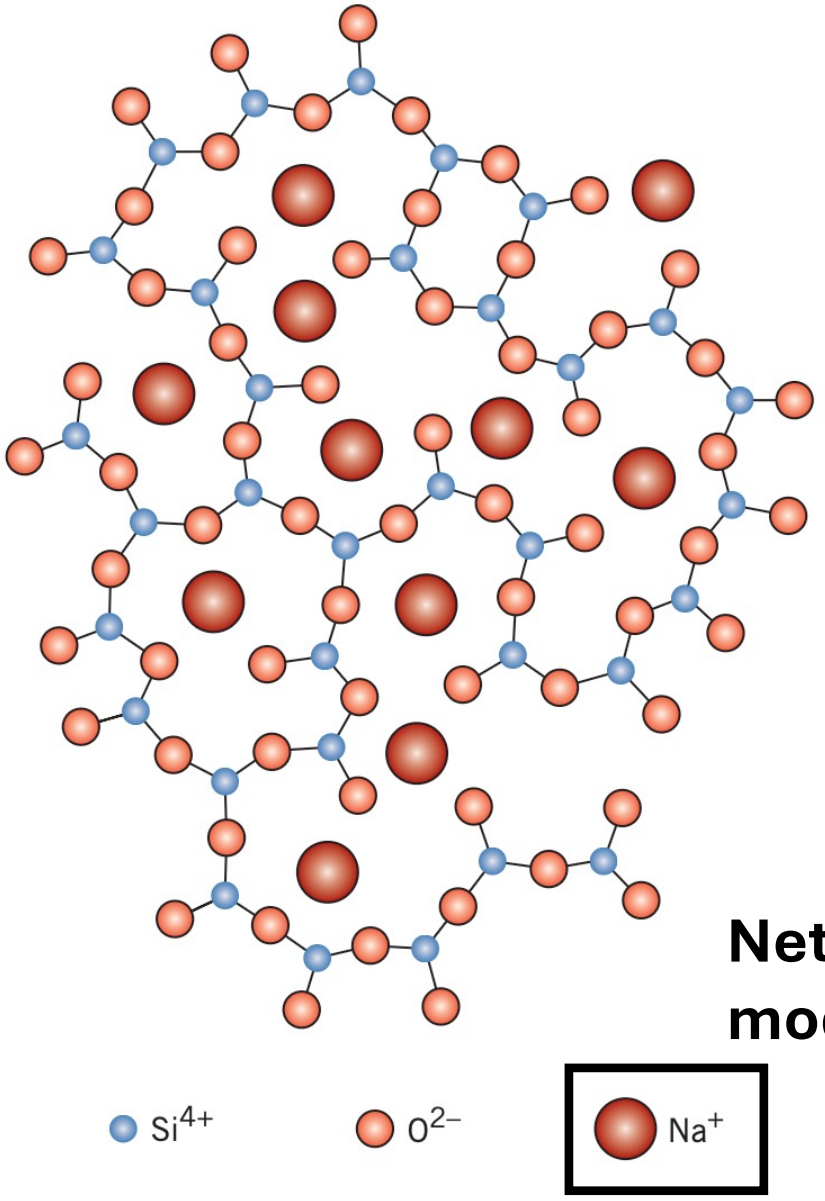


Common clays are layered silicates

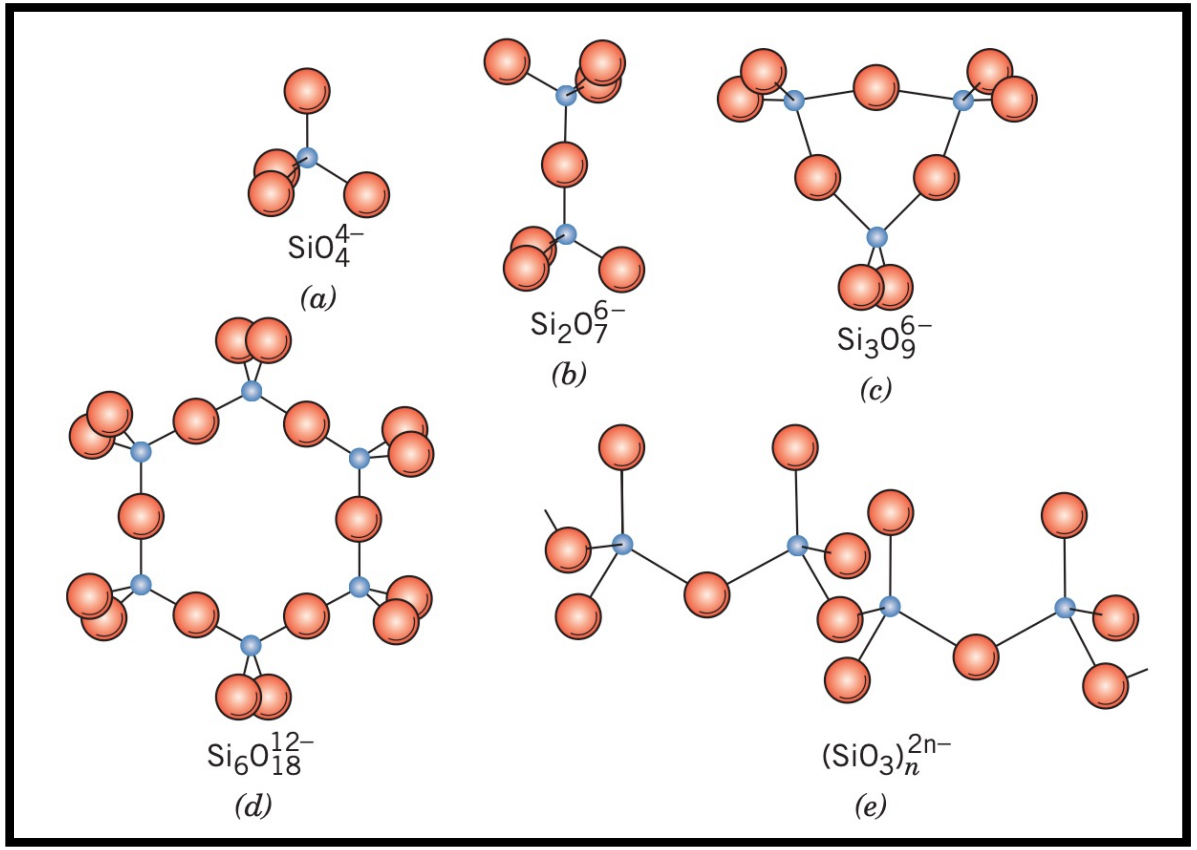
Notice the change in oxidation state – which of these form will often be dictated by what other elements we put in the structure.



Silica and silicate-based glasses



Because these tetrahedra can be arranged in so many ways, often they will form irregular **(amorphous) structures → glasses**



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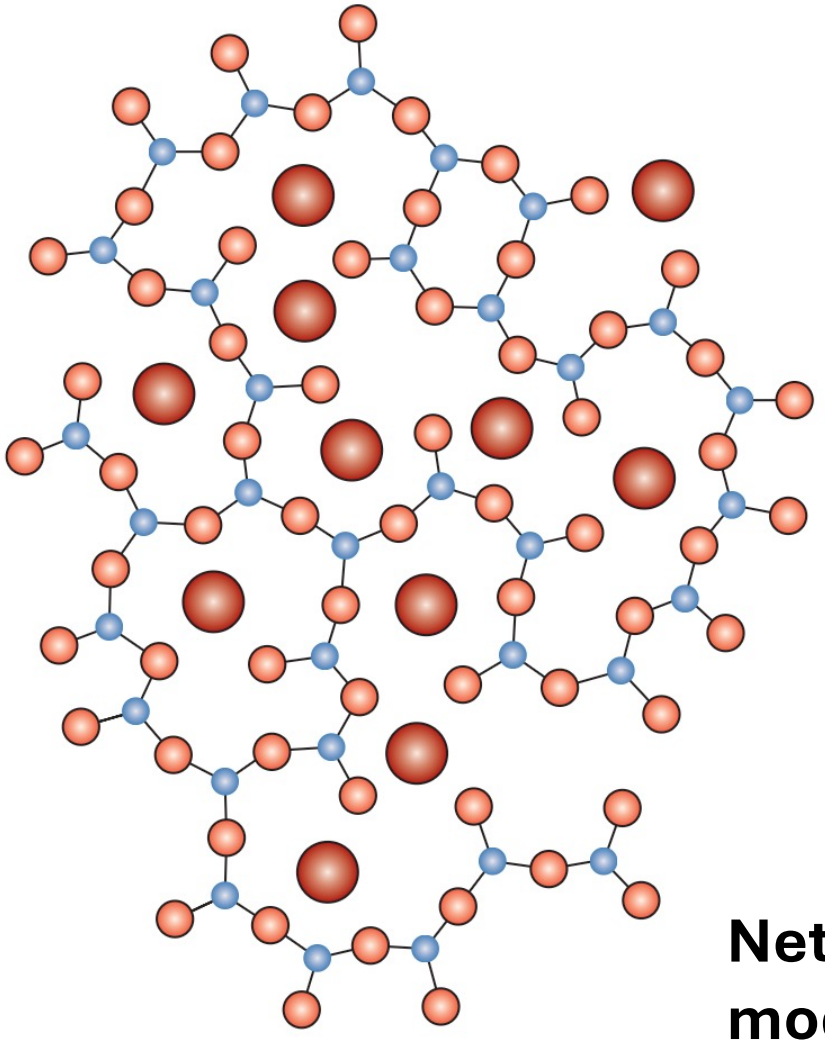

Network modifier

Amorphous → no (few) grain boundaries → transparent



Soda-lime glass → very common

(Na) (Ca)

Another special case: carbon

PERIODIC TABLE OF ELEMENTS

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 Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
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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
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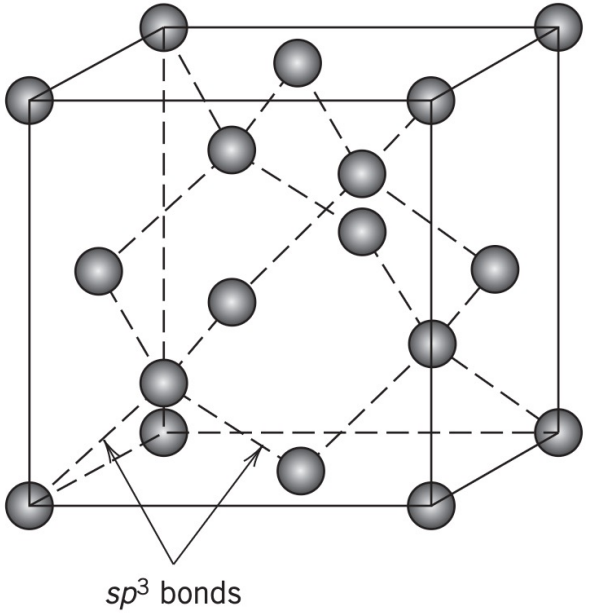
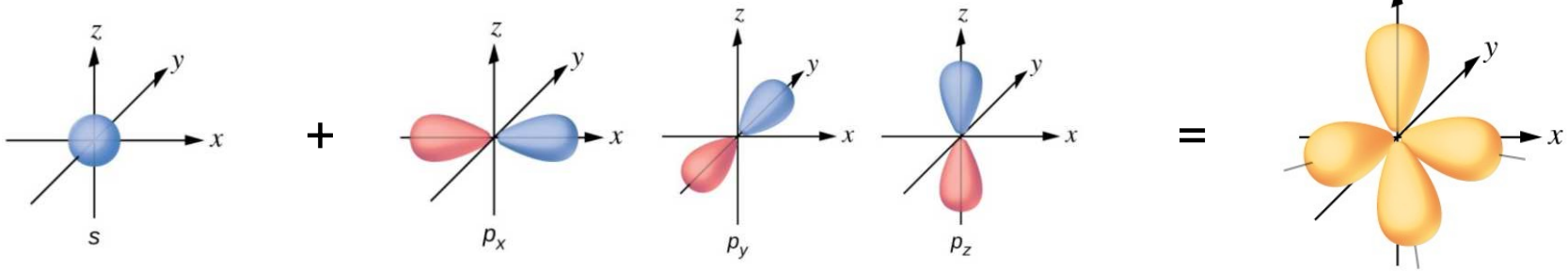


sp^3 bonds

Diamond



Very strong 3D covalent bonds
resulting from sp^3 hybridization



Another special case: carbon

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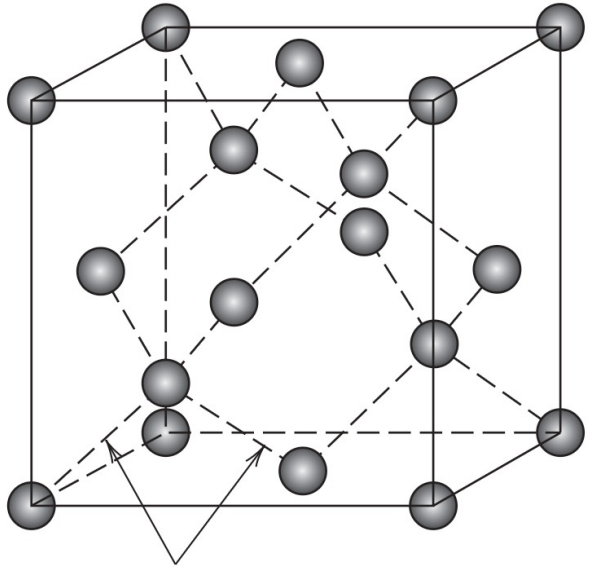


sp^3 bonds

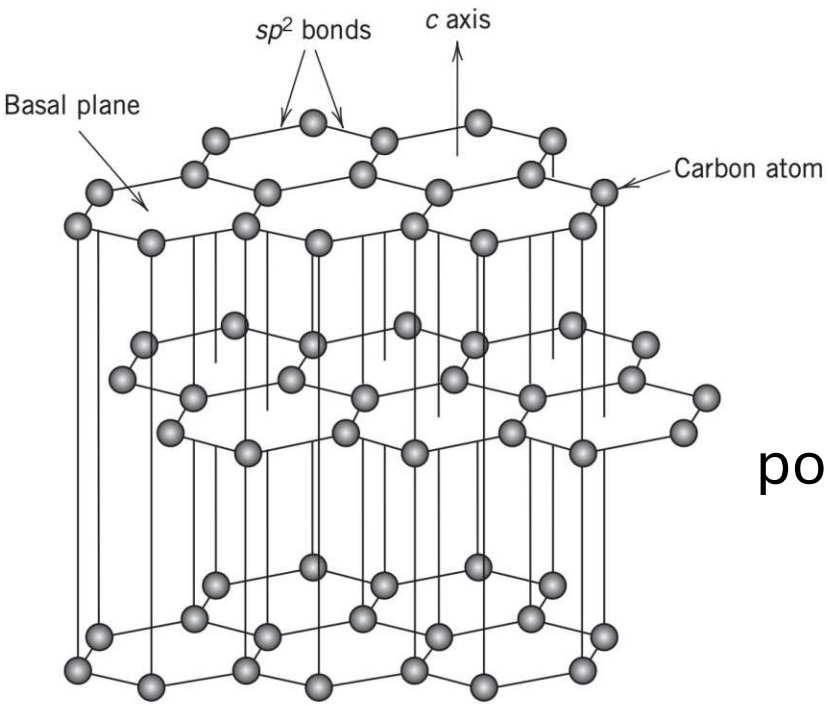
Diamond





Hardest known material! Used in cutting tools

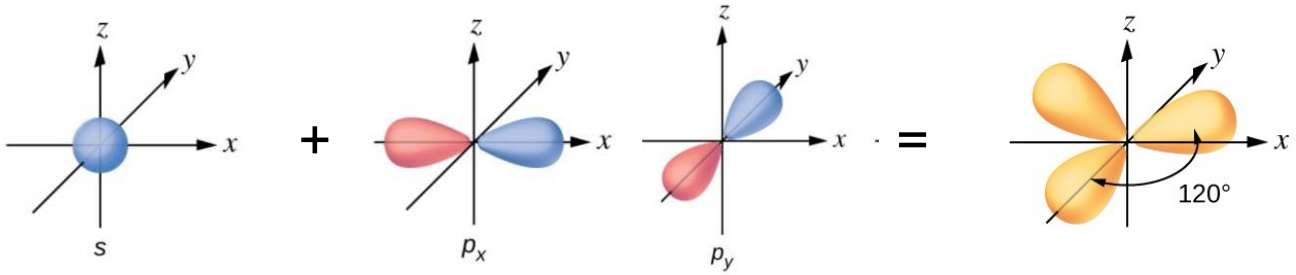
Another special case: carbon

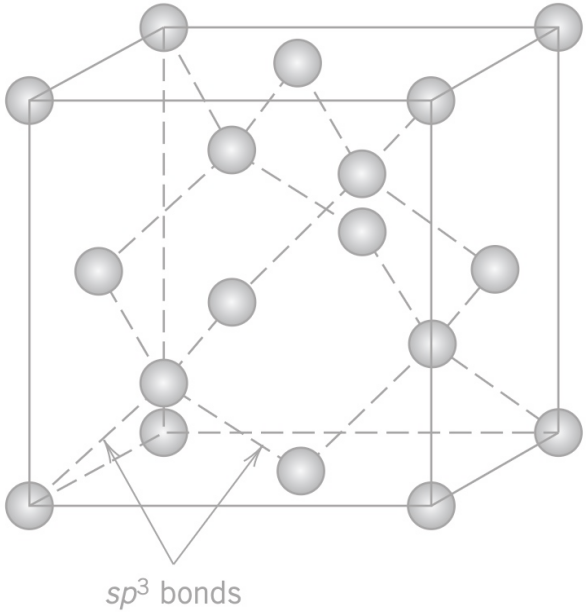




A more common polymorph of carbon is **graphite**

Strong covalent (sp^2) bonding in-plane, weak Van der Waals bonding out-of-plane





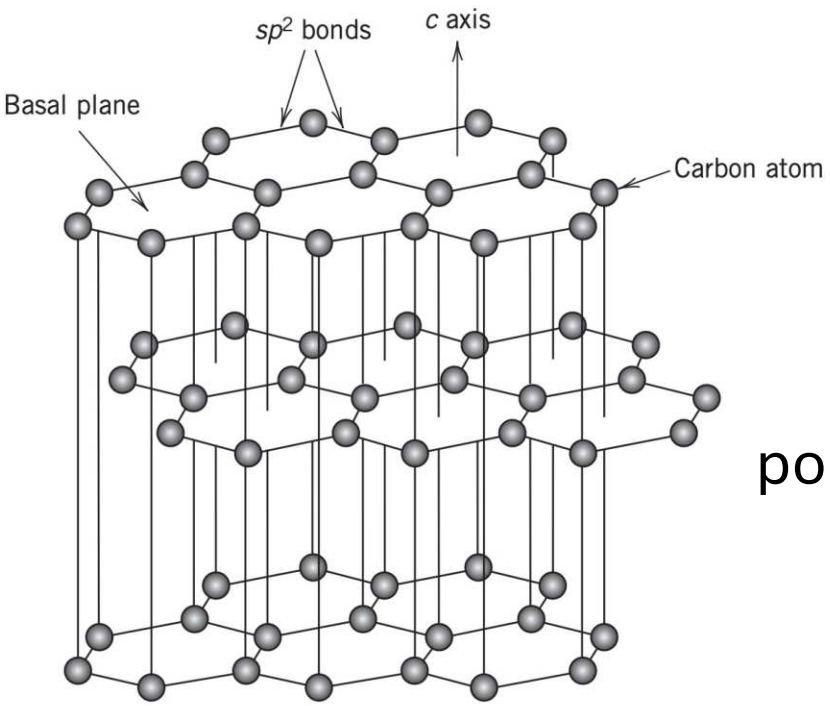
Diamond





Hardest known material! Used in cutting tools

Another special case: carbon





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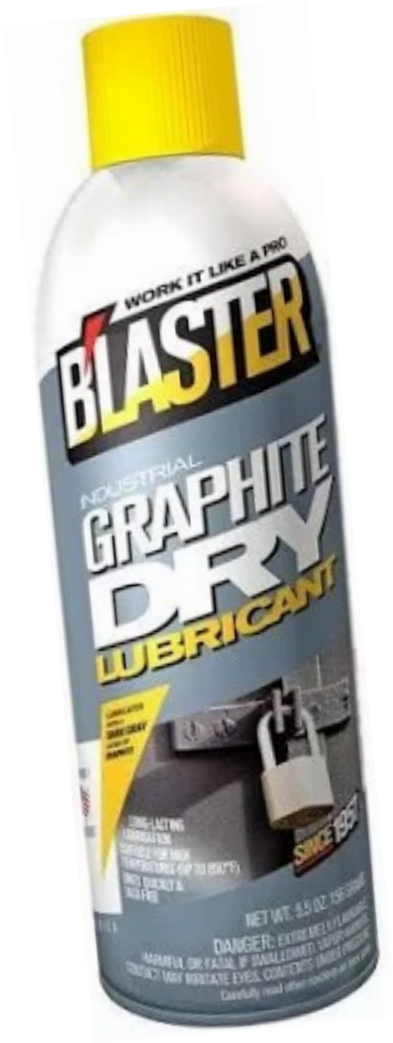
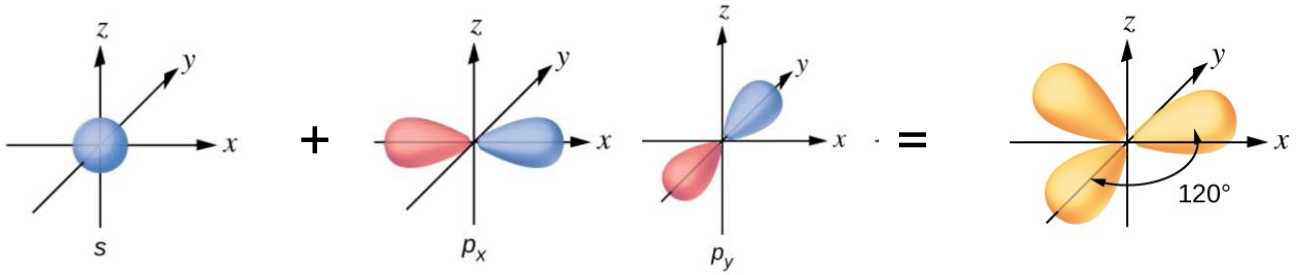
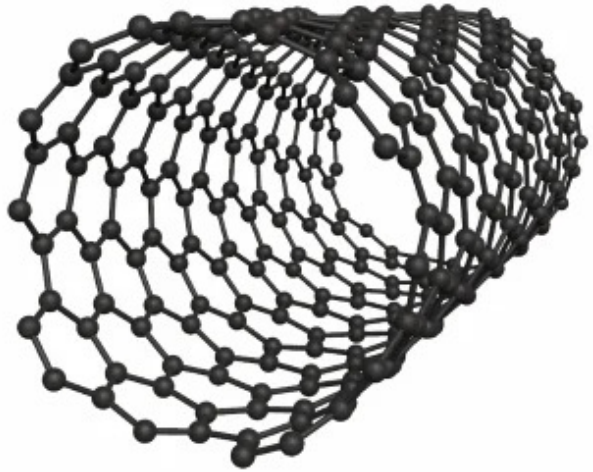


Used as a lubricant!

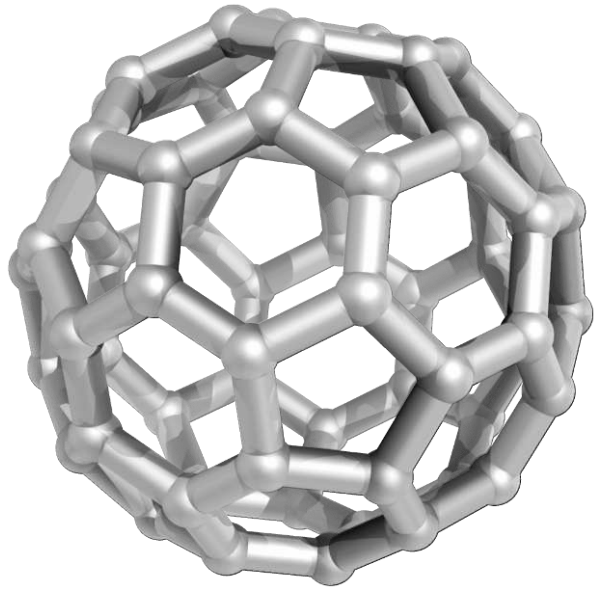
Strong covalent (sp^2) bonding in-plane, weak Van der Waals bonding out-of-plane



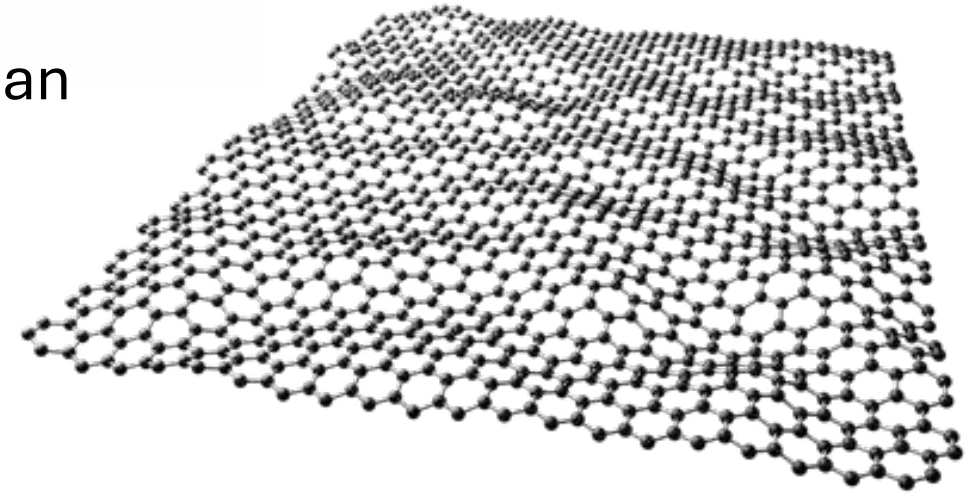
Another special case: carbon



Lots of carbon structure can be made!



~200× stronger than steel (by weight)!

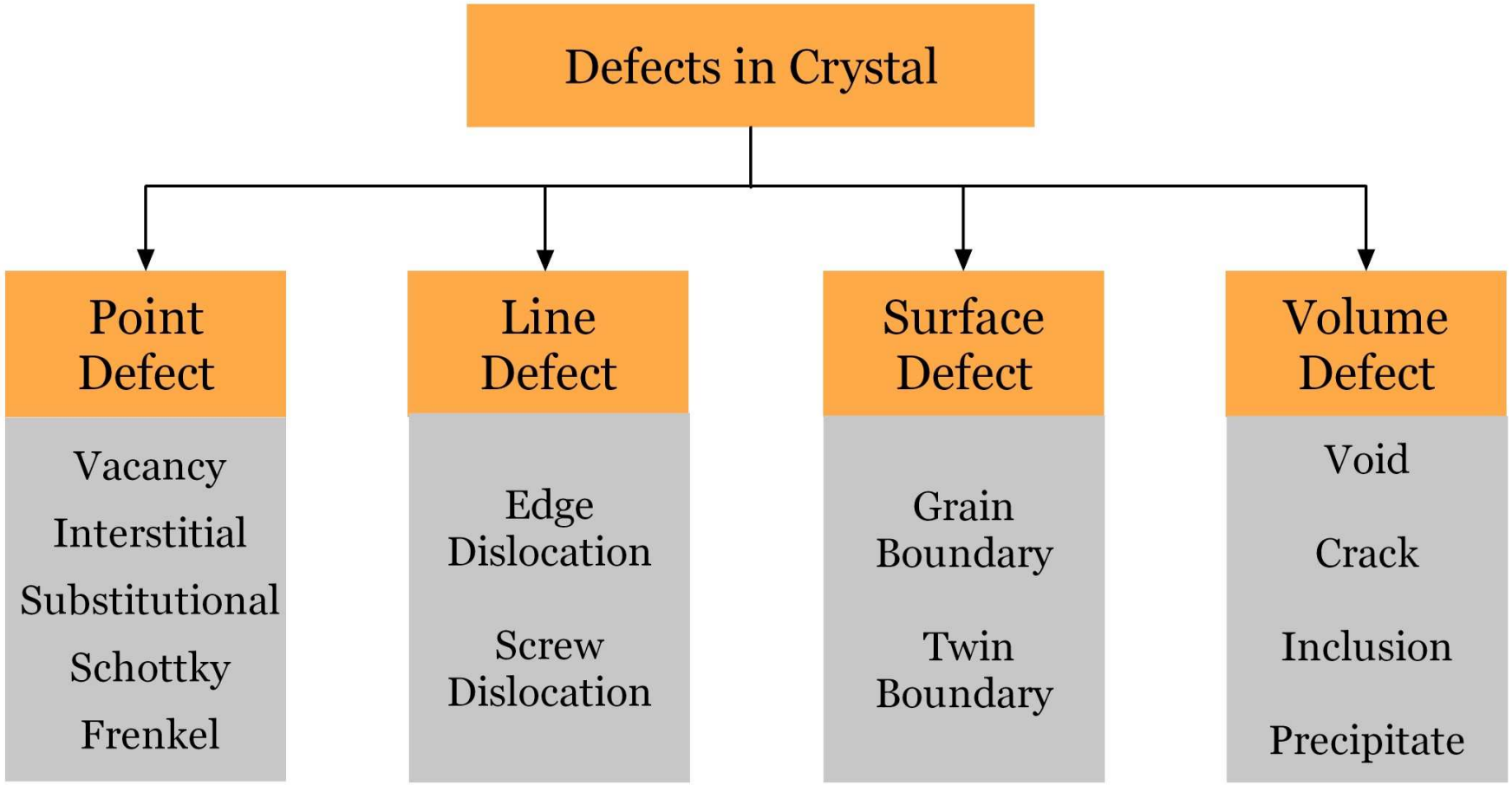


Questions on silicates and carbon?

Things to know:

- Silicates have tetrahedral building blocks that can be arranged in many ways (even randomly, as in glass)
- Carbon forms *very* strong bonds; however, this bonding can occur either 2D (graphite) or 3D (diamond)

How about defects in ceramic materials?



Single atom (0D)

A 1D line of atoms

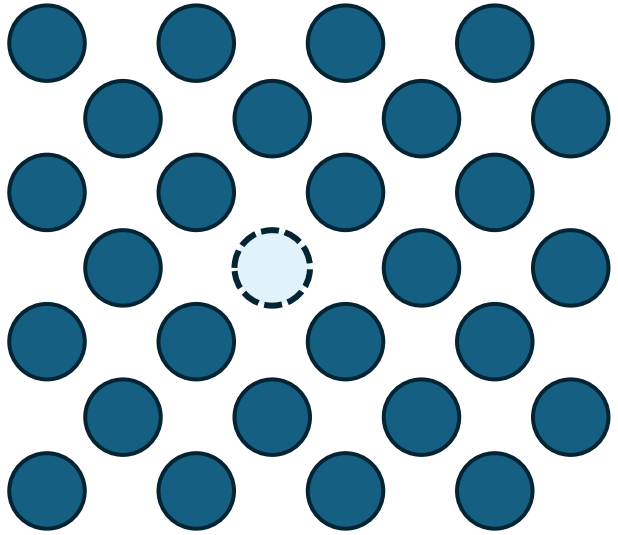
2D planes of atoms

3D chunks of atoms

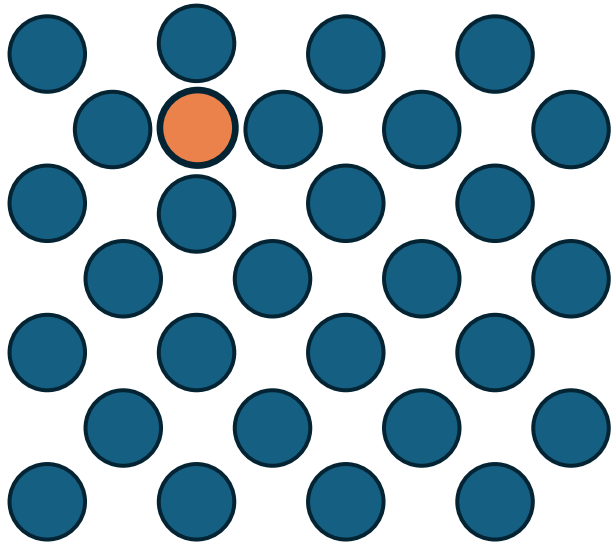
How about defects in ceramic materials?



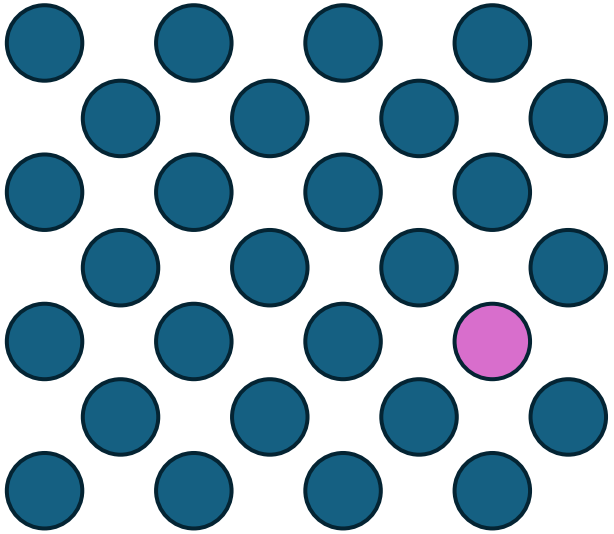
Single atom (0D)



Vacancy



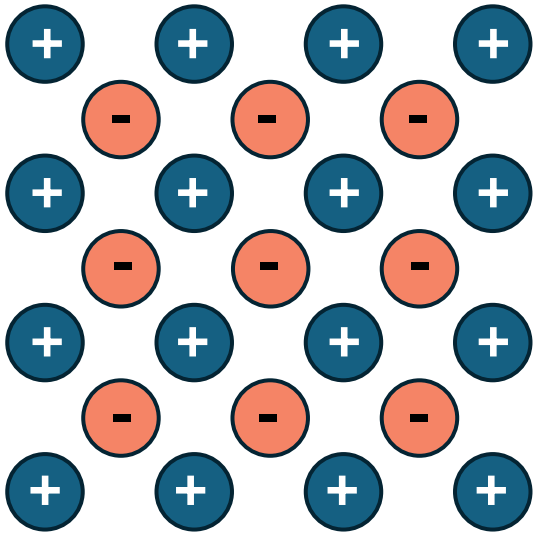
Interstitial



Substitution

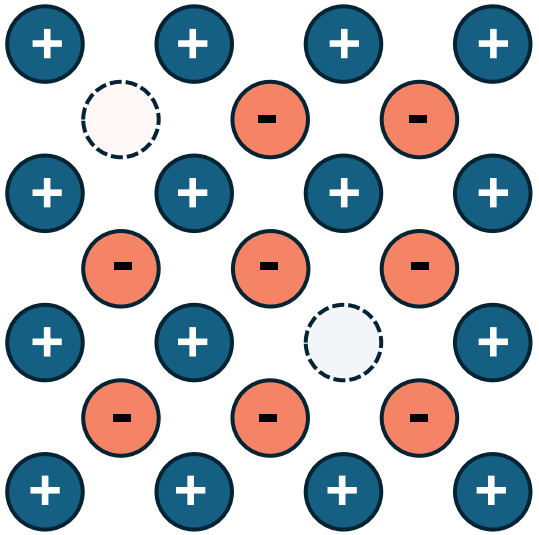
How about defects in ceramic materials?

Ceramics are complicated by the fact that we now have multiple species (cations and anions) which must removed or added in such a way that **maintains electroneutrality**



Na^+ Cl^-

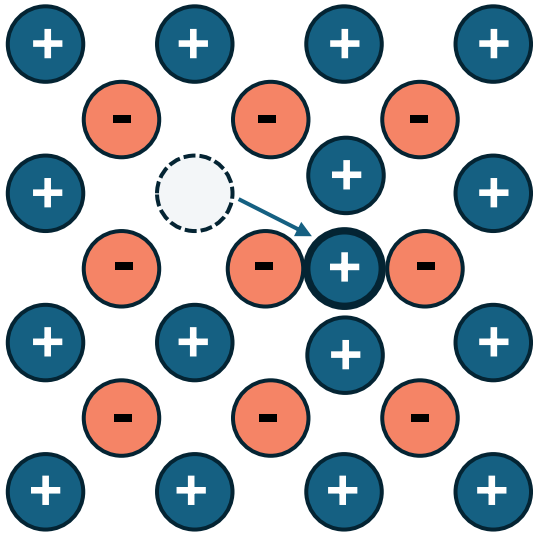
Schottky defect



Cation vacancy + anion vacancy

(Missing Na^+) -(+1) **(Missing Cl^-) -(-1)**

Frenkel defect



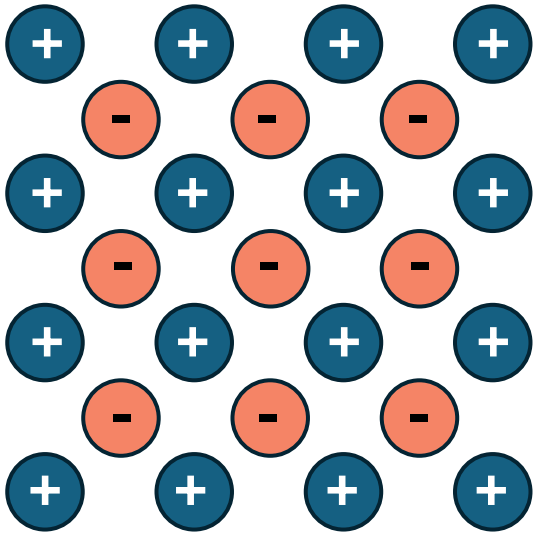
Vacancy + interstitial

(Missing Na^+) -(+1) **(Extra Na^+) +(+1)**

How about defects in ceramic materials?

Similar defect thermodynamics as before. Just the activation energies are different.

$$N_s = N \exp\left(-\frac{Q_s}{2kT}\right) \qquad N_{fr} = N \exp\left(-\frac{Q_{fr}}{2kT}\right)$$



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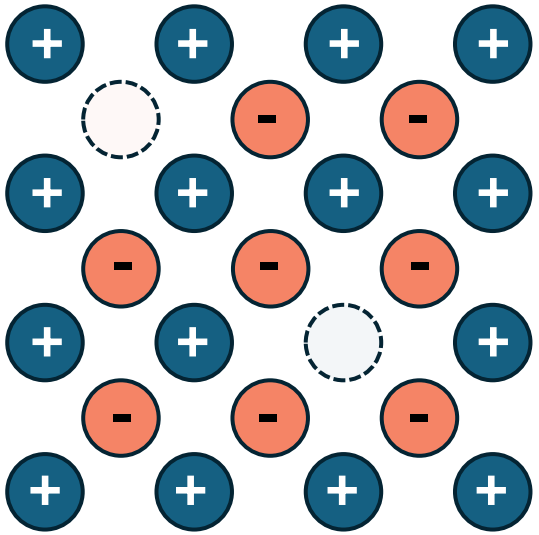
Schottky defect



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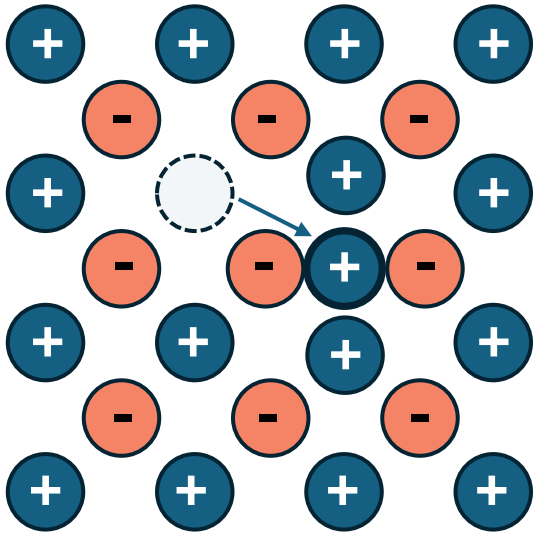
Frenkel defect



Vacancy + interstitial

How about defects in ceramic materials?

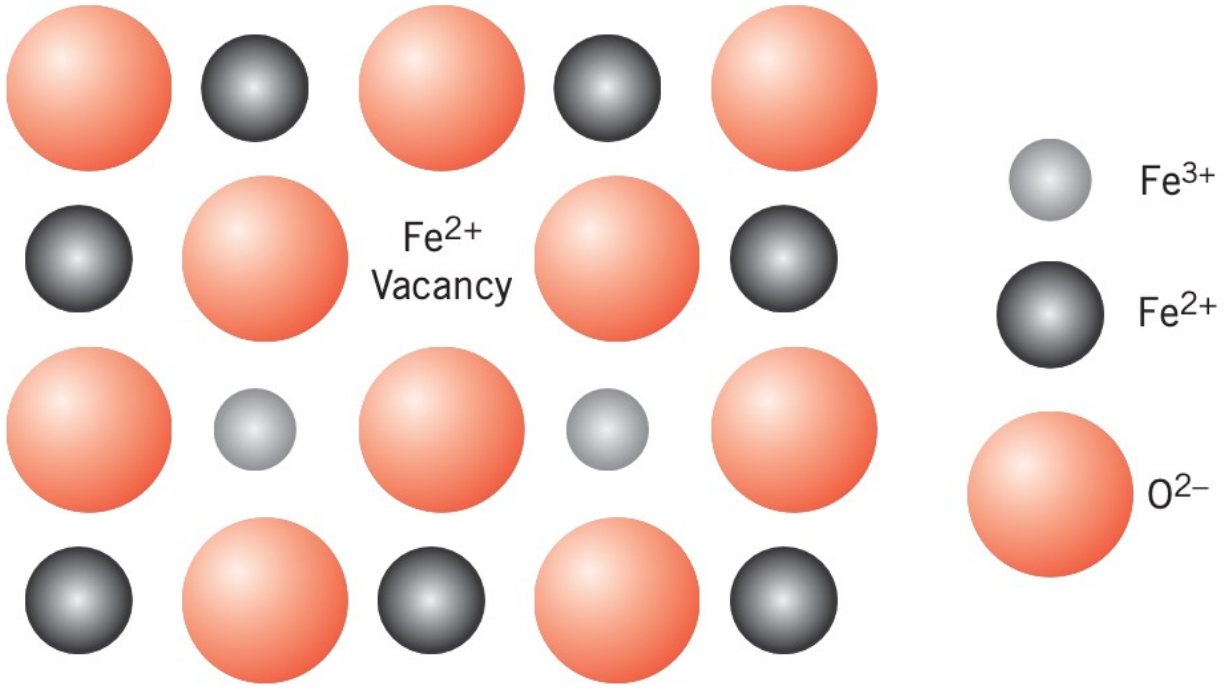


Figure 12.20 Schematic representation of an Fe^{2+} vacancy in FeO that results from the formation of two Fe^{3+} ions.

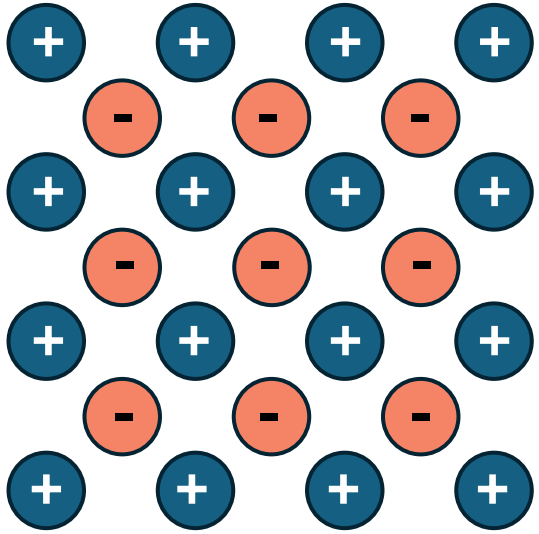
$Fe^{2+} \rightarrow$ Vacancy: $-(+2) = -2$

$2\,Fe^{2+} \rightarrow 2\,Fe^{3+} : 2(3-2) = +2$

These cancel out

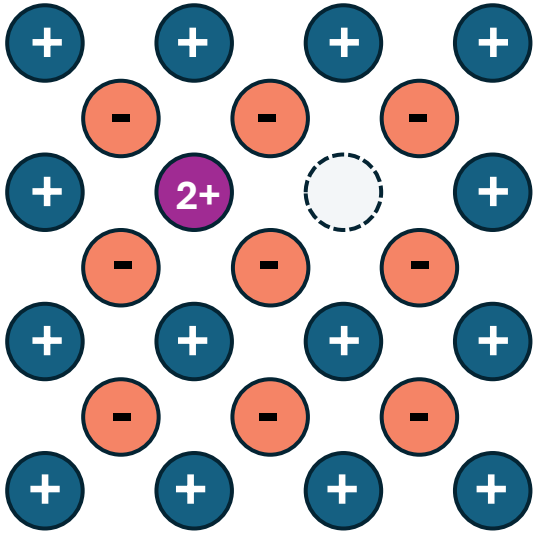
Frenkel/Schottky defects are not always necessary to maintain electroneutrality.
We can in some cases **oxidize or reduce nearby metals** to compensate.

Substitutional impurities in ceramics



Suppose we want to add a bit of **Mg to CsCl…**

Mg is 2+ **Cs is 1+**



If we substitute one Cs for one Mg, we also need to create one Cs vacancy

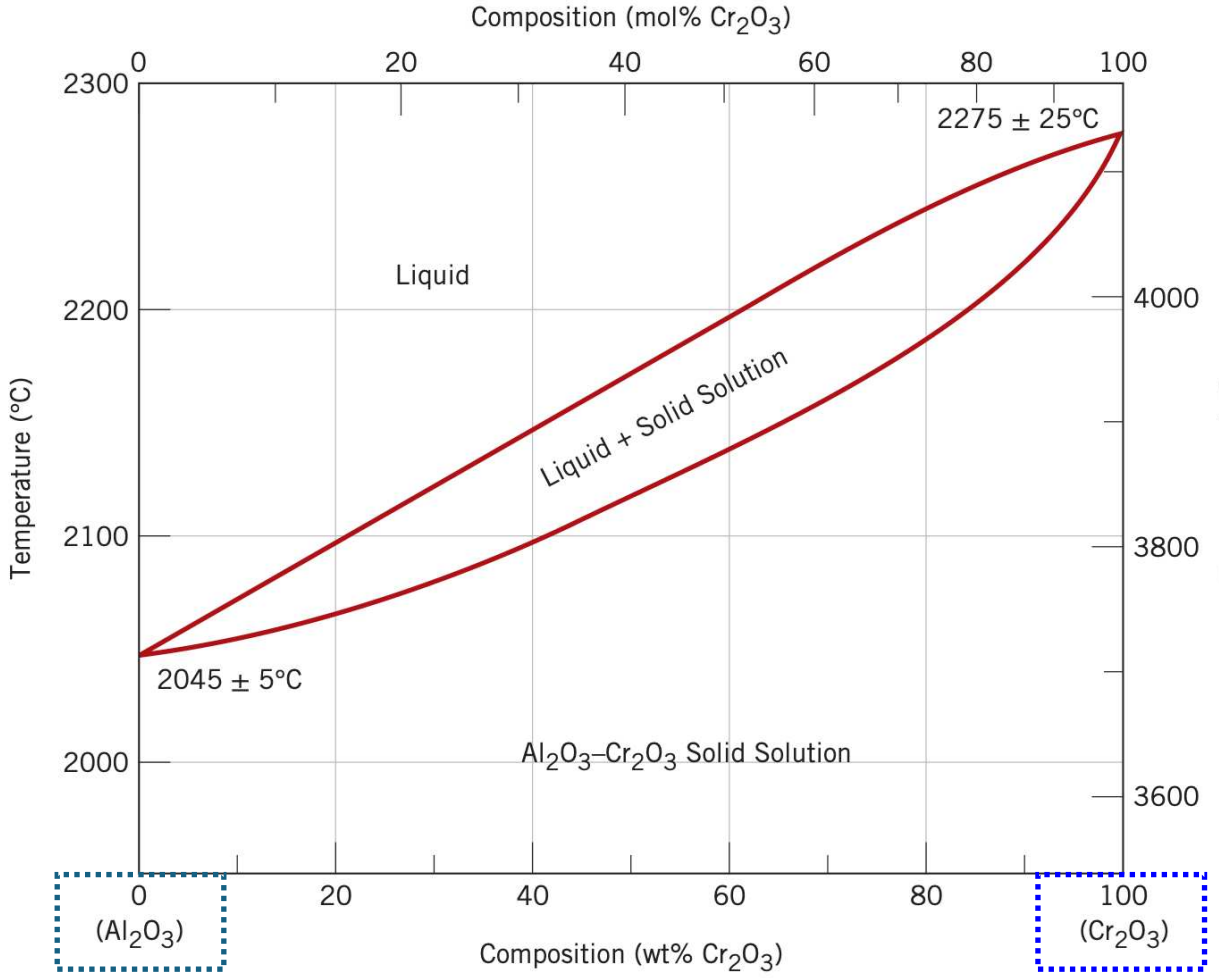
Generally, these types of substitutions have low solubility limits

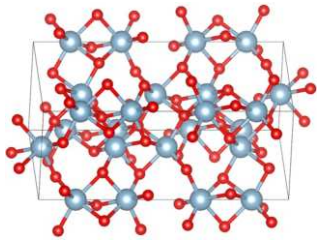
Substitutional impurities in ceramics

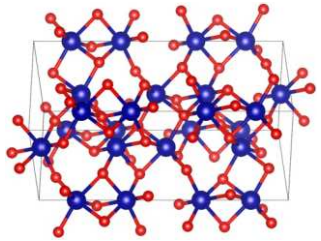
Recall the **Humes-Rothery rules**. Now adapted to ceramics…
A substitutional solid solution between *A* and *B* is likely when:

1) Their **atomic radius differs by < 15%**
2) They have **similar electronegativity** (are close on periodic table)
3) They have **the same crystal structures**
4) They have the **same oxidation state**

Phase diagrams of ceramics

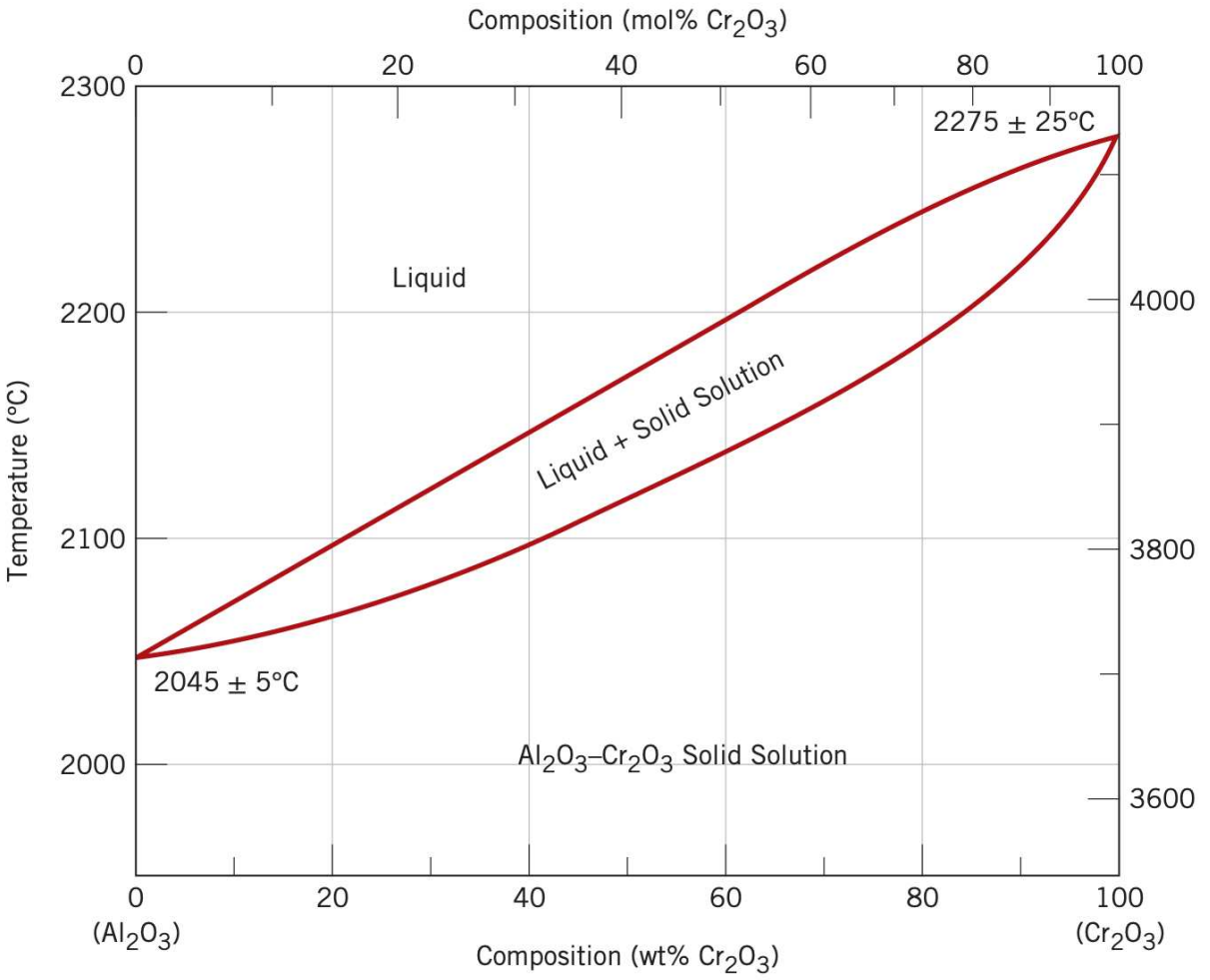


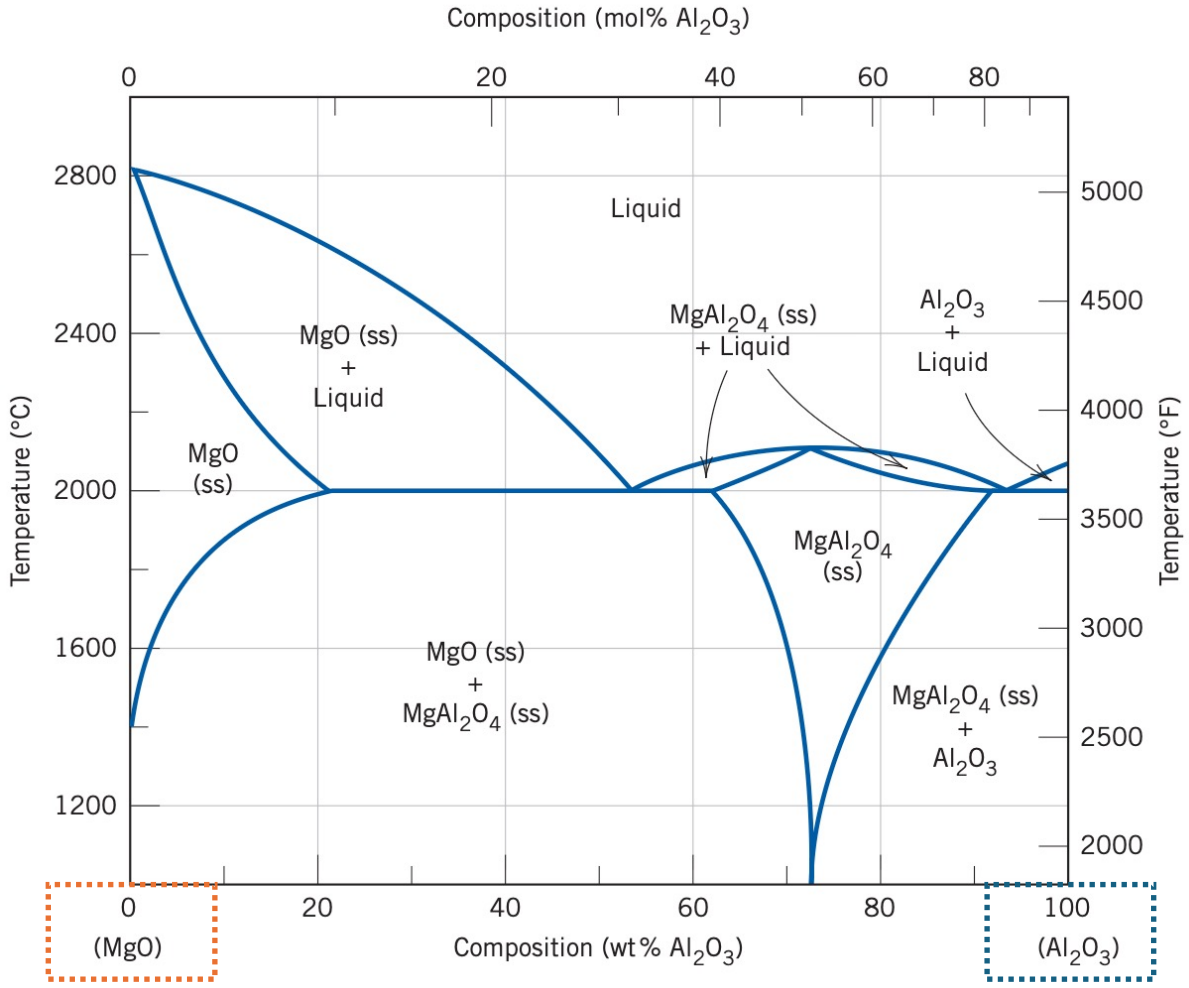


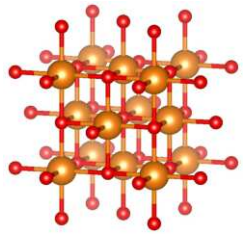


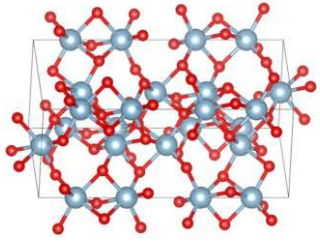
This is similar to the metal phase diagrams we have already seen – except now the **endpoints are compounds** (not elements)

Phase diagrams of ceramics





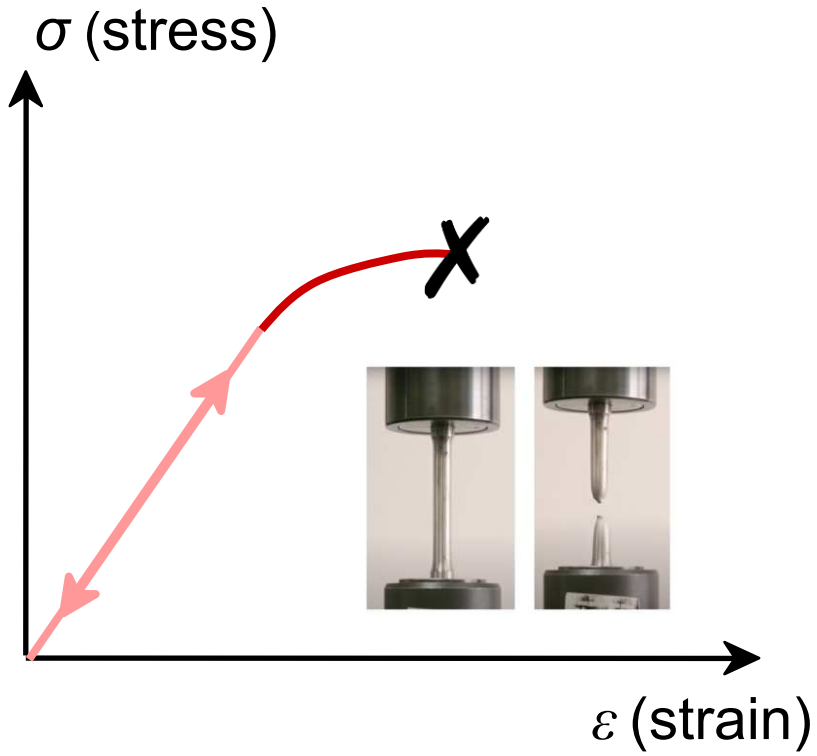


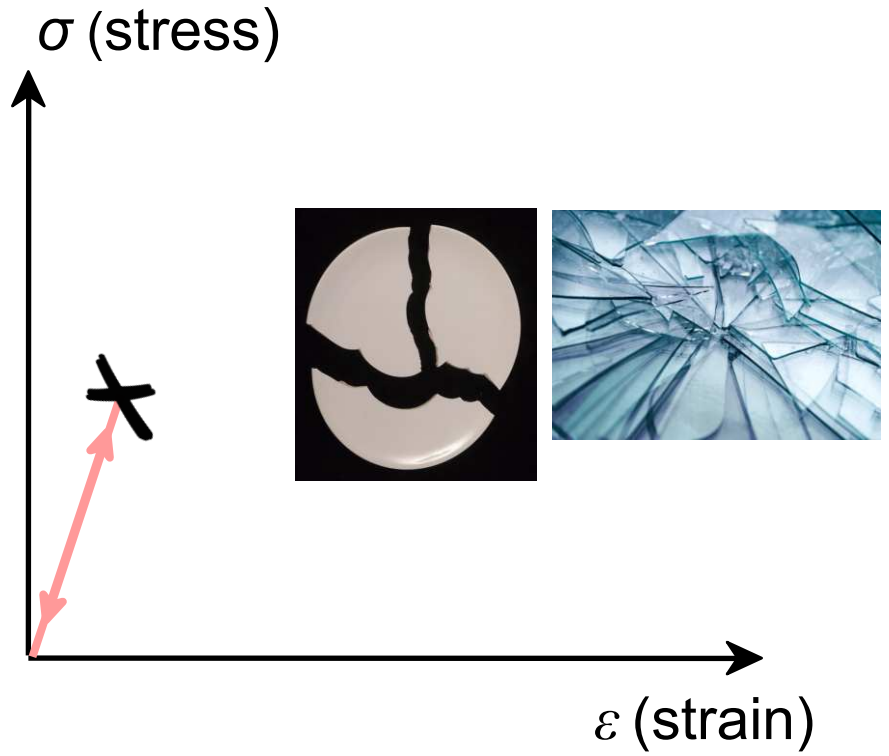


Questions on defects in ceramics?

Key: Must always maintain electroneutrality!

Mechanical properties of ceramics



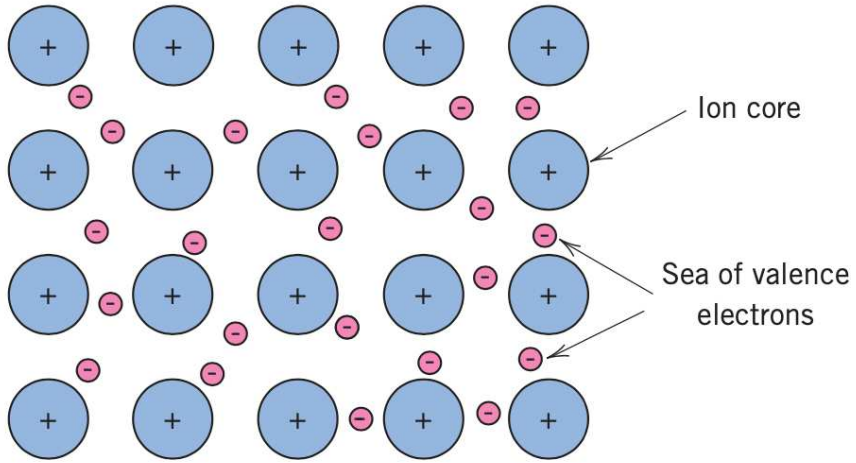


Recall: metals are often ductile, exhibiting substantial plastic deformation prior to fracture

Ceramics are often stiff and hard but also **very brittle,** exhibiting no plastic deformation prior to fracture

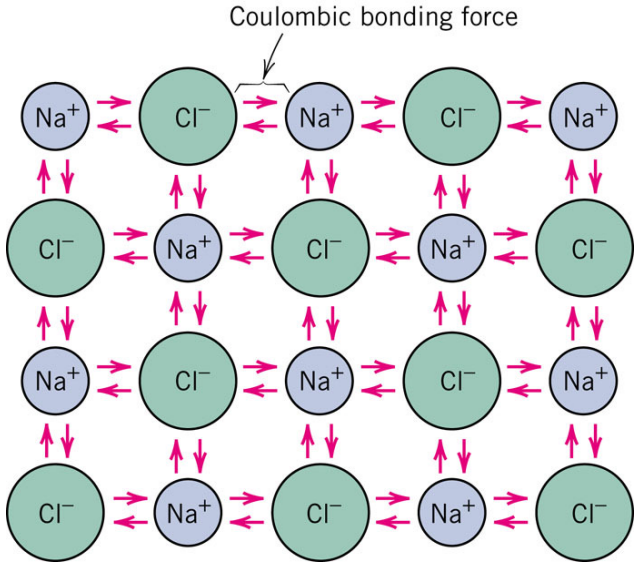
Ceramics often have deformation-resistant bonds

Metals



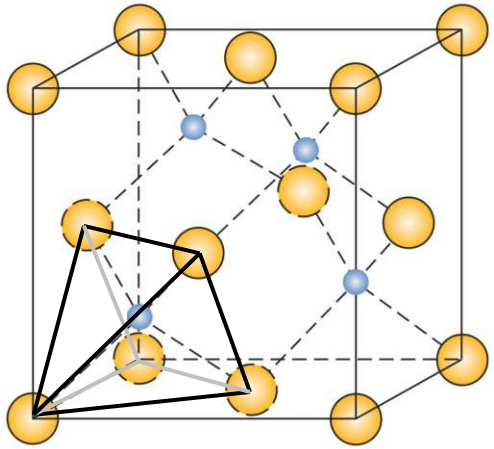
Atoms can “glide around” in the electron sea

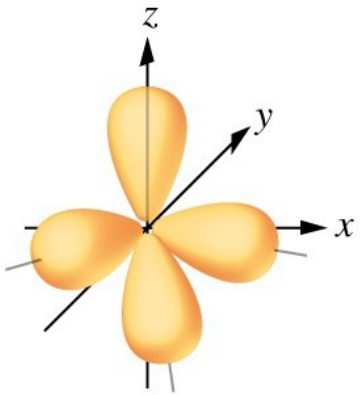
Deformation causes overlap between like ions



Ionic materials

Covalent materials

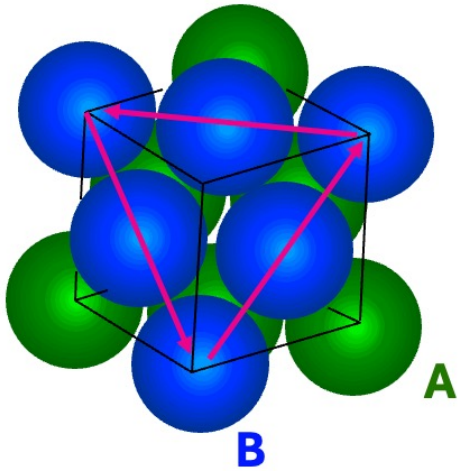


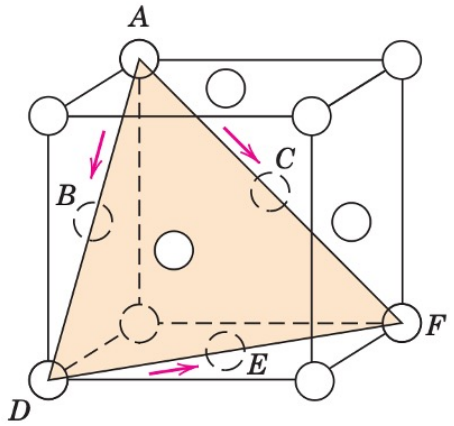


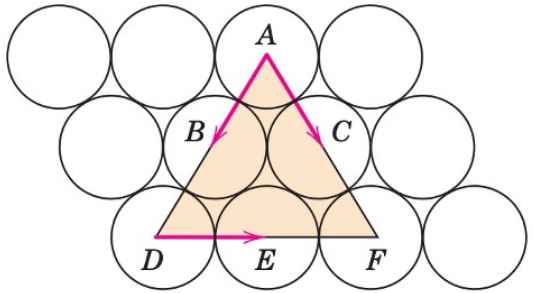
Deformation reduces orbital overlap

Ceramics also inhibit slip

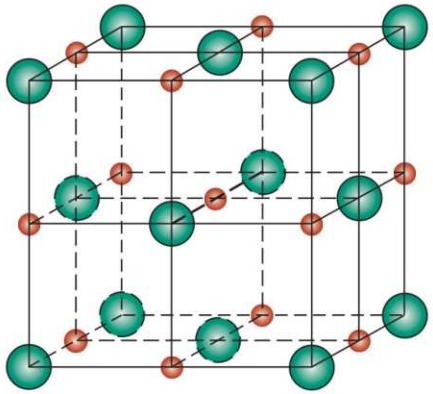
Recall: In **metals**, slip occurs along the **close-packed planes**

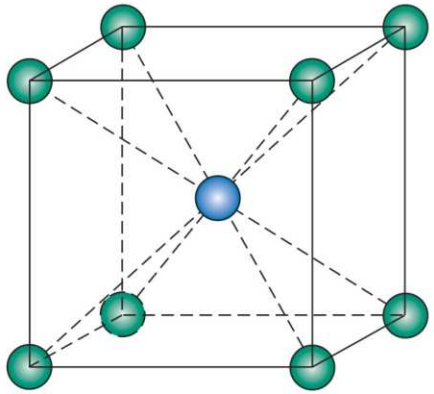


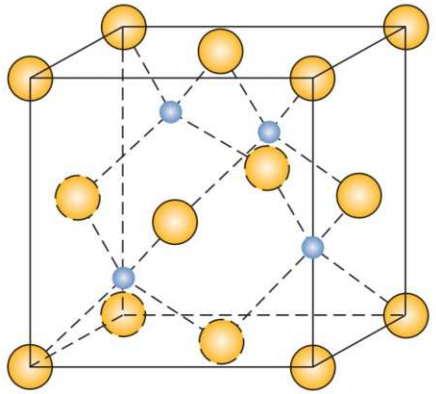




But in ceramic structures, we don't generally have close-packed planes

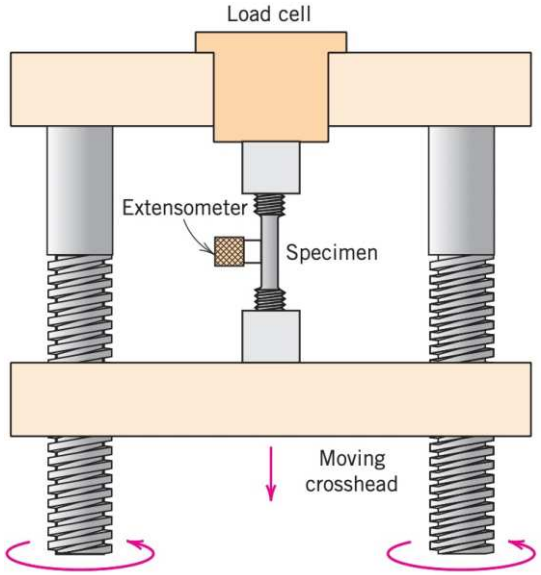




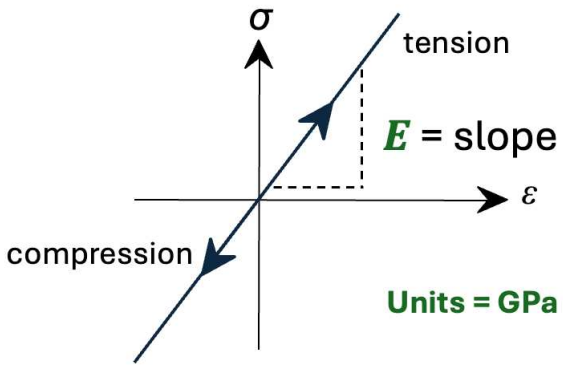


And slip would require some overlap of like ions → repulsion

Testing the mechanical properties of ceramics

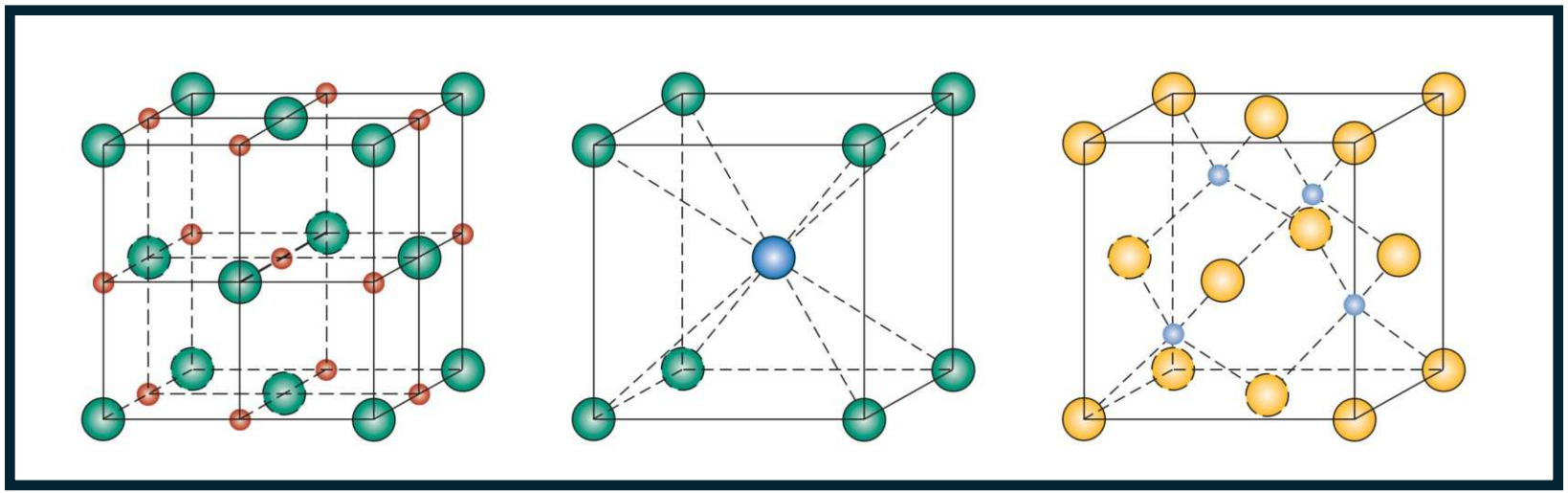






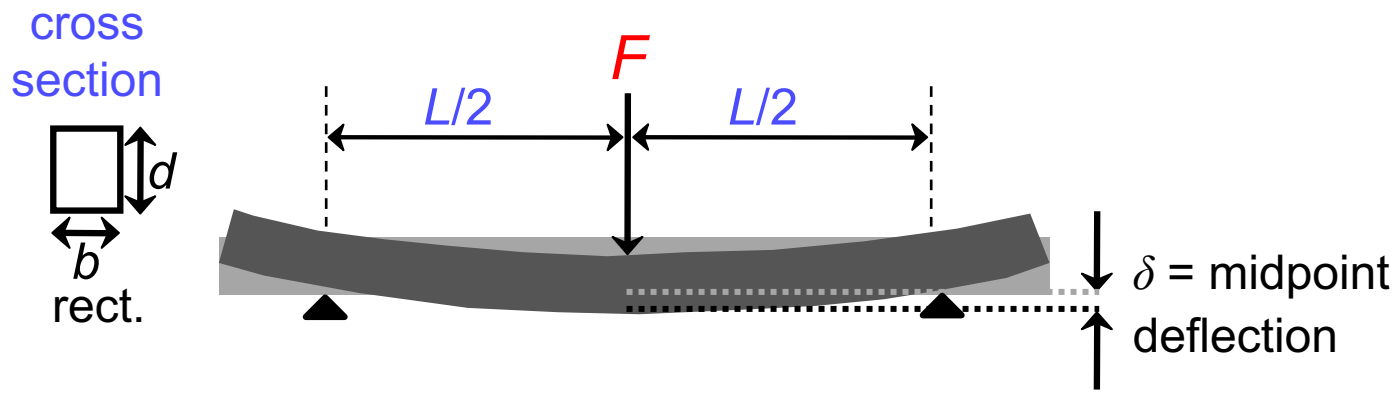
For metals, we'd tensile test. But ceramics are very prone to facture if we grip them hard or deform them even slightly, so tensile tests are usually impractical.

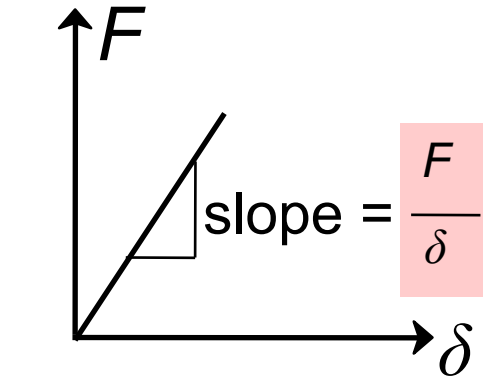
Let's focus on the **elastic properties** of ceramics



Testing the mechanical properties of ceramics

3-Point Bend Testing is instead used to measure how resistant ceramics are to deformation





linear-elastic behavior

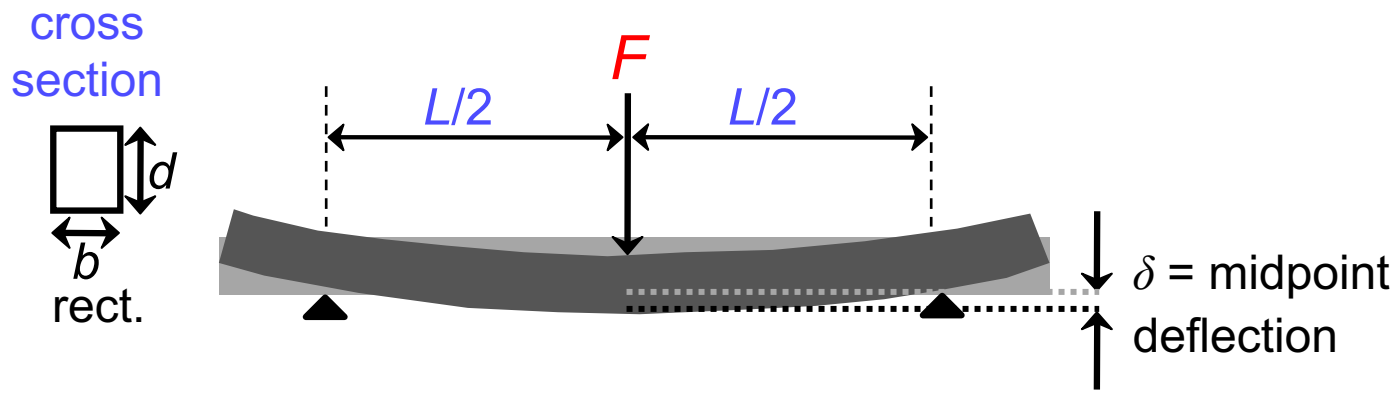
$$E = \frac{F}{\delta}\frac{L^3}{4bd^3}$$

Apply some force (F) and see how much the specimen bends (δ).

This gives the **"flexural modulus"** which is like the elastic modulus.

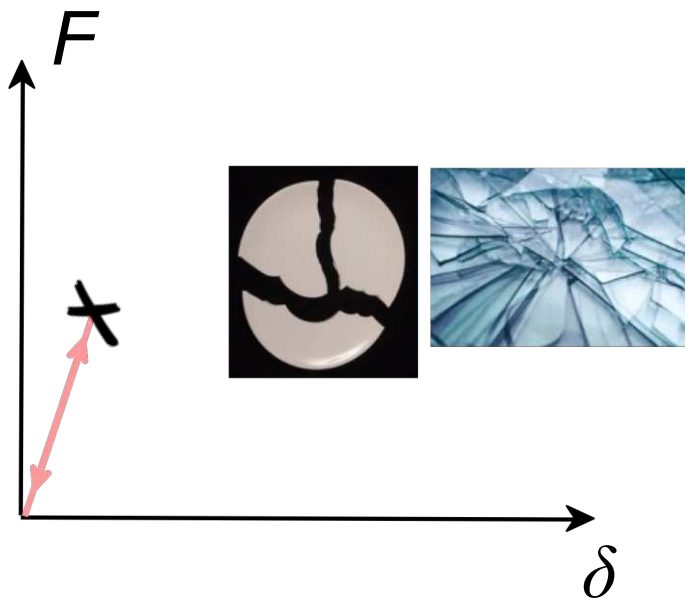
Testing the mechanical properties of ceramics

3-Point Bend Testing is instead used to measure how resistant ceramics are to deformation



Flexural strength is related to the load at fracture

$$\sigma_{fs} = \frac{3F_f L}{2bd^2}$$



High flexural strength implies the ceramic is very resistant to fracture

Questions on the mechanical properties of ceramics?

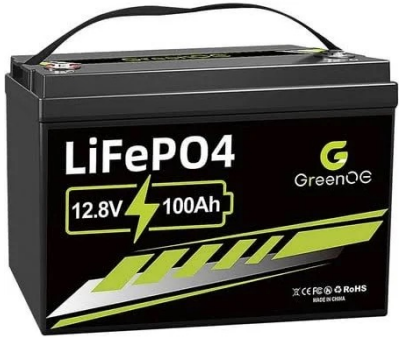
Know: they are generally stiff and very brittle

So...What are ceramics used for?





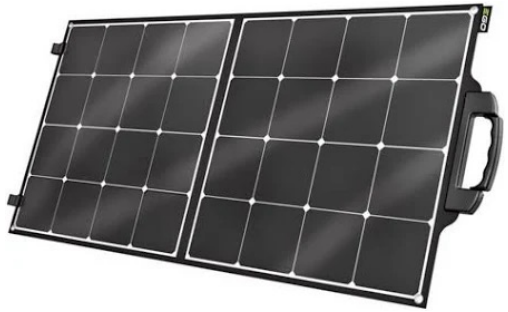




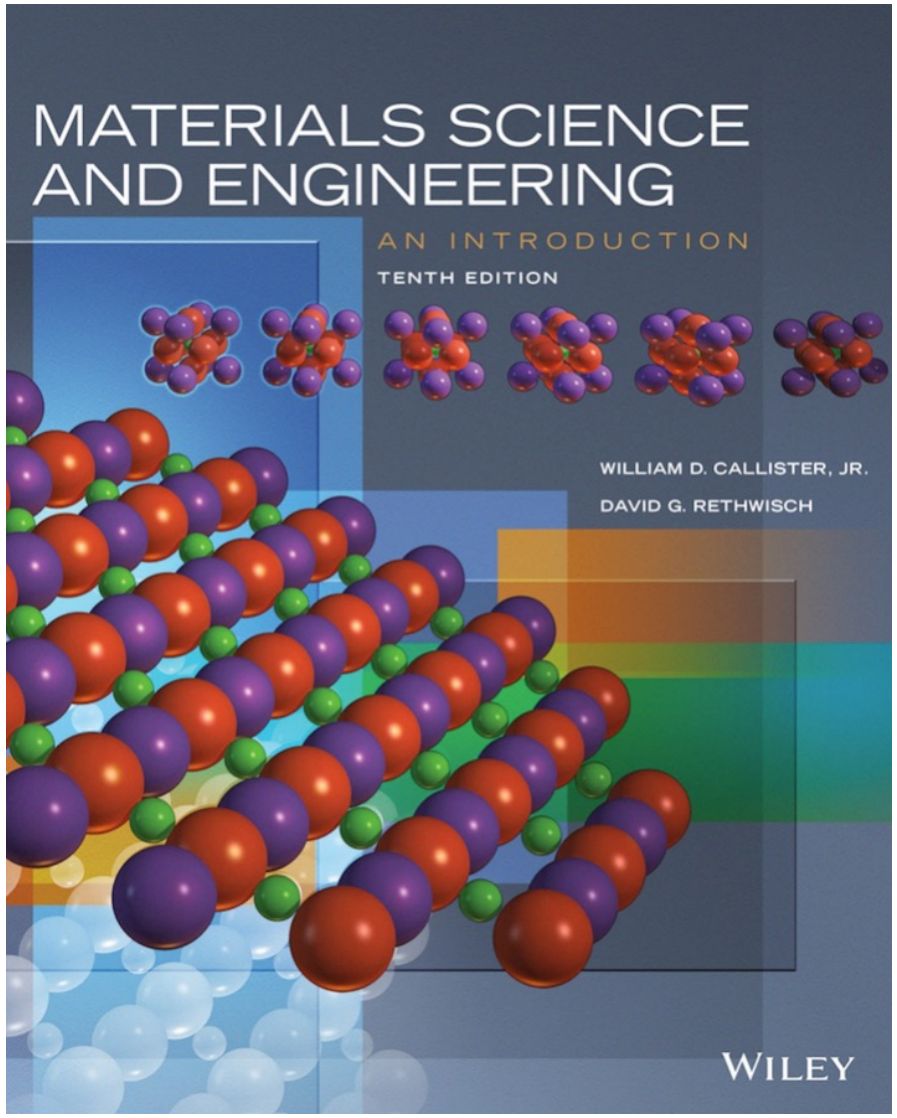








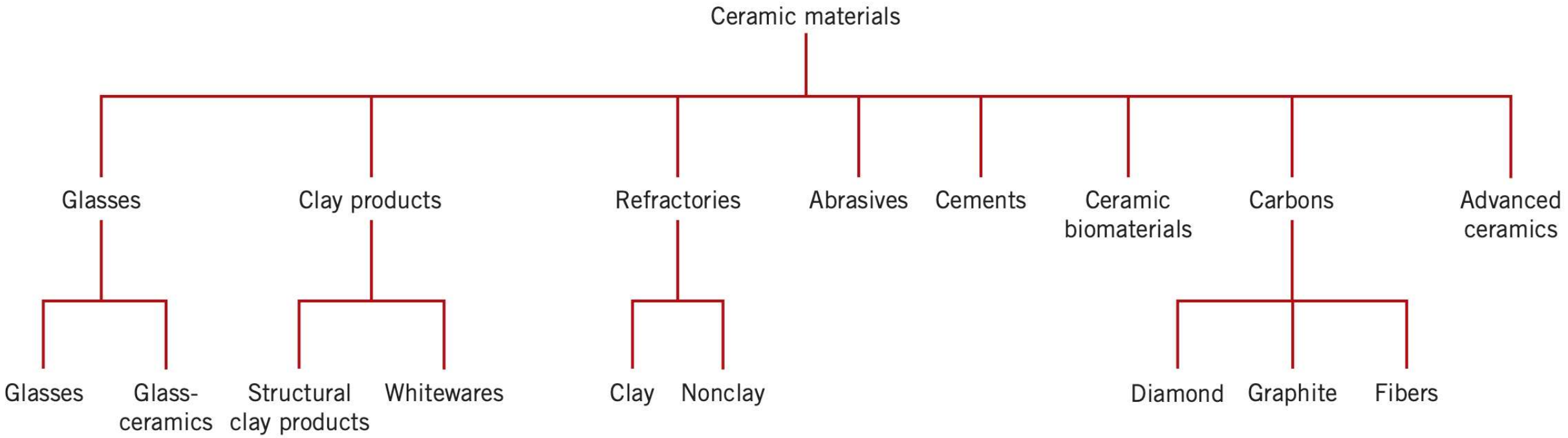
Reading for this subject



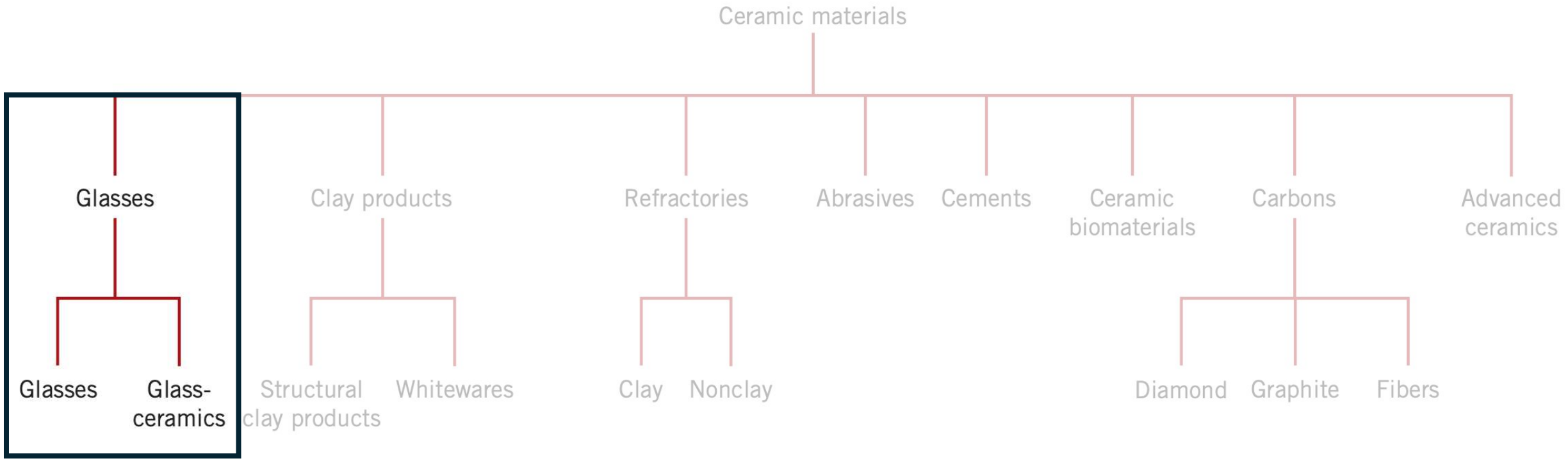
Chapter 13 Applications and Processing of Ceramics

This discussion will closely follow **Chapter 13** of Callister, **pages 443-476** of the 10th edition.

Types of ceramics and their applications

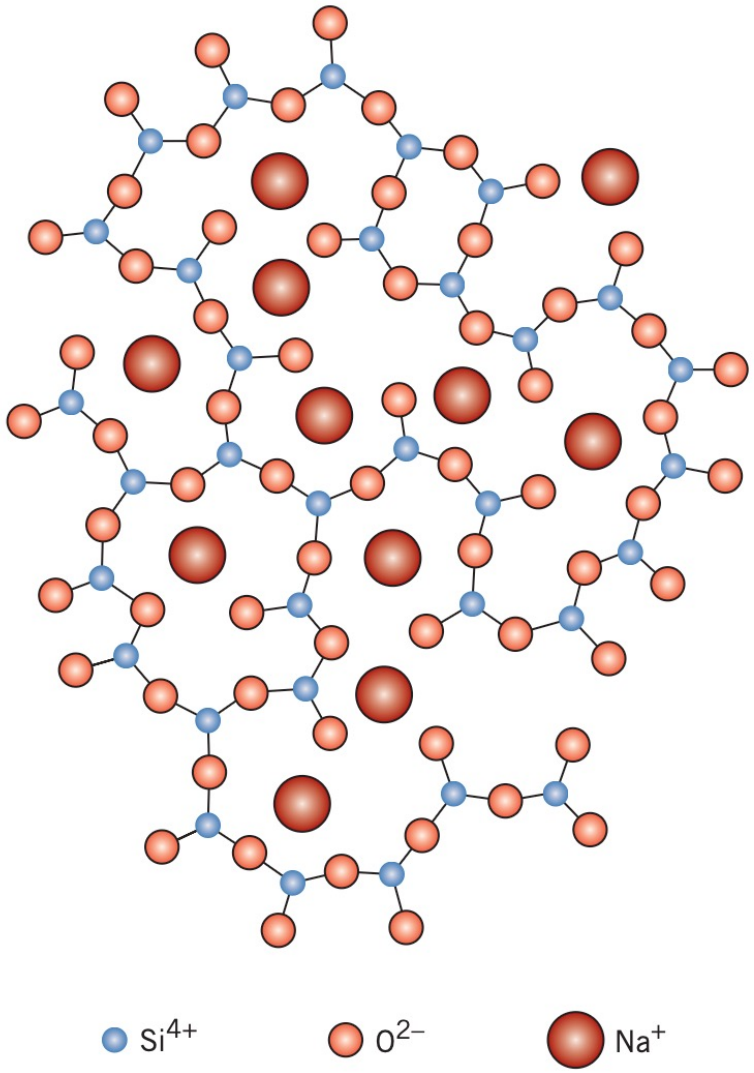


Types of ceramics and their applications





Glasses and glass-ceramics



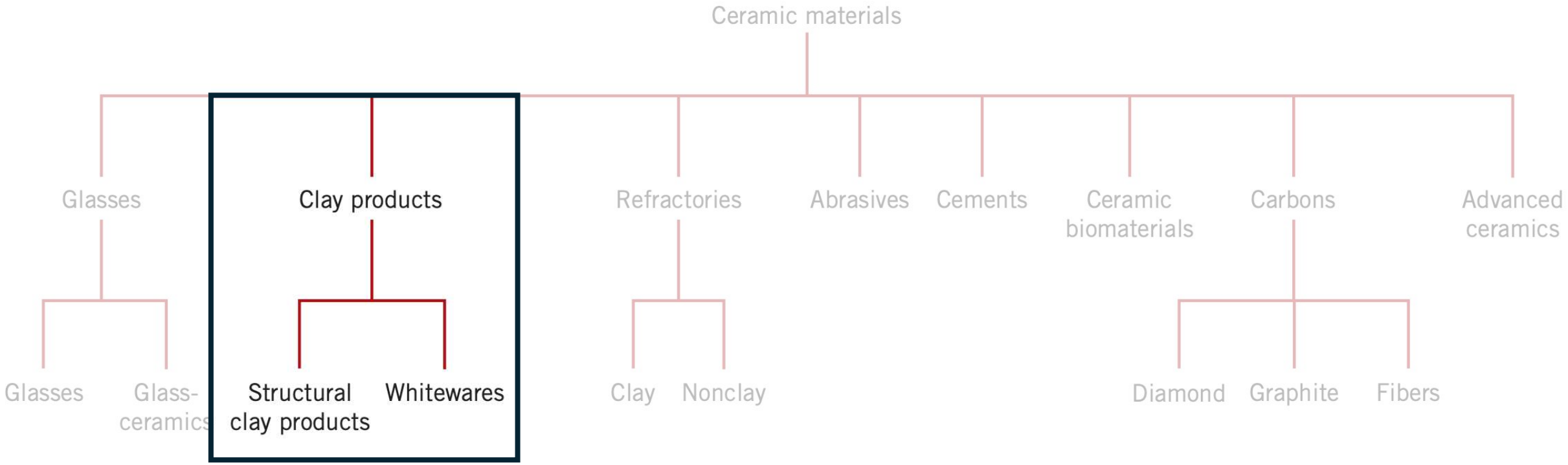
Glasses are largely based on **silica and silicates**, with **other elements** added to modify the properties as needed



Table 13.1 Compositions and Characteristics of Some Common Commercial Glasses

	Composition (wt%)						
Glass Type	*SiO_2*	*Na_2O*	*CaO*	*Al_2O_3*	*B_2O_3*	*Other*	*Characteristics and Applications*
Fused silica	>99.5						High melting temperature, very low coefficient of expansion (thermally shock-resistant)
96% Silica (Vycor)	96				4		Thermally shock- and chemically resistant—laboratory ware
Borosilicate (Pyrex)	81	3.5		2.5	13		Thermally shock- and chemically resistant—ovenware
Container (soda–lime)	74	16	5	1		4 MgO	Low melting temperature, easily worked, also durable
Fiberglass	55		16	15	10	4 MgO	Easily drawn into fibers—glass–resin composites
Optical flint	54	1				37 PbO, 8 K_2O	High density and high index of refraction—optical lenses
Glass-ceramic (Pyroceram)	43.5	14		30	5.5	6.5 TiO_2, 0.5 As_2O_3	Easily fabricated; strong; resists thermal shock—ovenware

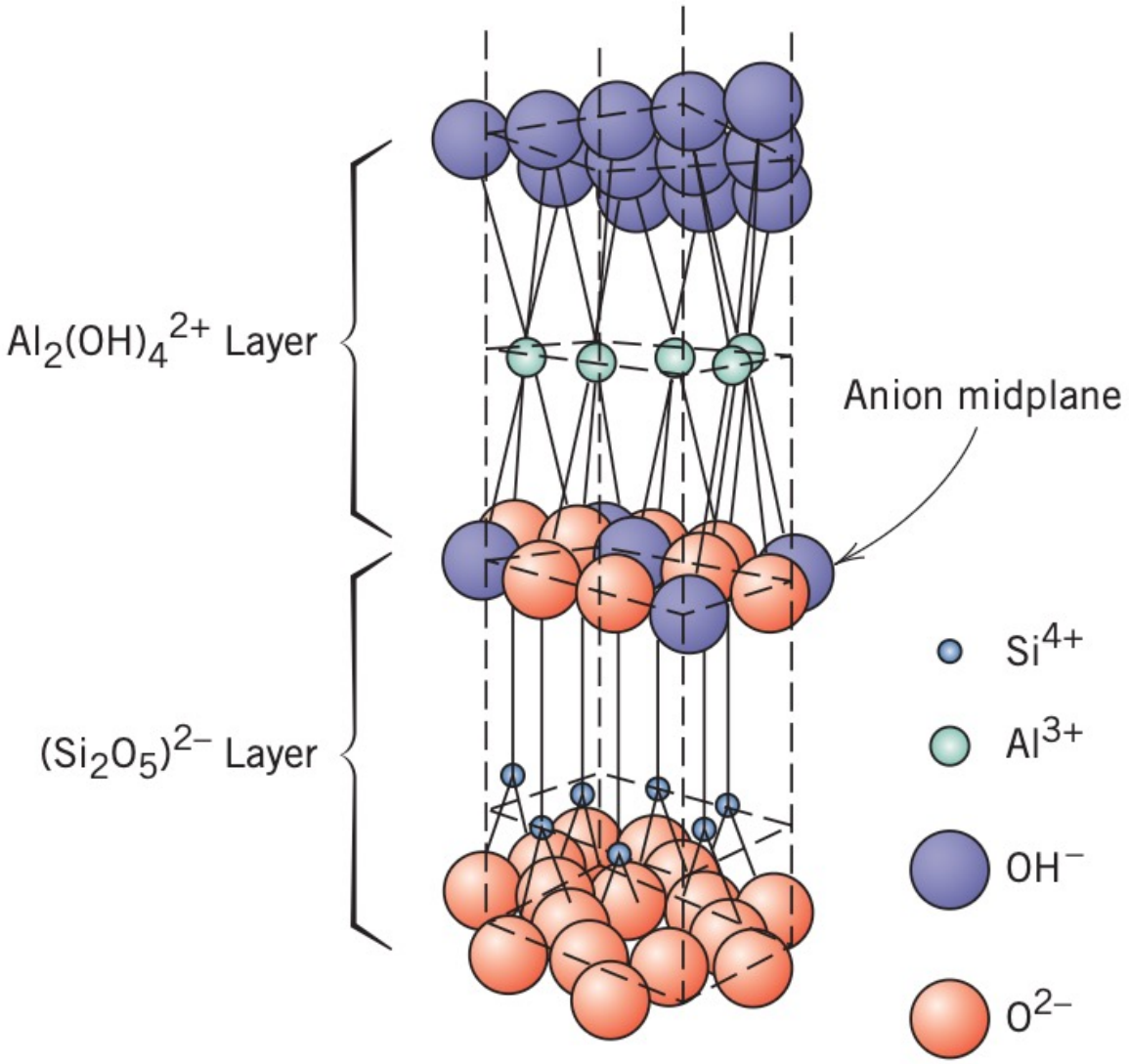
Types of ceramics and their applications







Structural clays and whitewares

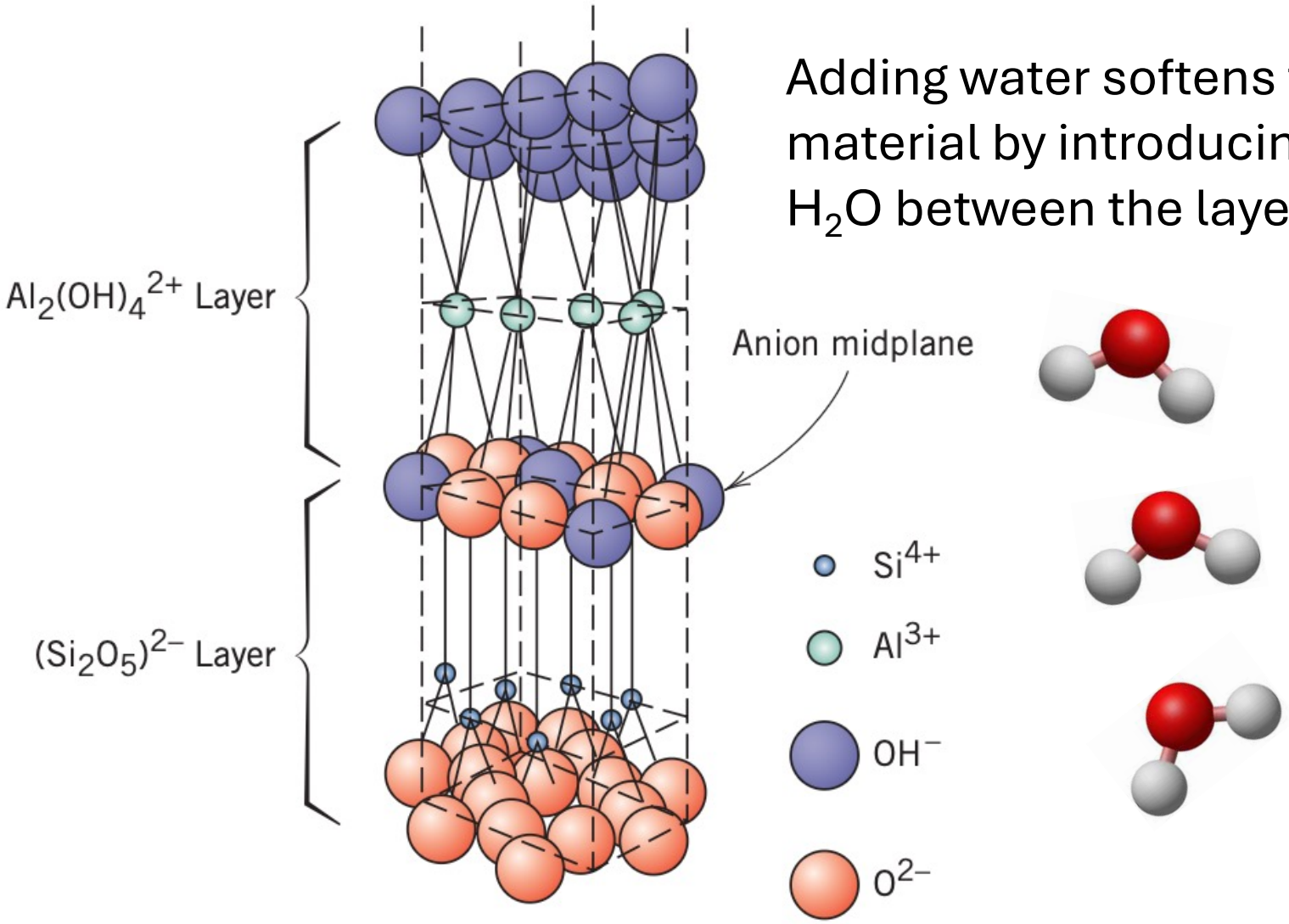


Typically **layered aluminosilicates** with other elements sometimes mixed in

Clay Mineral	Ideal Formula	Principal Missouri Occurence	Primary Use
Kaolinite Group	$Al_2Si_2O_5(OH)_4$	Bollinger and Cape Girardeau Counties	Paper filler, chinaware and most fire clays
Smectite Group	$\sim Ca_{0.17}(Al,MgFe)_2(Si,Al)_4O_{10}(OH)_2 \cdot nH_20$	Scott and Stoddard Counties	Pet absorbent and filler
Illite Group	$\sim K_{0.8}Al_2(AL_{0.8}Si_{3.2})O_{10}(OH)_2$	Most Misssouri Shales	Bricks and light weight aggregate for concrete
Chlorite Group	$(Mg,Fe,Al)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe,Al)_3(OH)_6$	Weathered igneous rocks from the St. Francois Mountains	None
Vermiculite	$\sim(Mg,Ca)_{0.3}(Mg,Fe^{2+},Fe^{3+},Al)_3(Si,Al)_4O_{10}(OH)_2$	Weathered igneous rocks from the St. Francois Mountains	Soil conditioner

They also tend to absorb water – which can be driven off by firing to form hard whitewares (*e.g.*, porcelain)

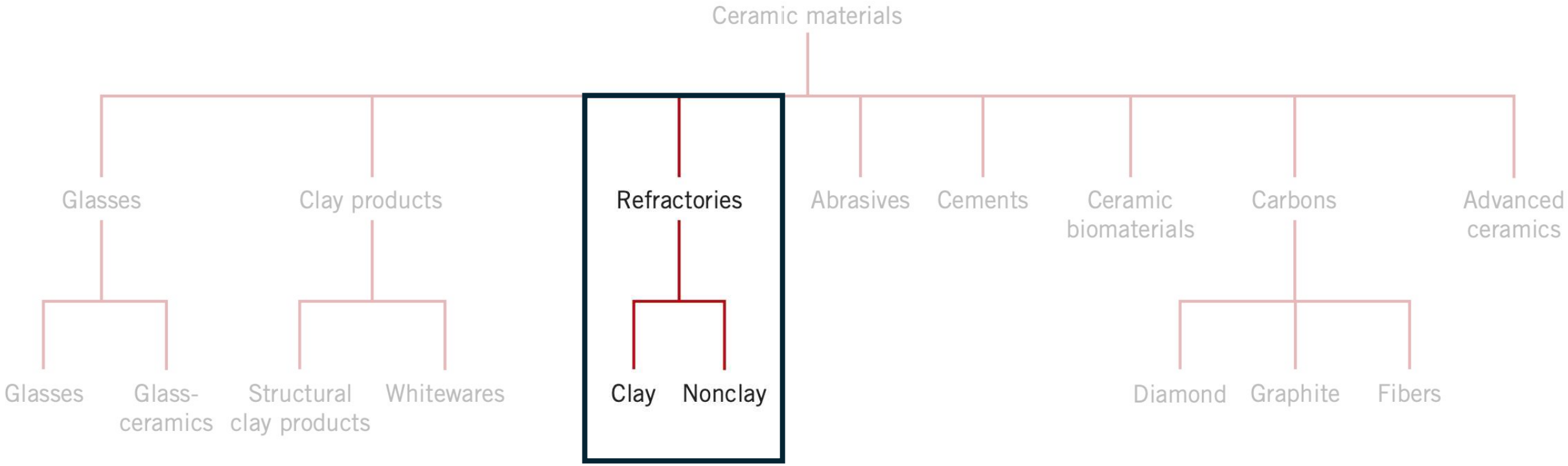
Structural clays and whitewares



Adding water softens the material by introducing H_2O between the layers



Types of ceramics and their applications



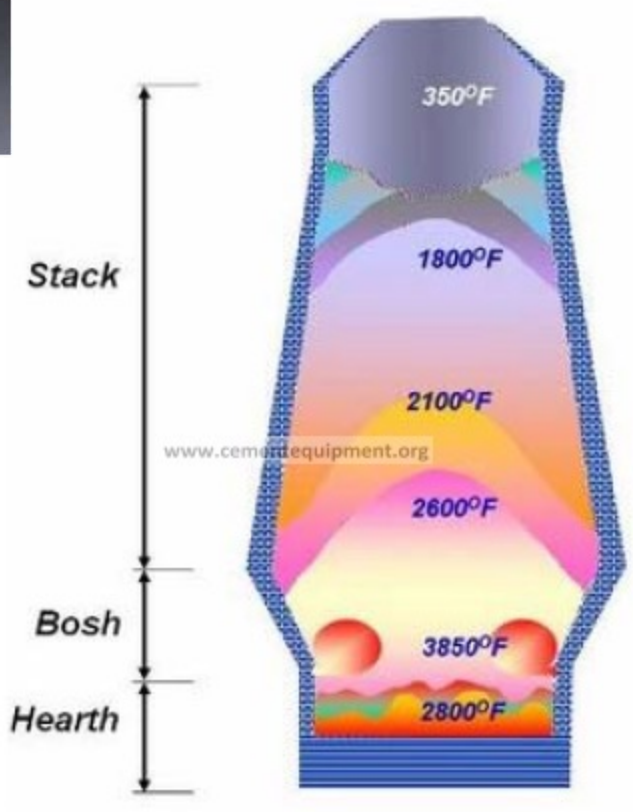




Refractory ceramics







Blast Furnace Temperature Zones





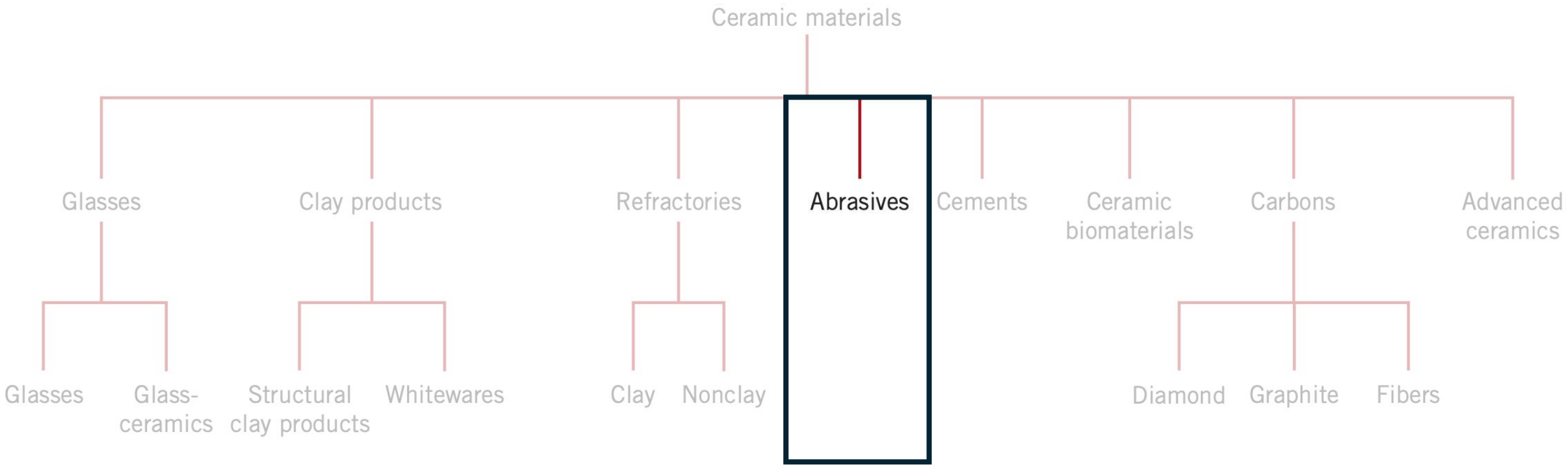
These are materials that can **withstand very high temperatures** *without* melting, decomposing, or reacting with anything

We often use natural materials: **binary oxides with strong bonds**

EX: ZrO_2, CaO, MgO, SiO_2, Al_2O_3

Non-Clays ***Clays***

Types of ceramics and their applications





Abrasives







These are materials that can **with exceptional hardness used in cutting/grinding applications**

These have some overlap with refractories as they tend to be **highly stable materials with strong covalent bonds:**

SiC, Al_2O_3, SiO_2, BC
(oxides and carbides)

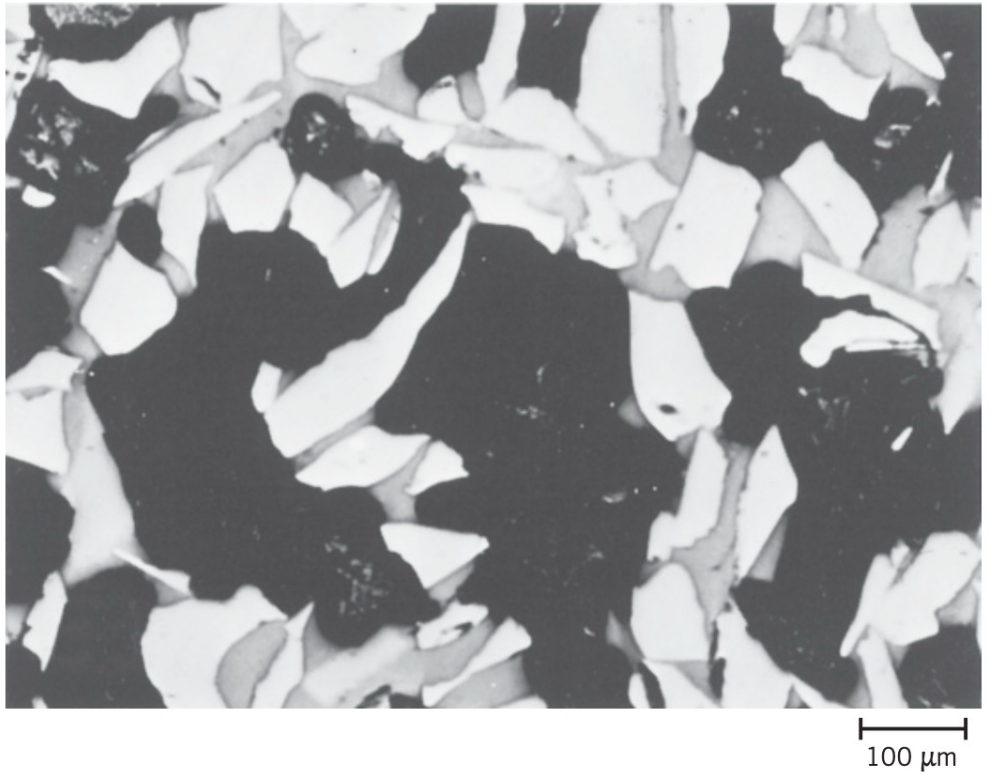
Diamond is the most effective (but expensive) abrasive

Abrasives



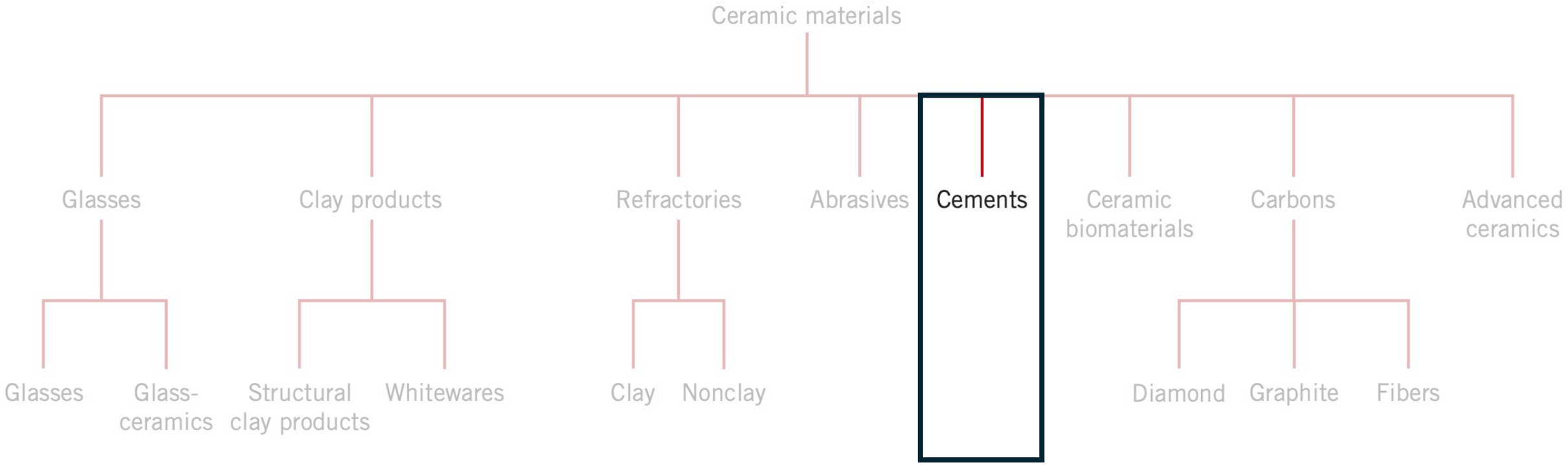






Microstructure matters! Larger grains tend to give a rougher and more abrasive surface.

Types of ceramics and their applications







Cements

These start off as a solid powder, but **when mixed with water, forms a paste that sets and hardens**



+





Initial solid powder

Hydration reaction forms a hard product

$$2CaO–SiO_2 + xH_2O \rightarrow 2CaO–SiO_2–xH_2O$$

Added water forms paste

Not drying that hardens it…
Quite the opposite

Cements



Cements are very important: **> 4 billion tons** are produced every year, contributing to more than **5% of all global CO_2 emissions!**

Primarily due to the high-*T* calcination step:

$$CaCO_3 \rightarrow CaO + CO_2$$





~1000 °C

Initial solid powder

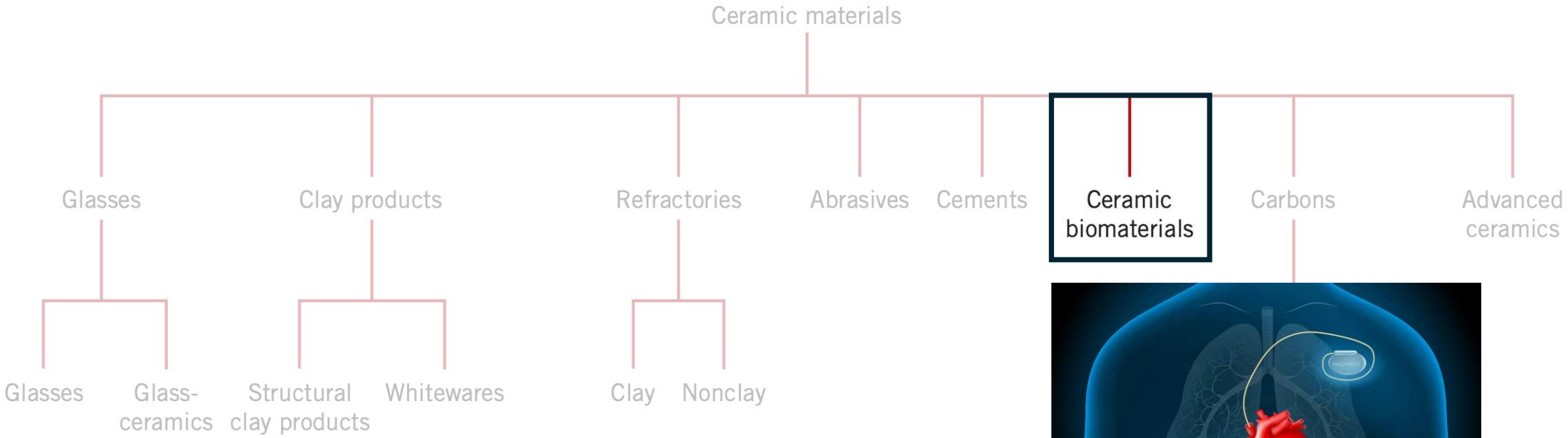
Hydration reaction forms a hard product

$$2CaO–SiO_2 + xH_2O \rightarrow 2CaO–SiO_2–xH_2O$$

Added water forms paste

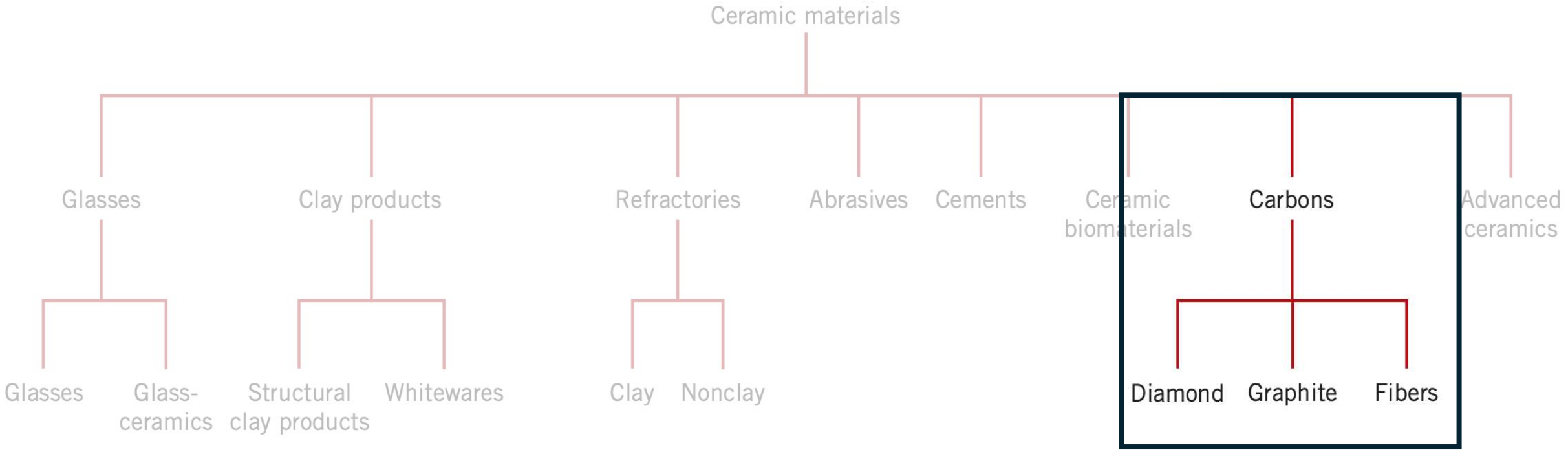
Not drying that hardens it…
Quite the opposite

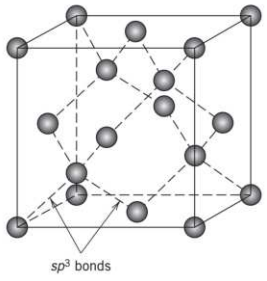
Types of ceramics and their applications



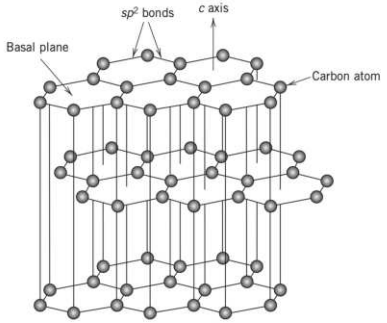
These must remain inert in your body

Types of ceramics and their applications

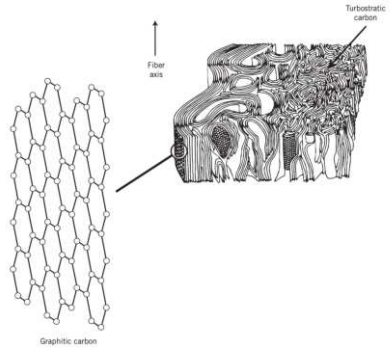


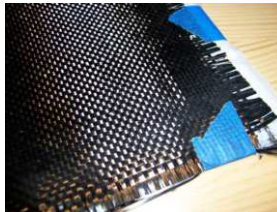




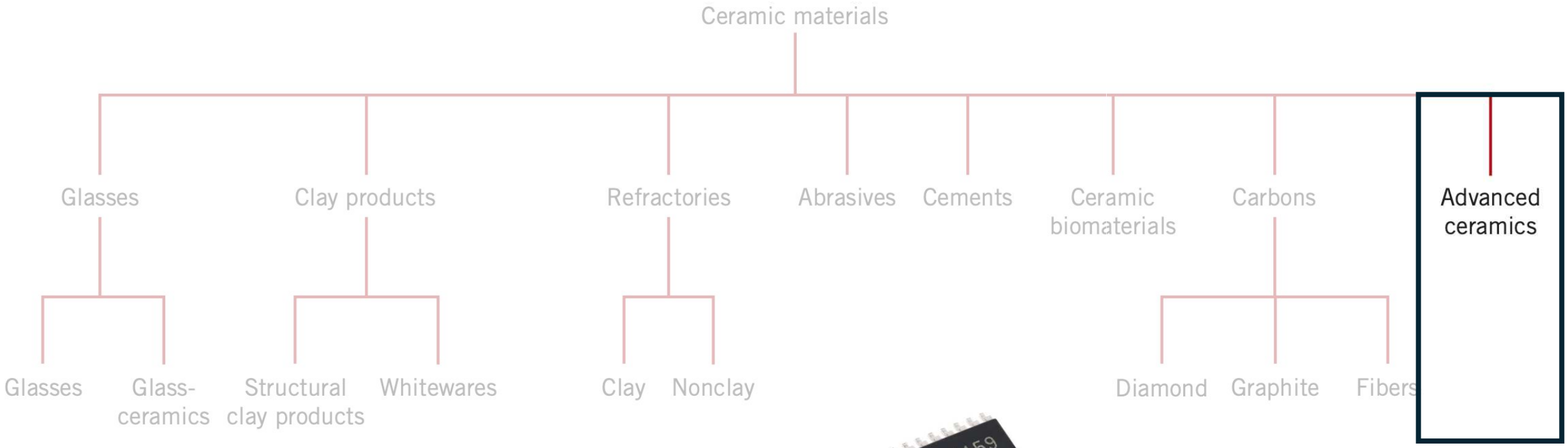




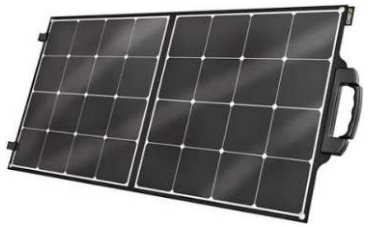




Types of ceramics and their applications



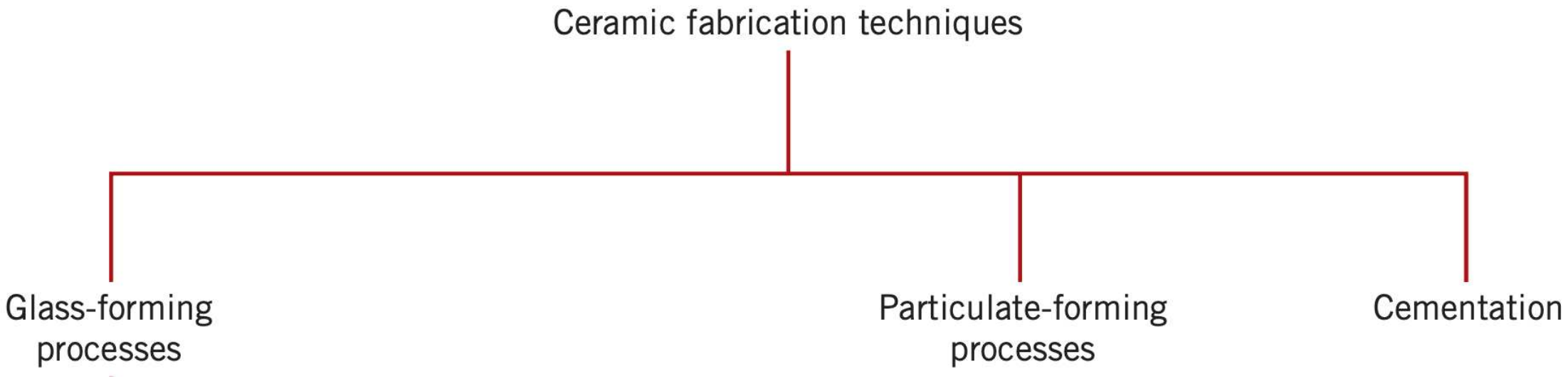




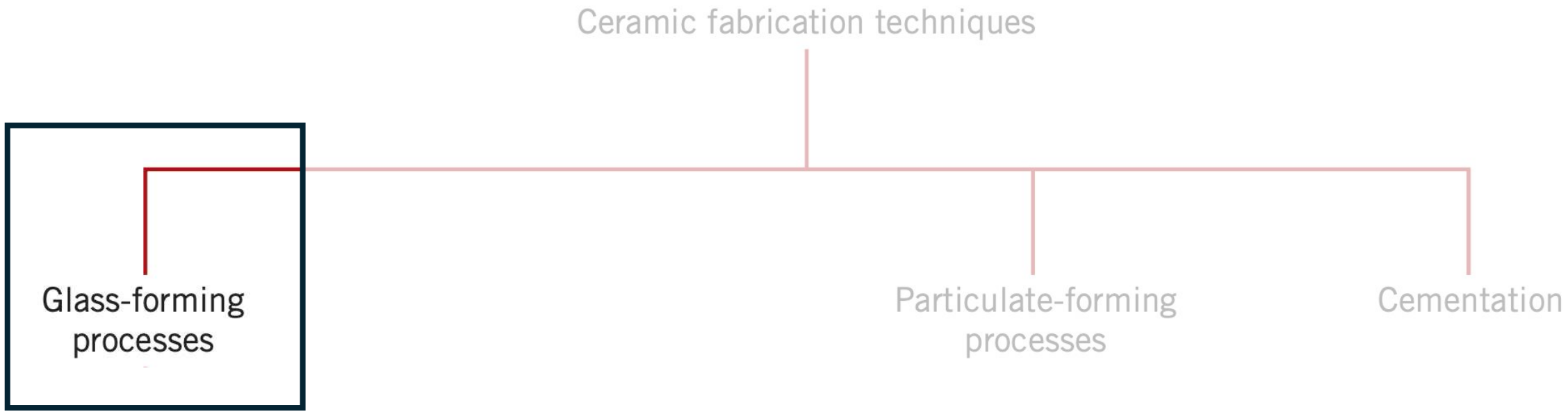


We'll cover these later when we discuss semiconductors and electrical properties

How do we make ceramics?

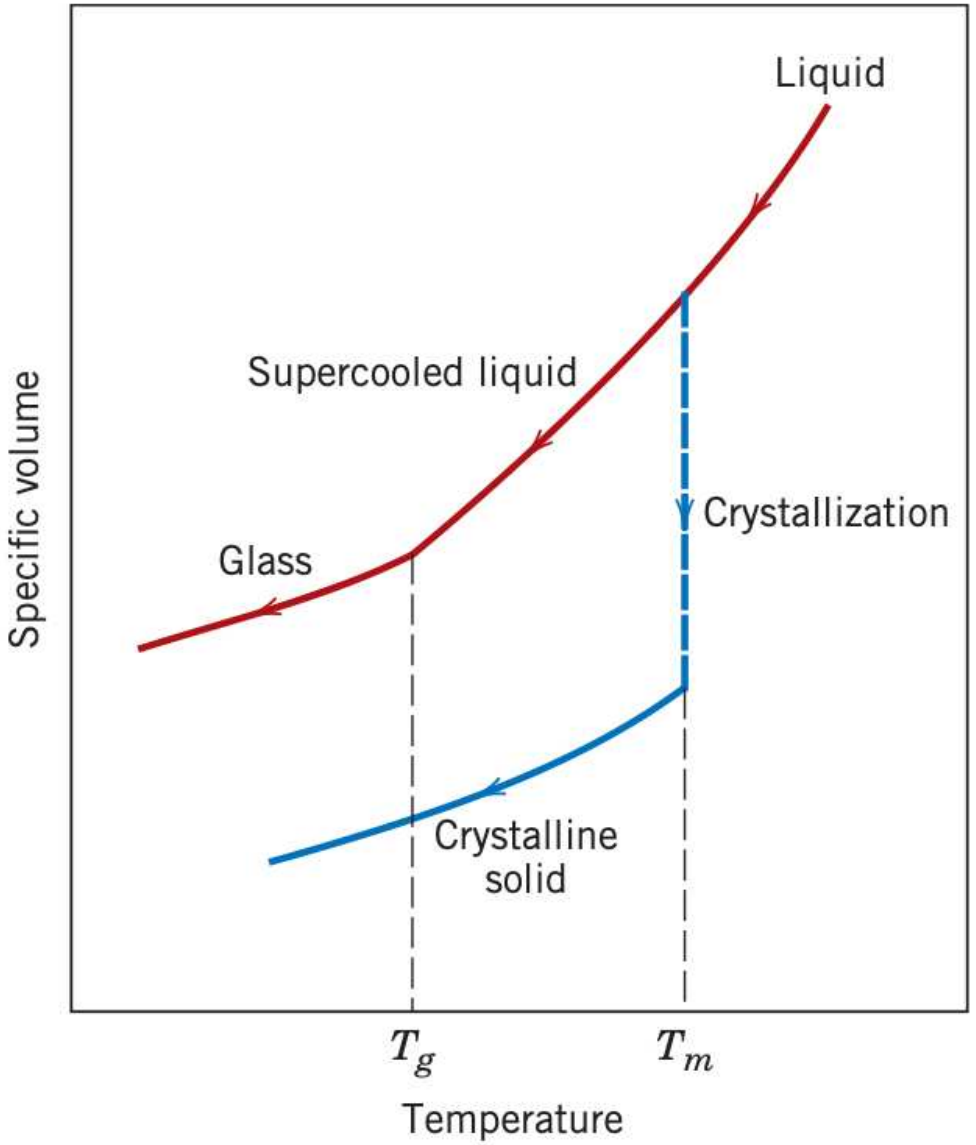


How do we make ceramics?

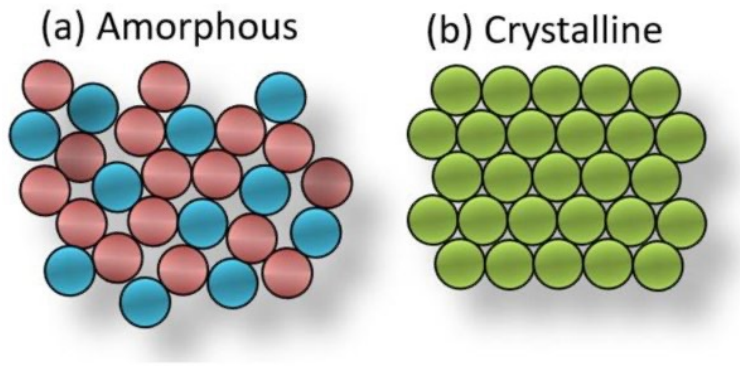


Usually involves some form of melting and casting

Glass forming processes

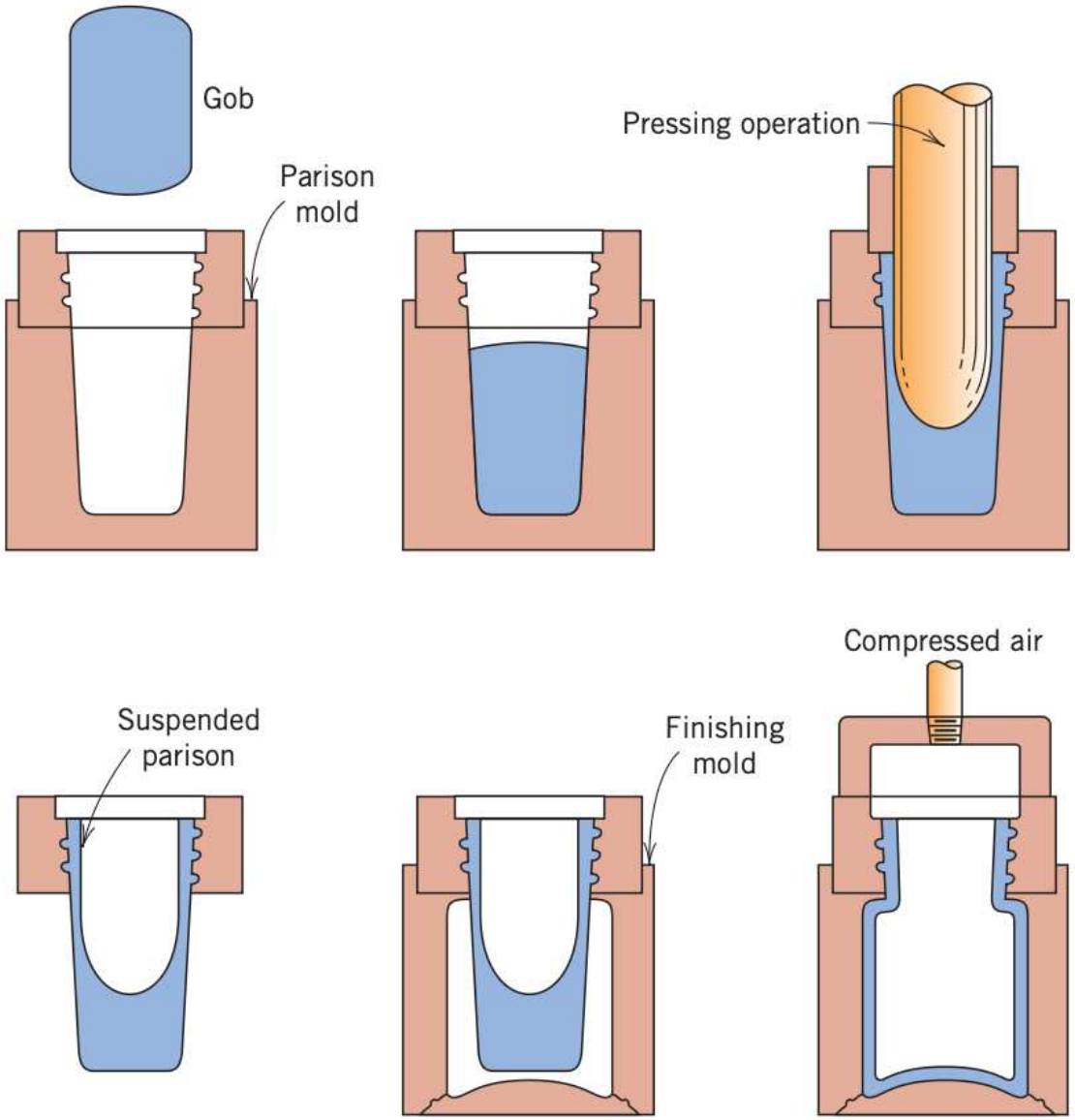






- Transforming a material from a melt into a solid crystal requires some diffusion of atoms
- If we can lower temperature fast enough to slow diffusion, we can prevent this transition entirely, leading to an amorphous (glass) solid

Glass forming processes: controlling final shape

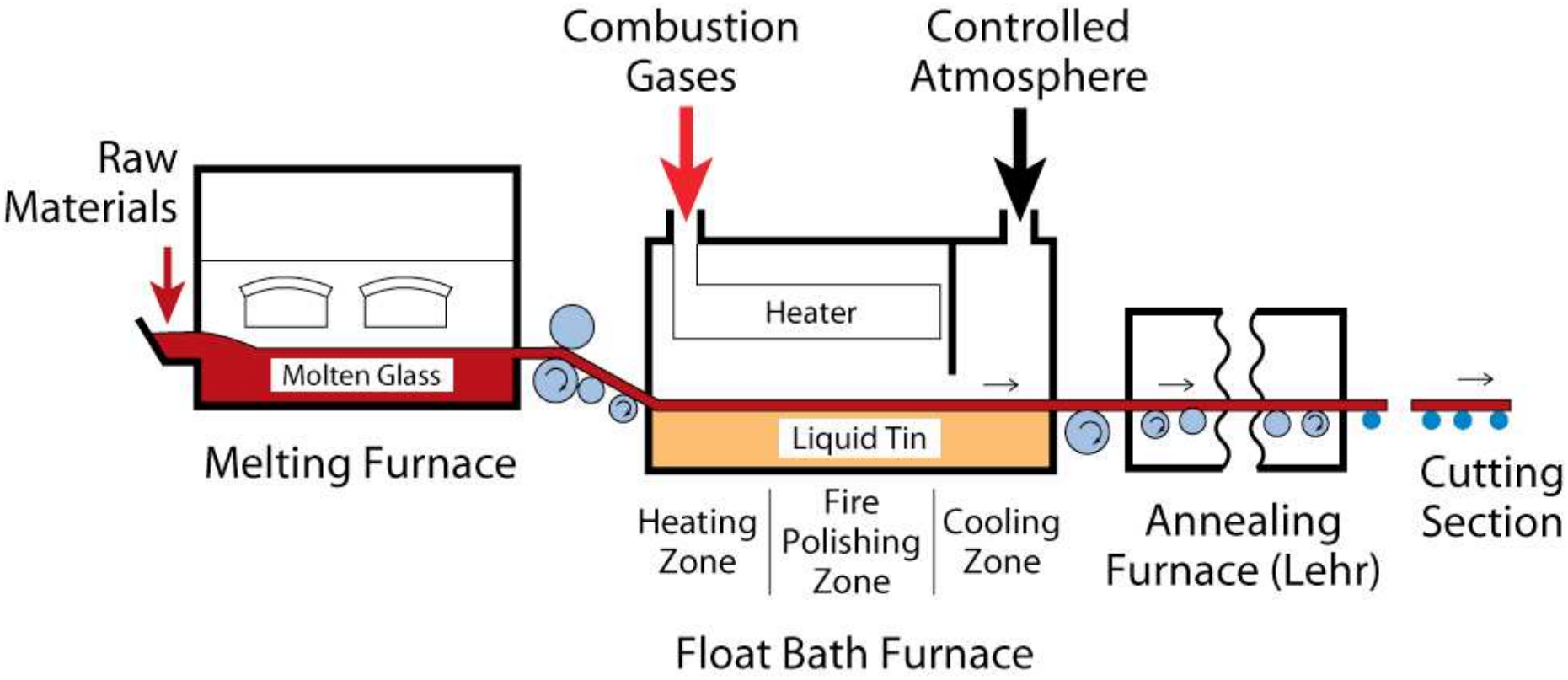


- The “press-and-blow” technique is widely used to make glasses, containers, *etc.*
- Final shape is dictated by choice of mold



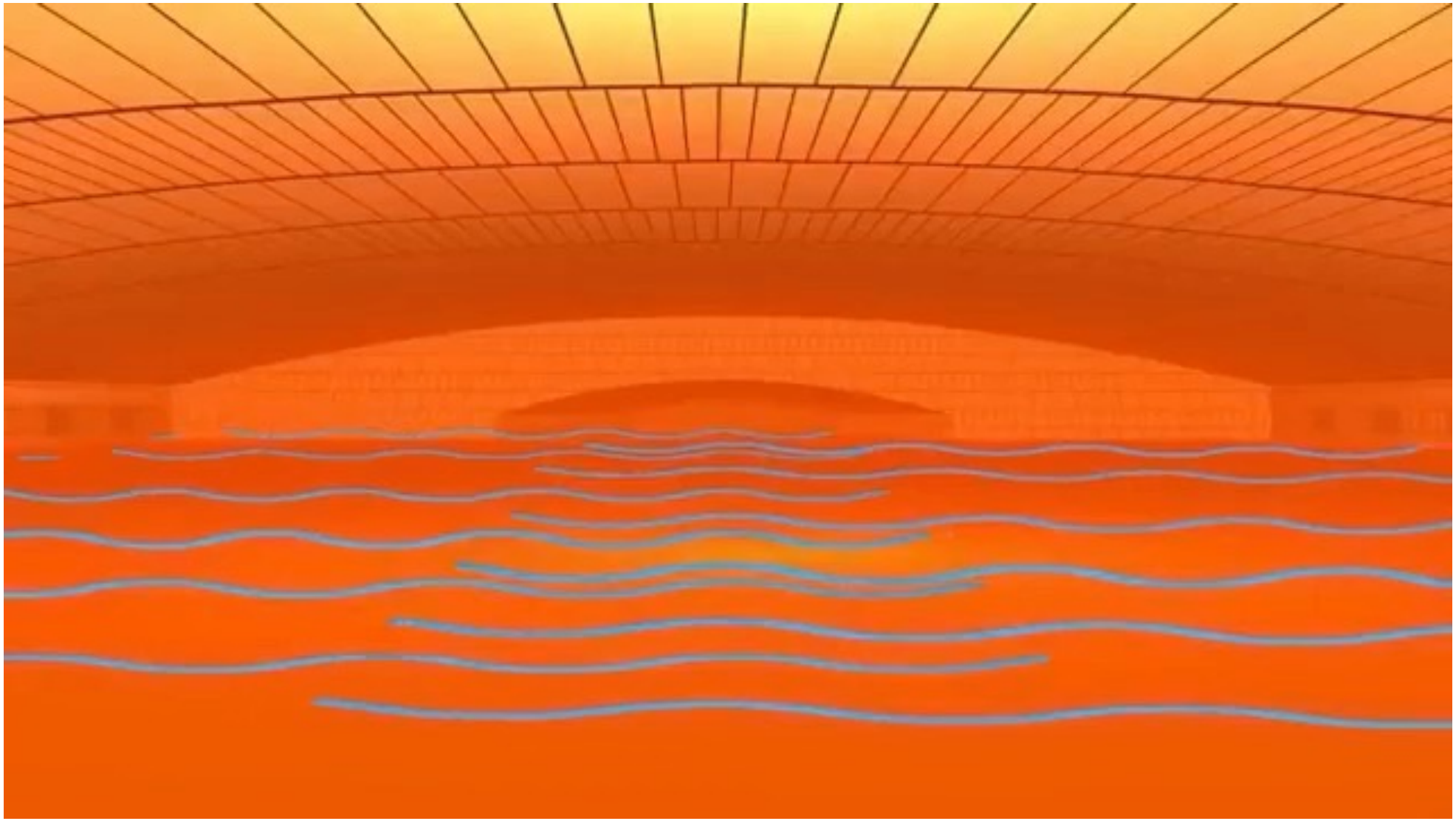
Glass forming processes: controlling final shape

If we instead want to form **sheets of glass** (*e.g.*, for windows)
we might use **continuous casting**

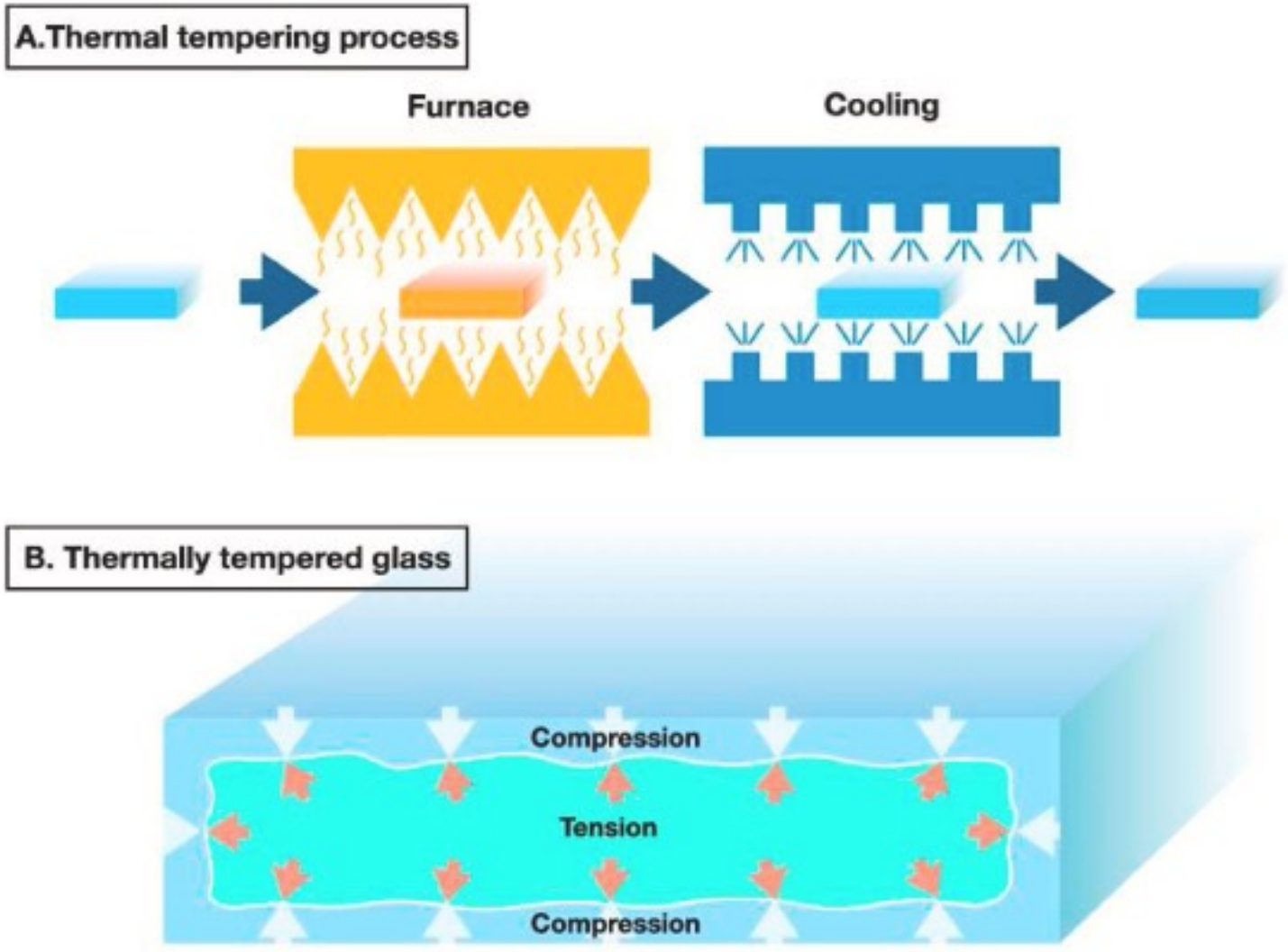


Many other methods – see textbook

Glass forming processes: controlling final shape



Heat treatments for tempered glass

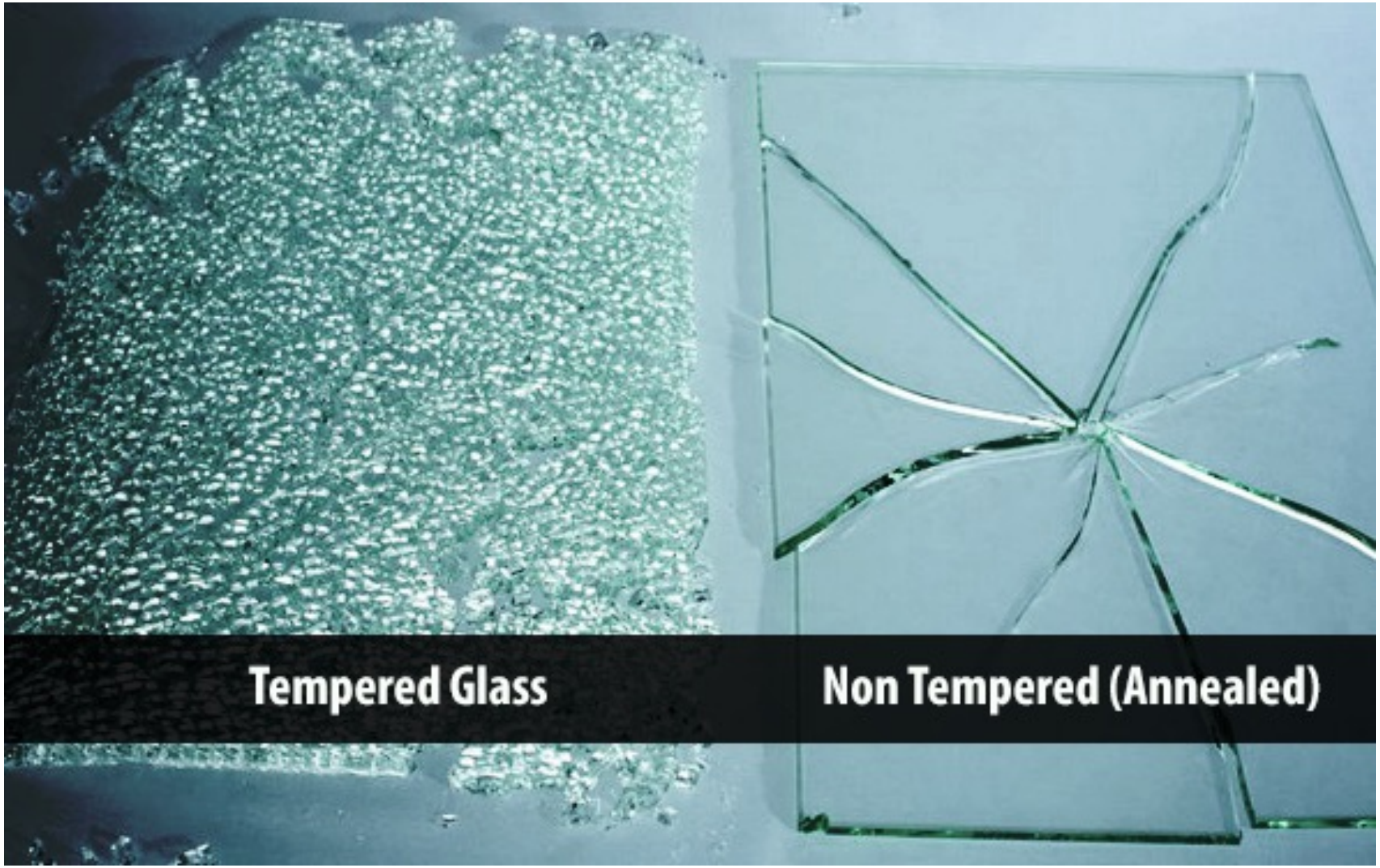


A sheet of glass is uniformly heated but then ***non*-uniformly cooled** through a jet of air

- **Outside** cools faster → remains **low density**
- **Inside** cools slower → relaxes to **high density**

Relative compression on the exterior **helps close any cracks that try to form**

Heat treatments for tempered glass



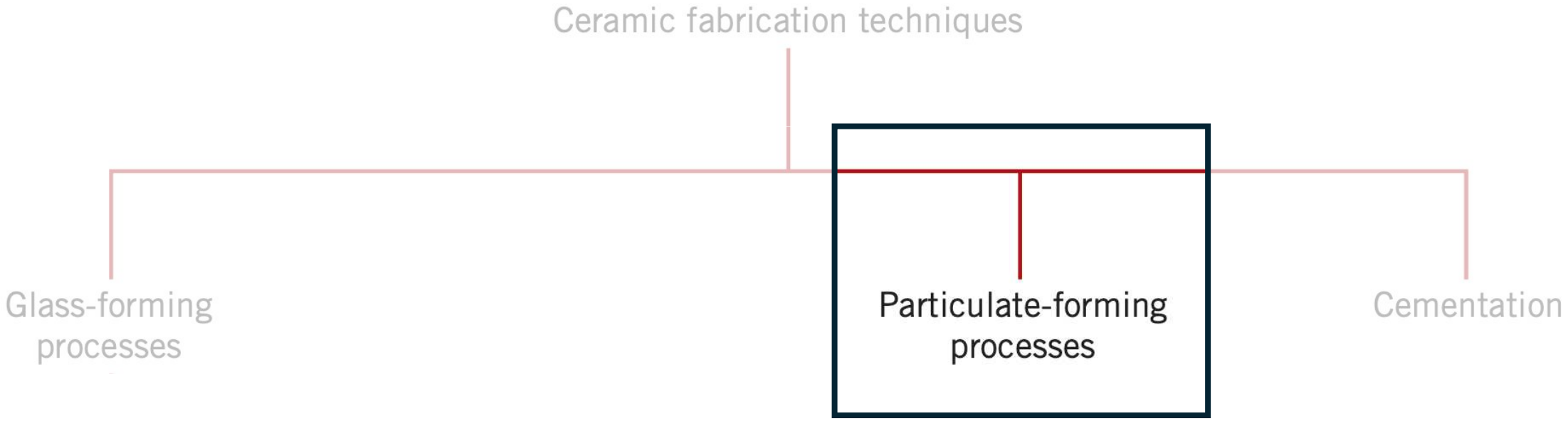
A cool example: Prince Rupert's drop



A cool example: Prince Rupert's drop

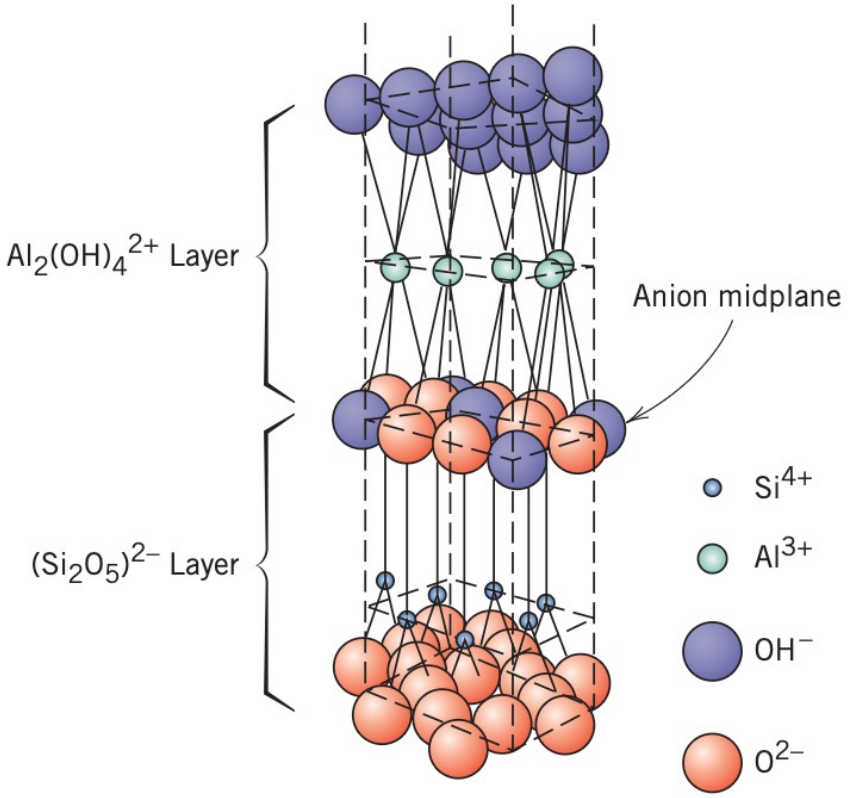


How do we make ceramics?



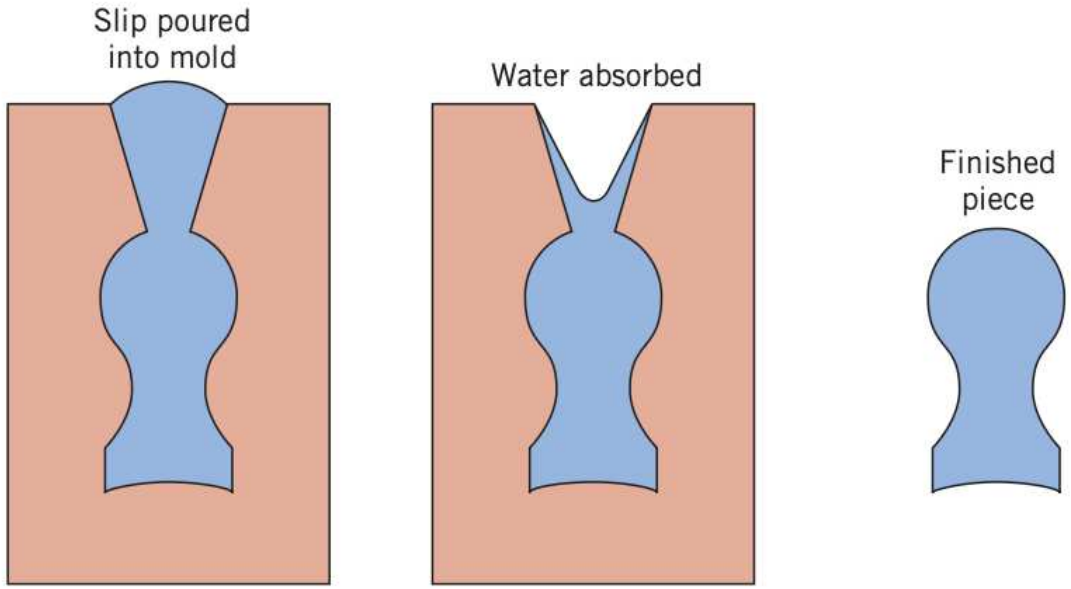
How do we turn powders into compact solids?

Particulate-forming methods: clays

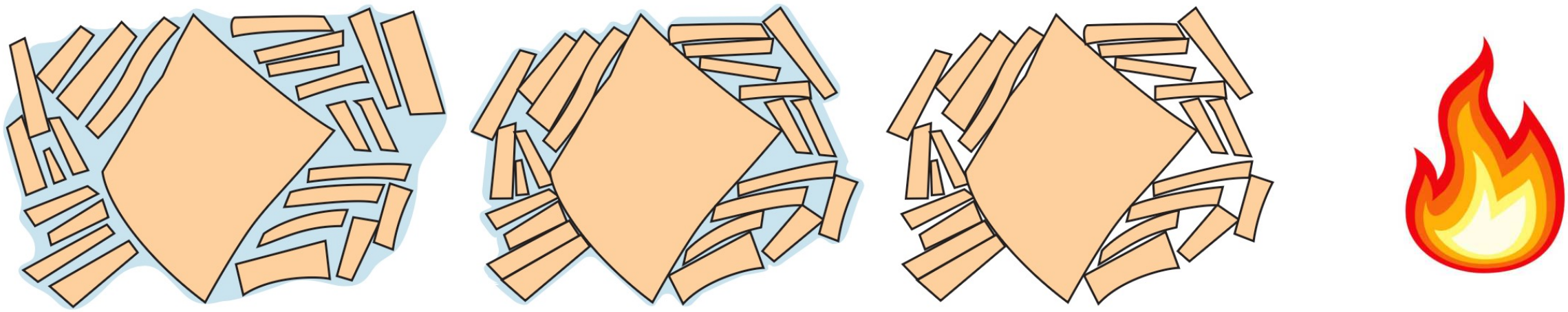




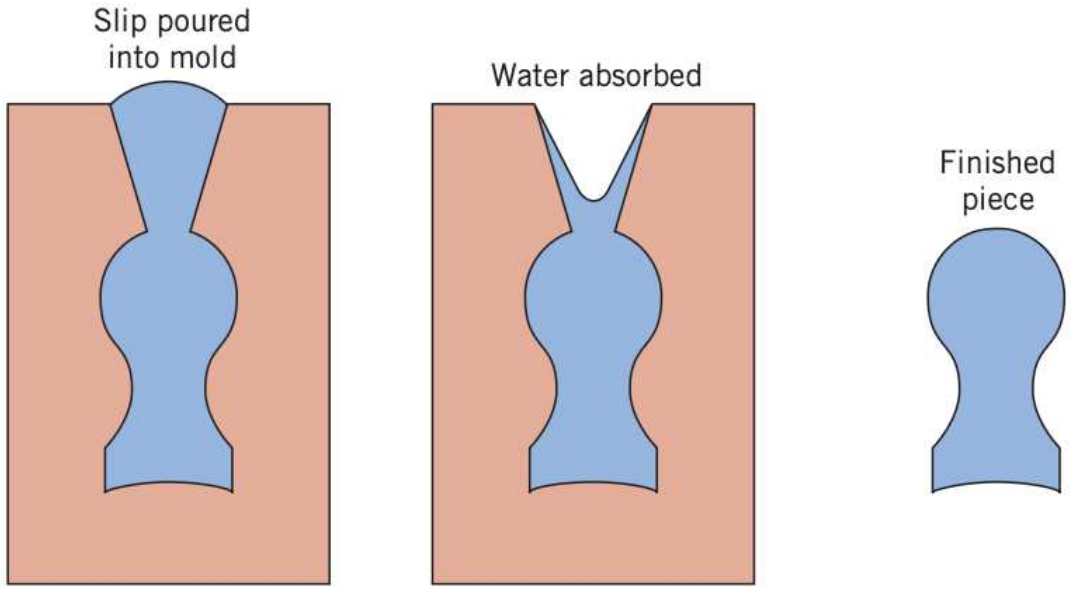
- Recall that **clays are layered aluminosilicates**, where the layers are bonded together through Van der Waals bonding
- **Adding water** to the structures puts H_2O in between the layers, weakening their bonds and **making the material easily molded**



Particulate-forming methods: clays



The water can then be removed to harden the material by **firing** it, but care should be taken to avoid cracking by heating slowly, since water removal causes some shrinkage



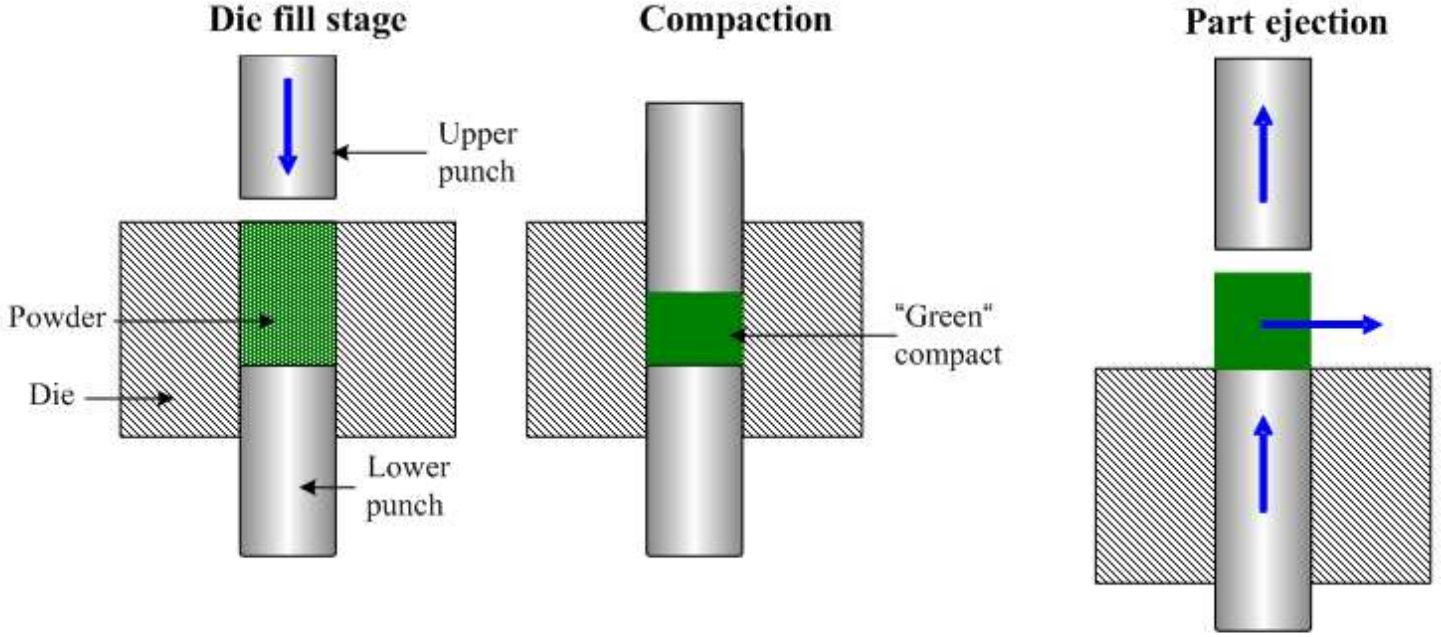
Particulate-forming methods: non-clay powders



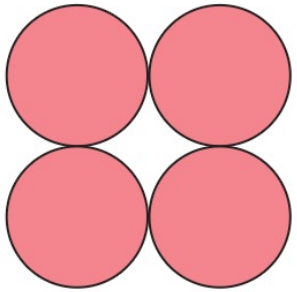
Many solid powders are not clays, meaning we can't just add water to them, but we'd still like to compact them into specific form factors

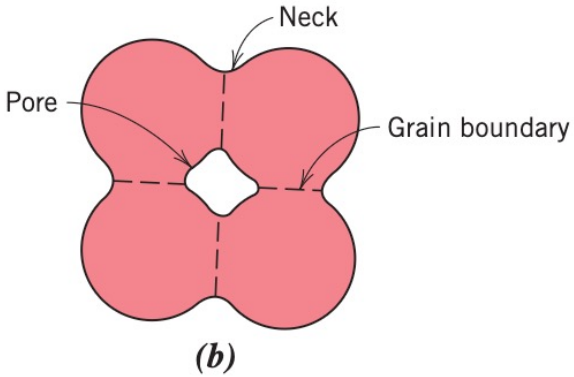
To do this, we can **press** them as shown below

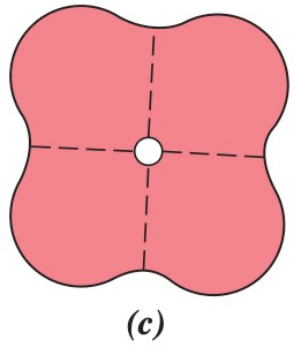
This leads to compact powders, but the individual **grains are still not chemically bonded**



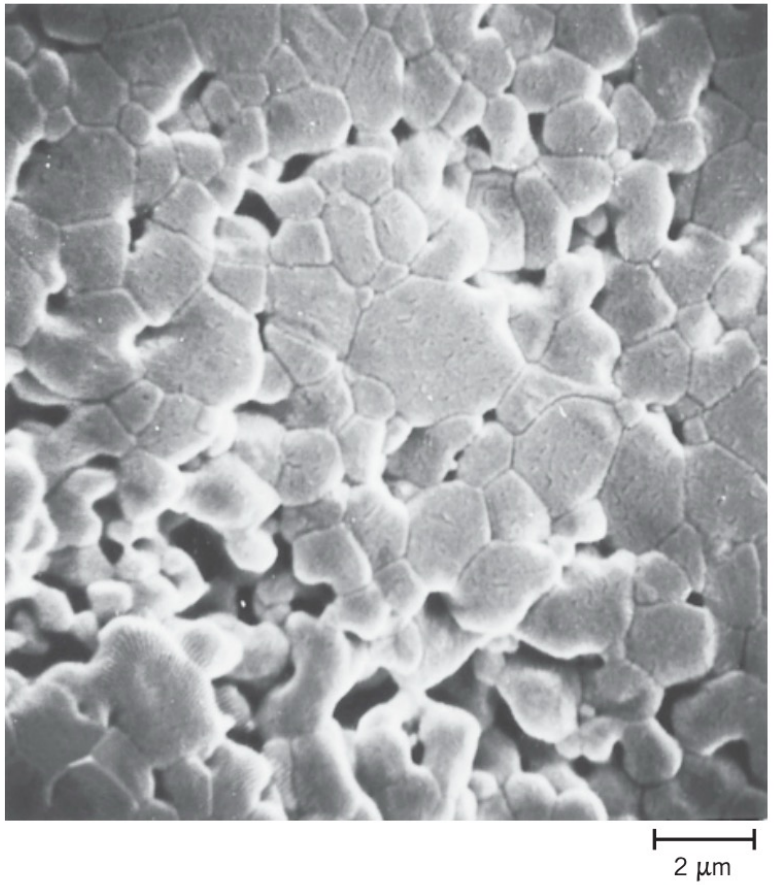
Particulate-forming methods: non-clay powders







The solution is **sintering:** heating the compact powders slightly below their melting point to chemically bond the grains



Remember, grain boundaries are thermodynamically unfavorable – they don't "want" to be there. We just need to give the system enough thermal energy so that diffusion solves the problem.

How do we make ceramics?



+



fabrication techniques



Particulate-forming processes

Cementation

In contrast to clays: adding water actually *hardens* cements because H_2O reacts with the material.