

Chapter 12: Structures & Properties of Ceramics

ISSUES TO ADDRESS...

- Structures of ceramic materials:
How do they differ from those of metals?
- Point defects:
How are they different from those in metals?
- Impurities:
How are they accommodated in the lattice and how do they affect properties?
- Mechanical Properties:
What special provisions/tests are made for ceramic materials?



Ceramic Bonding

- Bonding:
 - Mostly ionic, some covalent.
 - % ionic character increases with difference in electronegativity.
- Large vs small ionic bond character:

IA																		0	
H																			He
2.1	IIA											III A	IV A	V A	VIA	VII A		-	
Li	Be											B	C	N	O	F		Ne	
1.0	1.5											2.0	2.5	3.0	3.5	4.0		-	
Na	Mg											Al	Si	P	S	Cl		Ar	
0.9	1.2	IIIB	IVB	VB	VIB	VII B	VIII			IB	IIB	1.5	1.8	2.1	2.5	3.0		-	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br		Kr	
0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6	1.6	1.8	2.0	2.4	2.8		-	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I		Xe	
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5		-	
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At		Rn	
0.7	0.9	1.1-1.2	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.8	1.9	2.0	2.2		-	
Fr	Ra	Ac-No																	
0.7	0.9	1.1-1.7																	

CaF₂: large

SiC: small

Adapted from Fig. 2.7, *Callister 7e*. (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.



Ceramic Crystal Structures

Oxide structures

- oxygen anions much larger than metal cations
- close packed oxygen in a lattice (usually FCC)
- cations in the holes of the oxygen lattice



Site Selection

Which sites will cations occupy?

1. Size of sites

- does the cation fit in the site

2. Stoichiometry

- if all of one type of site is full the remainder have to go into other types of sites.

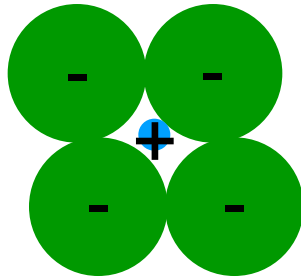
3. Bond Hybridization



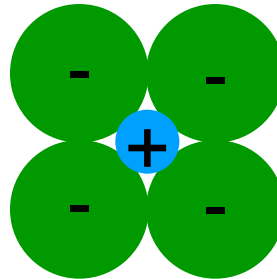
Ionic Bonding & Structure

1. Size - Stable structures:

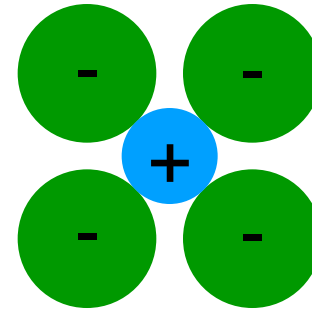
--maximize the # of nearest oppositely charged neighbors.



unstable



stable

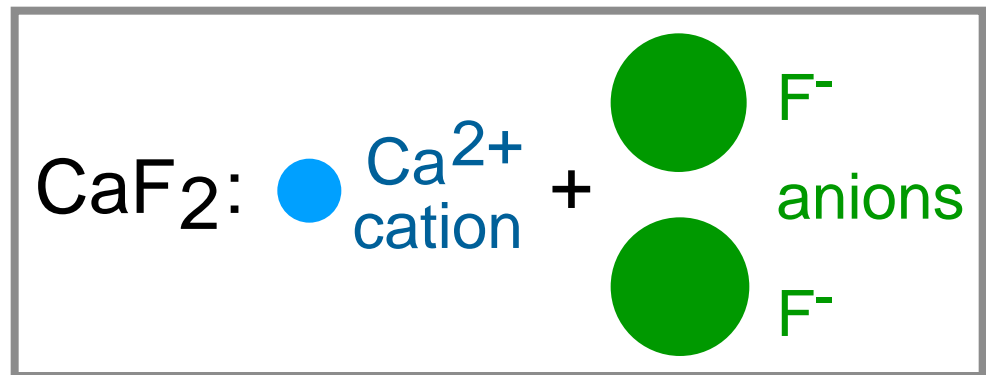


stable

Adapted from Fig. 12.1,
Callister 7e.

- **Charge Neutrality:**

--Net charge in the structure should be zero.



--General form: $A_m X_p$



m, p determined by charge neutrality



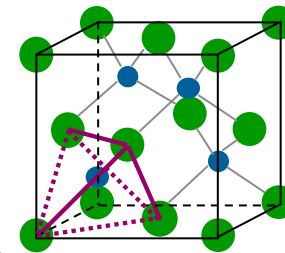
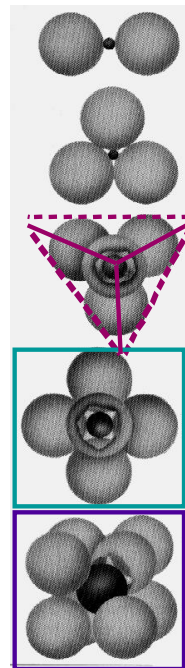
Coordination # and Ionic Radii

- Coordination # increases with $\frac{r_{\text{cation}}}{r_{\text{anion}}}$

Issue: How many anions can you arrange around a cation?

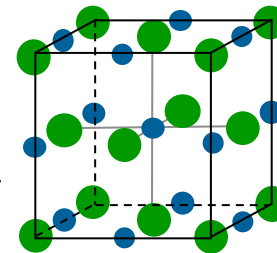
$\frac{r_{\text{cation}}}{r_{\text{anion}}}$	Coord #	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	T_D
0.414 - 0.732	6	O_H
0.732 - 1.0	8	cubic

Adapted from Table 12.2, Callister 7e.



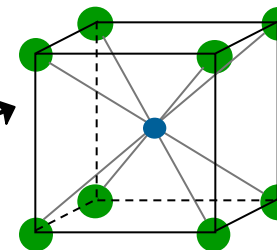
ZnS
(zincblende)

Adapted from Fig. 12.4, Callister 7e.



NaCl
(sodium chloride)

Adapted from Fig. 12.2, Callister 7e.



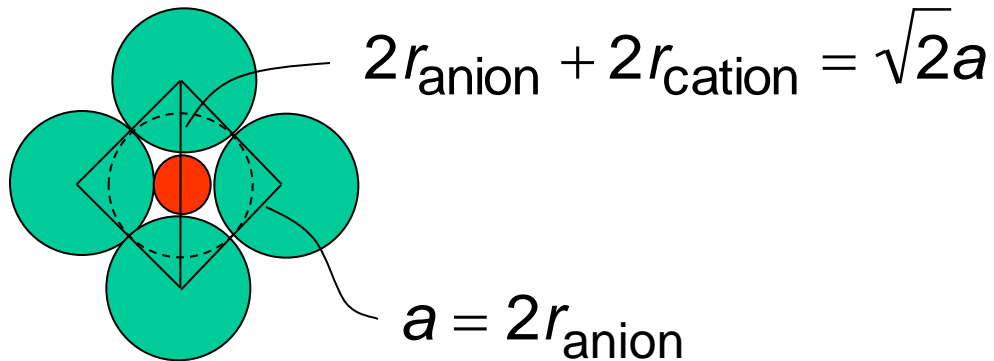
CsCl
(cesium chloride)

Adapted from Fig. 12.3, Callister 7e.



Cation Site Size

- Determine minimum $r_{\text{cation}}/r_{\text{anion}}$ for O_{H} site (C.N. = 6)



$$2r_{\text{anion}} + 2r_{\text{cation}} = 2\sqrt{2}r_{\text{anion}}$$

$$r_{\text{anion}} + r_{\text{cation}} = \sqrt{2}r_{\text{anion}} \quad r_{\text{cation}} = (\sqrt{2} - 1)r_{\text{anion}}$$

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = 0.414$$



Site Selection II

2. Stoichiometry

- If all of one type of site is full the remainder have to go into other types of sites.

Ex: FCC unit cell has 4 O_H and 8 T_D sites.

If for a specific ceramic each unit cell has 6 cations and the cations prefer O_H sites

4 in O_H

2 in T_D



Site Selection III

3. Bond Hybridization – significant covalent bonding

- the hybrid orbitals can have impact if significant covalent bond character present
- For example in SiC
 - $X_{\text{Si}} = 1.8$ and $X_{\text{C}} = 2.5$

$$\% \text{ ionic character} = 100 \{1 - \exp[-0.25(X_{\text{Si}} - X_{\text{C}})^2]\} = 11.5\%$$

- ca. 89% covalent bonding
- both Si and C prefer sp^3 hybridization
- Therefore in SiC get T_D sites



Example: Predicting Structure of FeO

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

Cation Ionic radius (nm)

Al³⁺ 0.053

Fe²⁺ 0.077

Fe³⁺ 0.069

Ca²⁺ 0.100

Anion

O²⁻ 0.140

Cl⁻ 0.181

F⁻ 0.133

- Answer:

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{0.077}{0.140} = 0.550$$

based on this ratio,

--coord # = 6

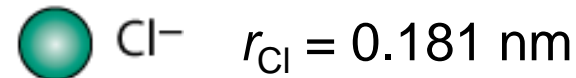
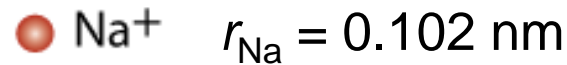
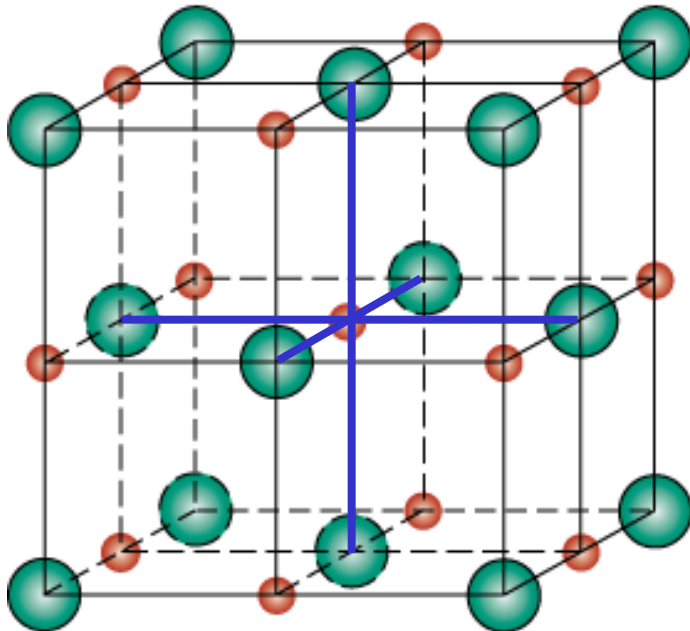
--structure = NaCl

Data from Table 12.3,
Callister 7e.



Rock Salt Structure

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



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

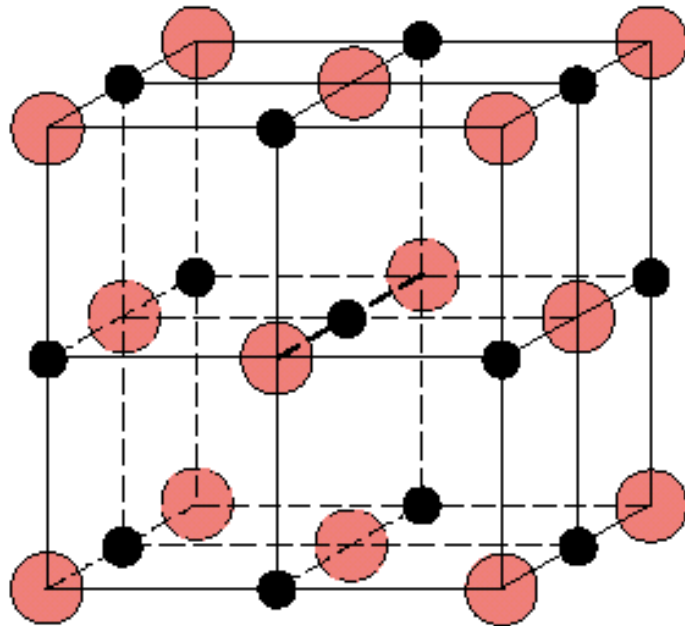
∴ cations prefer O_H sites

Adapted from Fig.
12.2, *Callister 7e*.



MgO and FeO

MgO and FeO also have the NaCl structure



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

∴ cations prefer O_{H} sites

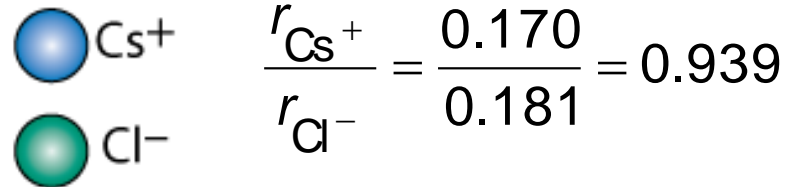
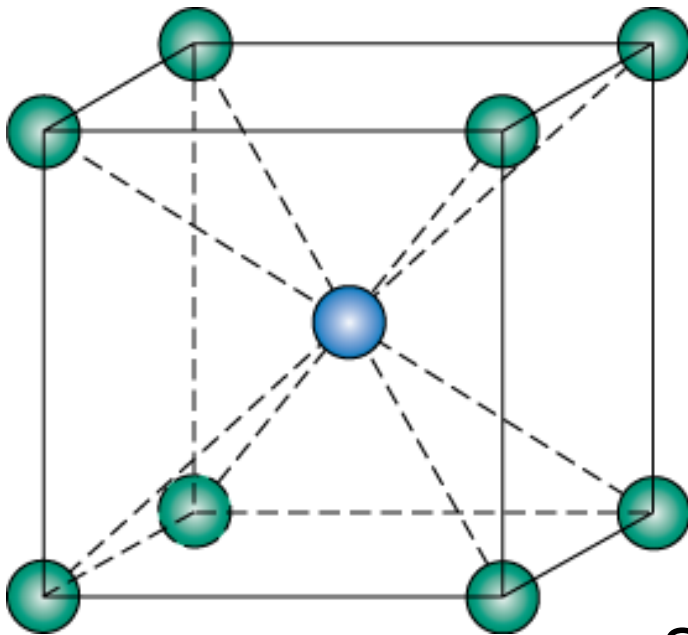
Adapted from Fig.
12.2, Callister 7e.

So each oxygen has 6 neighboring Mg²⁺

AX Crystal Structures

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

Cesium Chloride structure:



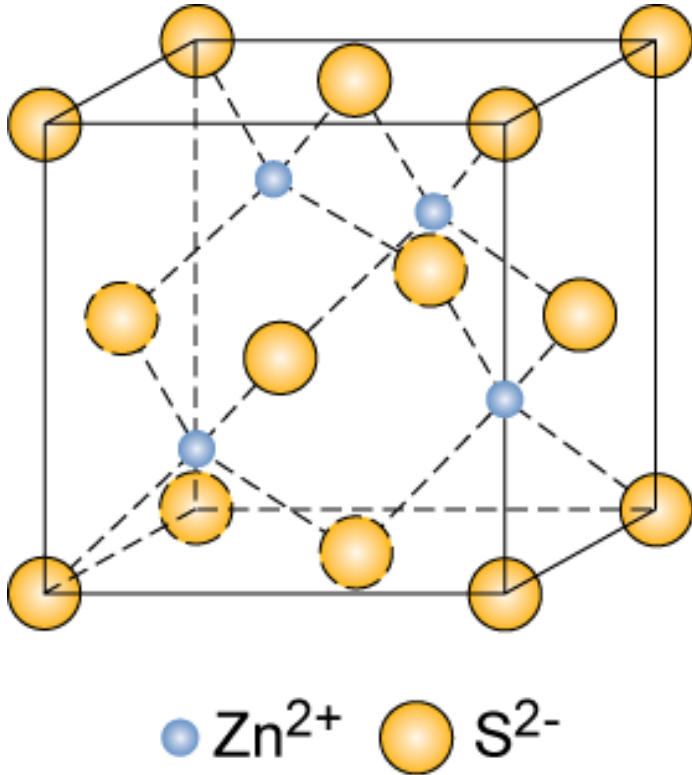
∴ cubic sites preferred

So each Cs⁺ has 8 neighboring Cl⁻

Adapted from Fig.
12.3, Callister 7e.

AX Crystal Structures

Zinc Blende structure



Adapted from Fig. 12.4, Callister 7e.

Ex: ZnO, ZnS, SiC

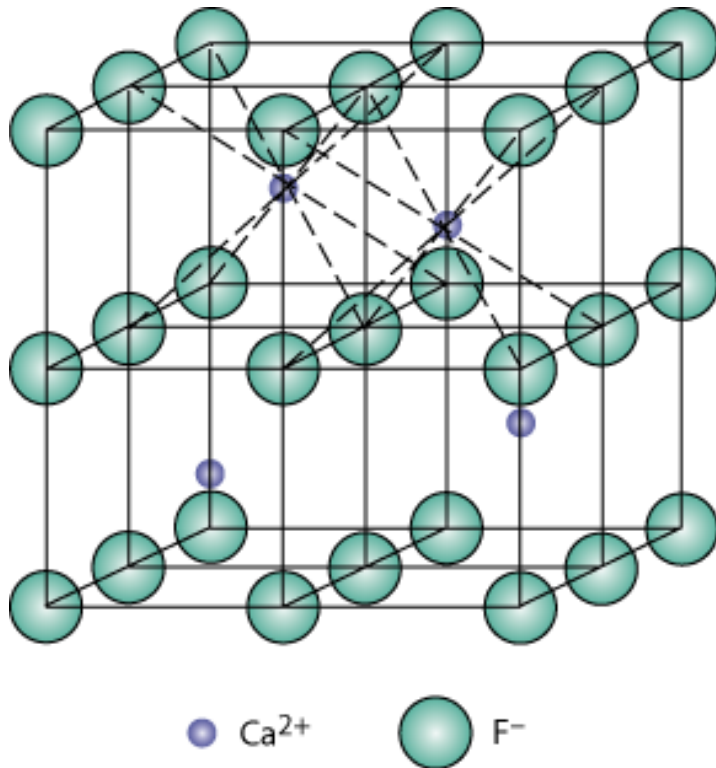
$$\frac{r_{\text{Zn}^{2+}}}{r_{\text{O}^{2-}}} = \frac{0.074}{0.140} = 0.529 \Rightarrow O_H??$$

- Size arguments predict Zn²⁺ in O_H sites,
- In observed structure Zn²⁺ in T_D sites
- Why is Zn²⁺ in T_D sites?
 - bonding hybridization of zinc favors T_D sites

So each Zn²⁺ has 4 neighboring O²⁻

AX₂ Crystal Structures

Fluorite structure



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

Adapted from Fig. 12.5, *Callister 7e*.

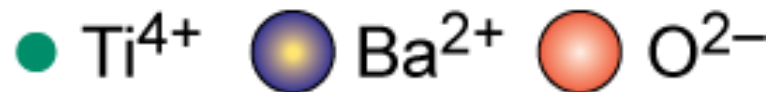
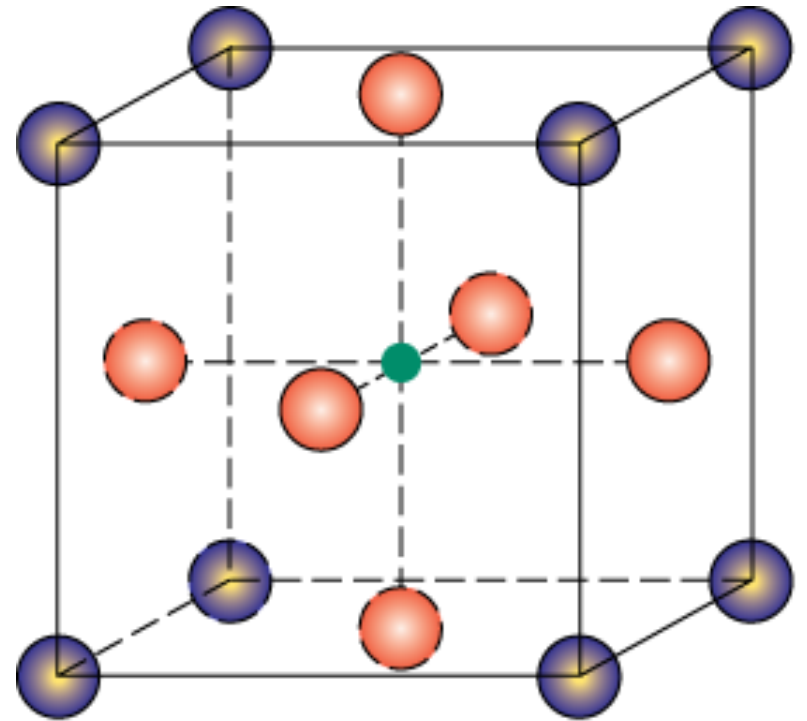


ABX₃ Crystal Structures

- Perovskite

Ex: complex oxide
BaTiO₃

Adapted from Fig.
12.6, *Callister 7e*.



Mechanical Properties

We know that ceramics are more brittle than metals. **Why?**

- Consider method of deformation
 - slippage along slip planes
 - in ionic solids this slippage is very difficult
 - too much energy needed to move one anion past another anion



Ceramic Density Computation

Number of formula units/unit cell

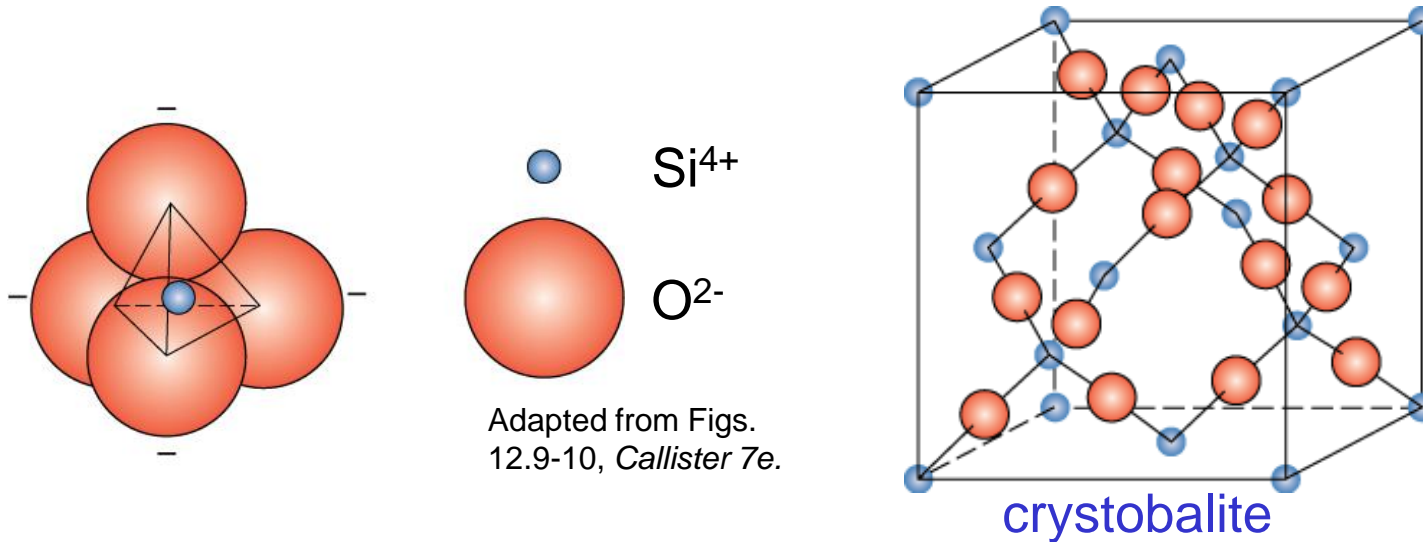
$$\rho = \frac{n'(\sum A_C + \sum A_A)}{V_C N_A}$$

Volume of unit cell



Silicate Ceramics

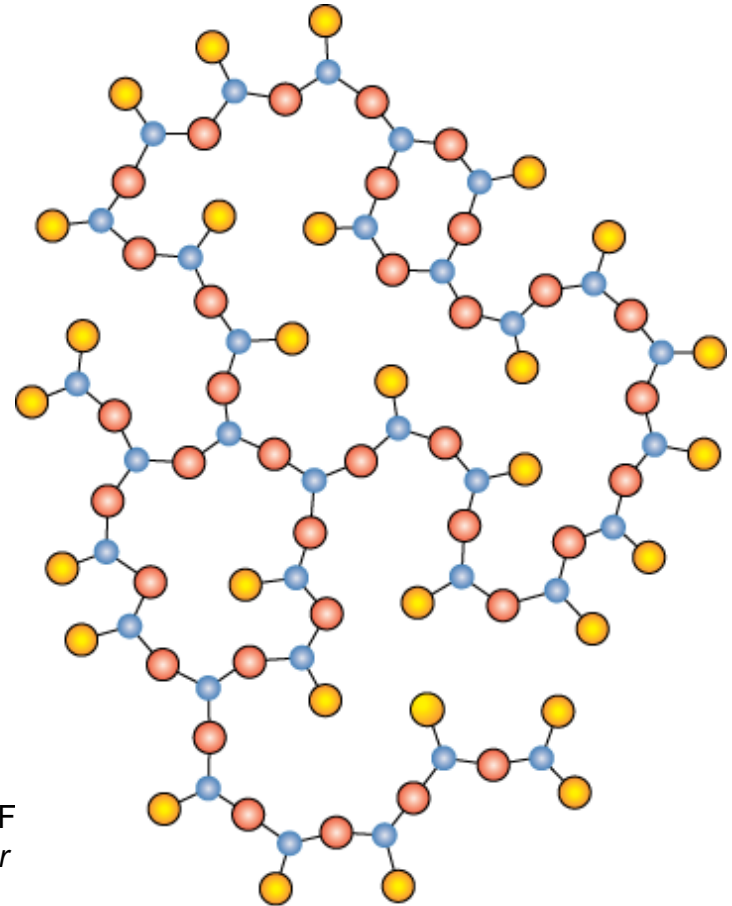
Most common elements on earth are Si & O



- SiO_2 (silica) structures are quartz, cristobalite, & tridymite
- The strong Si-O bond leads to a strong, high melting material (1710°C)

Amorphous Silica

- Silica gels - amorphous SiO_2
 - Si^{4+} and O^{2-} not in well-ordered lattice
 - Charge balanced by H^+ (to form OH^-) at “dangling” bonds
 - very high surface area $> 200 \text{ m}^2/\text{g}$
 - SiO_2 is quite stable, therefore unreactive
 - makes good catalyst support



Adapted from F
12.11, Callister



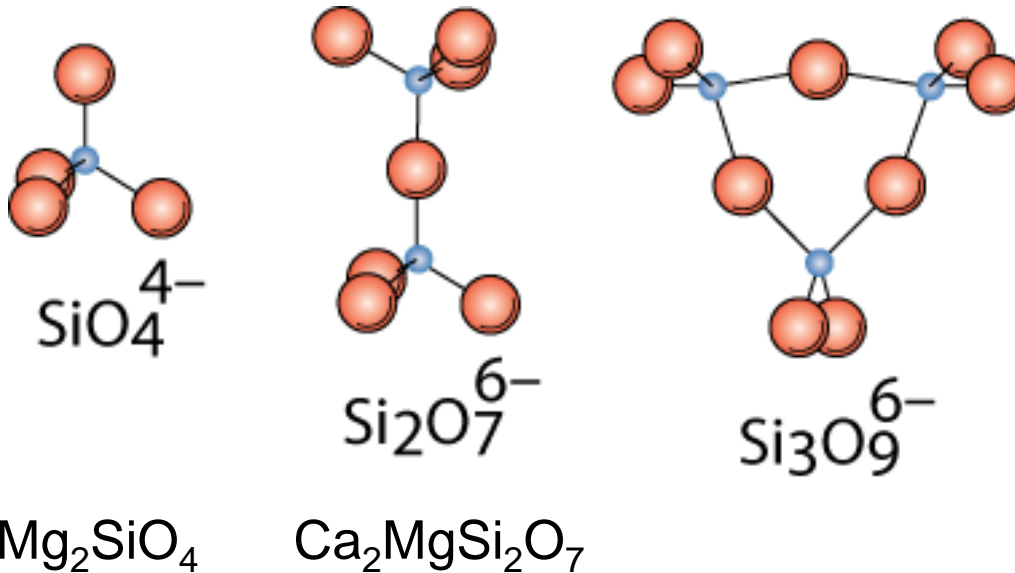
Silica Glass

- Dense form of amorphous silica
 - Charge imbalance corrected with “counter cations” such as Na^+
 - Borosilicate glass is the pyrex glass used in labs
 - better temperature stability & less brittle than sodium glass



Silicates

- Combine SiO_4^{4-} tetrahedra by having them share corners, edges, or faces

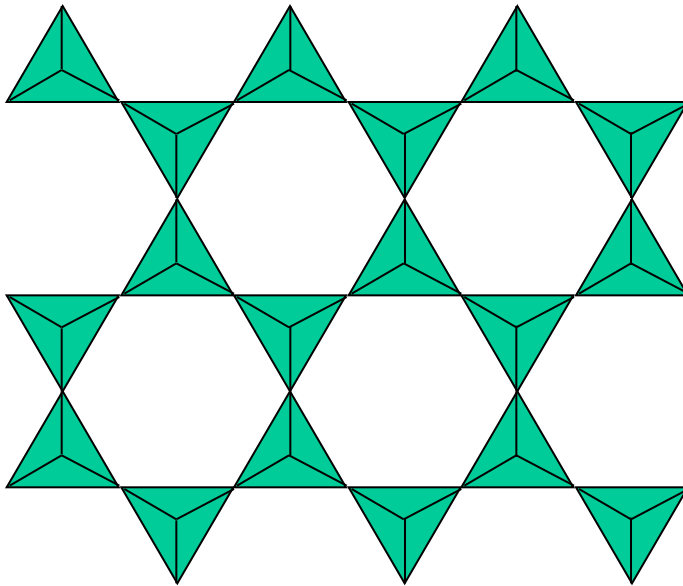


Adapted from Fig. 12.12, Callister 7e.

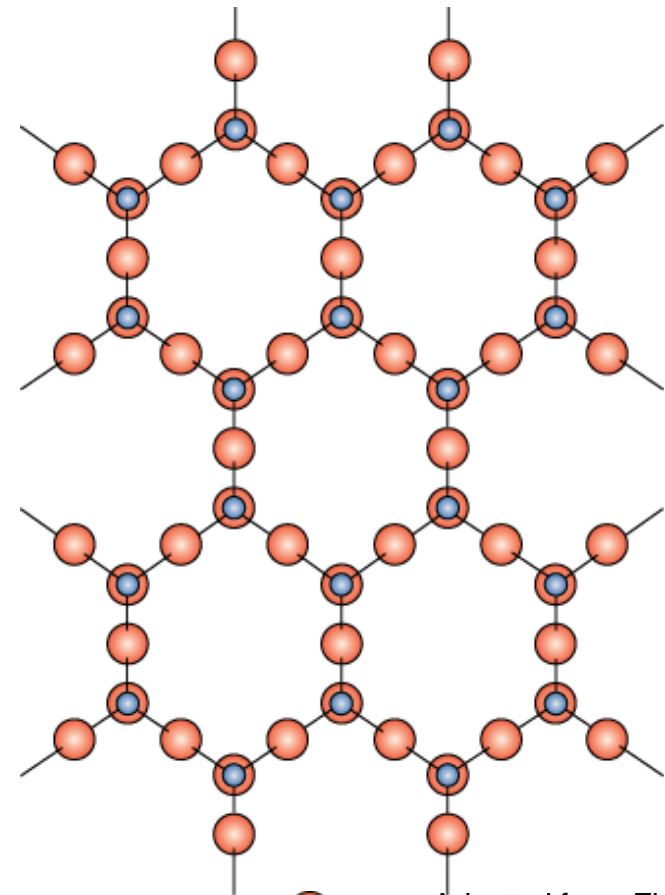
- Cations such as Ca^{2+} , Mg^{2+} , & Al^{3+} act to neutralize & provide ionic bonding

Layered Silicates

- Layered silicates (clay silicates)
 - SiO_4 tetrahedra connected together to form 2-D plane



- $(\text{Si}_2\text{O}_5)^{2-}$
- So need cations to balance charge



=

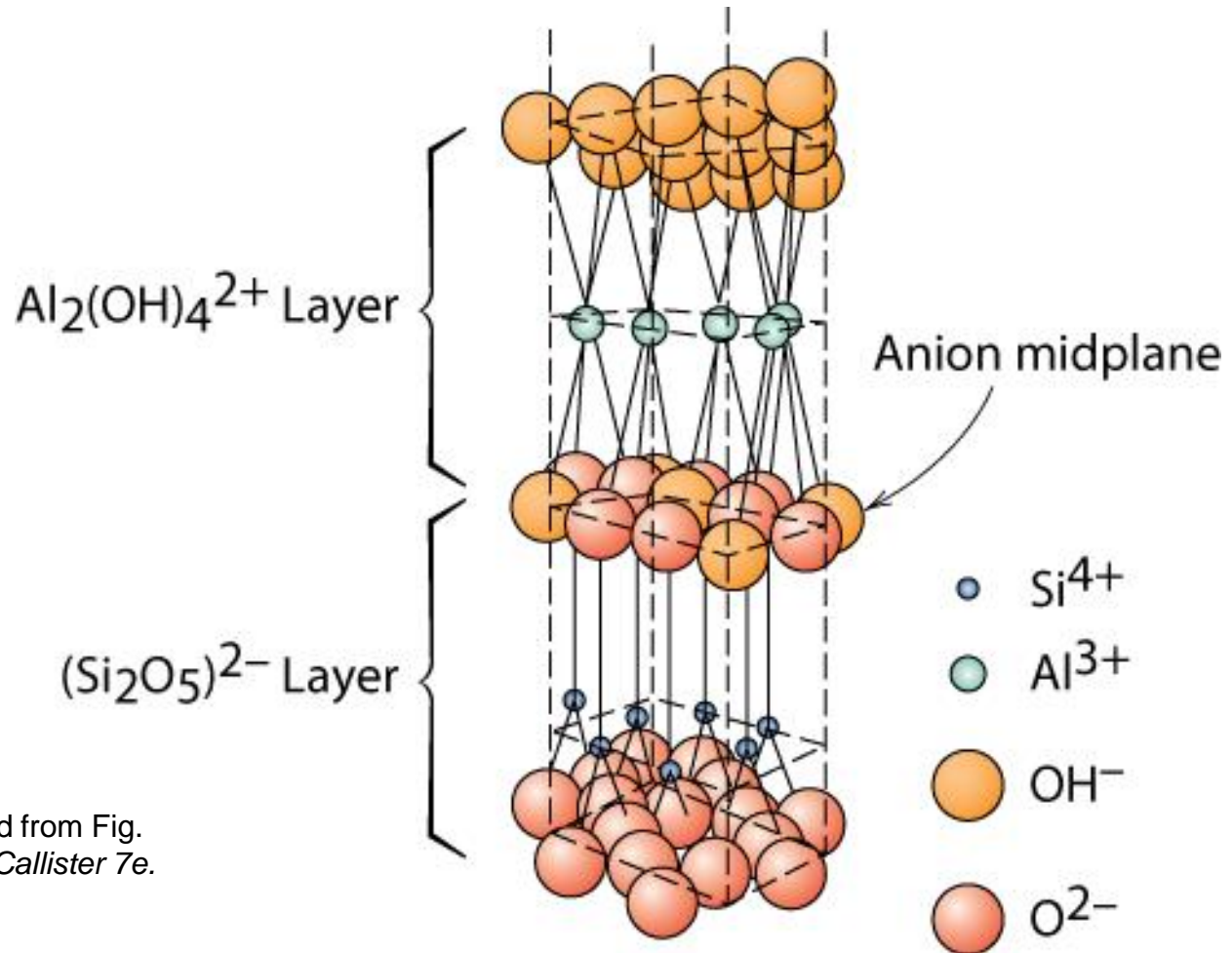


Adapted from Fig. 12.13, Callister 7e.



Layered Silicates

- Kaolinite clay alternates $(\text{Si}_2\text{O}_5)^{2-}$ layer with $\text{Al}_2(\text{OH})_4^{2+}$ layer



Adapted from Fig. 12.14, *Callister 7e*.

Note: these sheets loosely bound by van der Waal's forces



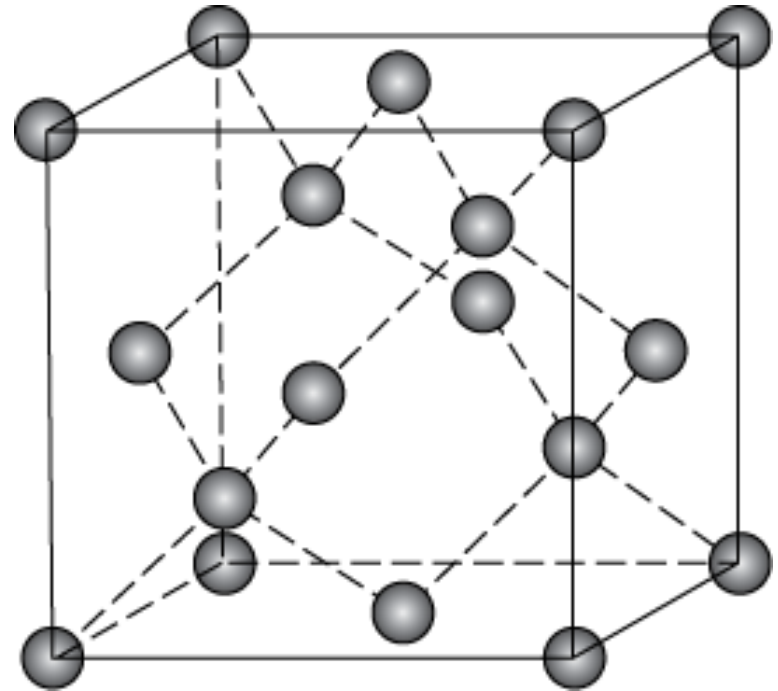
Layered Silicates

- Can change the counterions
 - this changes layer spacing
 - the layers also allow absorption of water
- Micas $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$
- Bentonite
 - used to seal wells
 - packaged dry
 - swells 2-3 fold in H_2O
 - pump in to seal up well so no polluted ground water seeps in to contaminate the water supply.



Carbon Forms

- Carbon black – amorphous – surface area ca. 1000 m²/g
- Diamond
 - tetrahedral carbon
 - hard – no good slip planes
 - brittle – can cut it
 - large diamonds – jewelry
 - small diamonds
 - often man made - used for cutting tools and polishing
 - diamond films
 - hard surface coat – tools, medical devices, etc.

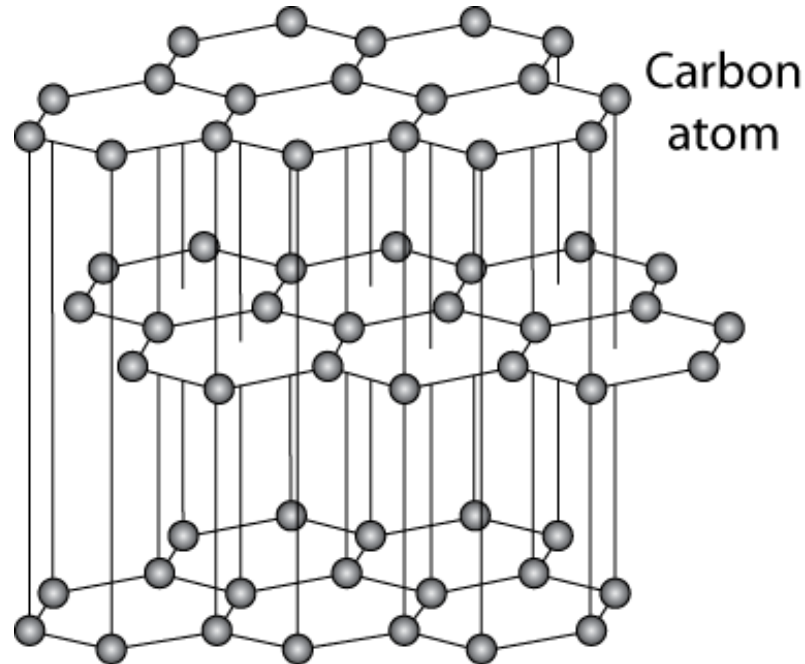


Adapted from Fig. 12.15, *Callister 7e*.



Carbon Forms - Graphite

- layer structure – aromatic layers

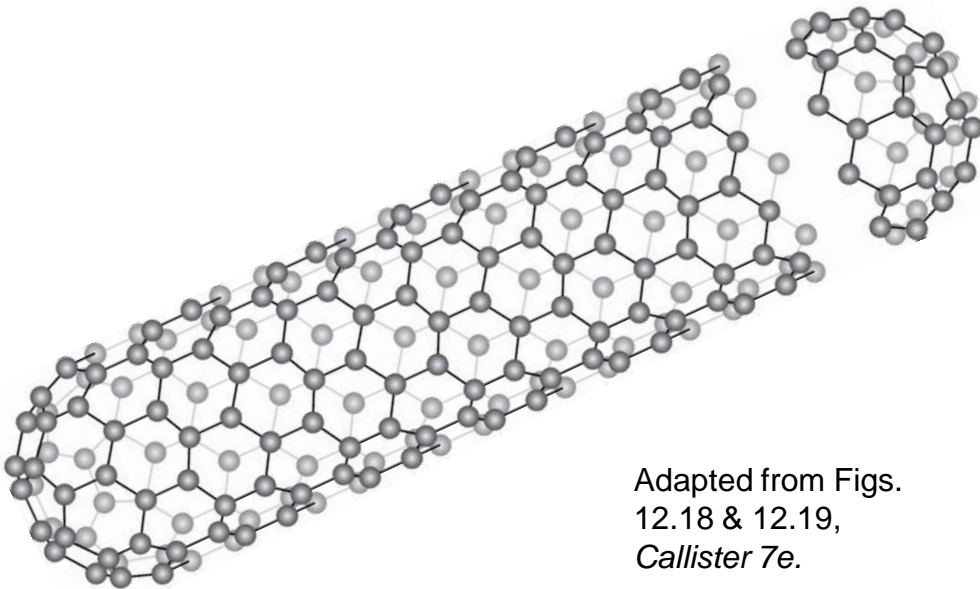


Adapted from Fig.
12.17, *Callister 7e*.

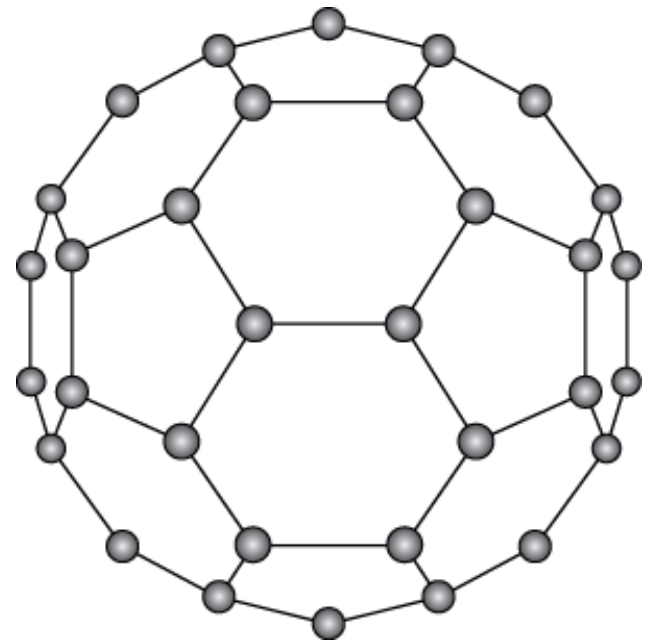
- weak van der Waal's forces between layers
- planes slide easily, good lubricant

Carbon Forms – Fullerenes and Nanotubes

- Fullerenes or carbon nanotubes
 - wrap the graphite sheet by curving into ball or tube
 - Buckminster fullerenes
 - Like a soccer ball C_{60} - also C_{70} + others

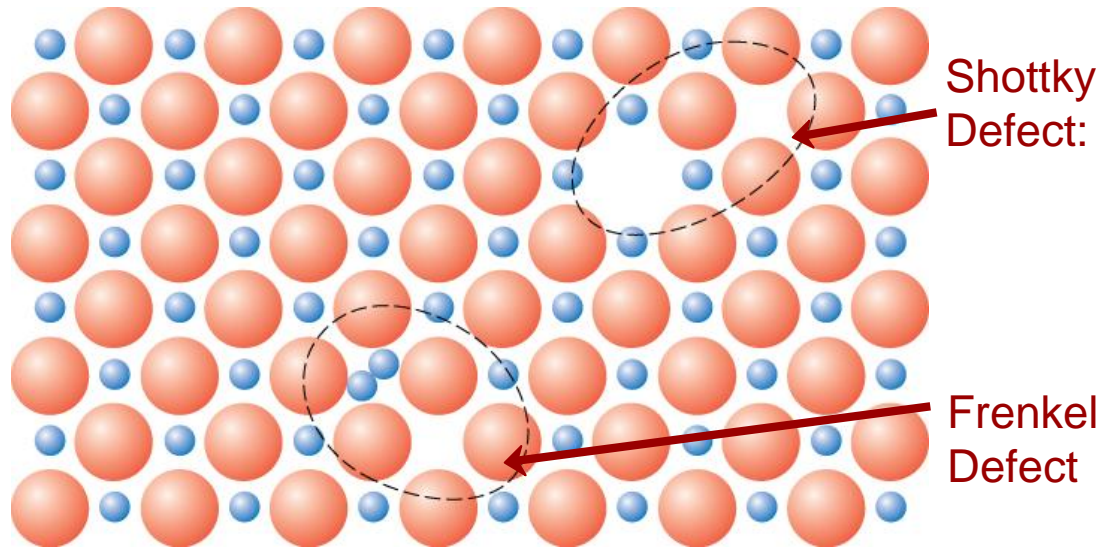


Adapted from Figs.
12.18 & 12.19,
Callister 7e.



Defects in Ceramic Structures

- Frenkel Defect
--a cation is out of place.
- Shottky Defect
--a paired set of cation and anion vacancies.



Adapted from Fig. 12.21, *Callister 7e*. (Fig. 12.21 is from W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, John Wiley and Sons, Inc., p. 78.)

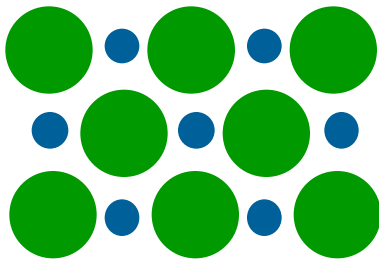
- Equilibrium concentration of defects $\sim e^{-Q_D / kT}$

Impurities

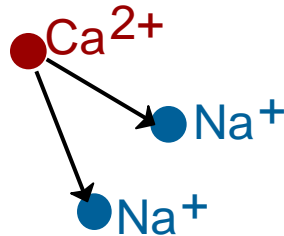
- Impurities must also satisfy **charge balance** = Electroneutrality



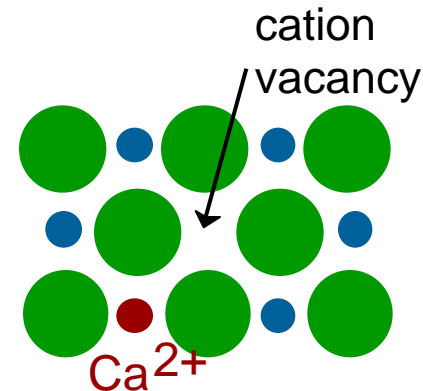
- Substitutional cation impurity



initial geometry

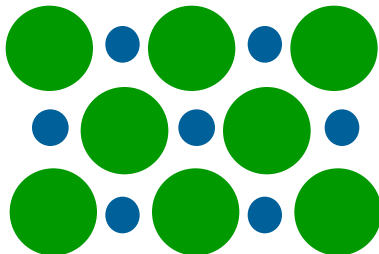


Ca^{2+} impurity

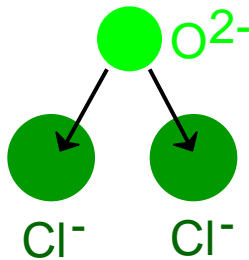


resulting geometry

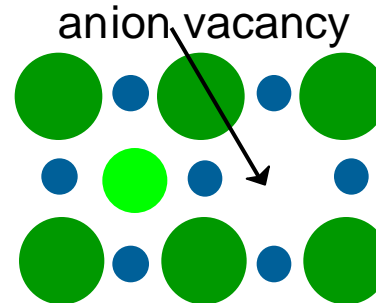
- Substitutional anion impurity



initial geometry



O^{2-} impurity

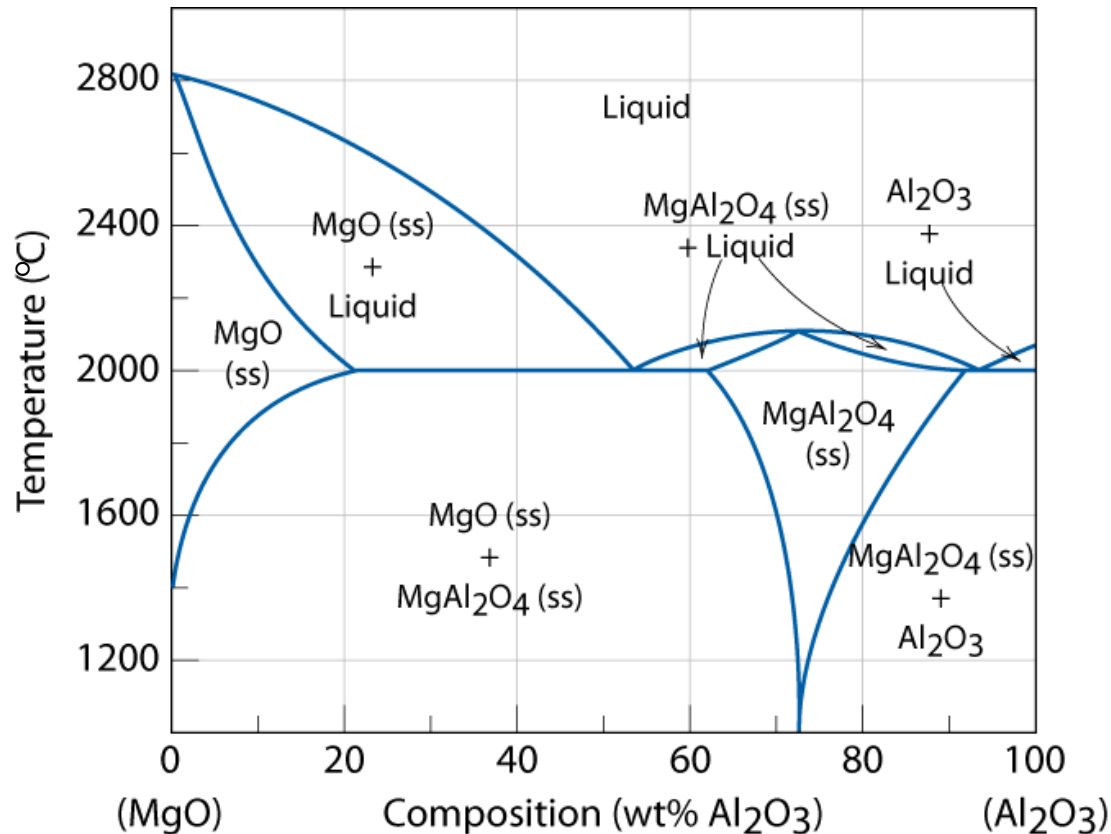


resulting geometry



Ceramic Phase Diagrams

MgO-Al₂O₃ diagram:

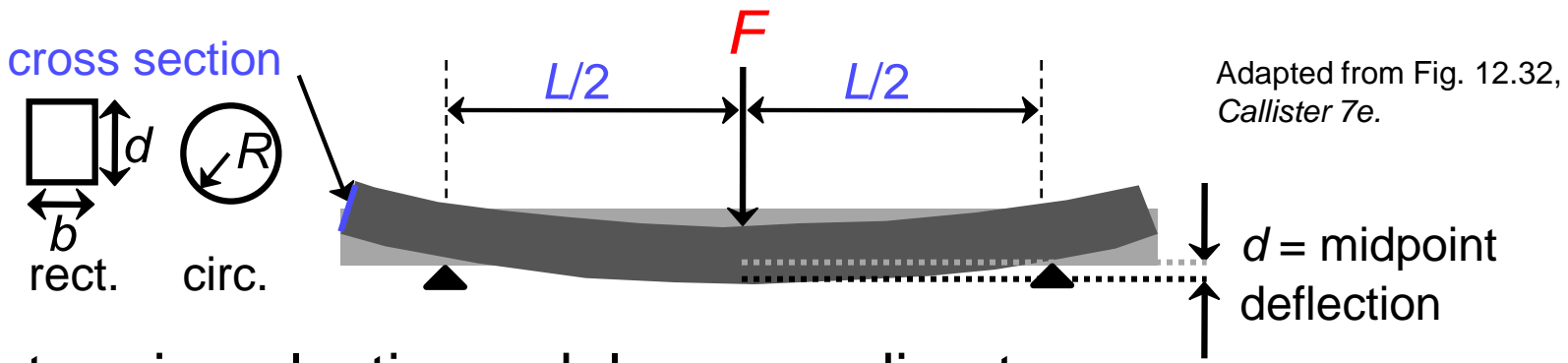


Adapted from Fig. 12.25, Callister 7e.

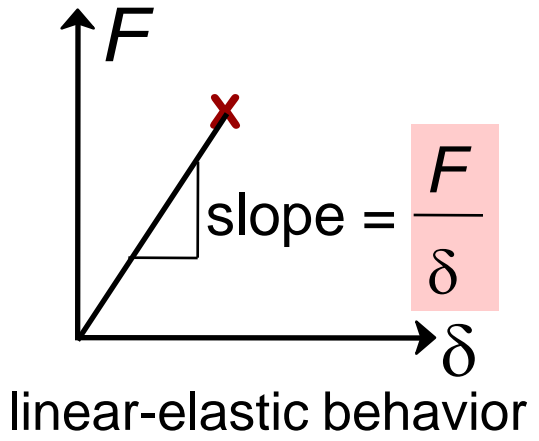


Measuring Elastic Modulus

- 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:

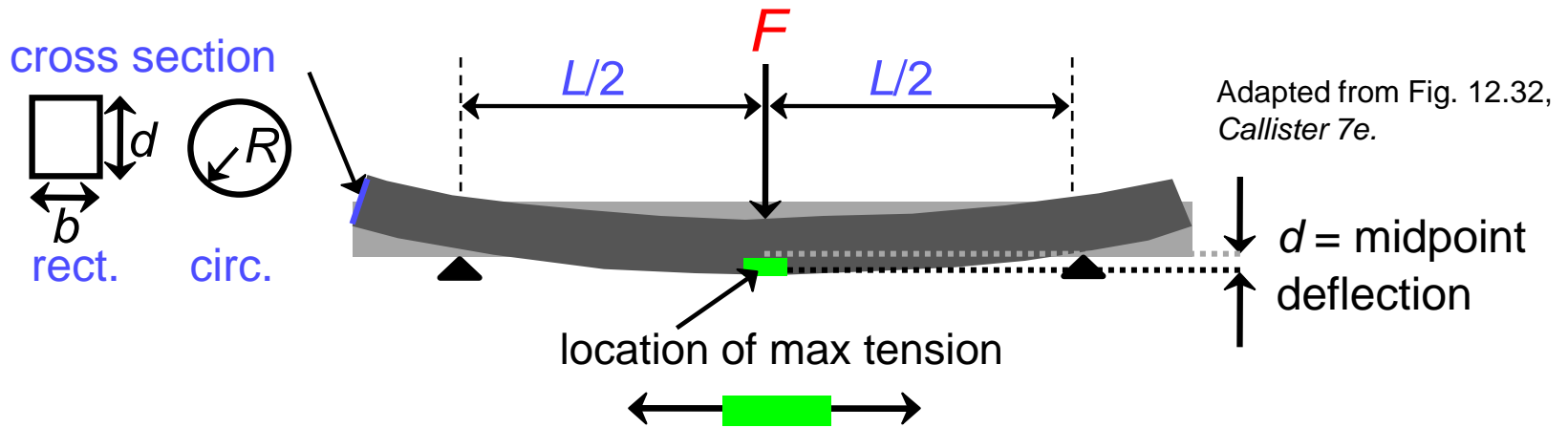


$$E = \frac{F}{\delta} \frac{L^3}{4bd^3} = \frac{F}{\delta} \frac{L^3}{12\pi R^4}$$

rect. cross section circ. cross section

Measuring Strength

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



- Flexural strength:

$$\sigma_{fs} = \frac{1.5F_f L}{bd^2 \text{ rect.}} = \frac{F_f L}{\pi R^3}$$

F

F_f

δ

δ_{fs}

- Typ. values:

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

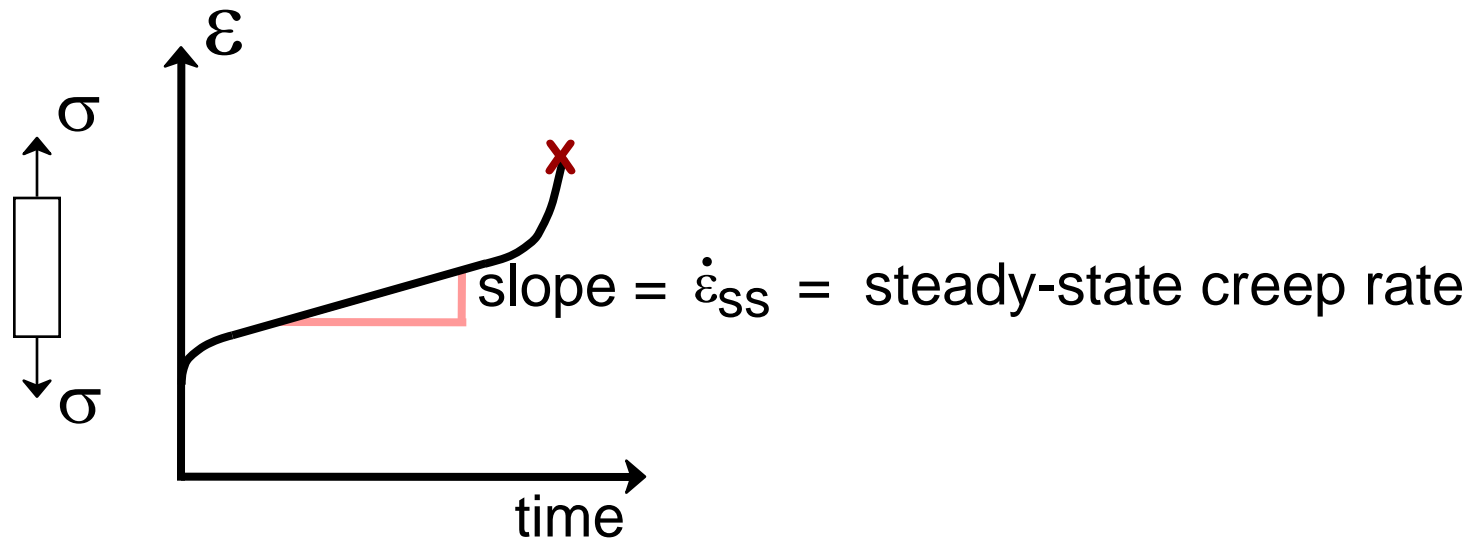
Data from Table 12.5, Callister 7e.



Measuring Elevated T Response

- Elevated Temperature Tensile Test ($T > 0.4 T_m$).

creep test



Summary

- Ceramic materials have covalent & ionic bonding.
- Structures are based on:
 - charge neutrality
 - maximizing # of nearest oppositely charged neighbors.
- Structures may be predicted based on:
 - ratio of the cation and anion radii.
- Defects
 - must preserve charge neutrality
 - have a concentration that varies exponentially w/ T .
- Room T mechanical response is elastic, but fracture is brittle, with negligible deformation.
- Elevated T creep properties are generally superior to those of metals (and polymers).



ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems:

