

Chapter 12: Structures & Properties of Ceramics

- 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	IIA												He					
2.1													-					
Li	Be												Ne					
1.0	1.5												-					
Na	Mg	IIIB	IVB	VB	VIB	VII B	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	Ar	
0.9	1.2											Al	Si	P	S	Cl	-	
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 (arrow from Ca to F)

SiC: small (arrows from Si and C)

Adapted from Fig. 2.7, Callister 7e.

Ionic Crystals

Table 12.1 For Several Ceramic Materials, Percent Ionic Character of the Interatomic Bonds

<i>Material</i>	<i>Percent Ionic Character</i>	<u>Cation Radius (nm)</u>	<u>Anion Radius (nm)</u>
CaF ₂	89	0.100	0.133
MgO	73	0.072	0.14
NaCl	67	0.102	0.182
Al ₂ O ₃	63	0.053	0.140
SiO ₂	51	0.040	0.140
Si ₃ N ₄	30		
ZnS	18		
SiC	12		

Note: larger anion radius



Most ionic crystals can be considered as close-packed structure of anions with cations in the interstitial sites.

Cations: metallic ions, positively charged

Anions: nonmetallic ions, negatively charged

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

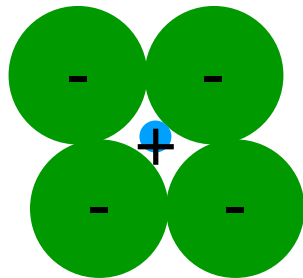
- if all of one type of site is full, the remainder have to go into other types of sites.

3. Bond Hybridization

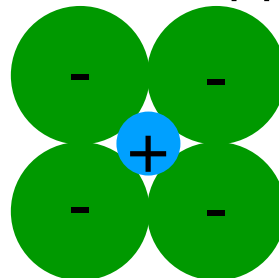
Ionic Bonding & Structure

1. Size - Stable structures:

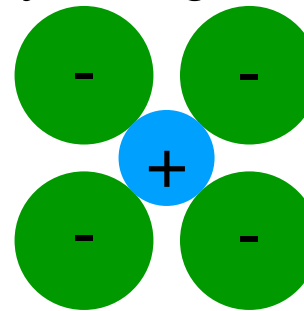
--maximize the # of nearest oppositely charged neighbors.



unstable



stable

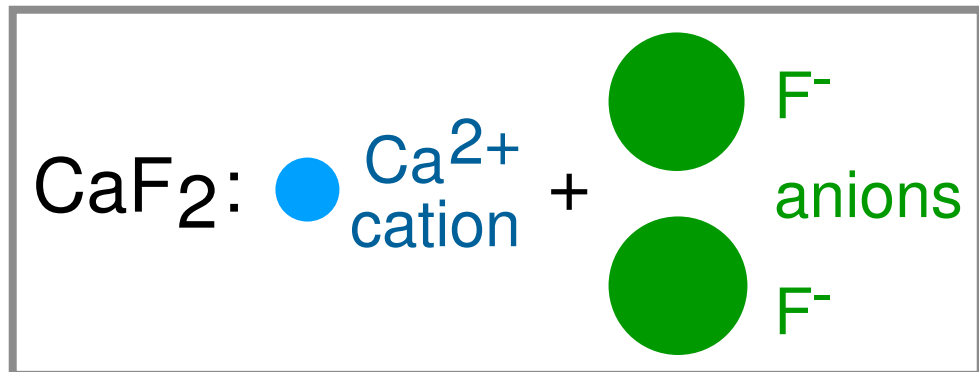


stable

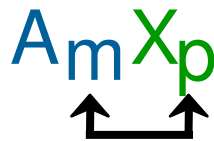
Adapted from Fig. 12.1,
Callister 7e.

- **Charge Neutrality:**

--Net charge in the structure should be zero.



--General form:



m, p determined by charge neutrality

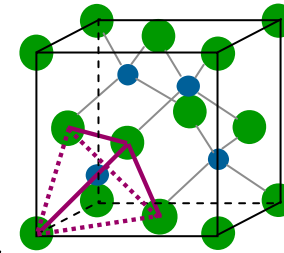
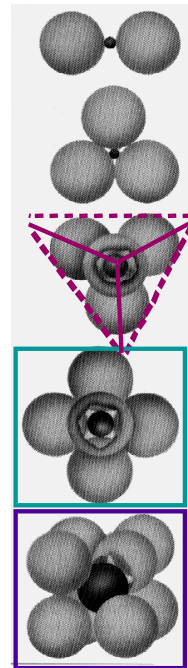
Coordination # and Ionic Radii

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

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

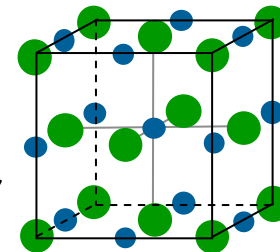
$\frac{r_{\text{cation}}}{r_{\text{anion}}}$	Coord #	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	T_D
0.414 - 0.732	6	O_H
0.732 - 1.0	8	cubic

Adapted from Table 12.2, Callister 7e.



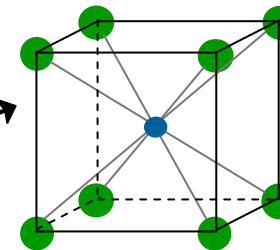
ZnS
(zincblende)

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-anion stable configuration

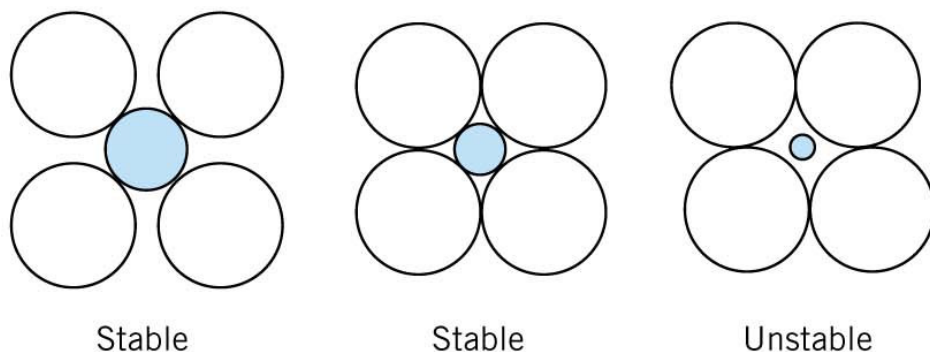
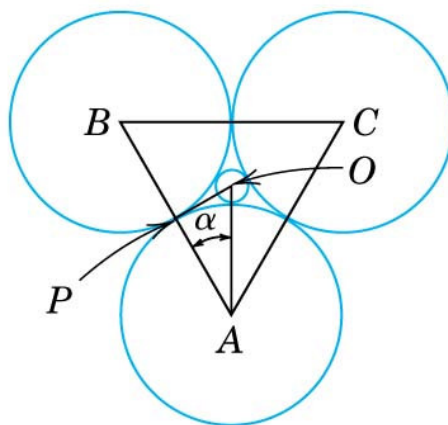
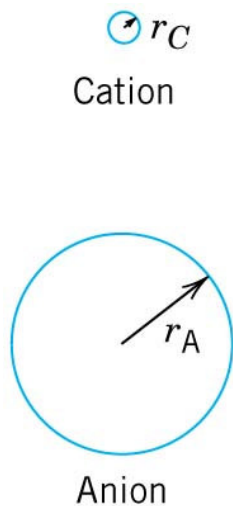


FIGURE 12.1 Stable and unstable anion–cation coordination configurations. Open circles represent anions; colored circles denote cations.

e.g. 3-coordinate



when $\cos \alpha = \frac{r_A}{r_A + r_C}$

Rewrite as

$$\frac{r_C}{r_A} = \frac{1}{\cos \alpha} - 1$$

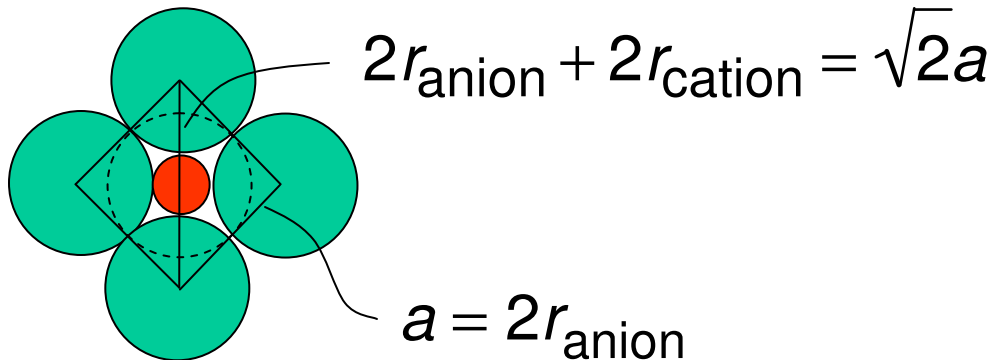
With $\alpha = 30^\circ$

Minimum ratio for 3-coordinate

$$\frac{r_C}{r_A} = 0.155$$

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.

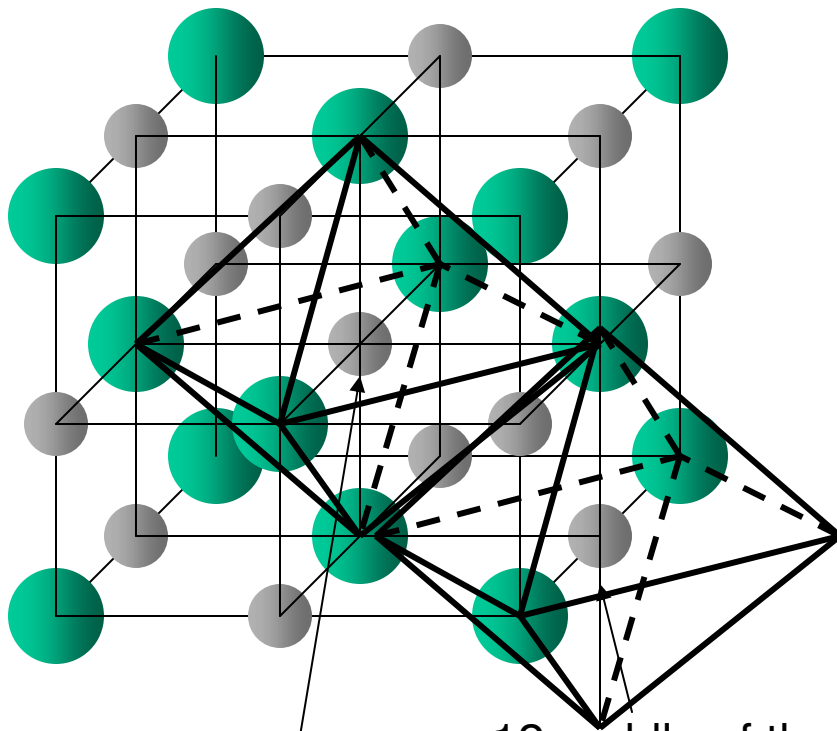
If for a specific ceramic each unit cell has 6 cations and the cations prefer O_H sites

4 in O_H

2 in T_D

Interstitial sites in FCC

Octahedral (O_h) sites

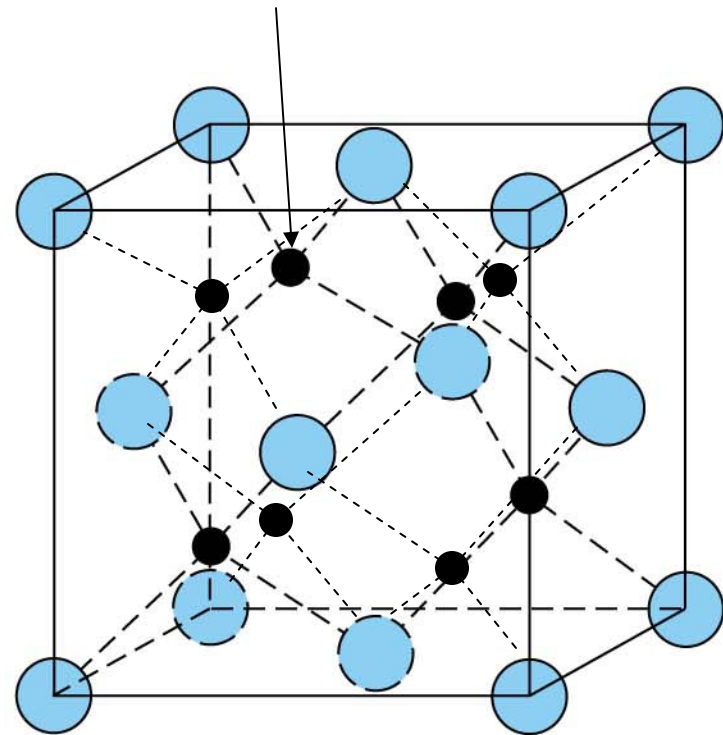


1 at the center

Net 4 O_h sites/unit cell

12 middle of the
edge sites (each
shared by 4 unit
cells)

Tetrahedral (T_d) sites



Net 8 T_d sites/unit cell

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,

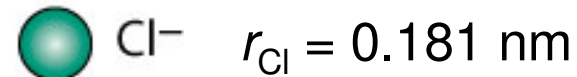
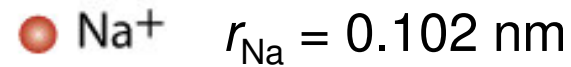
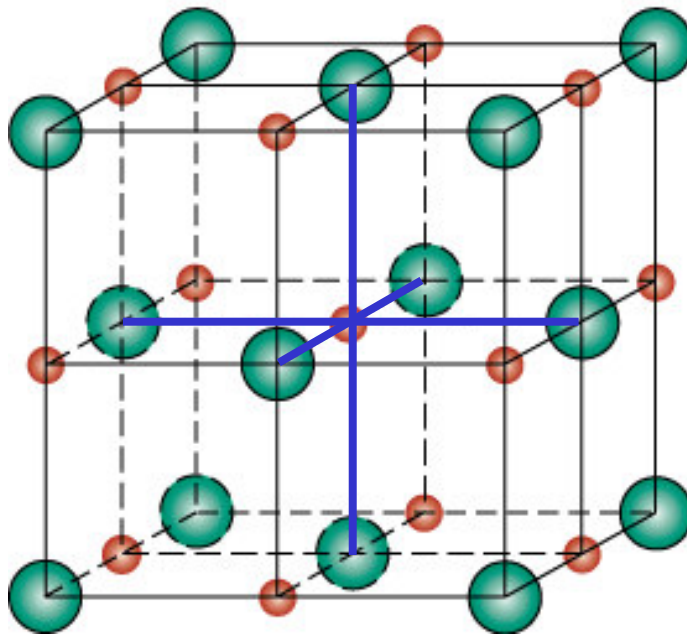
--coord # = 6

--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



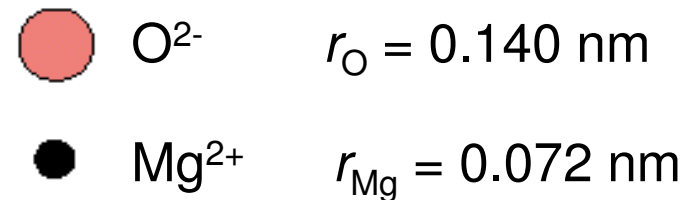
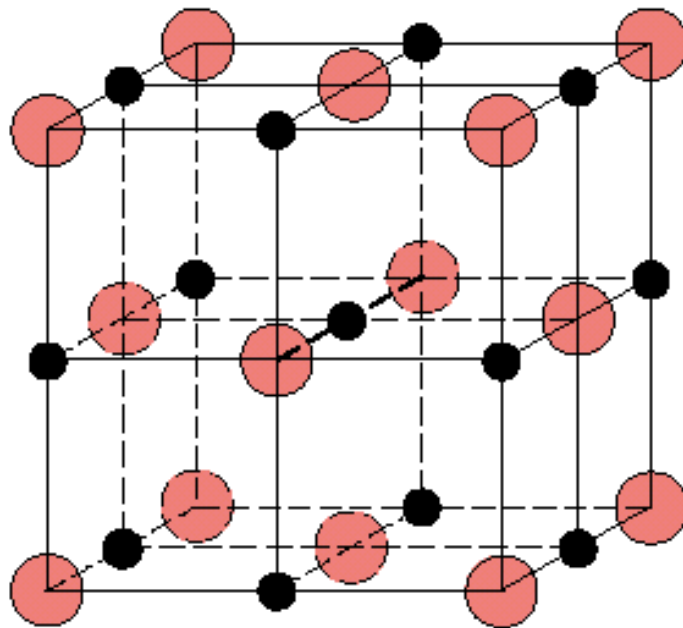
$$r_{\text{Na}}/r_{\text{Cl}} = 0.564$$

∴ 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

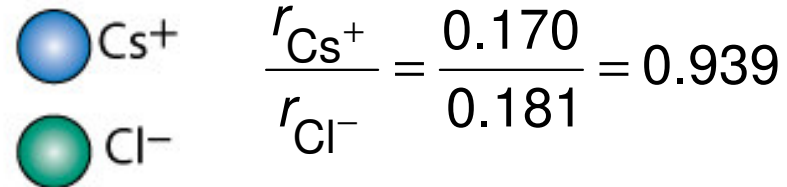
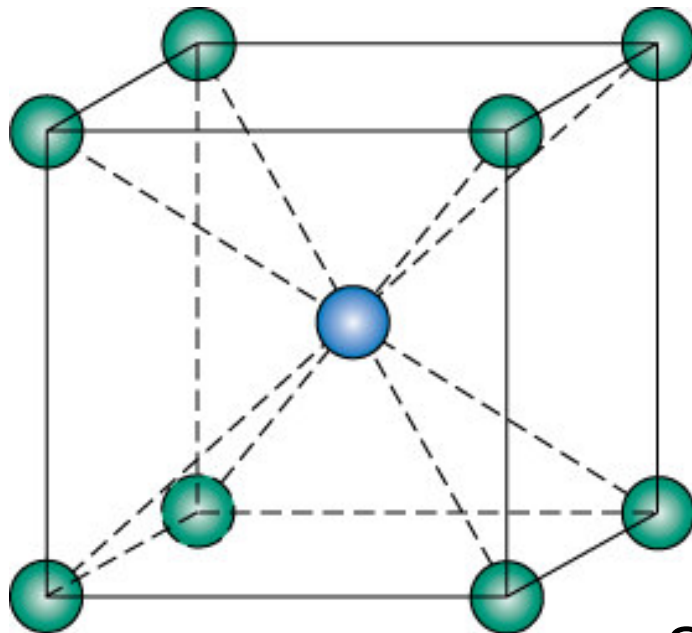
Adapted from Fig.
12.2, *Callister 7e*.

So each oxygen has 6 neighboring Mg²⁺

AX Crystal Structures

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

Cesium Chloride structure:



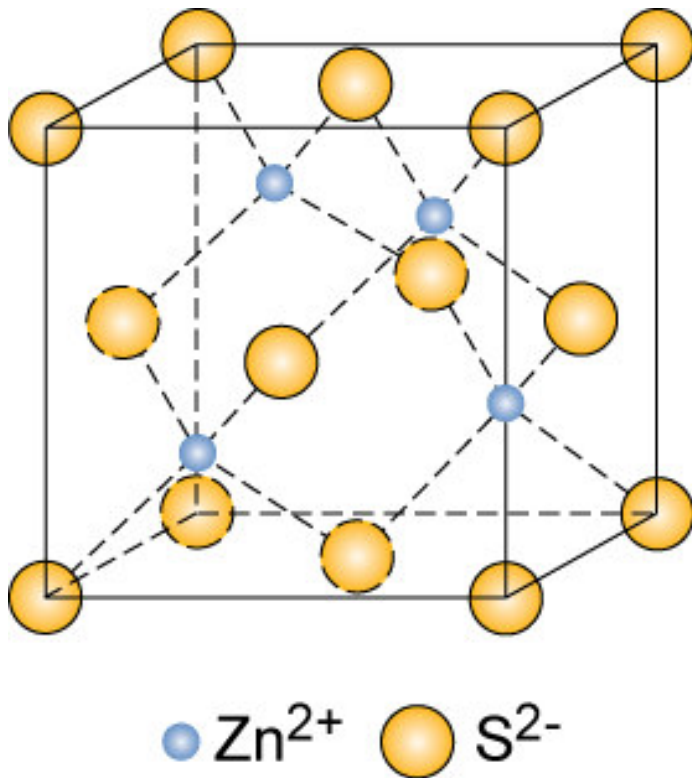
∴ cubic sites preferred

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.

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

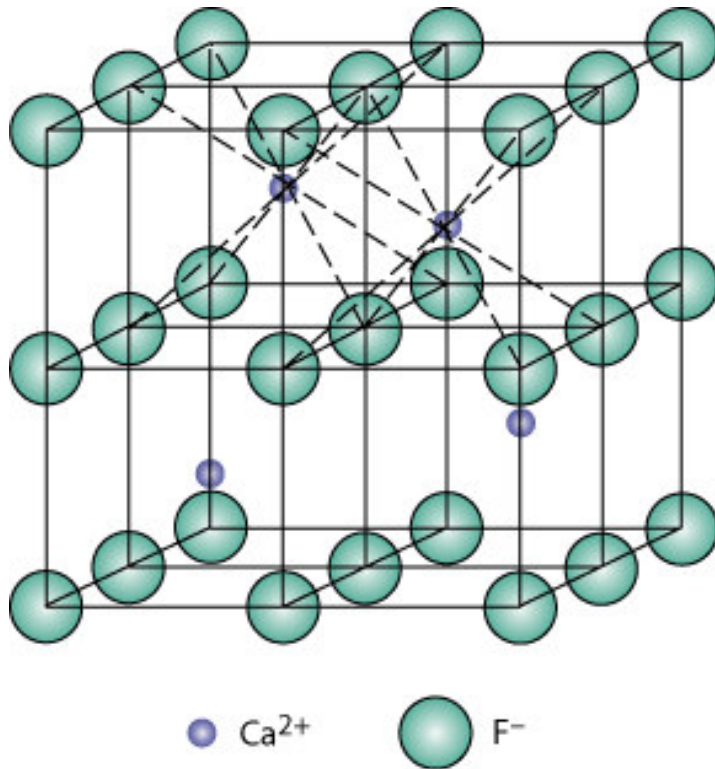
- Size arguments predict Zn²⁺ in O_H sites,
- In observed structure Zn²⁺ in T_D sites
- Why is Zn²⁺ in T_D sites?
 - bonding hybridization of zinc favors T_D sites

So each Zn²⁺ has 4 neighboring O²⁻

Ex: ZnO, ZnS, SiC

AX₂ Crystal Structures

Fluorite structure



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

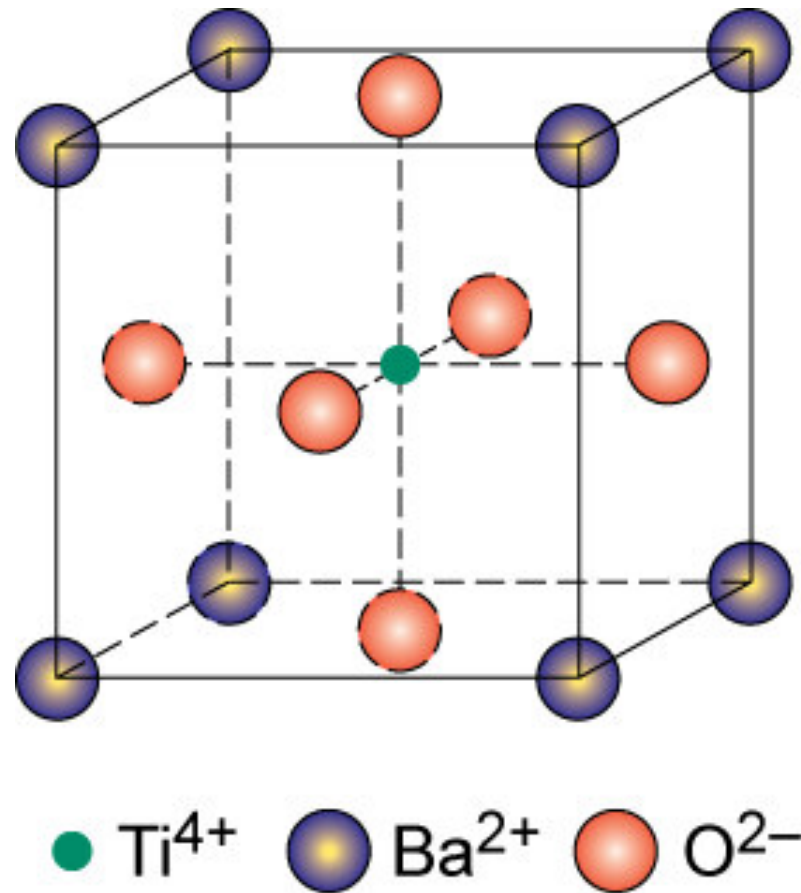
- Calcium Fluorite (CaF₂)
- cations in cubic sites
- UO₂, ThO₂, ZrO₂, CeO₂
- antifluorite structure –
cations and anions
reversed

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

n' = number of cations in unit cell

A_C = atomic weight of cation

n_A = number of anions in unit cell

A_A = atomic weight of anion

V_C = volume of unit cell

N_A = Avogadro's number

Theoretical Density Calculation of NaCl

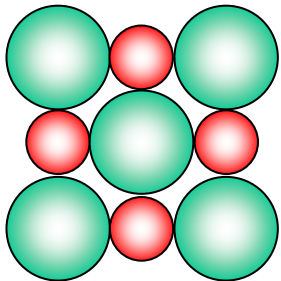
$$\rho = \frac{n'(\Sigma A_C + \Sigma A_A)}{V_C N_A}$$

$$A_{Na} = 22.99 \text{ g/mol}$$

$$A_{Cl} = 35.45 \text{ g/mol}$$

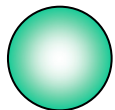
$$a = 2(r_{Na^+} + r_{Cl^-})$$

$$a = 2(r_{Na^+} + r_{Cl^-}) = 2(0.102 + 0.181) \text{ nm}$$



$$\text{Thus, } V_c = a^3 = (2r_{Na^+} + 2r_{Cl^-})^3$$

And n' is 4 pair of Na and Cl in one unit cell finally,



Cl⁻

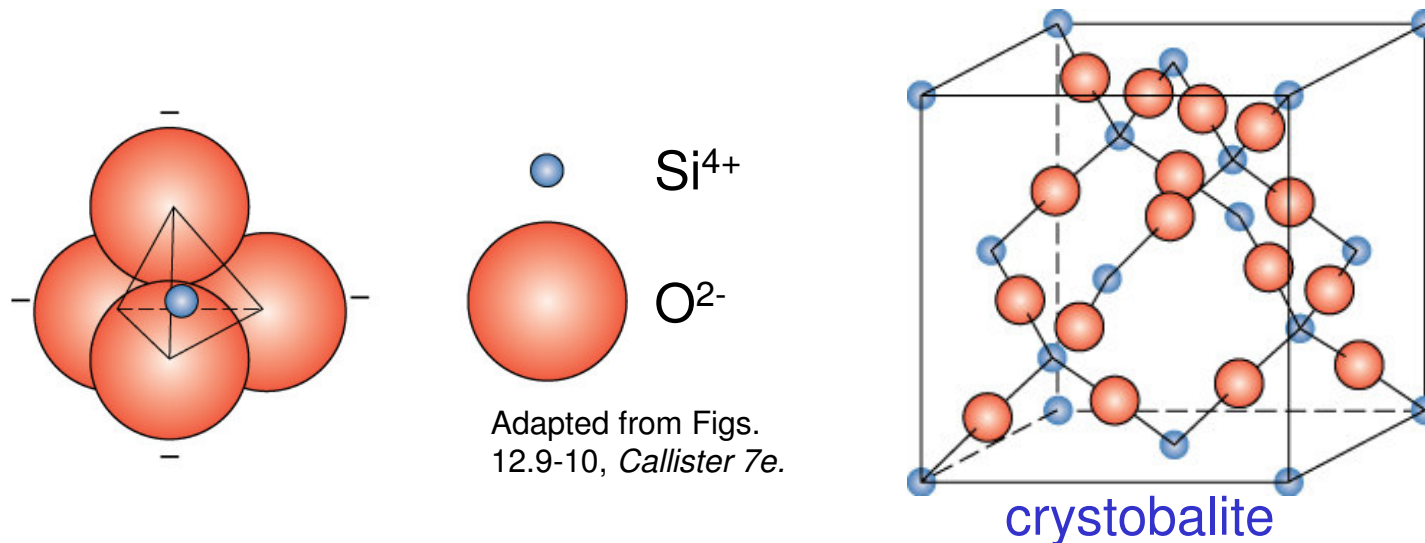


Na⁺

$$\rho = \frac{n'(A_{Na} + A_{Cl})}{(2r_{Na^+} + 2r_{Cl^-})^3 N_A} = 2.14 \text{ g/cm}^3$$

Silicate Ceramics

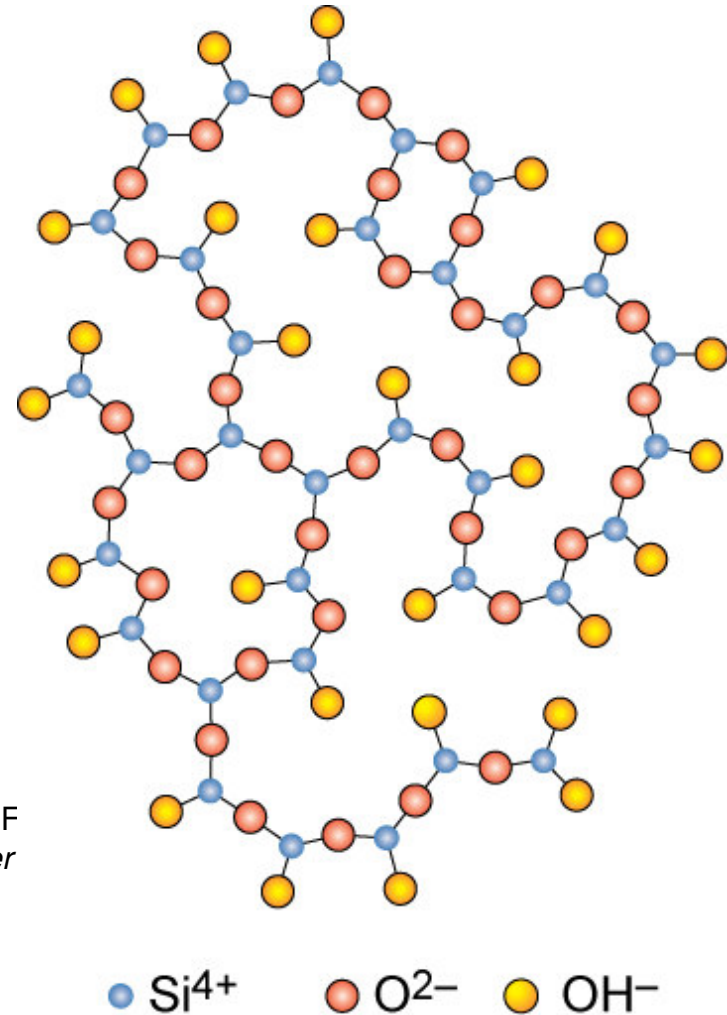
Most common elements on earth are Si & O



- 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



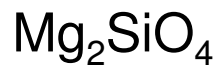
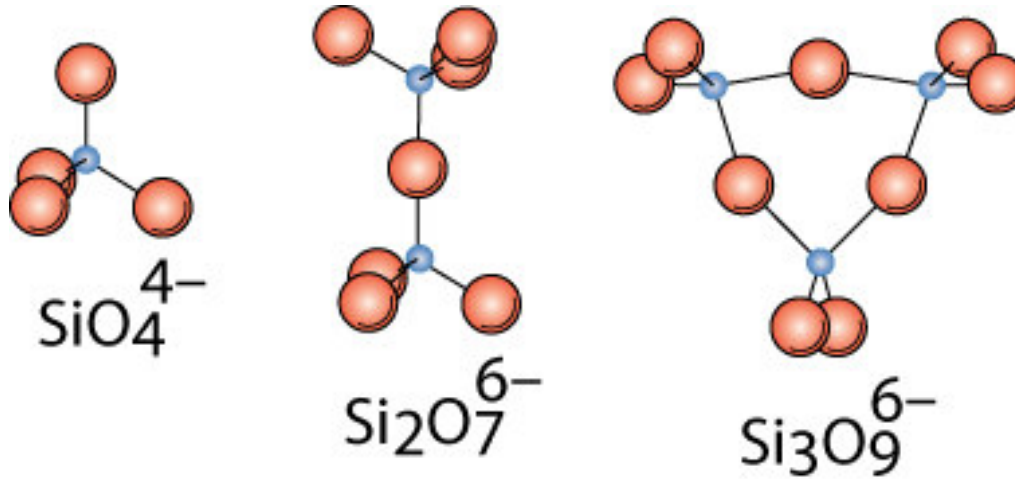
Adapted from F
12.11, *Callister*

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

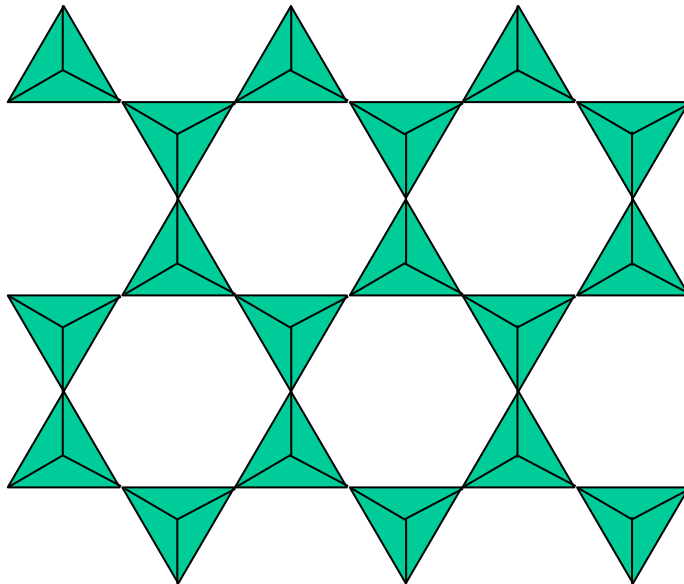


Adapted from Fig. 12.12, *Callister 7e*.

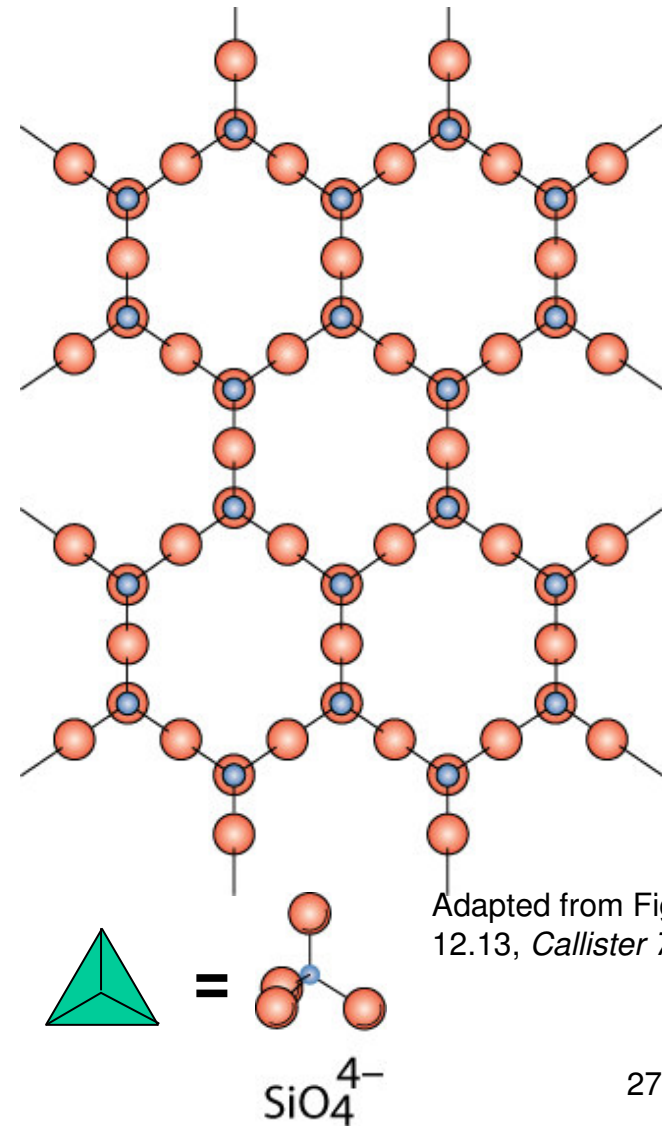
- Cations such as Ca^{2+} , Mg^{2+} , & Al^{3+} act to neutralize & provide ionic bonding

Layered Silicates

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

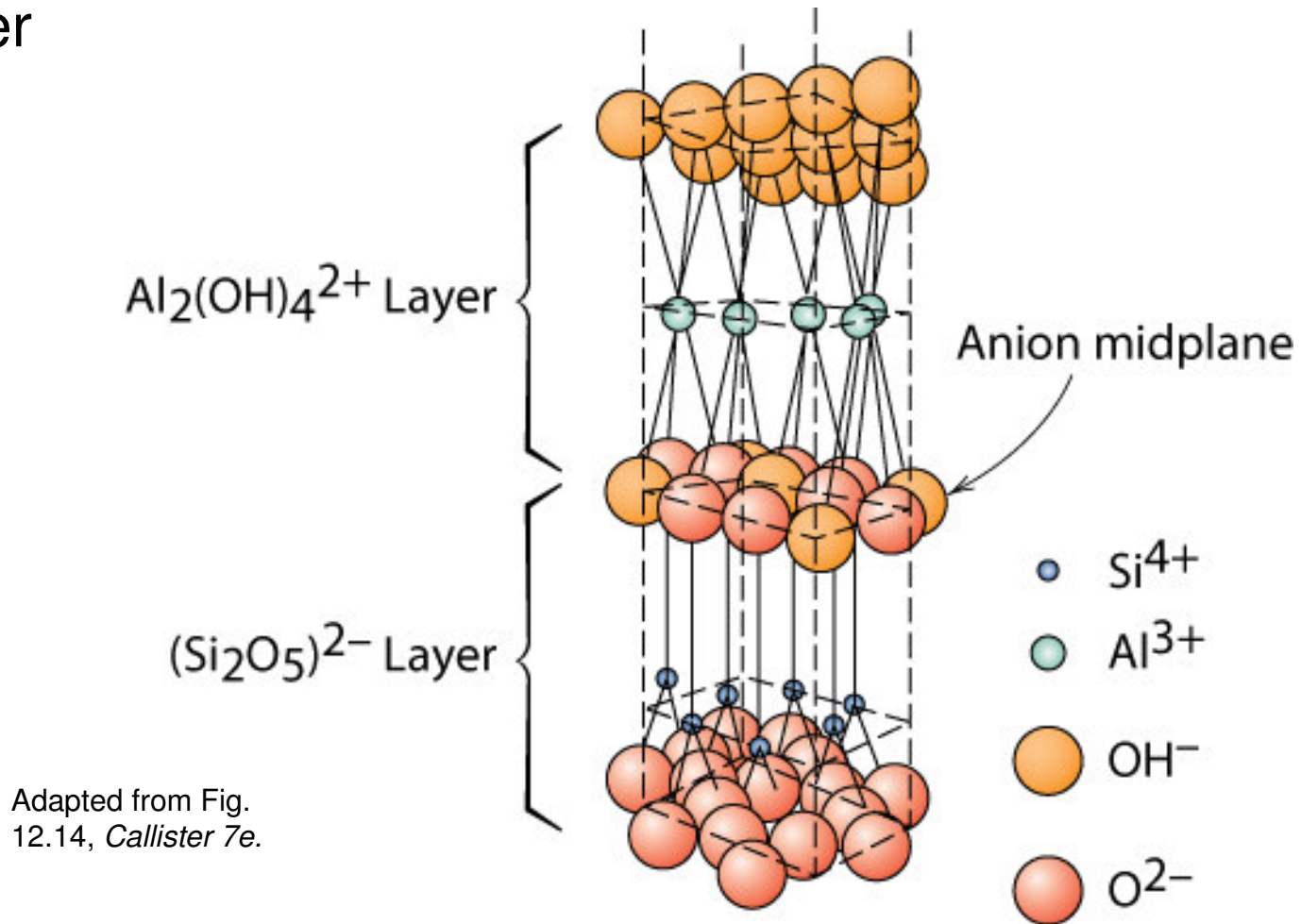


- $(\text{Si}_2\text{O}_5)^{2-}$
- So need cations to balance charge



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*.

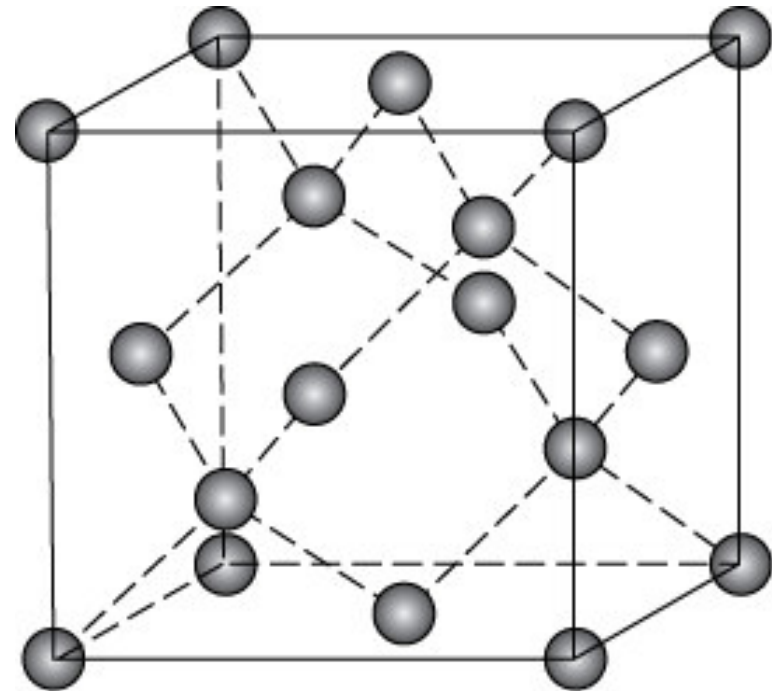
Note: these sheets loosely bound by van der Waal's forces

Layered Silicates

- Can change the counterions
 - this changes layer spacing
 - the layers also allow absorption of water
- Micas $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$
 - smooth surface for AFM sample holder
- 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

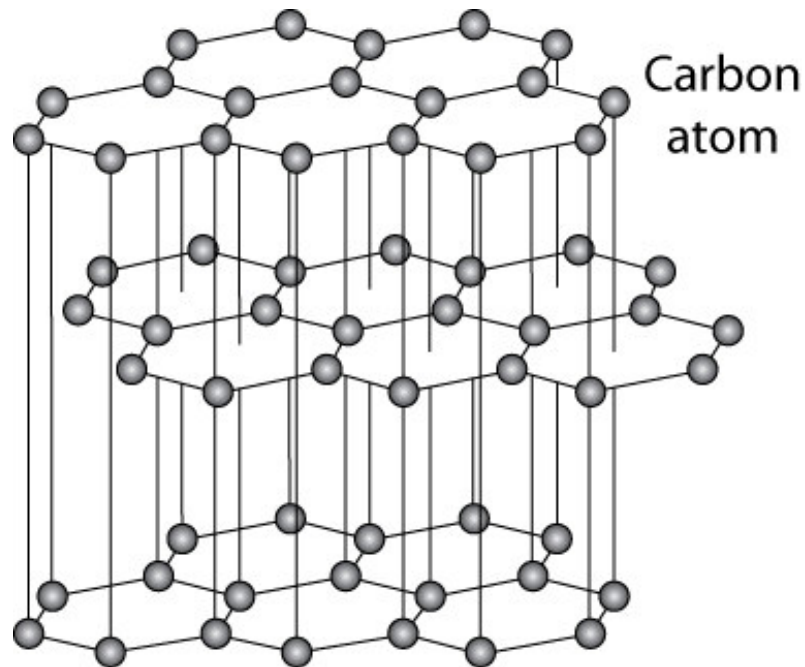
- Carbon black – amorphous – surface area ca. 1000 m²/g
- Diamond
 - tetrahedral carbon
 - hard – no good slip planes
 - brittle – can cut it
 - large diamonds – jewelry
 - small diamonds
 - often man made - used for cutting tools and polishing
 - diamond films
 - hard surface coat – tools, medical devices,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



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

Carbon Forms - Graphite

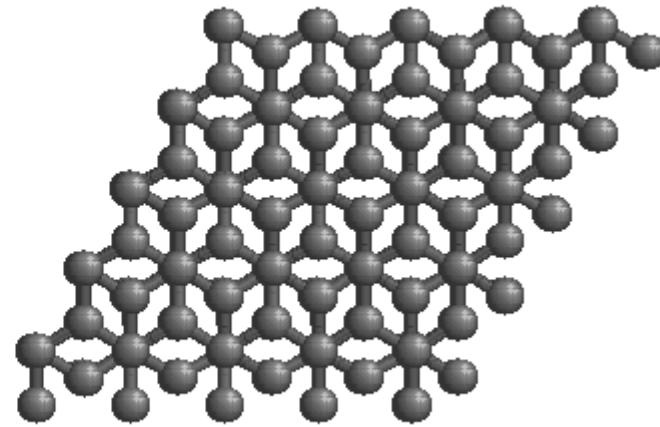
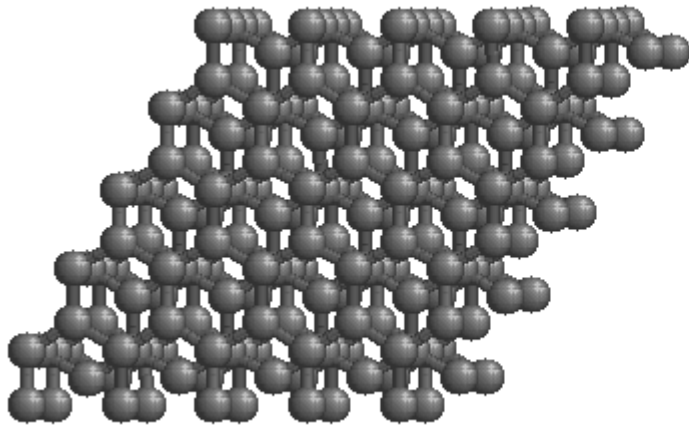
- layer structure – aromatic layers



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

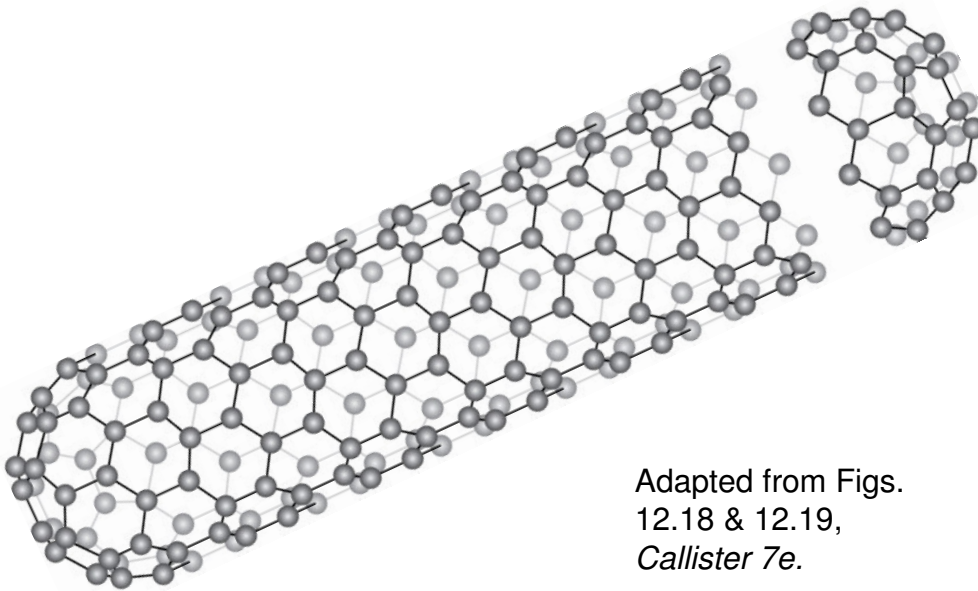
- weak van der Waal's forces between layers
- planes slide easily, good lubricant

Carbon Forms - Graphite

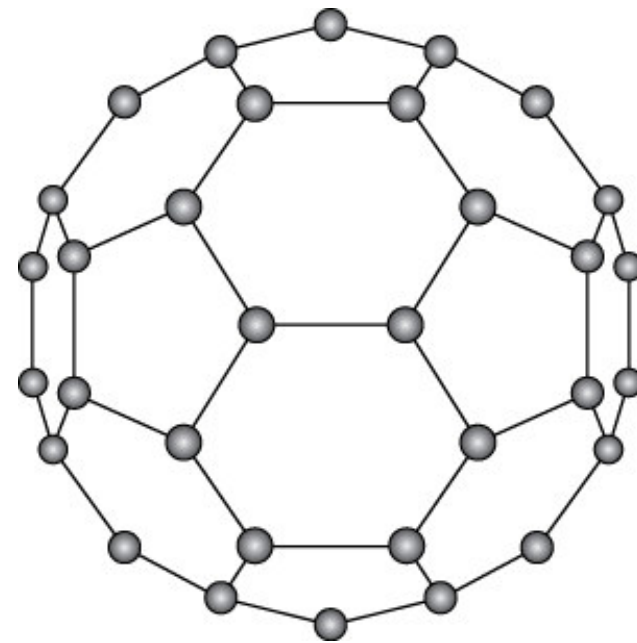


Carbon Forms – Fullerenes and Nanotubes

- 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

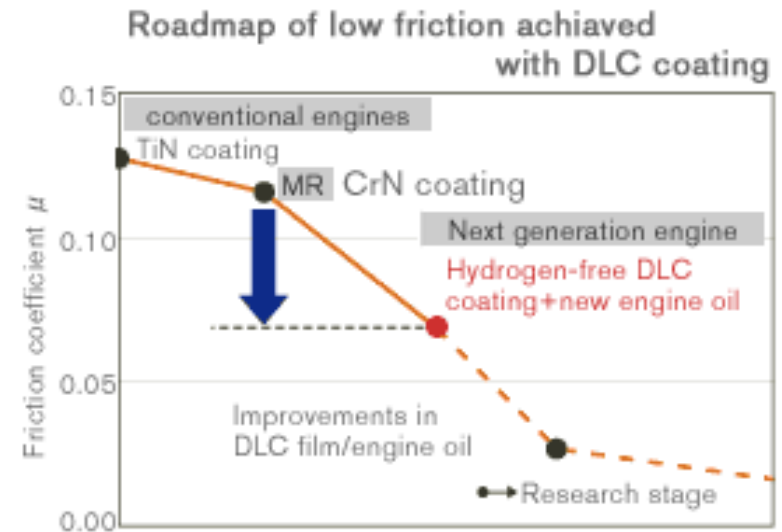
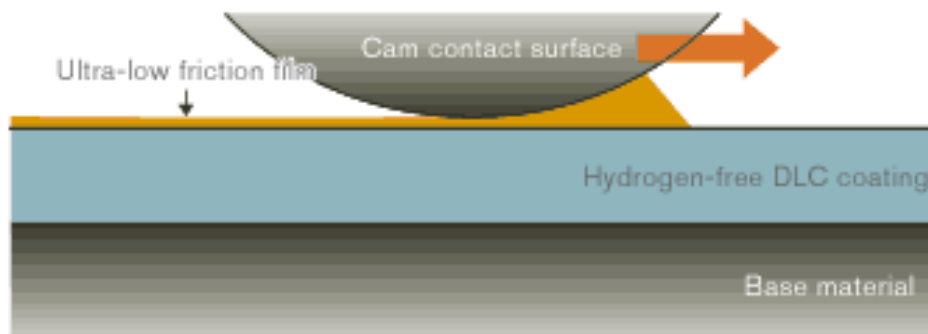


Adapted from Figs.
12.18 & 12.19,
Callister 7e.



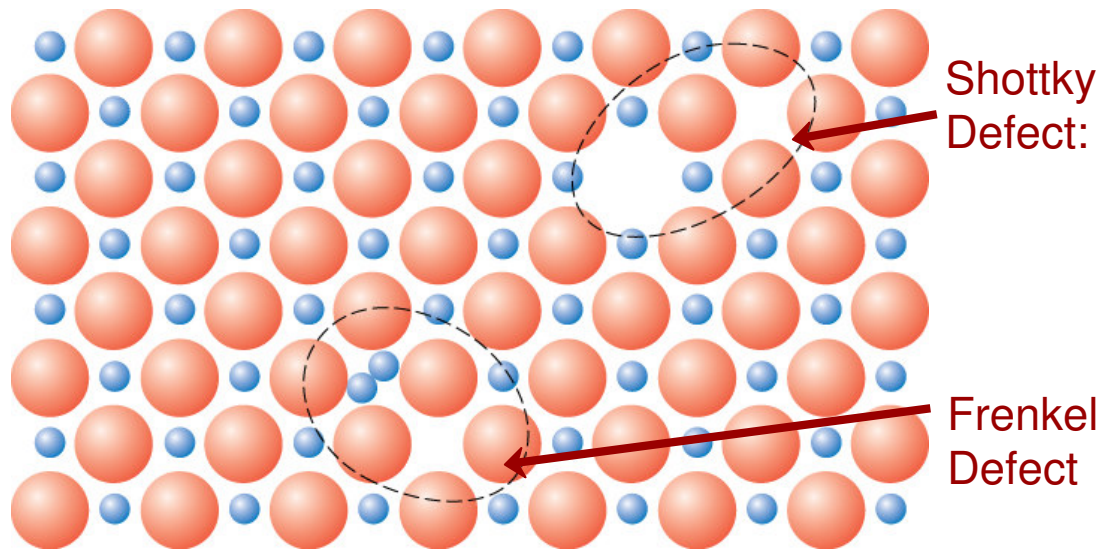
Diamond-like Carbon Film

- **Ultralow friction surface**
- **http://en.wikipedia.org/wiki/Diamond-like_carbon**



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.)

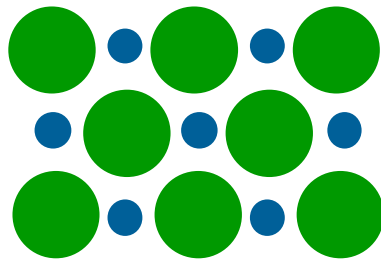
- Equilibrium concentration of defects $\sim e^{-Q_D / kT}$

Impurities

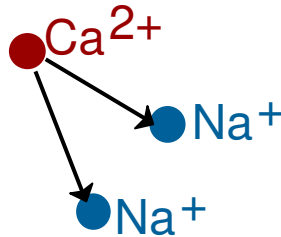
- Impurities must also satisfy **charge balance** = Electroneutrality



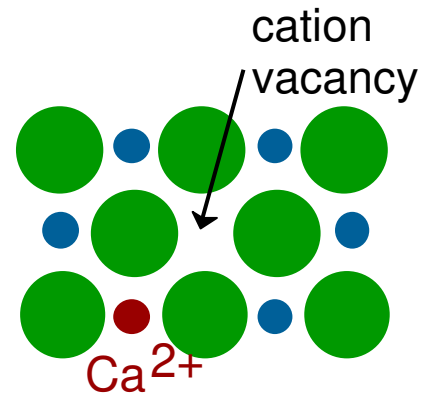
- Substitutional cation impurity



initial geometry

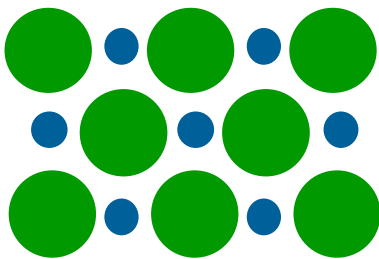


Ca^{2+} impurity

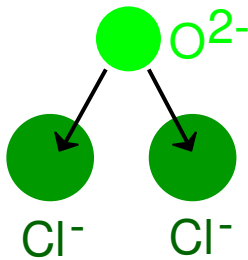


resulting geometry

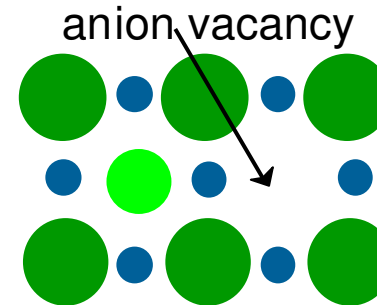
- Substitutional anion impurity



initial geometry

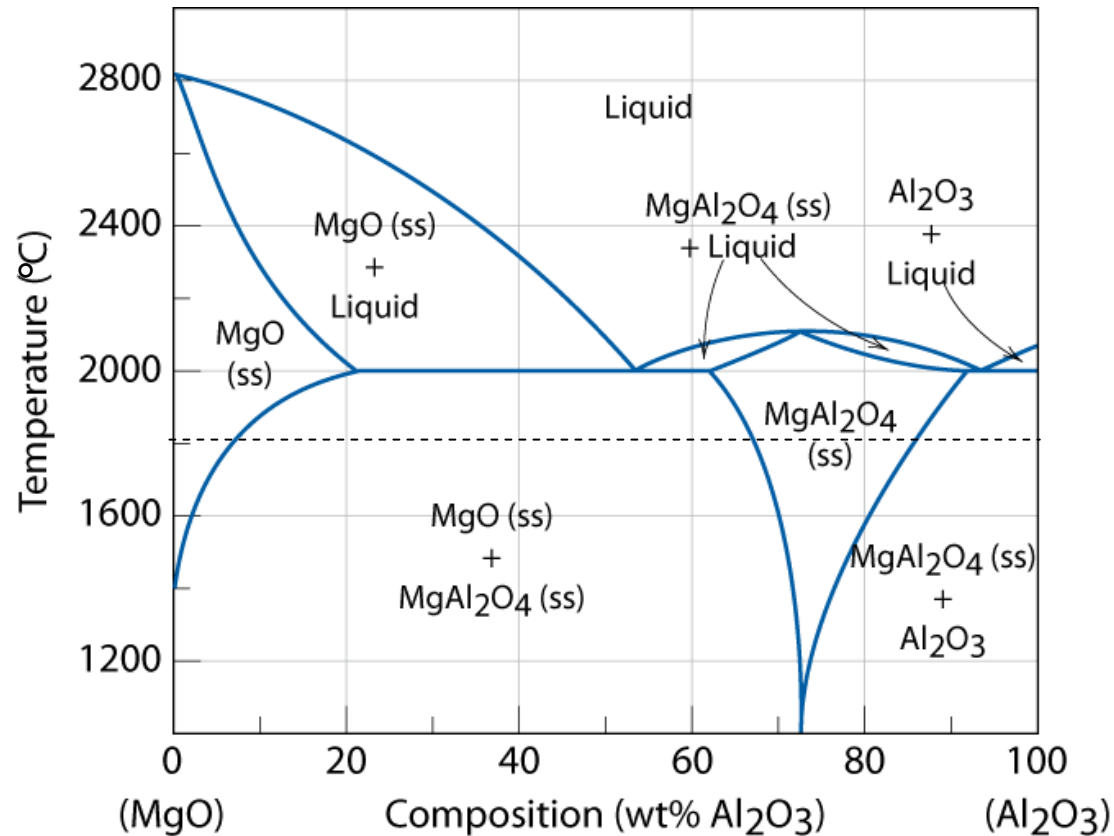


O^{2-} impurity



resulting geometry

Ceramic Phase Diagrams



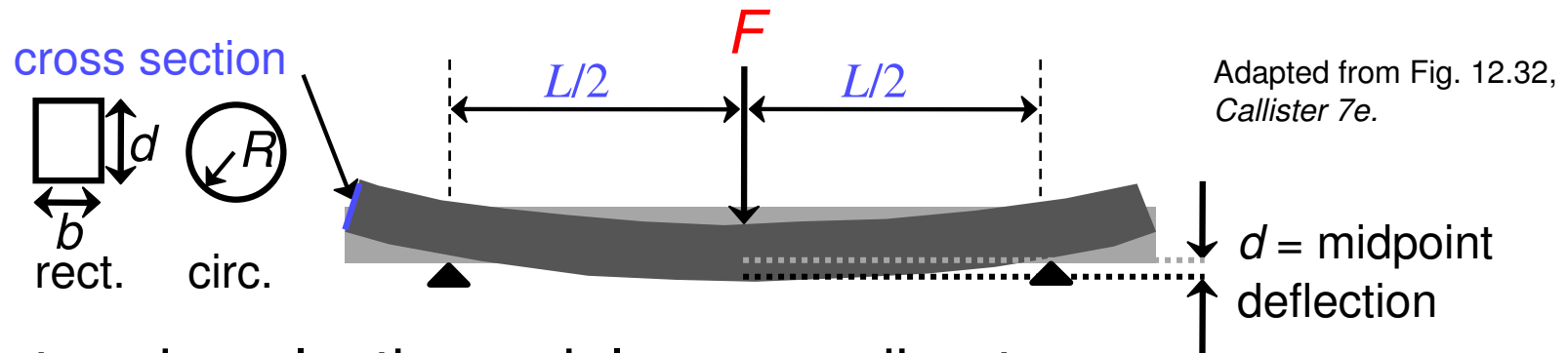
For the MgO/Al₂O₃ phase diagram, what are the:

- Composition of the MgO (ss) phase for a 40 wt% Al₂O₃ alloy at 1800°C?
- Chemical formula of the interceramic compound?
- Composition of the eutectic alloy with the lowest MgO composition?
- Primary phase for a 30 wt% Al₂O₃ alloy cooled from the liquid phase to room temperature?
- Solubility of Al₂O₃ in MgO at 1900°C?

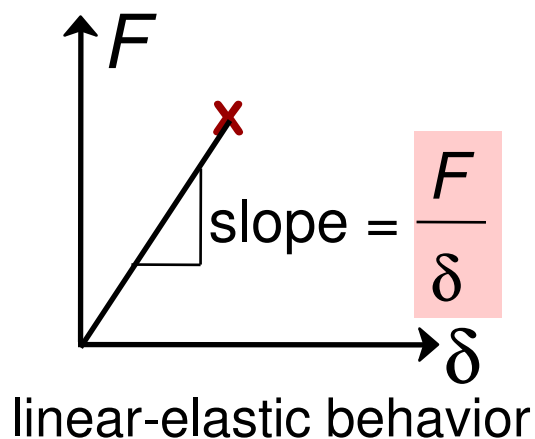
- a) **Composition of the MgO(ss) phase:**
MgO: 92-93 wt% , Al₂O₃: 7-8 wt%
- b) **Chemical formula of the interceramic compound:**
MgAl₂O₄
- c) **Composition of the eutectic alloy with the lowest MgO composition:**
MgO: 6-7 wt% , Al₂O₃: 93-94 wt%
- d) **Primary phase for a 30 wt% Al₂O₃ alloy cooled from the liquid phase to room temperature:**
MgO(ss)
- e) **Solubility of Al₂O₃ in MgO at 1900 °C:**
12-13 wt%

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 ($\epsilon < 0.1\%$).



- Determine elastic modulus according to:

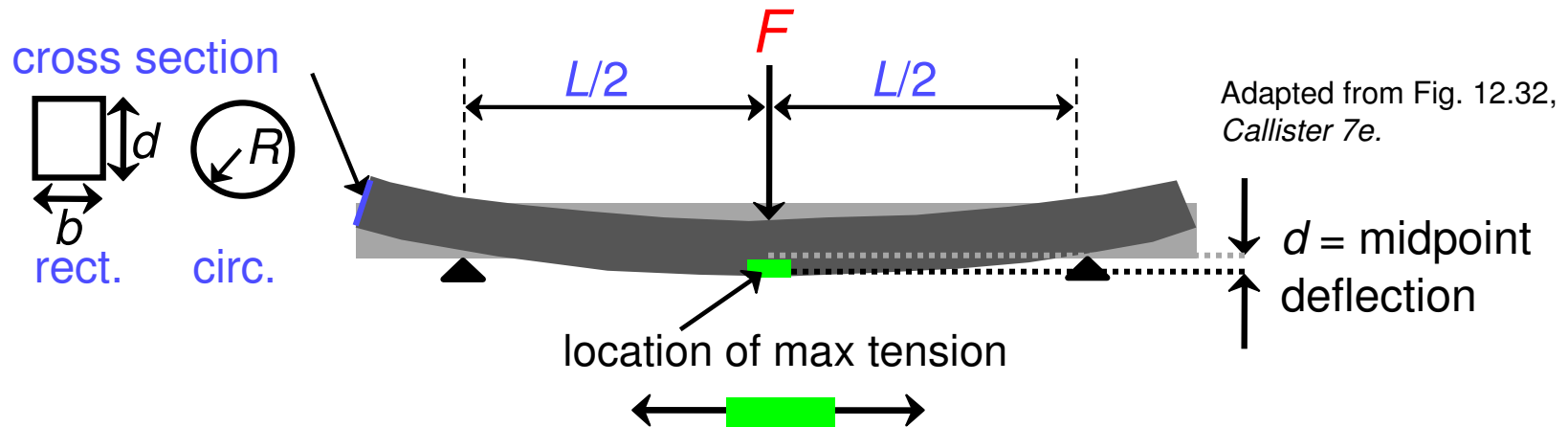


$$E = \frac{F}{\delta} \frac{L^3}{4bd^3} = \frac{F}{\delta} \frac{L^3}{12\pi R^4}$$

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:

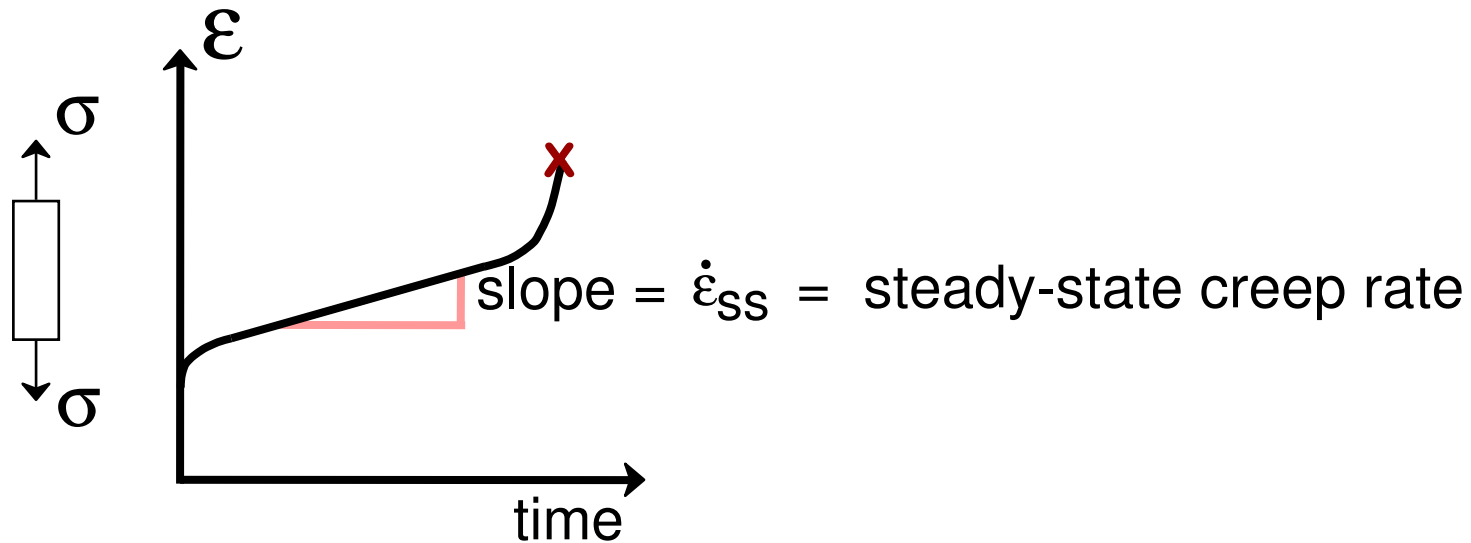
Material	σ_{fs} (MPa)	E (GPa)
Si nitride	250-1000	304
Si carbide	100-820	345
Al oxide	275-700	393
glass (soda)	69	69

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).