Chemical Engineering 378

Science of Materials Engineering

Lecture 8

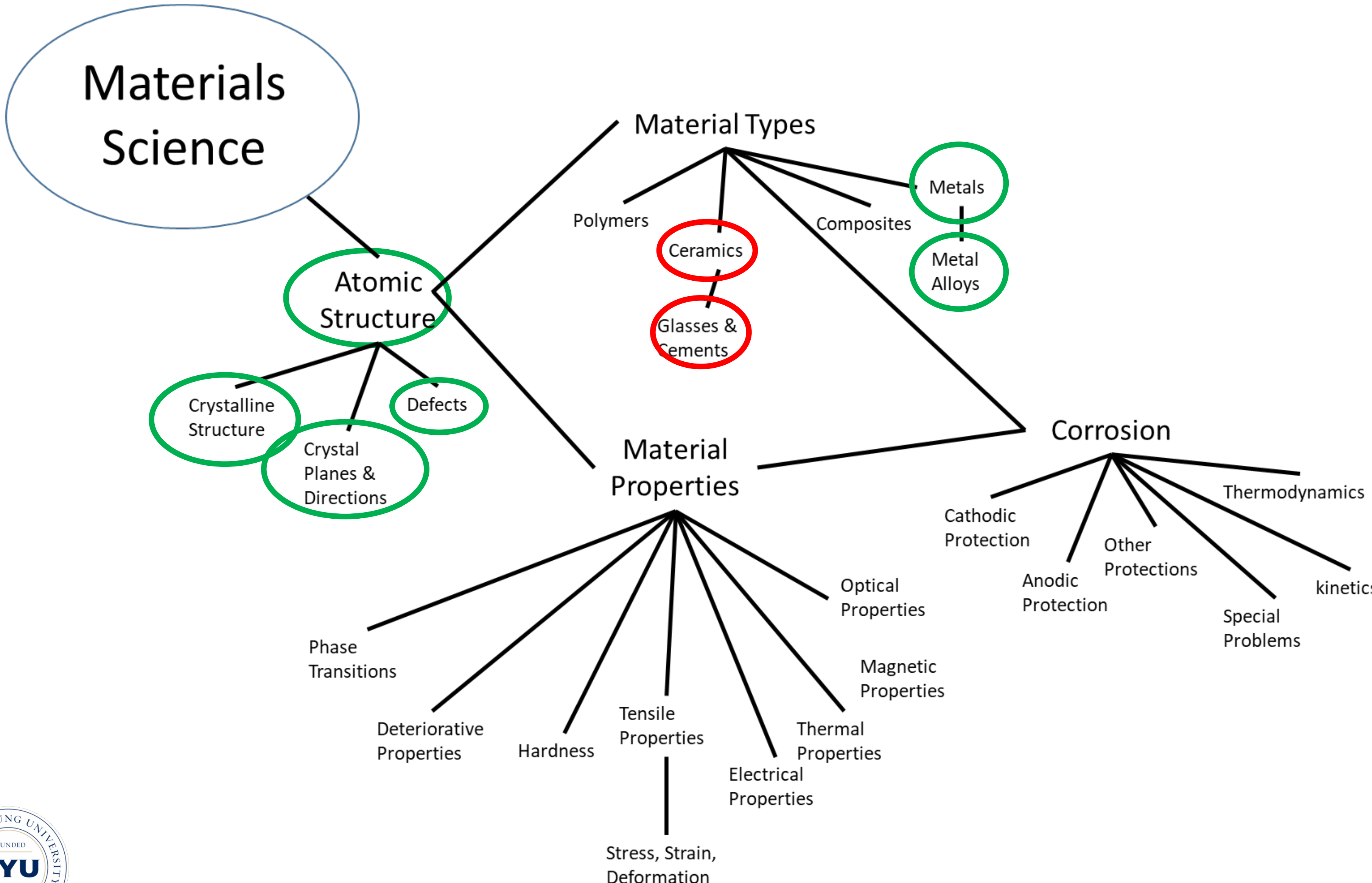
Glasses and Ceramics

Spiritual Thought

"More than anything, our Father wants His children to *choose* to return home to Him. Everything He does is motivated by His yearning desire. The entire reason we are here on earth is to qualify to live with Him forever. We do that by using our agency to find and stay on the covenant path that leads back to our heavenly home."

-President Russel M. Nelson

Materials Roadmap



Atomic Bonding in Ceramics

- Bonding:
  - -- Can be ionic and/or covalent in character.
  - -- % ionic character increases with difference in electronegativity of atoms.

- Degree of ionic character may be large or small:

CaF_2: large

SiC: small

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

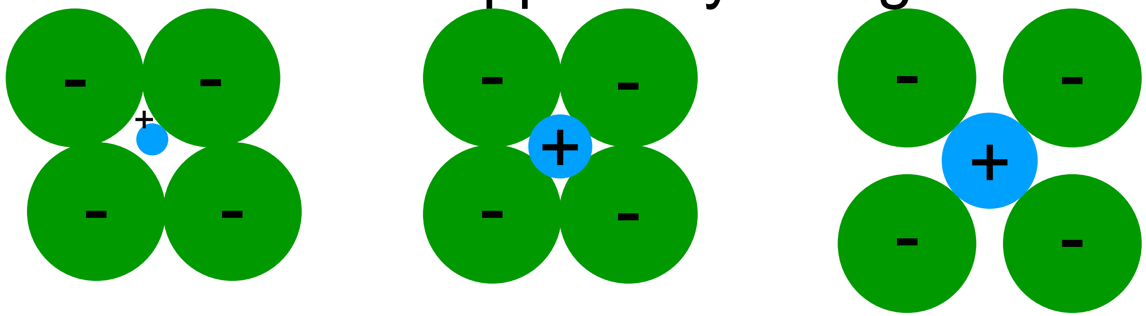
Ceramic Crystal Structures

Oxide structures

- oxygen anions larger than metal cations
- close packed oxygen in a lattice (usually FCC)
- cations fit into interstitial sites among oxygen ions

Factors that Determine Crystal Structure

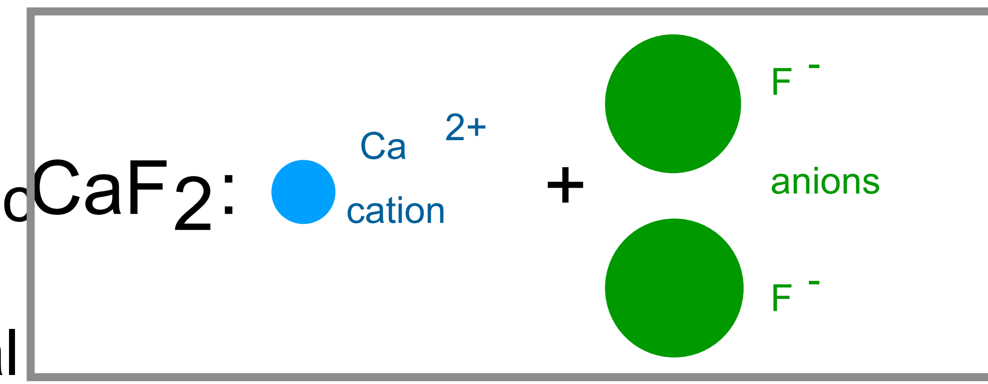
1. Relative sizes of ions – Formation of stable structures:
   --maximize the # of oppositely charged ion neighbors.



unstable   stable   stable

Adapted from Fig. 12.1, *Callister & Rethwisch 10e.*

2. Maintenance of Charge Neutrality :
   --Net charge in ceramic should be zero.
   --Reflected in chemical formula: A_mX_p



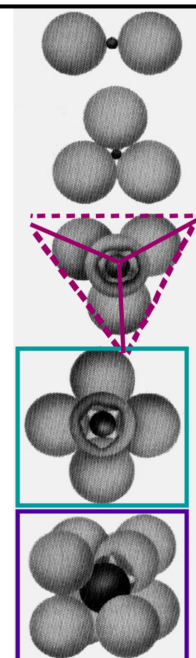
m, p values to achieve charge neutrality

Coordination Number and Ionic Radii

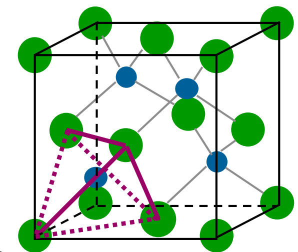
- Coordination Number increases with $\dfrac{r_{cation}}{r_{anion}}$

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

$\dfrac{r_{cation}}{r_{anion}}$	Coord. Number	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	tetrahedral
0.414 - 0.732	6	octahedral
0.732 - 1.0	8	cubic

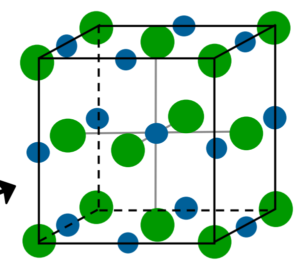


Adapted from Table 12.2, *Callister & Rethwisch 10e.*



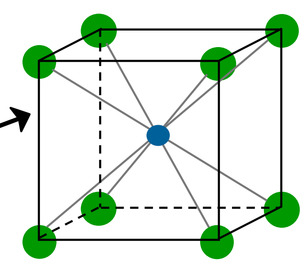
ZnS (zinc blende)

Adapted from Fig. 12.4, *Callister & Rethwisch 10e.*



NaCl (sodium chloride)

Adapted from Fig. 12.2, *Callister & Rethwisch 10e.*

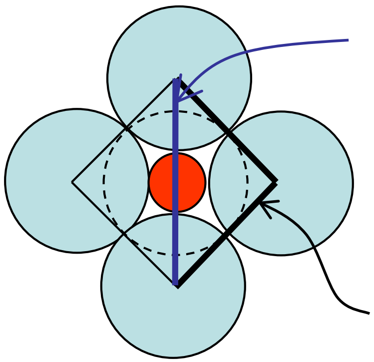


CsCl (cesium chloride)

Adapted from Fig. 12.3, *Callister & Rethwisch 10e.*

Computation of Minimum Cation-Anion Radius Ratio

- Determine minimum r_{cation}/r_{anion} for an octahedral site (C.N. = 6)



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

$$a = 2r_{anion}$$

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

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

$$\boxed{\frac{r_{cation}}{r_{anion}} = \sqrt{2} - 1 = 0.414}$$

Bond Hybridization

Bond Hybridization is possible when there is significant covalent bonding

- hybrid electron orbitals form
- For example for SiC
  - X_{Si} = 1.8 and X_C = 2.5

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

- ~ 89% covalent bonding
- Both Si and C prefer *sp*^{3} hybridization
- Therefore, for SiC, Si atoms occupy tetrahedral sites

Example Problem: Predicting the Crystal Structure of FeO

- 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	
O^{2-}	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 because

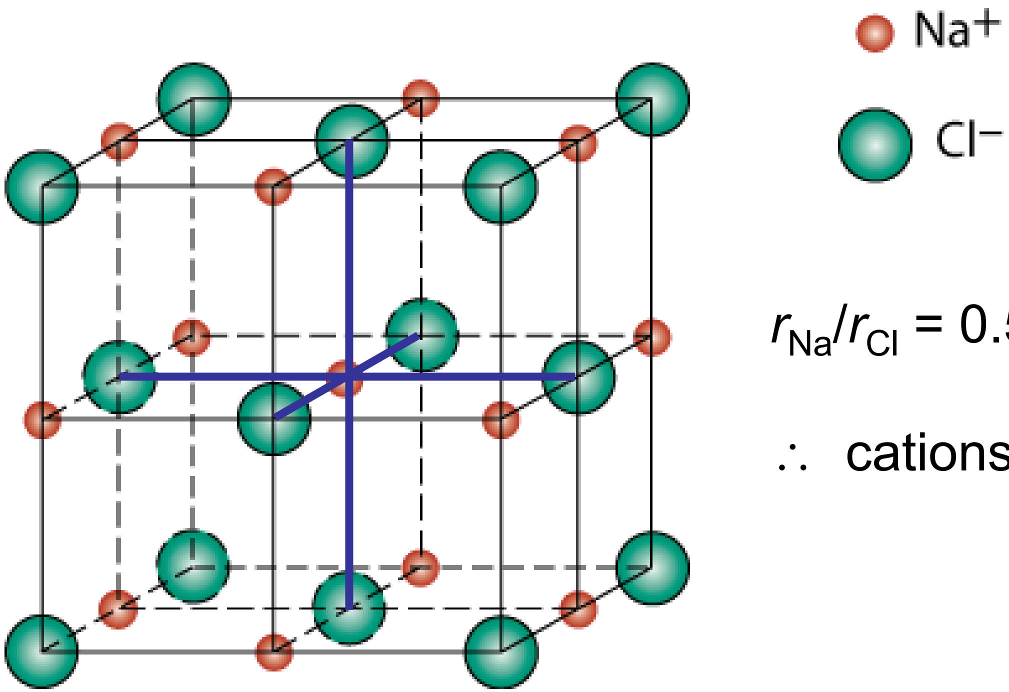
$0.414 < 0.550 < 0.732$

-- crystal structure is NaCl

Data from Table 12.3, *Callister & Rethwisch 10e.*

Rock Salt Structure

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



$r_{Na} = 0.102$ nm

$r_{Cl} = 0.181$ nm

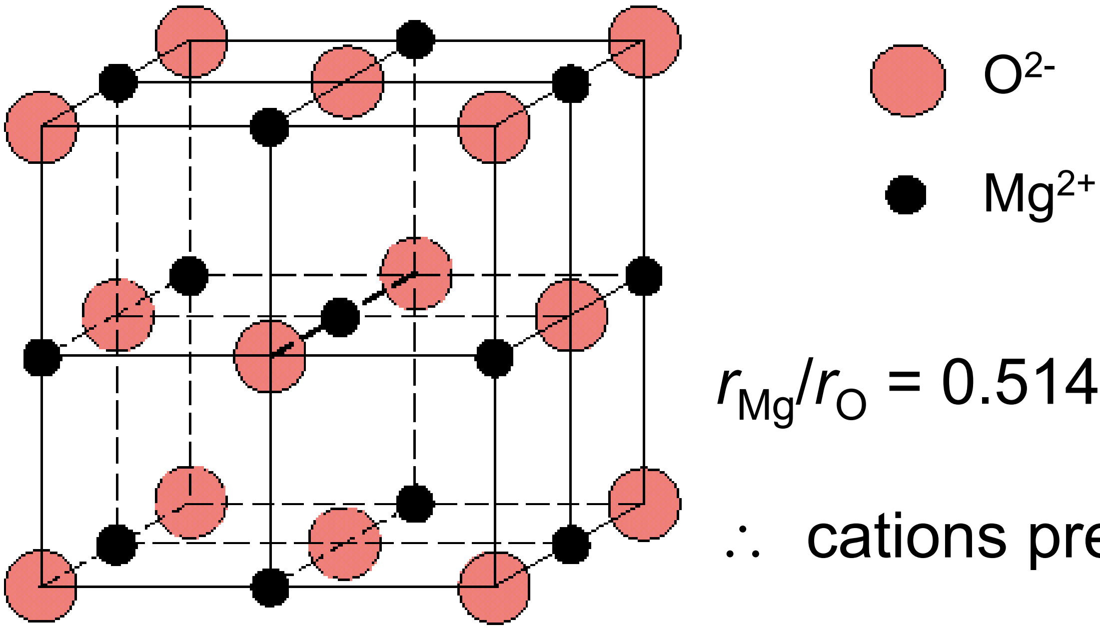
$r_{Na}/r_{Cl} = 0.564$

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

Adapted from Fig. 12.2,
Callister & Rethwisch 10e.

MgO and FeO

MgO and FeO also have the NaCl structure



Adapted from Fig. 12.2, *Callister & Rethwisch 10e.*

$r_{Mg}/r_O = 0.514$

$\therefore$ cations prefer octahedral sites

So each Mg^{2+} (or Fe^{2+}) has 6 neighbor oxygen atoms

AX Crystal Structures

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

Cesium Chloride structure:

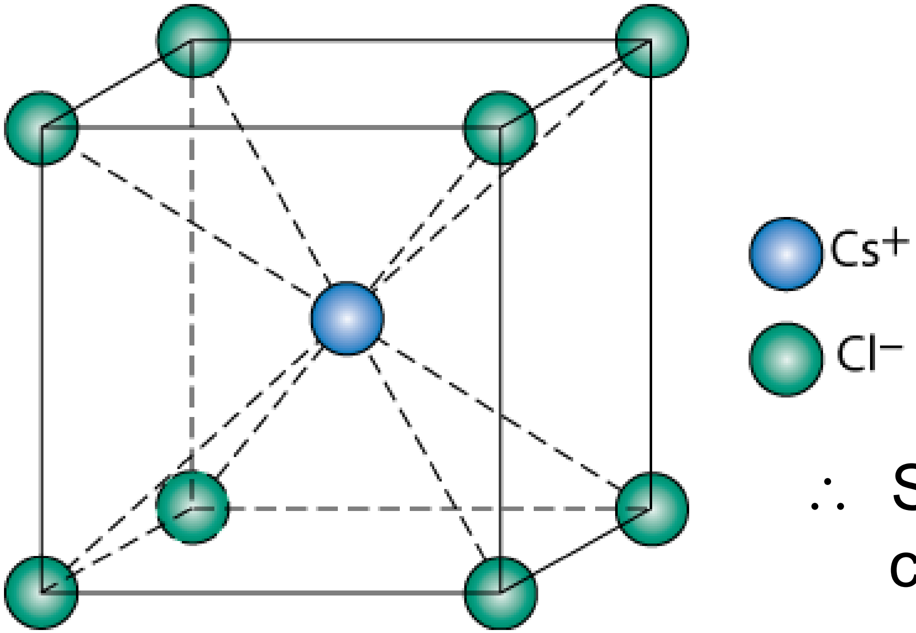


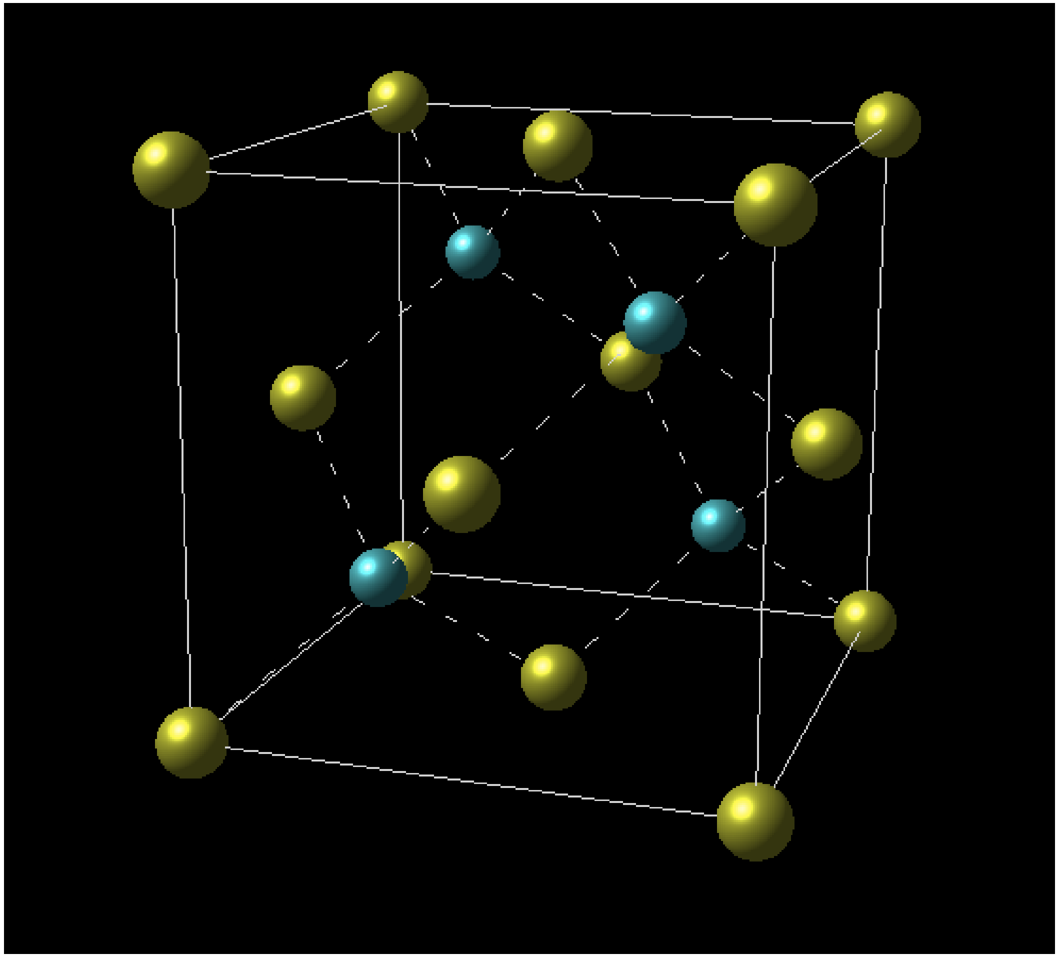
Fig. 12.3, *Callister & Rethwisch 10e.*

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

$\therefore$ Since $0.732 < 0.939 < 1.0$, cubic sites preferred

So each Cs^+ has 8 neighbor Cl^-

VMSE Screenshot – Zinc Blende Unit Cell



AX_2 Crystal Structures

Fluorite structure

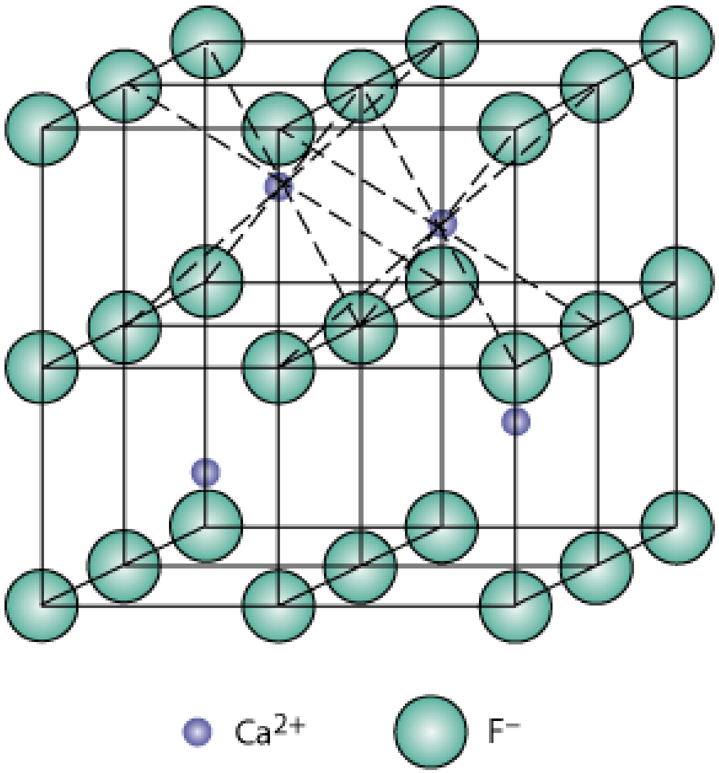


Fig. 12.5, *Callister & Rethwisch 10e.*

- Calcium Fluorite (CaF_2)
- Cations in cubic sites
- UO_2, ThO_2, ZrO_2, CeO_2
- Antifluorite structure – positions of cations and anions reversed

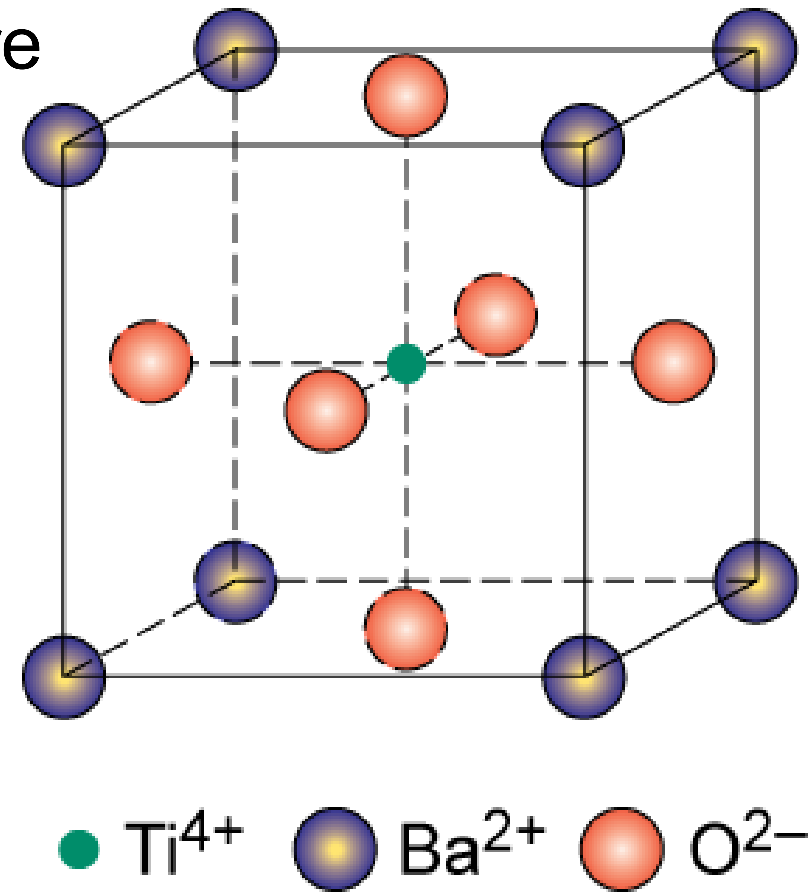
ABX_3 Crystal Structures

- Perovskite structure

Ex: complex oxide

$BaTiO_3$

Fig. 12.6, *Callister & Rethwisch 10e.*



Density Computations for Ceramics

Number of formula units/unit cell

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

Avogadro's number

Volume of unit cell

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

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

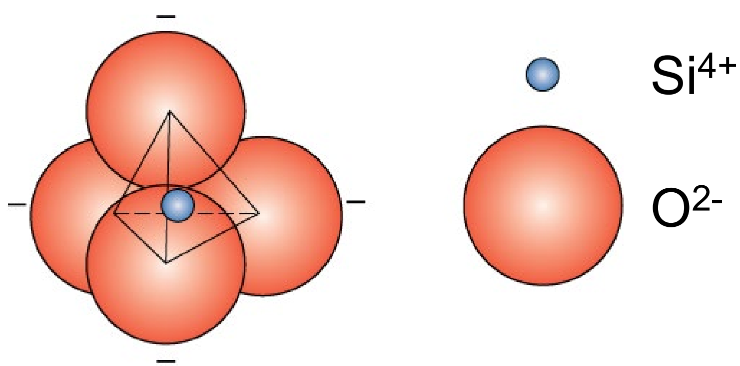
Example

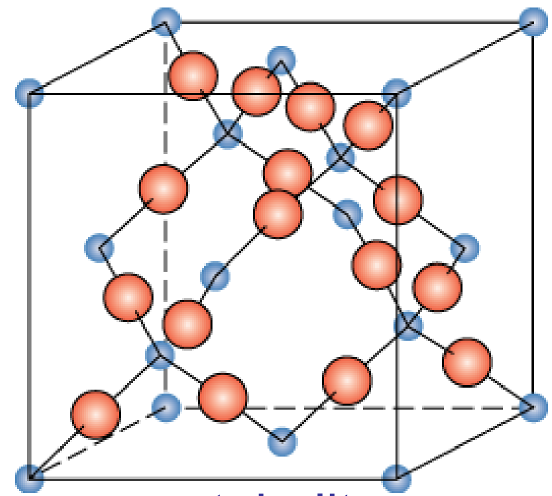
- What is the theoretical density of NaCl?

- NaCl structure? (alternating FCC)
  - $\Sigma A_C = A_{Na} = 22.99 g/mol$
  - $\Sigma A_C = A_{Na} = 35.45 g/mol$
- a =$2_{r_{Na^+}} + 2_{r_{Cl^-}}$
- V = a^3
- $\rho = \frac{4(22.99+35.45)}{(2[.102\times10^{-7}]+2[.181\times10^{-7}])^3(6.022\times10^{23})} =$ $2.14 g/mol$

Silicate Ceramics

Most common elements on earth are Si & O





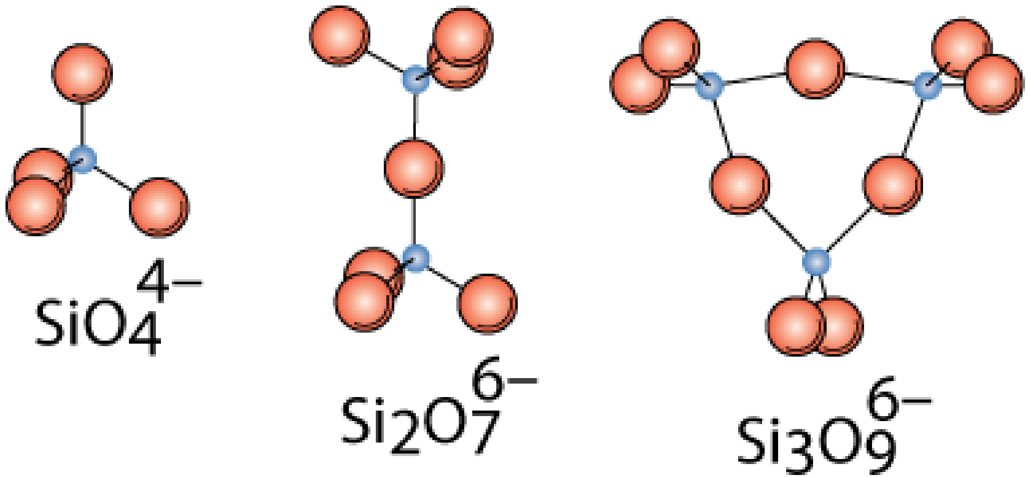
Figs. 12.9 & 12.10, *Callister & Rethwisch 10e*

crystobalite

- SiO_2 (silica) polymorphic forms are quartz, crystobalite, & tridymite
- The strong Si-O bonds lead to a high melting temperature (1710ºC) for this material

Silicates

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



Adapted from Fig. 12.12, *Callister & Rethwisch 10e.*

Mg_2SiO_4 $Ca_2MgSi_2O_7$

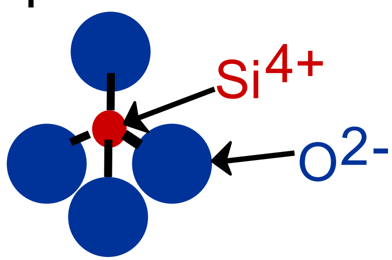
Presence of cations such as Ca^{2+}, Mg^{2+}, & Al^{3+}

1. maintain charge neutrality, and
2. ionically bond SiO_4^{4-} to one another

Glass Structure

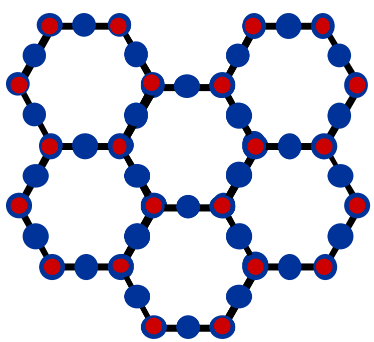
- Basic Unit:

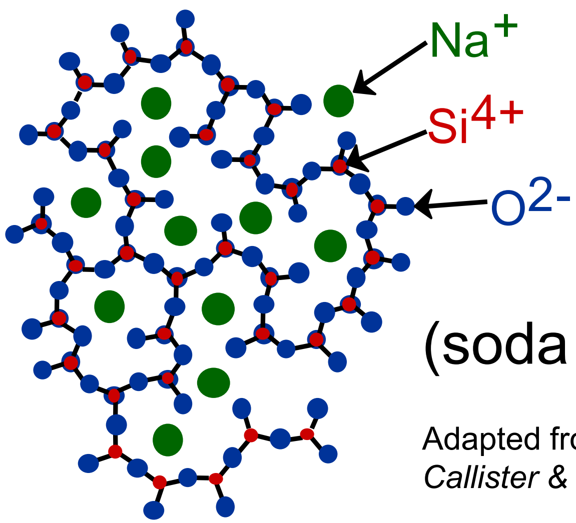
SiO_4^{4-} tetrahedron



Glass is noncrystalline (amorphous)
- Fused silica is SiO_2 to which no impurities have been added
- Other common glasses contain impurity ions such as Na^+, Ca^{2+}, Al^{3+}, and B^{3+}

- Quartz is crystalline SiO_2:





(soda glass)

Adapted from Fig. 12.11, *Callister & Rethwisch 10e*.

Layered Silicates

- Layered silicates (e.g., clays, mica, talc)
  - SiO_4 tetrahedra connected together to form 2-D plane
- A net negative charge is associated with each $(Si_2O_5)^{2-}$ unit
- Negative charge balanced by adjacent plane rich in positively charged cations

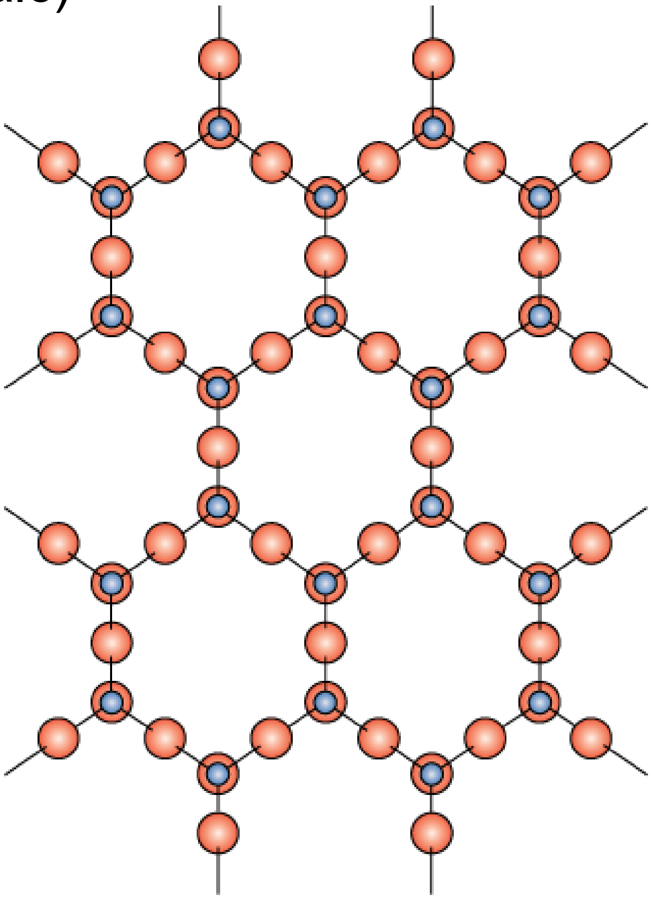


Fig. 12.13, *Callister & Rethwisch 10e.*

Layered Silicates (cont)

- Kaolinite clay alternates $(Si_2O_5)^{2-}$ layer with $Al_2(OH)_4^{2+}$ layer

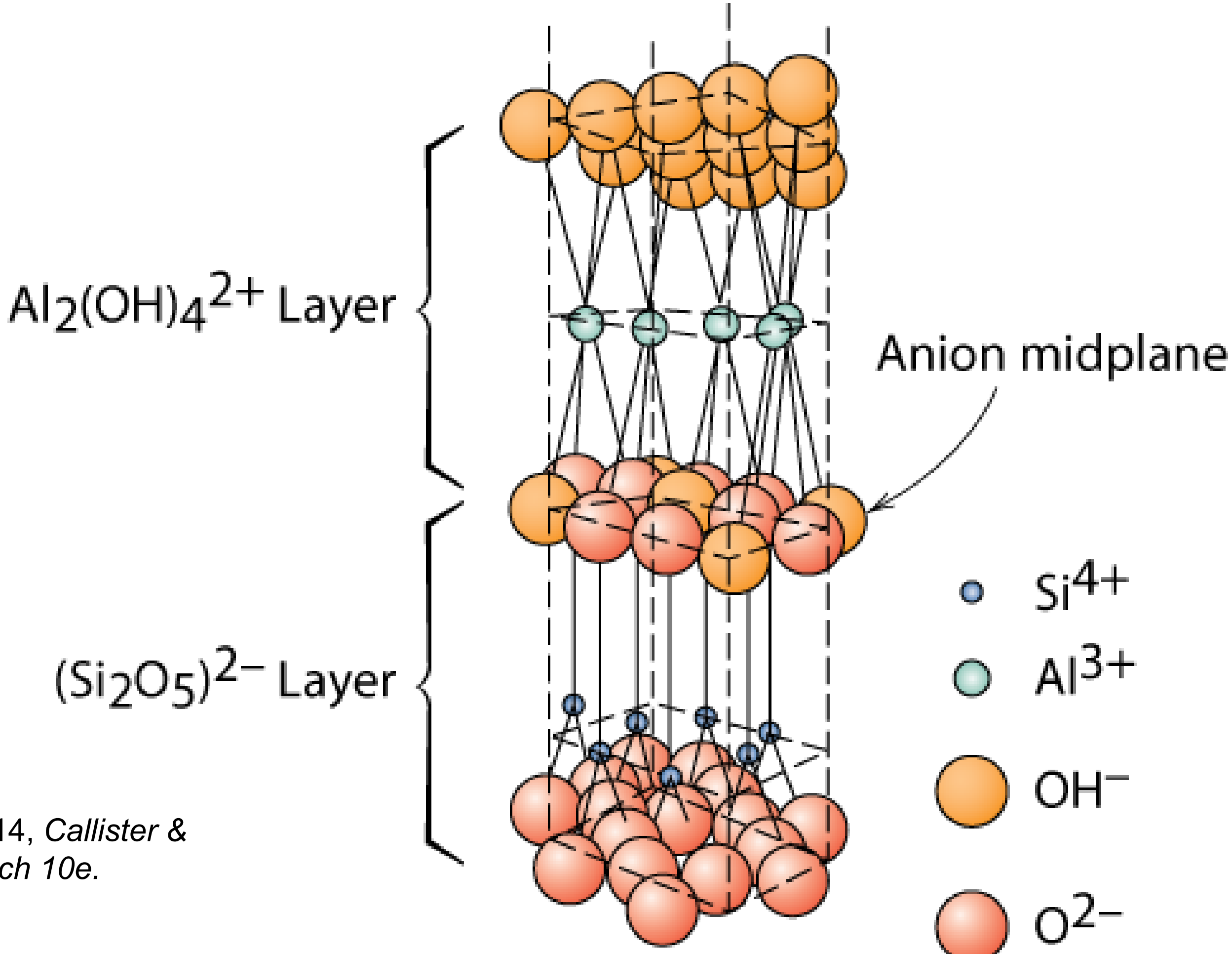


Fig. 12.14, *Callister & Rethwisch 10e.*

Note: Adjacent sheets of this type are loosely bound to one another by van der Waal's forces.

Polymorphic Forms of Carbon

Diamond

- tetrahedral bonding of carbon
  - hardest material known
  - very high thermal conductivity
- large single crystals – gem stones
- small crystals – used to grind/cut other materials
- diamond thin films
  - hard surface coatings – used for cutting tools, medical devices, etc.

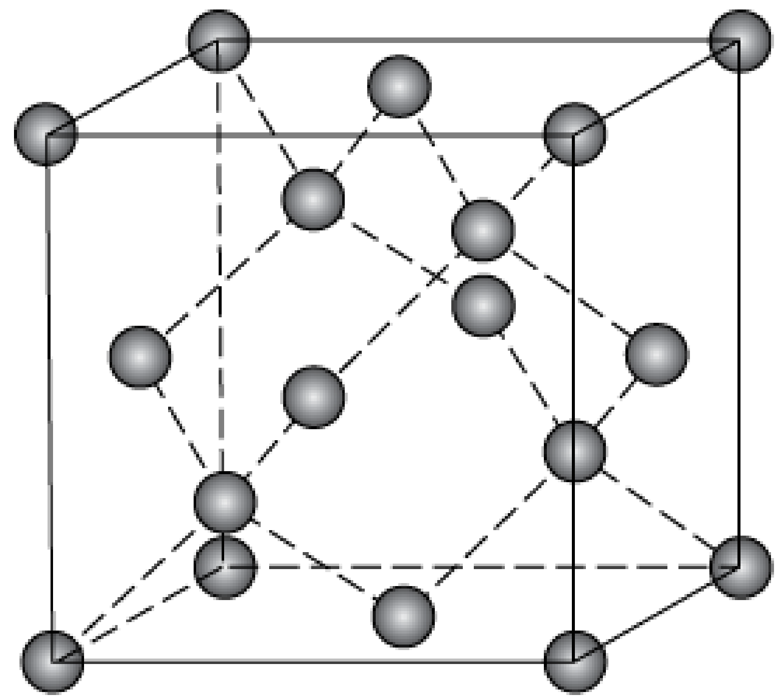


Fig. 12.16, *Callister & Rethwisch 10e.*

Polymorphic Forms of Carbon (cont)

Graphite

– layered structure – parallel hexagonal arrays of carbon atoms

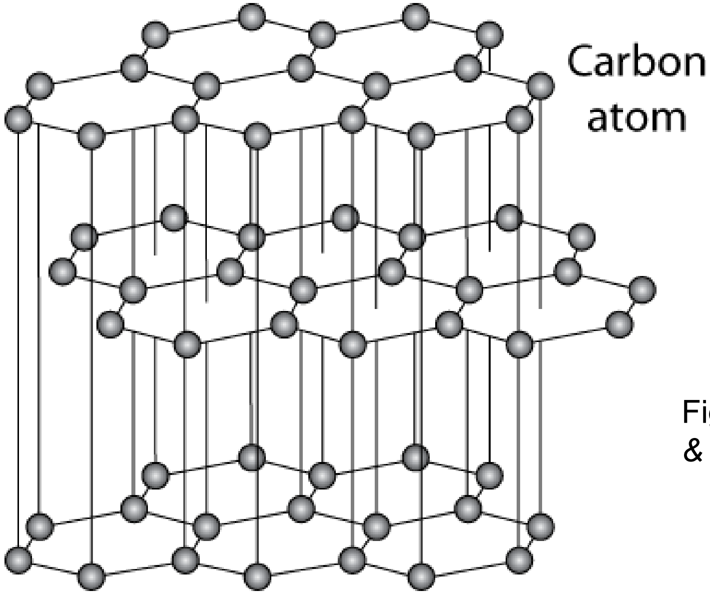


Fig. 12.17, *Callister & Rethwisch 10e.*

– weak van der Waal's forces between layers

– planes slide easily over one another -- good lubricant

Point Defects in Ceramics (i)

- Vacancies

  -- vacancies exist in ceramics for both cations and anions

- Interstitials

  -- interstitials exist for cations

  -- interstitials are not normally observed for anions because anions are large relative to the interstitial sites

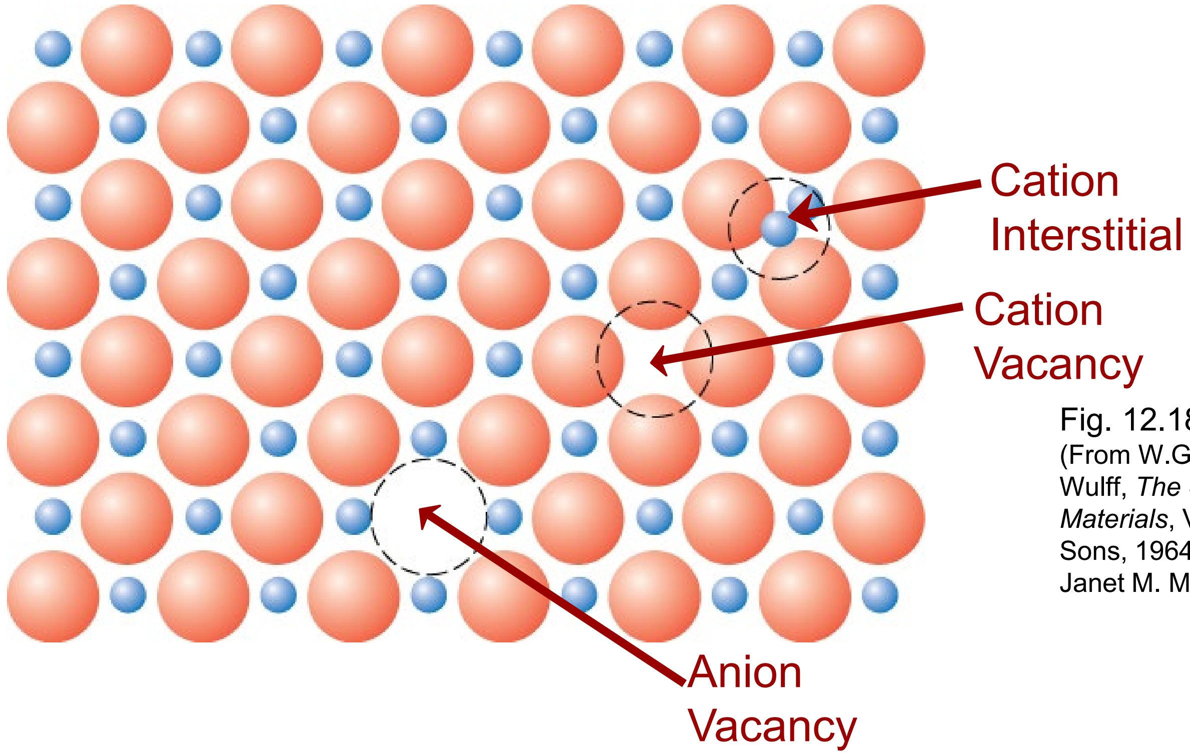


Fig. 12.18, *Callister & Rethwisch 10e.* (From W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, John Wiley & Sons, 1964. Reproduced with permission of Janet M. Moffatt.)

Point Defects in Ceramics (ii)

- Frenkel Defect

  -- a cation vacancy-cation interstitial pair.

- Shottky Defect

  -- a paired set of cation and anion vacancies.

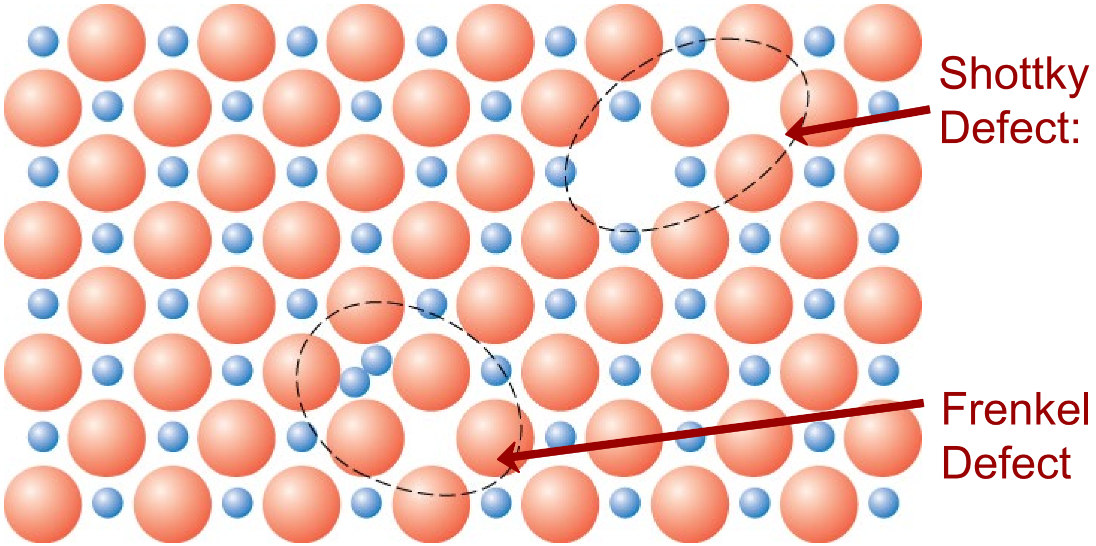


Fig. 12.19, *Callister & Rethwisch 10e.* (From W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, John Wiley & Sons, 1964. Reproduced with permission of Janet M. Moffatt.)

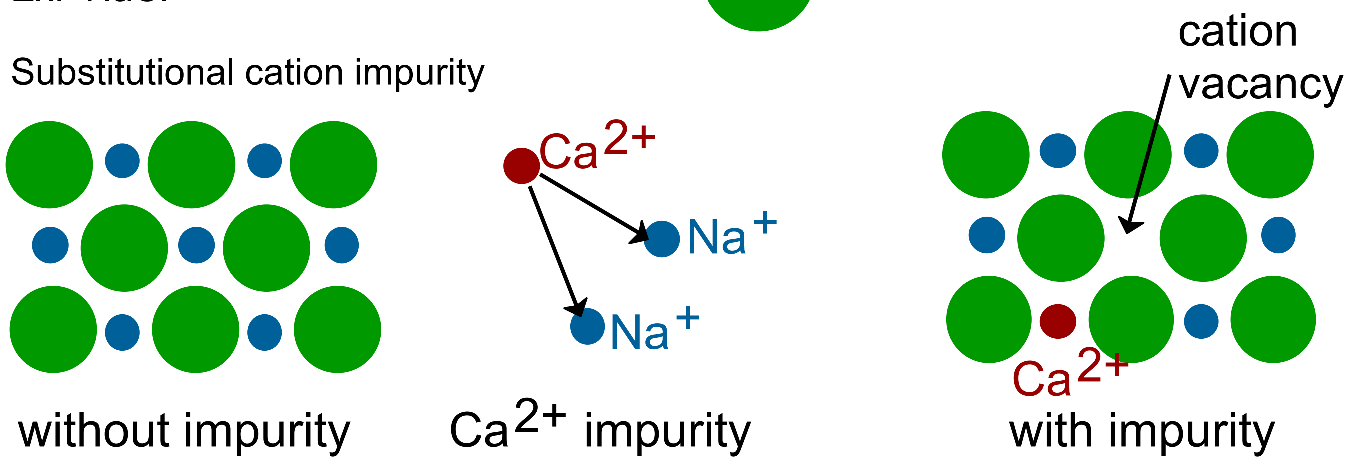
- Equilibrium concentration of defects

$$\propto e^{-Q_D/kT}$$

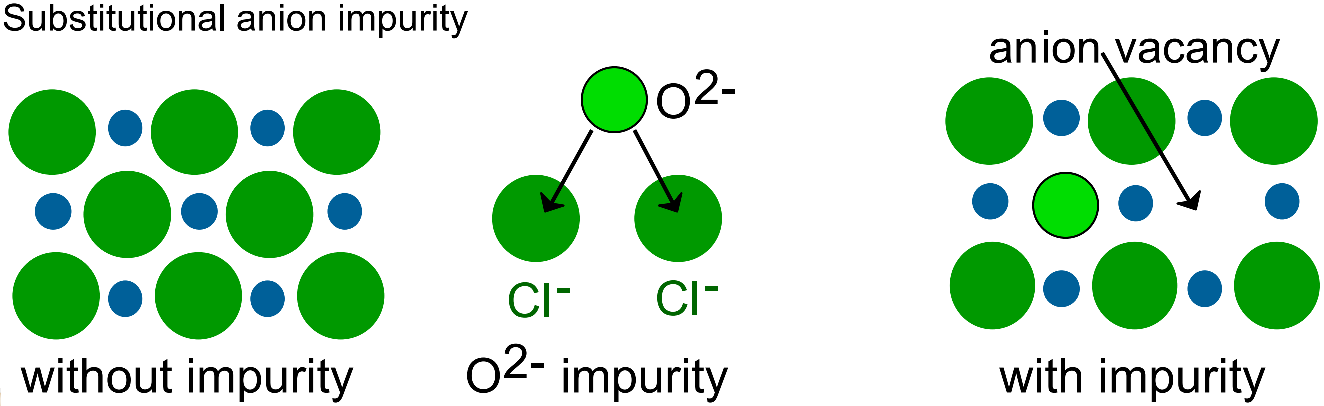
Imperfections in Ceramics

- Electroneutrality (charge balance) must be maintained when impurities are present
- Ex: NaCl

- Substitutional cation impurity



- Substitutional anion impurity



Ceramic Phase Diagrams

MgO-Al_2O_3 diagram:

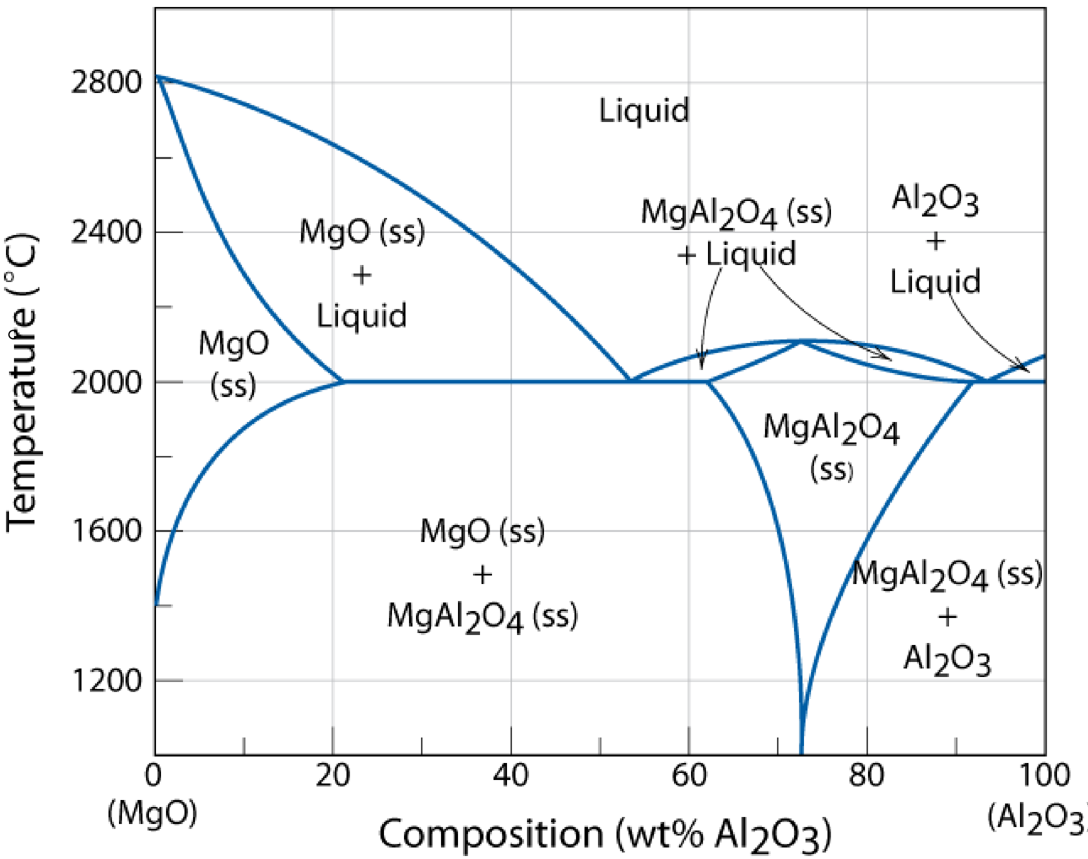


Fig. 12.23, Callister & Rethwisch 10e.
[Adapted from B. Hallstedt, "Thermodynamic Assessment of the System MgO–Al_2O_3," *J. Am. Ceram. Soc.*, 75[6], 1992, p.1502. Reprinted by permission of the American Ceramic Society.]