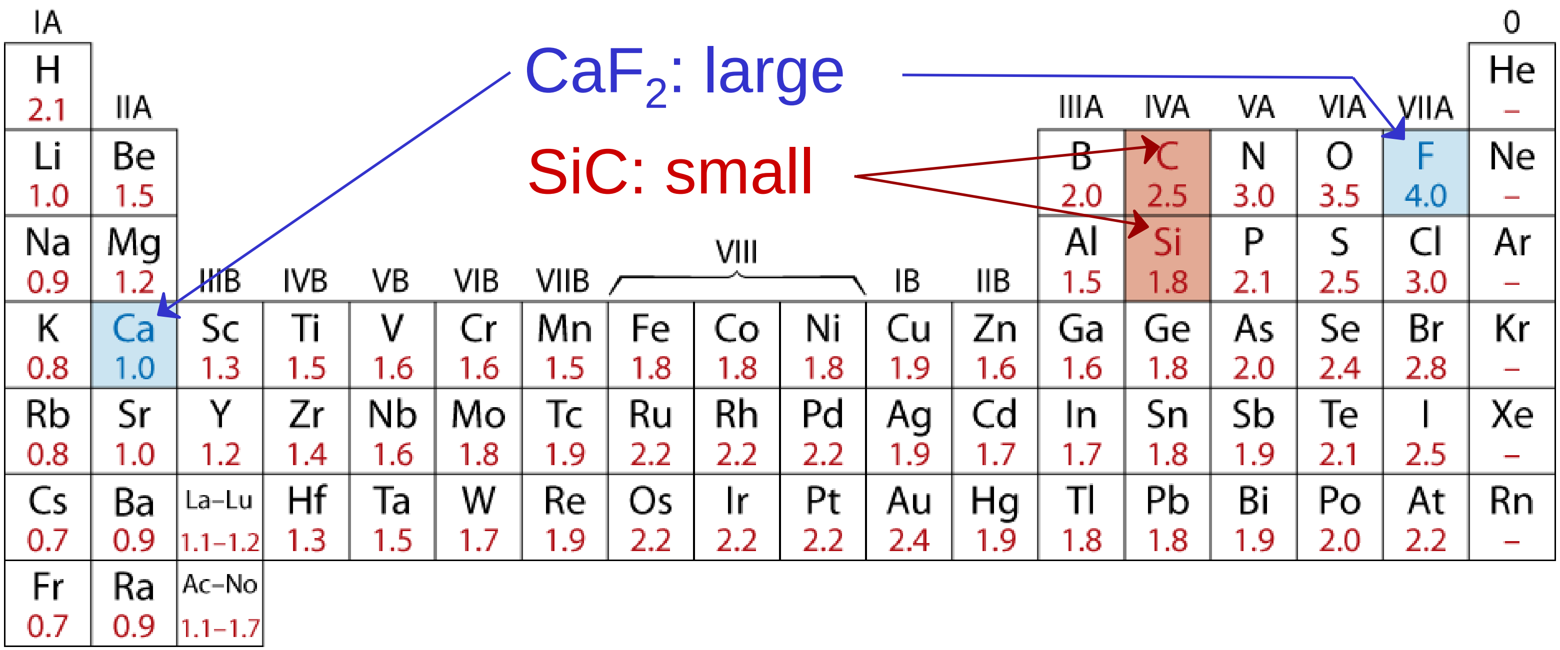
Chapter 12: Structures & Properties of Ceramics

ISSUES TO ADDRESS...

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

Atomic Bonding in Ceramics

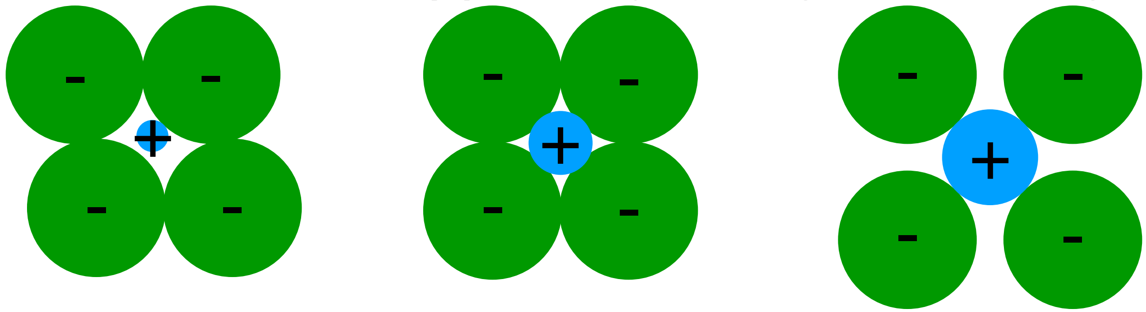
- Bonding:
  - -- Can be ionic and/or covalent in character.
  - -- % ionic character increases with difference in electronegativity of atoms.
- Degree of ionic character may be large or small:



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.)

Factors that Determine Crystal Structure

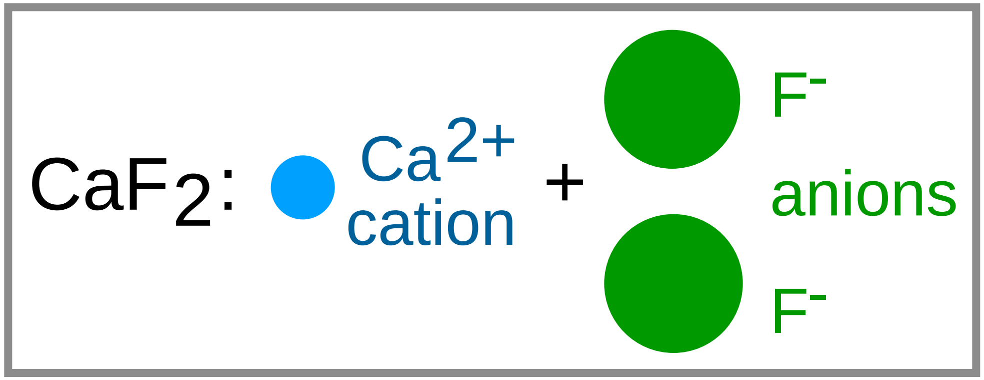
1. Relative sizes of ions – Formation of stable structures:
   --maximize the # of oppositely charged ion neighbors.



unstable | stable | stable

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

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



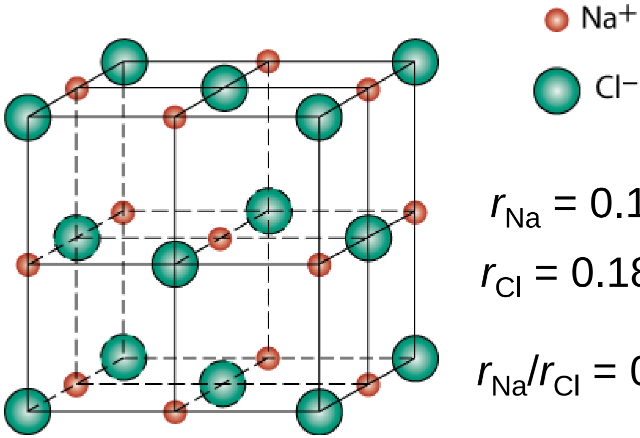
$A_m X_p$

m, p values to achieve charge neutrality

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

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

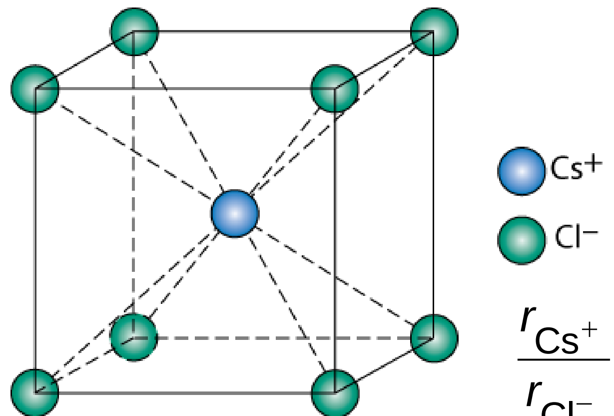
∴ cations (Na^+) prefer octahedral sites

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

AX Crystal Structures

AX–Type Crystal Structures include CsCl, and zinc blende

Cesium Chloride structure:



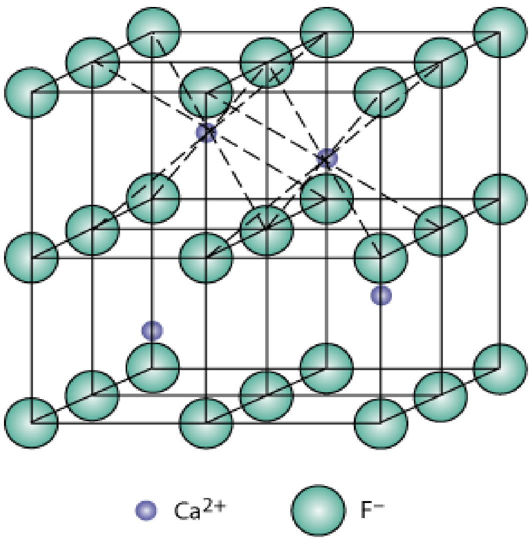
$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{0.170}{0.181} = 0.939$$

∴ Since 0.732 < 0.939 < 1.0, cubic sites preferred

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

AX_2 Crystal Structures

Fluorite structure



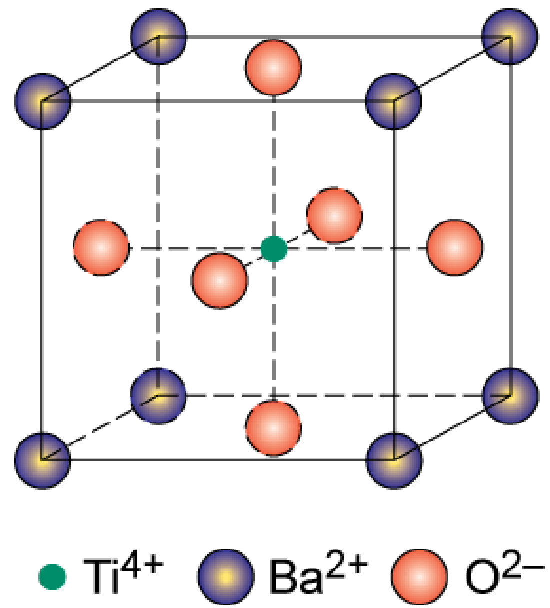
- Calcium Fluorite (CaF_2)
- Cations in cubic sites
- UO_2, ThO_2, ZrO_2, CeO_2

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

ABX_3 Crystal Structures

- Perovskite structure

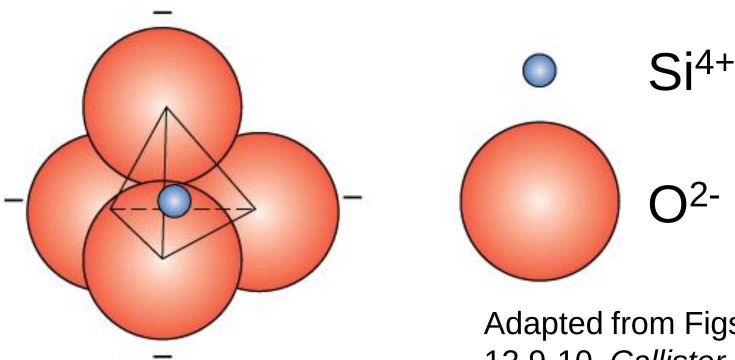
Ex: complex oxide $BaTiO_3$



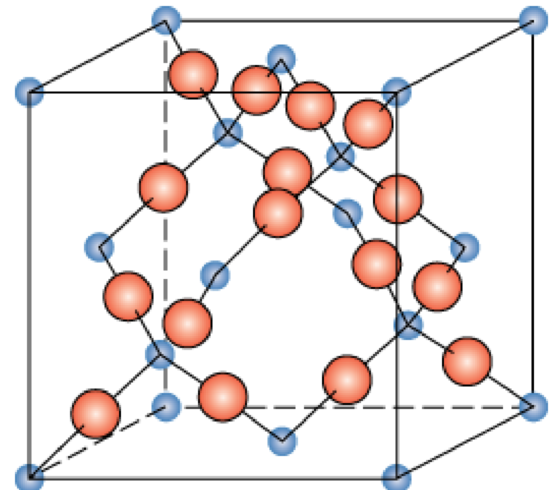
Adapted from Fig. 12.6,
Callister & Rethwisch 8e.

Silicate Ceramics

Most common elements on earth are Si & O



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



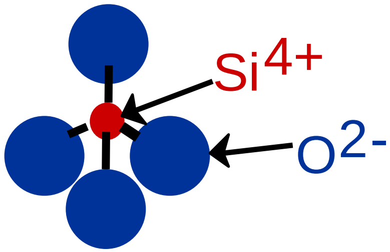
crystobalite

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

Glass Structure

- Basic Unit:

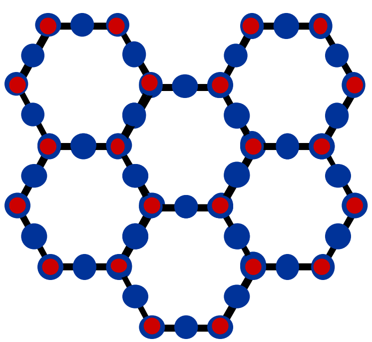
$Si0_4^{4-}$ tetrahedron

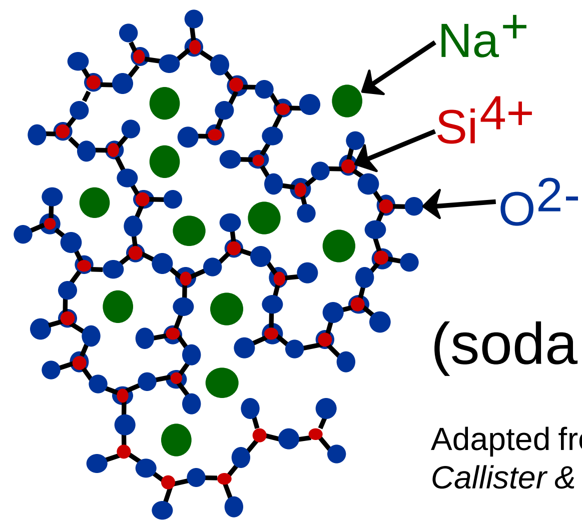


Glass is noncrystalline (amorphous)

- 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:





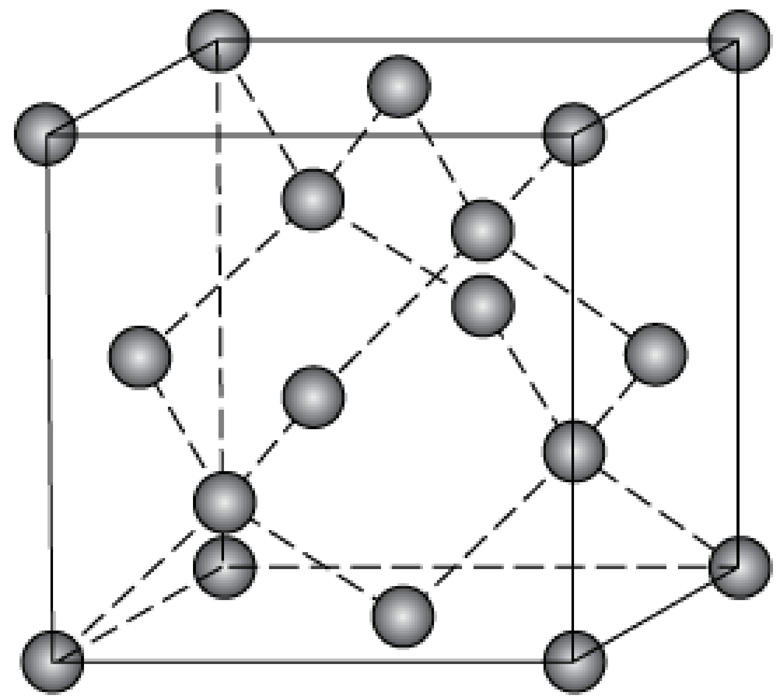
(soda glass)

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

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.

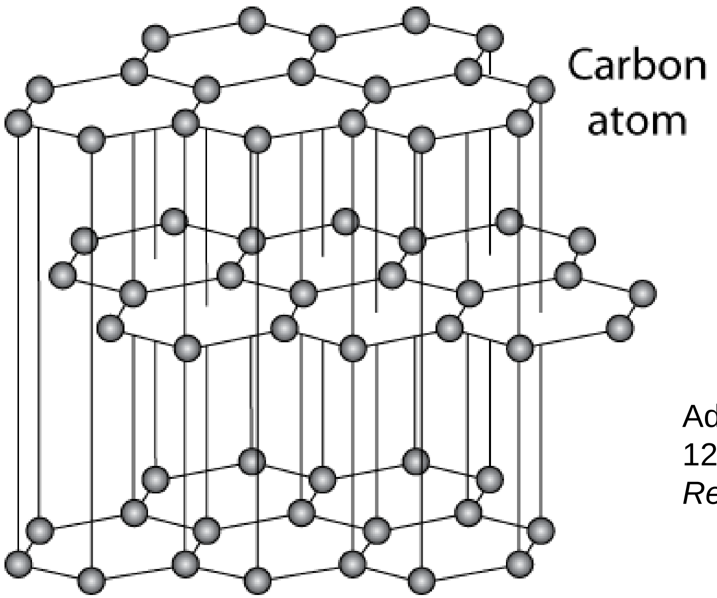


Adapted from Fig. 12.15, *Callister & Rethwisch 8e.*

Polymorphic Forms of Carbon (cont)

Graphite

– layered structure – parallel hexagonal arrays of carbon atoms



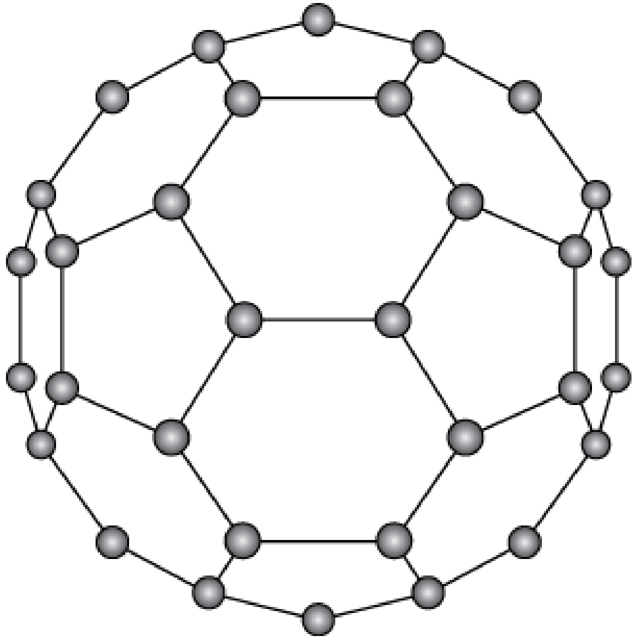
Adapted from Fig. 12.17, *Callister & Rethwisch 8e.*

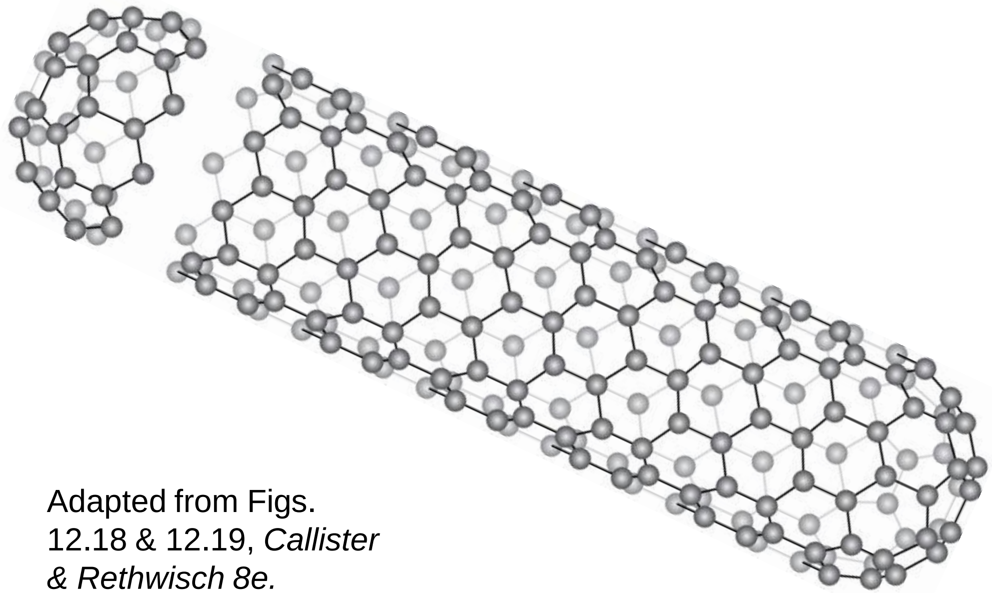
– weak van der Waal's forces between layers

– planes slide easily over one another -- good lubricant

Polymorphic Forms of Carbon (cont) Fullerenes and Nanotubes

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

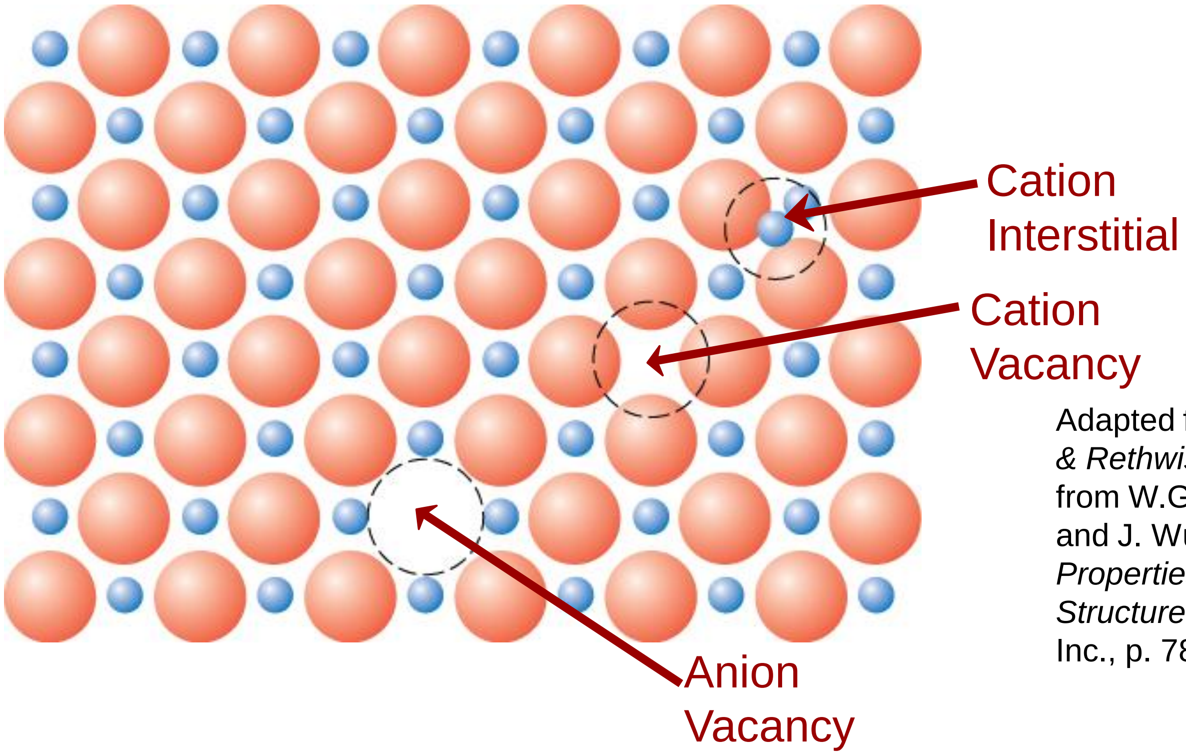




Adapted from Figs. 12.18 & 12.19, *Callister & Rethwisch 8e.*

Point Defects in Ceramics (i)

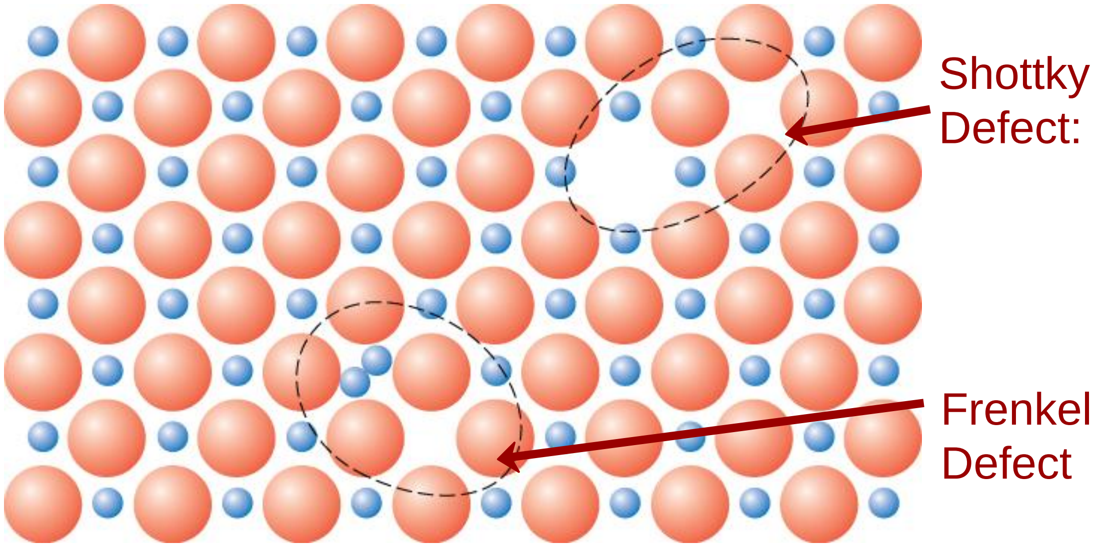
- Vacancies
  -- vacancies exist in ceramics for both cations and anions
- Interstitials
  -- interstitials exist for cations
  -- interstitials are not normally observed for anions because anions are large relative to the interstitial sites



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
  -- a cation vacancy-cation interstitial pair.
- Shottky Defect
  -- a paired set of cation and anion vacancies.

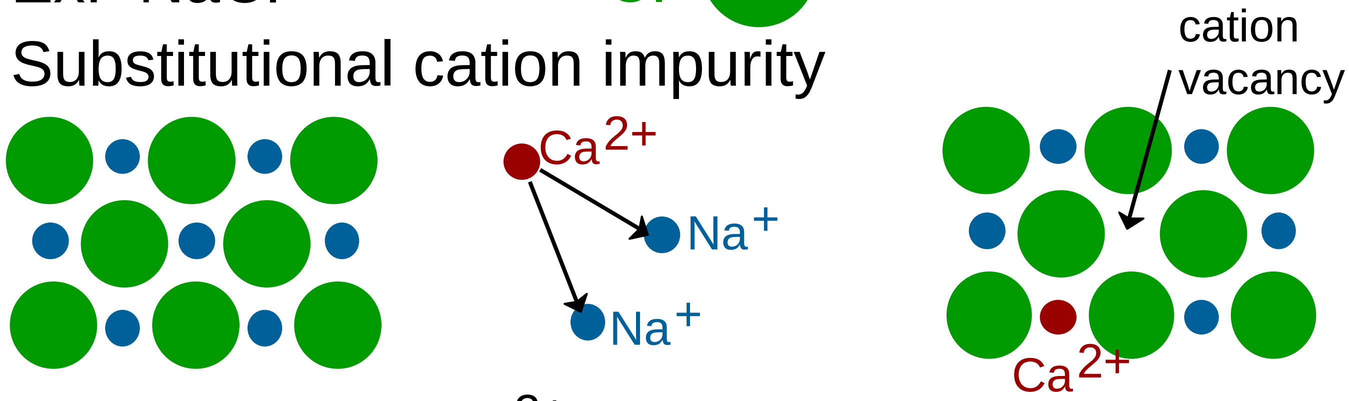


Adapted from Fig.12.21, *Callister & Rethwisch 8e.* (Fig. 12.21 is from W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, John Wiley and Sons, Inc., p. 78.)

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

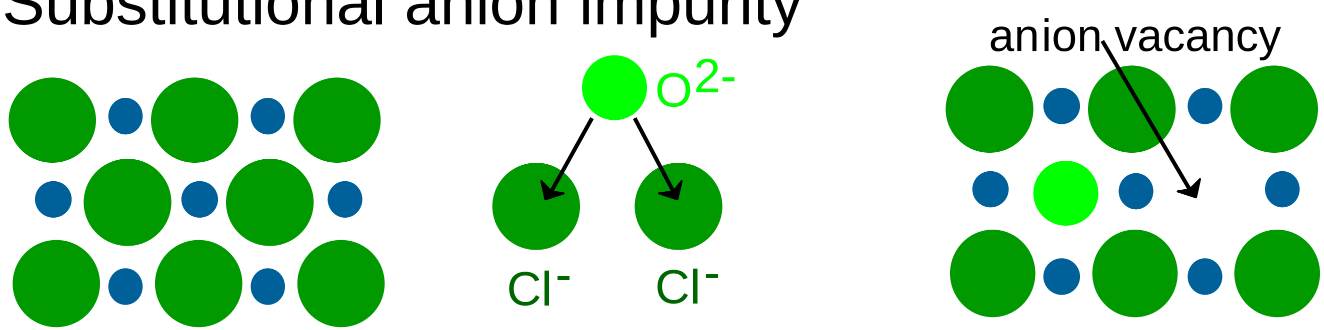
Imperfections in Ceramics

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



without impurity | Ca^{2+} impurity | with impurity

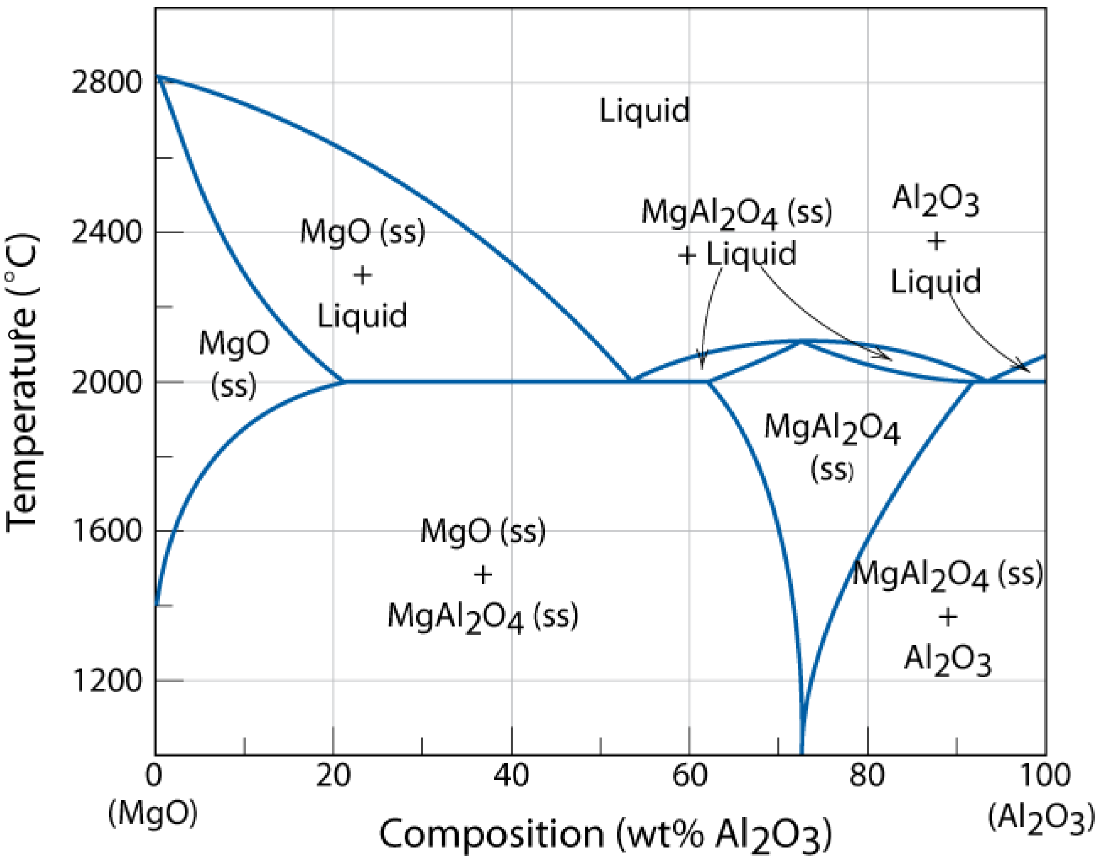
- Substitutional anion impurity



without impurity | O^{2-} impurity | with impurity

Ceramic Phase Diagrams

MgO-Al_2O_3 diagram:



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

Mechanical Properties

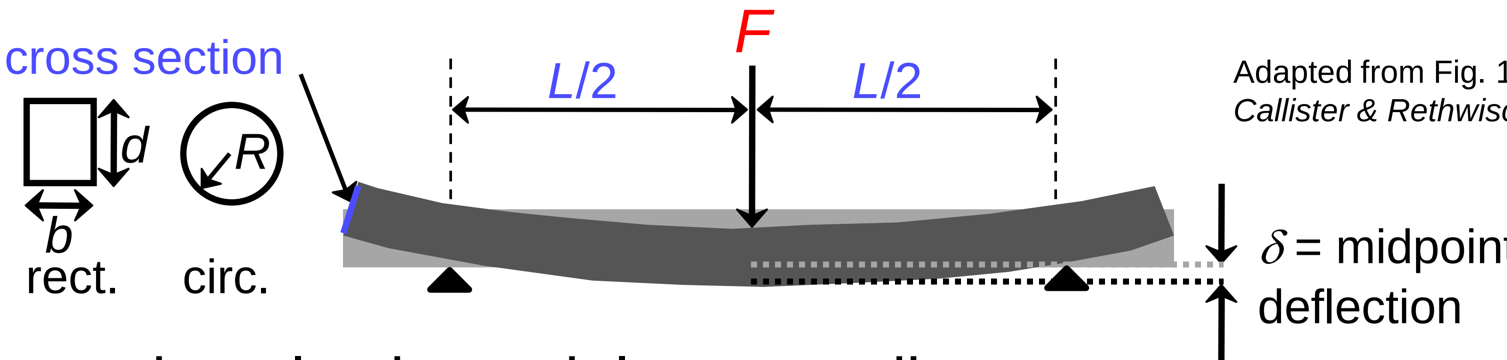
Ceramic materials are more brittle than metals.

Why is this so?

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

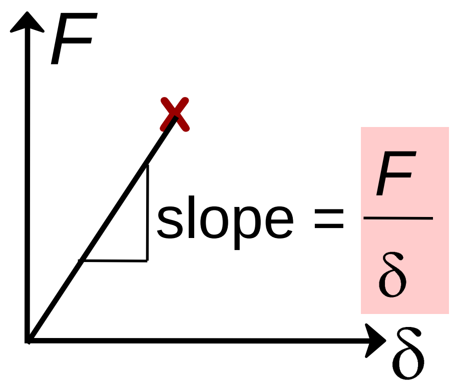
Flexural Tests – Measurement of Elastic Modulus

- Room *T* behavior is usually elastic, with brittle failure.
- 3-Point Bend Testing often used.
  -- tensile tests are difficult for brittle materials.



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

- Determine elastic modulus according to:



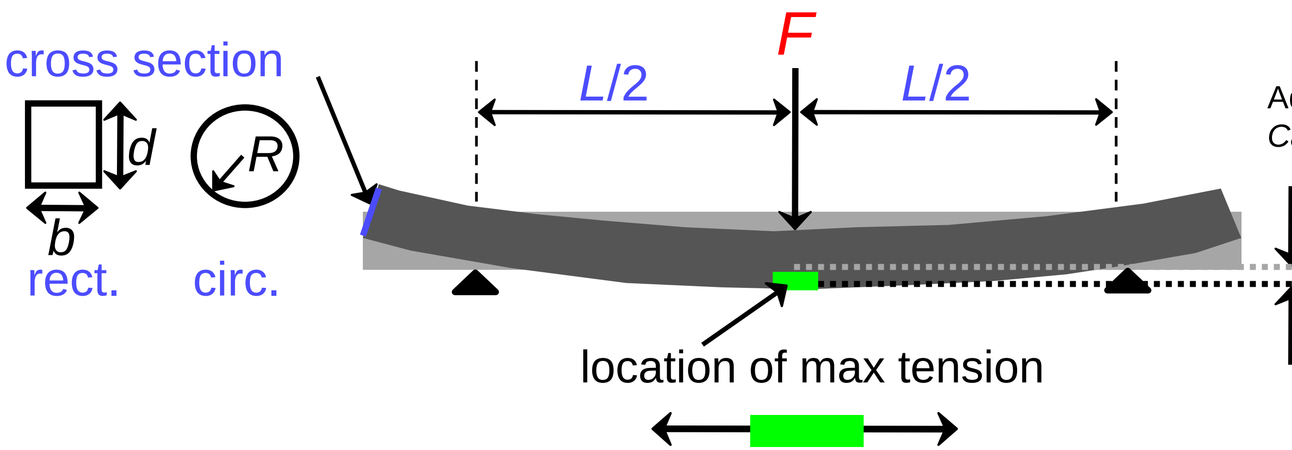
linear-elastic behavior

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

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

Flexural Tests – Measurement of Flexural Strength

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



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

- Flexural strength:

$$\sigma_{fs} = \frac{3F_f L}{2bd^2} \quad \text{(rect. cross section)}$$

$$\sigma_{fs} = \frac{F_f L}{\pi R^3} \quad \text{(circ. cross section)}$$

- 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