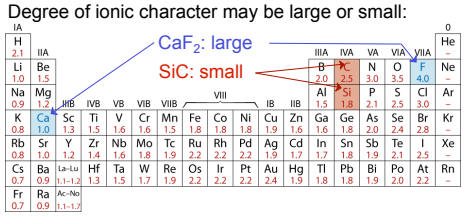
Chapter 12: Structures & Properties of Ceramics

ISSUES TO ADDRESS...

- How do the crystal structures of _____ materials differ from those for _____?
- How do _____ defects in ceramics differ from those defects found in metals?
- How are _____ accommodated in the ceramic lattice?
- In what ways are _____ phase diagrams different from phase diagrams for metals?
- How are the mechanical properties of ceramics _____, and how do they differ from those for metals?

Atomic Bonding in Ceramics

- Bonding:
  -- _____.
  -- % ionic character _____ with difference in electronegativity of atoms.
- Degree of ionic character may be large or small:



Adapted from Fig. 2.7, *Callister & Rethwisch 8e.* (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.)

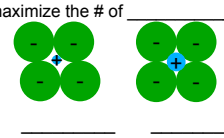
Ceramic Crystal Structures

Oxide structures

- oxygen anions _____ than metal cations
- close _____ oxygen in a _____ (usually ____)
- cations fit into _____ sites among _____ ions

Factors that Determine Crystal Structure

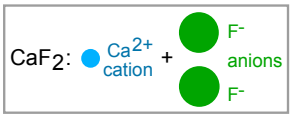
1. Relative sizes of ions – _____:
   --maximize the # of _____.



Adapted from Fig. 12.1, *Callister & Rethwisch 8e.*

_____ _____ stable

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



m, p values to achieve charge neutrality

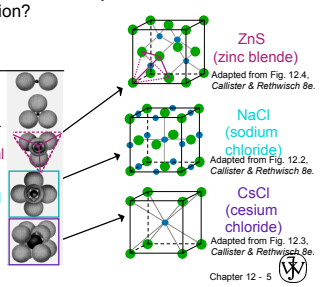
Coordination # and Ionic Radii

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

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

$\frac{r_{cation}}{r_{anion}}$	Coord #	
< 0.155	2	linear
0.155 - 0.225	3	_____
0.225 - 0.414	4	tetrahedral
0.414 - 0.732	6	octahedral
0.732 - 1.0	8	_____

Adapted from Table 12.2, *Callister & Rethwisch 8e.*



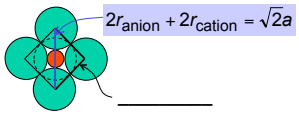
ZnS (zinc blende)
Adapted from Fig. 12.4, *Callister & Rethwisch 8e.*

NaCl (sodium chloride)
Adapted from Fig. 12.2, *Callister & Rethwisch 8e.*

CsCl (cesium chloride)
Adapted from Fig. 12.3, *Callister & Rethwisch 8e.*

Computation of Minimum Cation-Anion Radius Ratio

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



_____

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

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

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

Bond Hybridization

Bond Hybridization is possible when there is significant _____ bonding

– _____

– For example for SiC
  - X_{Si} = 1.8 and X_C = 2.5

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

  - ~ 89% _____ bonding
  - Both Si and C prefer sp^3 hybridization
  - Therefore, for SiC, Si atoms occupy _____ sites

Example Problem: Predicting the Crystal Structure of FeO

- On the basis of ionic radii, what _____ 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

Data from Table 12.3, *Callister & Rethwisch 8e.*

- Answer:

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

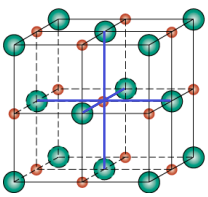
based on this ratio,
-- coord # = ___ because

0.414 < 0.550 < 0.732

-- crystal structure is ____

Rock Salt Structure

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



Adapted from Fig. 12.2, *Callister & Rethwisch 8e.*

Na^+ r_{Na} = 0.102 nm

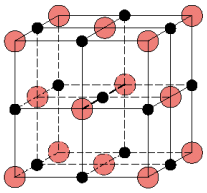
Cl^- r_{Cl} = _____ nm

r_{Na}/r_{Cl} = _____

∴ cations (Na^+) prefer _____ sites

MgO and FeO

MgO and FeO also have the NaCl structure



Adapted from Fig. 12.2, *Callister & Rethwisch 8e.*

O^{2-} r_O = 0.140 nm

Mg^{2+} r_{Mg} = 0.072 nm

r_{Mg}/r_O = _____

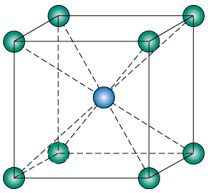
∴ _____ prefer octahedral sites

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

AX Crystal Structures

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

Cesium Chloride structure:



Adapted from Fig. 12.3, *Callister & Rethwisch 8e.*

Cs^+

Cl^-

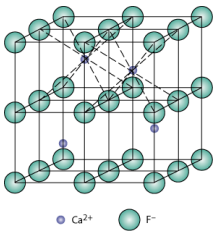
$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{0.170}{0.181}$ = _____

∴ Since 0.732 < ____ < 1.0,
_____ sites preferred

So each Cs^+ has __ neighbor Cl^-

AX_2 Crystal Structures

Fluorite structure



Ca^{2+} F^-

Adapted from Fig. 12.5, *Callister & Rethwisch 8e.*

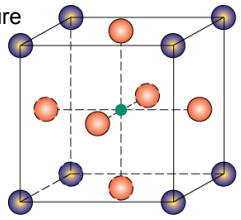
- Calcium _____ (CaF_2)
- Cations in _____ sites
- UO_2, ThO_2, ZrO_2, CeO_2
- _____ structure – positions of cations and anions reversed

ABX_3 Crystal Structures

- _____ structure

Ex: complex oxide

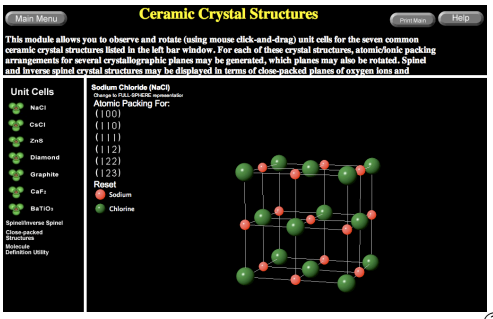
_____



Adapted from Fig. 12.6, *Callister & Rethwisch 8e.*

● Ti^{4+} ● Ba^{2+} ● O^{2-}

VMSE: Ceramic Crystal Structures



Density Computations for Ceramics

Number of formula units/unit cell

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

_____ number

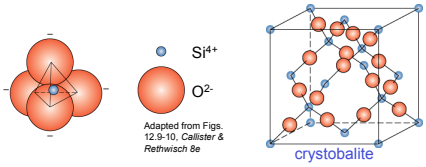
Volume of unit cell

ΣA_C = sum of atomic weights of _____

ΣA_A = sum of atomic weights of _____

Silicate Ceramics

Most common _____

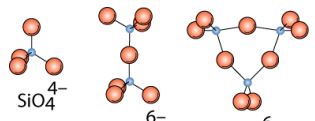


Adapted from Figs. 12.9-10, *Callister & Rethwisch 8e*

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

Silicates

Bonding of adjacent SiO_4^{4-} accomplished by the sharing of common _____



Adapted from Fig. 12.12, *Callister & Rethwisch 8e.*

Mg_2SiO_4 $Ca_2MgSi_2O_7$

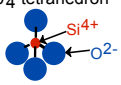
Presence of cations such as Ca^{2+}, Mg^{2+}, & Al^{3+}

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

Glass Structure

- Basic Unit:

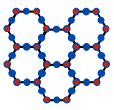
SiO_4^{4-} tetrahedron

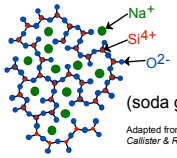


Glass is _____ (_____)

- _____ is SiO_2 to which no impurities have been added
- Other common _____ contain impurity ions such as Na^+, Ca^{2+}, Al^{3+}, and B^{3+}

- Quartz is _____ SiO_2:



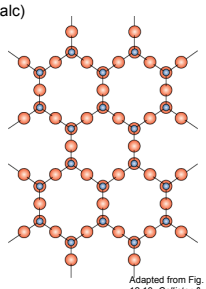


(soda glass)

Adapted from Fig. 12.11, *Callister & Rethwisch 8e.*

Layered Silicates

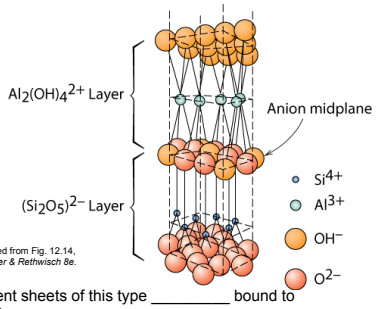
- Layered _____ (e.g., clays, mica, talc)
  - SiO_4 _____ connected together to form 2-D plane
- A net negative charge is associated with each $(Si_2O_5)^{2-}$ unit
- Negative charge balanced by _____ plane rich in positively charged _____



Adapted from Fig. 12.13, *Callister & Rethwisch 8e.*

Layered Silicates (cont.)

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



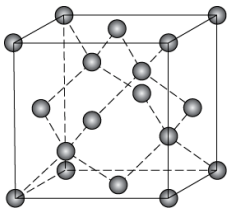
Adapted from Fig. 12.14, *Callister & Rethwisch 8e.*

Note: Adjacent sheets of this type _____ bound to one another by _____.

Polymorphic Forms of Carbon

Diamond

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

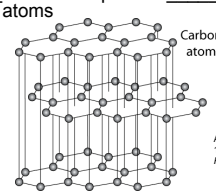


Adapted from Fig. 12.15, *Callister & Rethwisch 8e.*

Polymorphic Forms of Carbon (cont)

_____

– _____ structure – parallel _____ arrays of carbon atoms

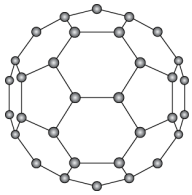


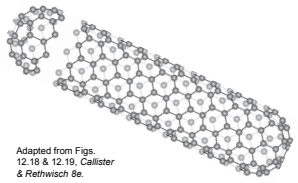
Adapted from Fig. 12.17, *Callister & Rethwisch 8e.*

– weak van der Waal's forces between layers
– planes slide easily over one another -- good lubricant

Polymorphic Forms of Carbon (cont) Fullerenes and Nanotubes

- _____ – spherical cluster of 60 carbon atoms, C_{60}
  – Like a soccer ball
- Carbon _____ – sheet of graphite rolled into a tube
  – Ends capped with fullerene _____

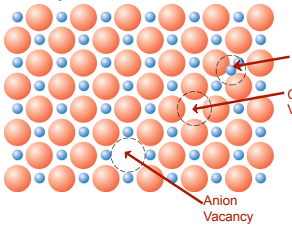




Adapted from Figs. 12.18 & 12.19, *Callister & Rethwisch 8e.*

Point Defects in Ceramics (i)

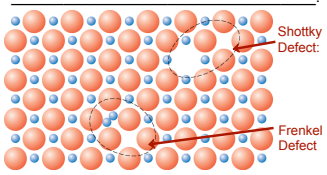
- Vacancies
  -- vacancies exist in _____ for both _____
- Interstitials
  -- interstitials exist for _____
  -- interstitials are not normally observed for _____ are large relative to the interstitial sites



Adapted from Fig. 12.20, *Callister & Rethwisch 8e.* (Fig. 12.20 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.)

Point Defects in Ceramics (ii)

- Frenkel Defect
  -- _____.
- Shottky Defect
  -- _____.

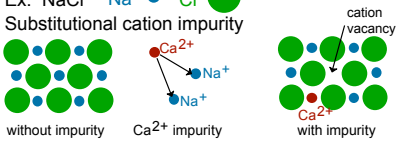


Adapted from Fig.12.21, *Callister & Rethwisch 8e.* (Fig. 12.21 is from W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, John Wiley and Sons, Inc., p. 78.)

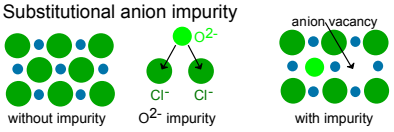
- Equilibrium concentration of defects $\propto e^{-Q_D/kT}$

Imperfections in Ceramics

- _____ (charge _____) must be maintained when impurities are present
- Ex: NaCl Na^+ Cl^-
- Substitutional cation impurity

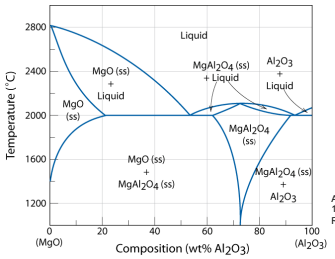


- Substitutional anion impurity



Ceramic Phase Diagrams

MgO-Al_2O_3 diagram:



Adapted from Fig. 12.25, Callister & Rethwisch 8e.

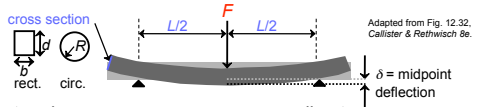
Mechanical Properties

_____ materials are more brittle than _____.
Why is this so?

- Consider _____
  - In crystalline, by _____ motion
  - In highly ionic solids, dislocation motion is difficult
    - few _____
    - resistance to motion of ions of like charge (e.g., anions) past one another

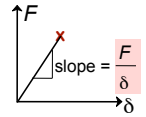
Flexural Tests – Measurement of Elastic Modulus

- Room *T* behavior is usually _____, with _____ failure.
- _____ often used.
  -- tensile tests are difficult for _____ materials.



Adapted from Fig. 12.32, *Callister & Rethwisch 8e.*

- Determine _____ according to:



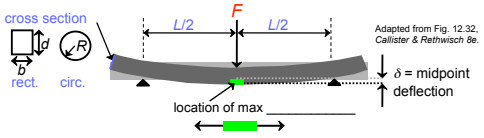
linear-elastic behavior

$$E = \frac{F}{\delta}\frac{L^3}{4bd^3}$$ (rect. cross section)

$$E = \frac{F}{\delta}\frac{L^3}{12\pi R^4}$$ (circ. cross section)

Flexural Tests – Measurement of _____ Strength

- _____ test to measure room-*T* flexural strength.



Adapted from Fig. 12.32, *Callister & Rethwisch 8e.*

- _____ strength:

$$\sigma_{fs} = \frac{3F_f L}{2bd^2}$$ (rect. _____)

$$\sigma_{fs} = \frac{F_f L}{\pi R^3}$$ (circ. _____)

- Typical values:

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

Data from Table 12.5, *Callister & Rethwisch 8e.*

SUMMARY

- Interatomic bonding in ceramics is ionic and/or covalent.
- Ceramic crystal structures are based on:
  -- maintaining charge neutrality
  -- cation-anion radii ratios.
- Imperfections
  -- Atomic point: vacancy, interstitial (cation), Frenkel, Schottky
  -- Impurities: substitutional, interstitial
  -- Maintenance of charge neutrality
- Room-temperature mechanical behavior – flexural tests
  -- linear-elastic; measurement of elastic modulus
  -- brittle fracture; measurement of flexural modulus