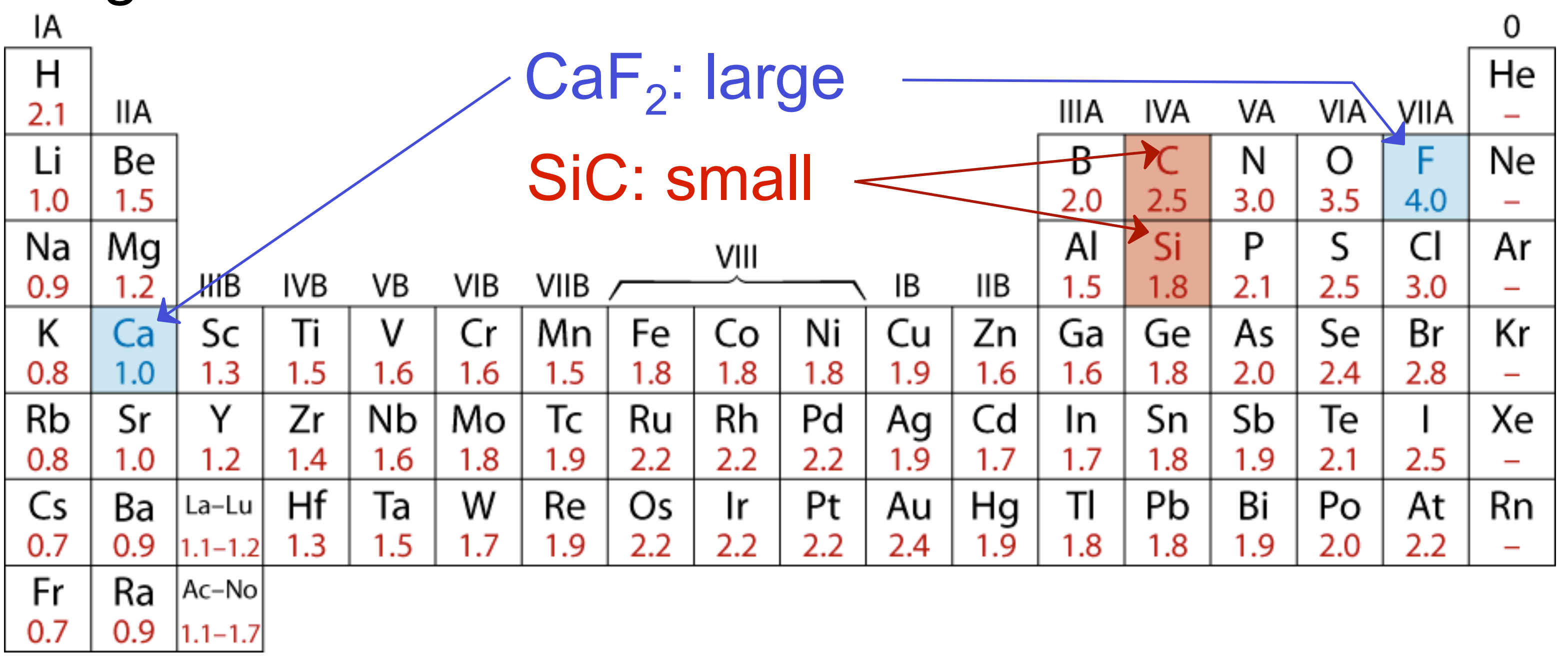
Chapter 12: Structures & Properties of Ceramics

Review: 12.1-12.4
Read: 12.6-12.7 and 12.11
Study: 12.8-12.10

- 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?

Bonding in ceramics

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

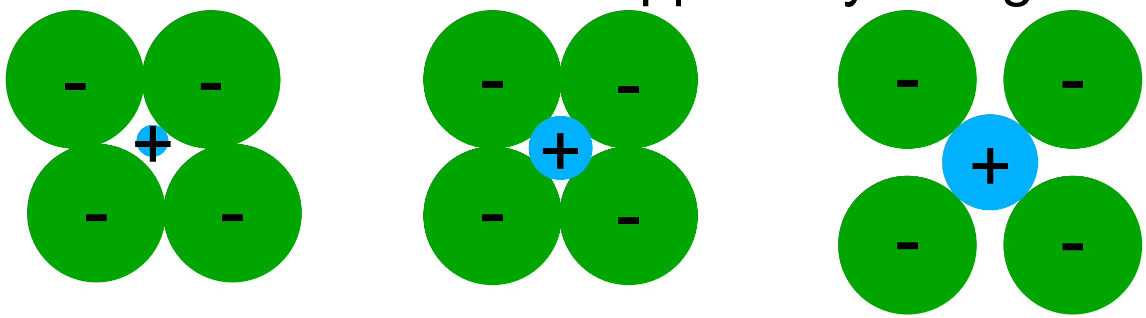


Adapted from Fig. 2.7, *Callister 7e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

Ionic Bonding & Structure

1. Size - Stable structures:

--maximize the # of nearest oppositely charged neighbors.

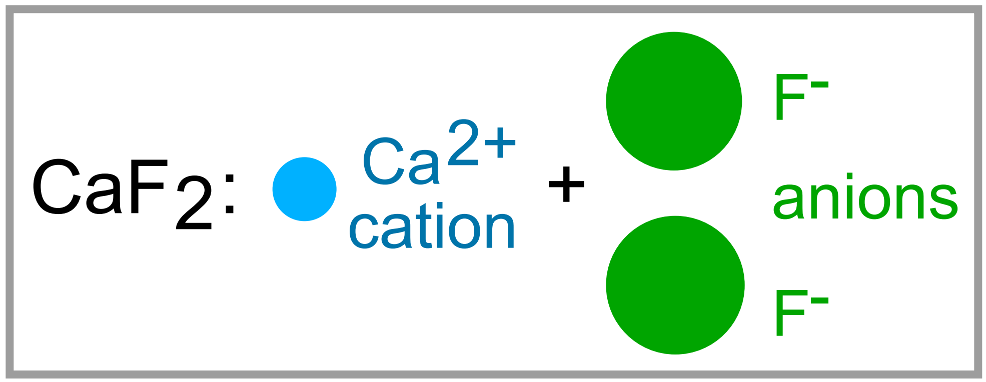


unstable stable stable

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

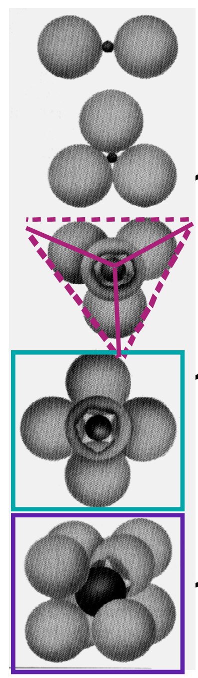
Coordination # and Ionic Radii

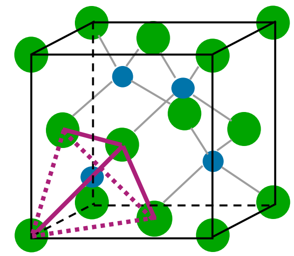
- Coordination # increases with $\frac{r_{cation}}{r_{anion}}$

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

$\frac{r_{cation}}{r_{anion}}$	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

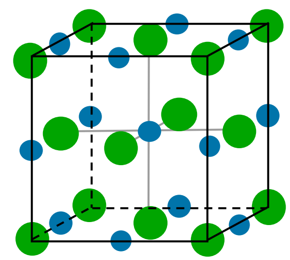
Adapted from Table 12.2, *Callister 7e.*





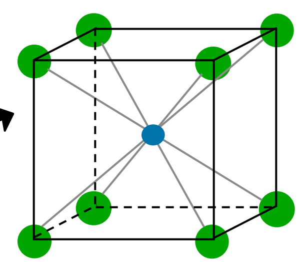
ZnS (zincblende)

Adapted from Fig. 12.4, *Callister 7e.*



NaCl (sodium chloride)

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



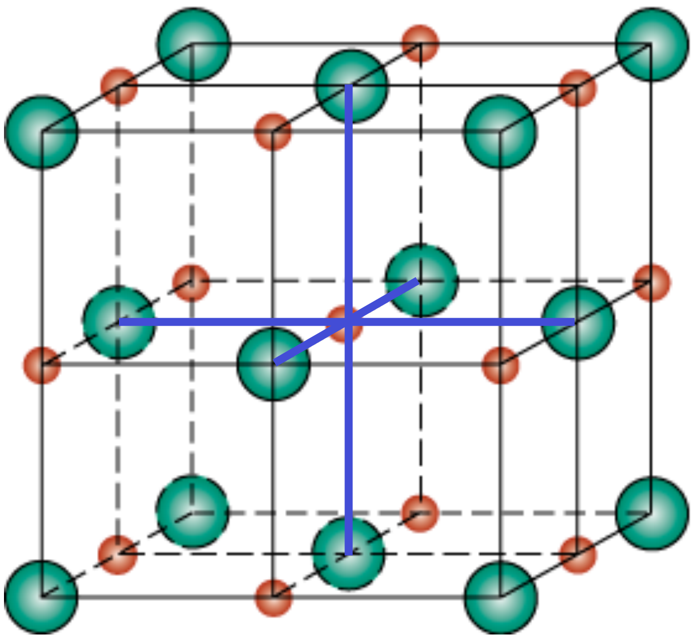
CsCl (cesium chloride)

Adapted from Fig. 12.3, *Callister 7e.*

Rock Salt Structure

Same concepts can be applied to ionic solids in general.

Example: NaCl (rock salt) structure



Na^+ $r_{Na} = 0.102$ nm

Cl^- $r_{Cl} = 0.181$ nm

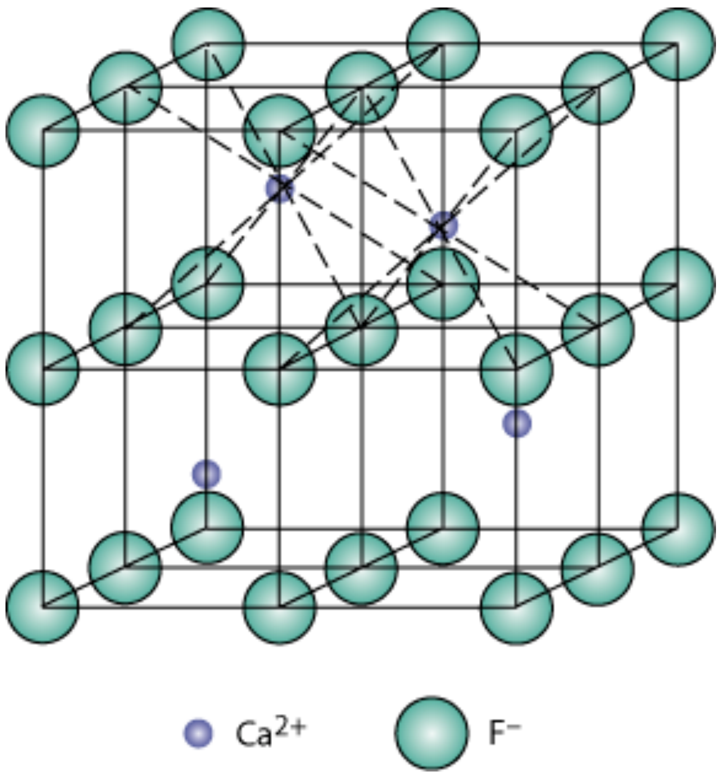
$r_{Na}/r_{Cl} = 0.564$

$\therefore$ cations prefer O_H sites

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

AX_2 Crystal Structures

Fluorite structure



- Calcium Fluorite (CaF_2)
- cations in cubic sites

- UO_2, ThO_2, ZrO_2, CeO_2

- antifluorite structure – cations and anions reversed

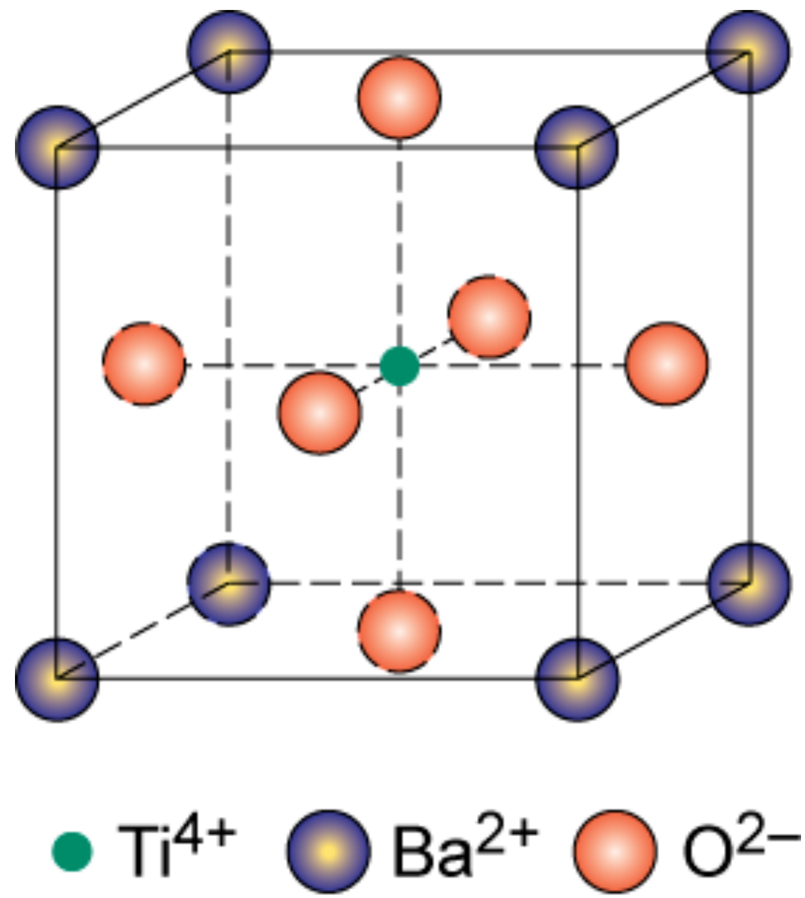
Adapted from Fig. 12.5, *Callister 7e.*

ABX_3 Crystal Structures

- Perovskite

Ex: complex oxide

$BaTiO_3$



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

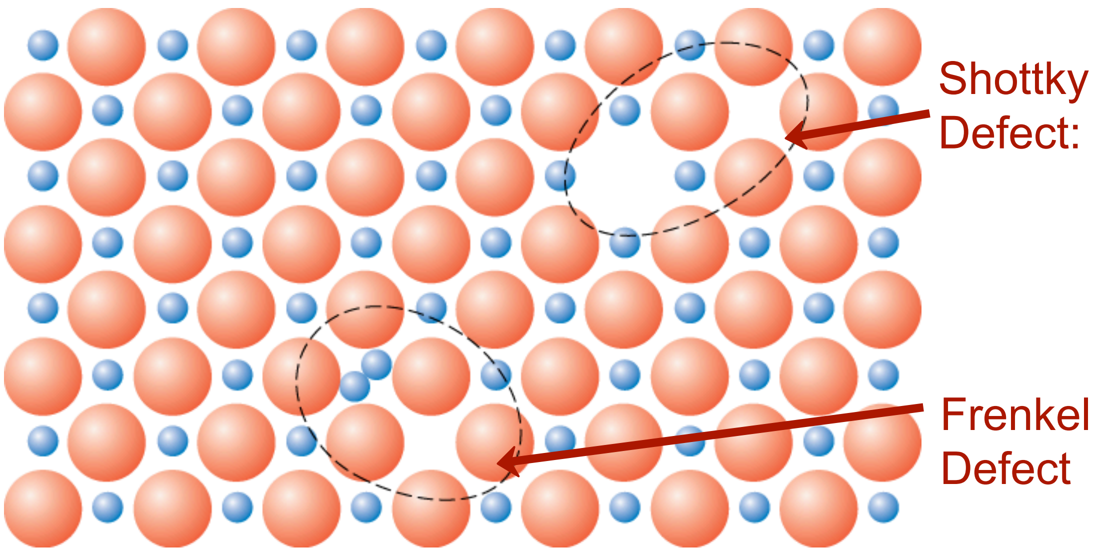
Defects in Ceramic Structures

- Frenkel Defect

  --a cation is out of place.

- Shottky Defect

  --a paired set of cation and anion vacancies.

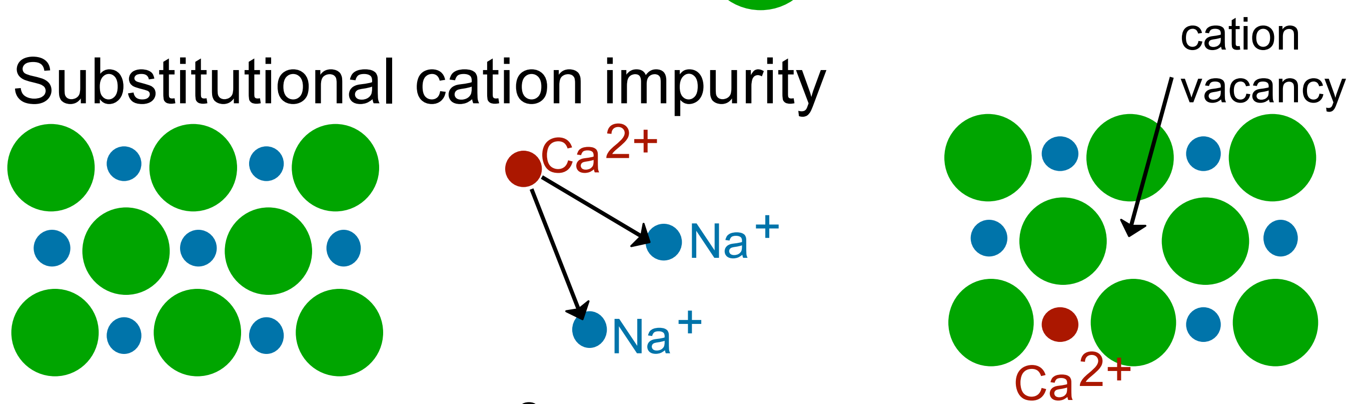


Adapted from Fig. 12.21, *Callister 7e.* (Fig. 12.21 is from W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, John Wiley and Sons, Inc., p. 78.)

- Equilibrium concentration of defects $\sim e^{-Q_D/2kT}$

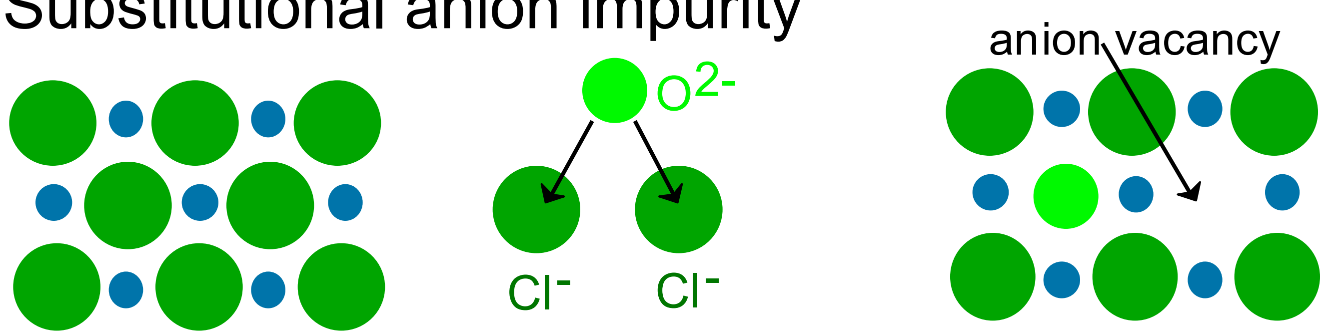
Impurities

- Impurities must also satisfy charge balance = Electroneutrality
- Ex: NaCl Na^{+} Cl^{-}
- Substitutional cation impurity



initial geometry Ca^{2+} impurity resulting geometry

- Substitutional anion impurity



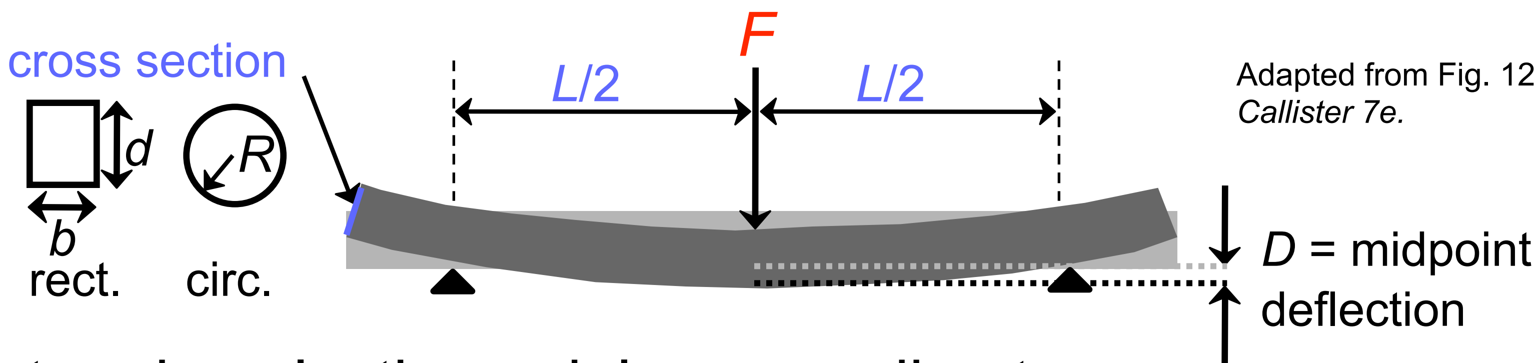
initial geometry O^{2-} impurity resulting geometry

Stress-strain behavior

- **Flectural testing replaces tensile testing**
- **Reasons not to perform a standard tension test**
  - difficult to prepare and test specimens having a required geometry
  - difficult to grip brittle materials without fracturing them
  - ceramics fail after only about 0.1% strain and samples are difficult to align without experiencing bending stress

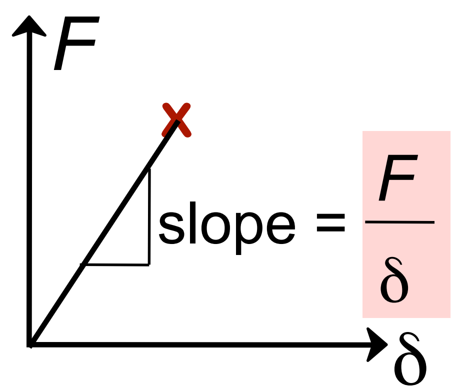
Measuring Elastic Modulus

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



Adapted from Fig. 12.32, *Callister 7e.*

- Determine elastic modulus according to:



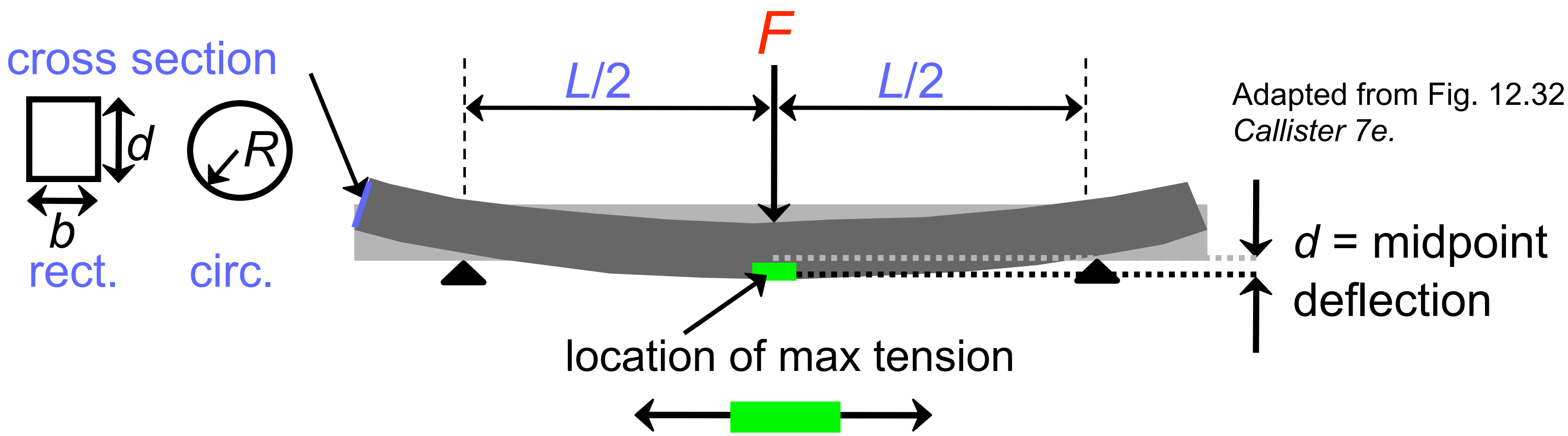
linear-elastic behavior

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

rect. cross section | circ. cross section

Measuring Strength

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

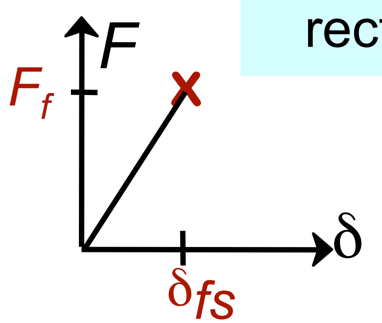


Adapted from Fig. 12.32, *Callister 7e.*

- Flexural strength:

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

rect.



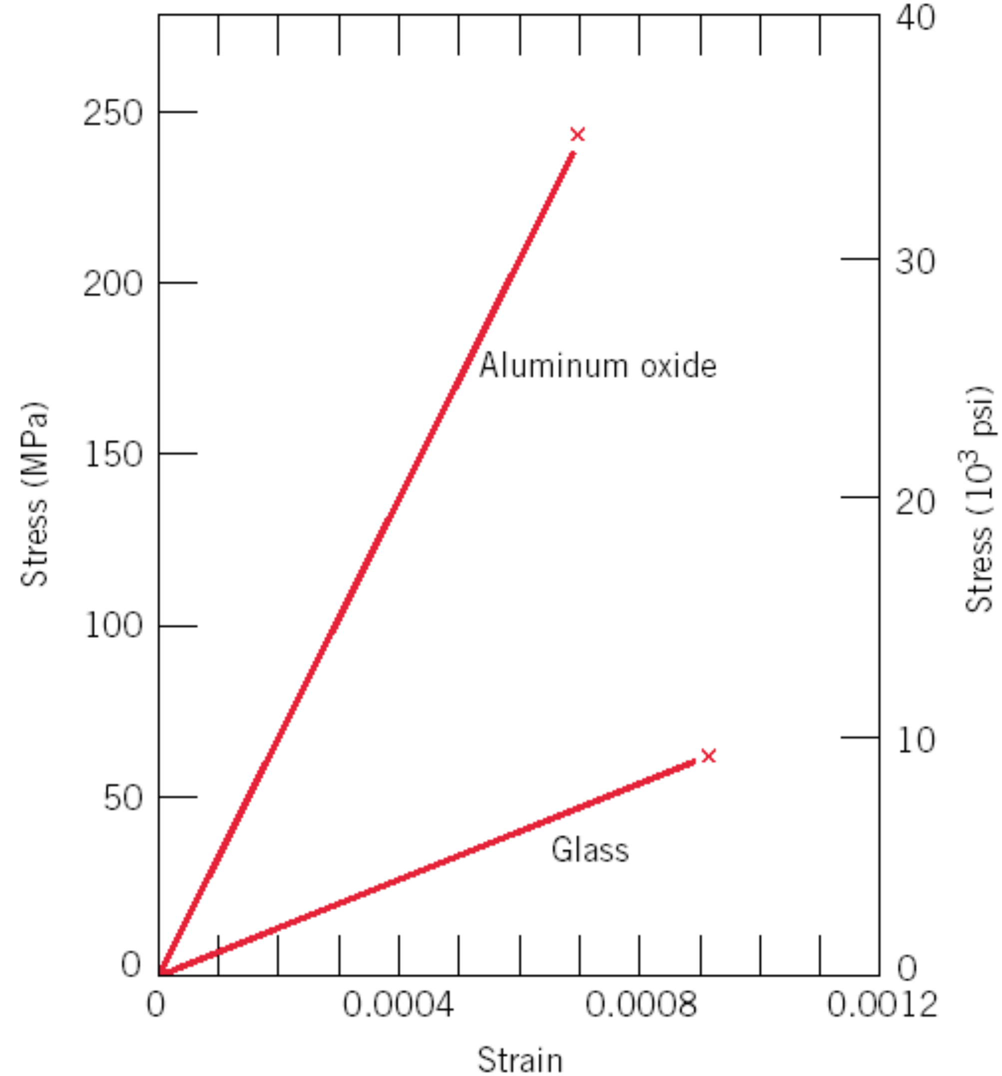
- Typ. values:

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.*

Elastic behavior

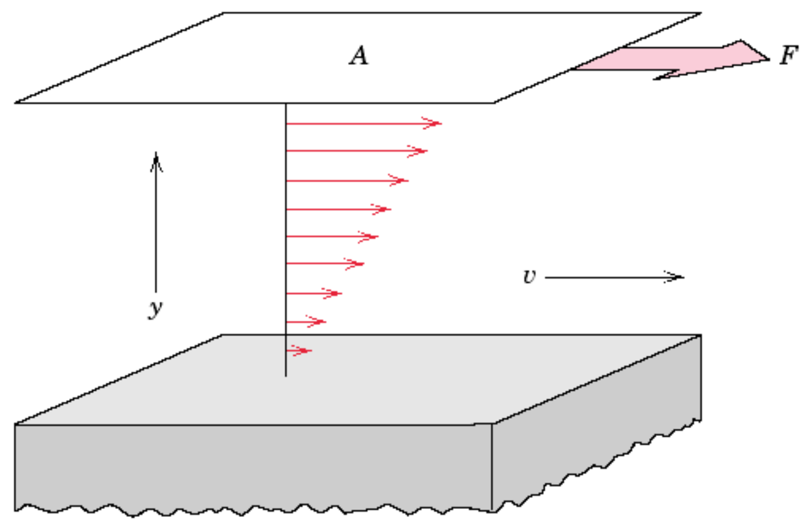
- **Typical stress-strain behavior to fracture for aluminum oxide and glass**



Mechanisms of plastic deformation

- **Crystalline ceramics are brittle**
  - Covalent bonds are relatively strong
  - There are limited numbers of slip systems
  - Dislocation structures are complex

- **Noncrystalline ceramics**
  - Plastic deformation does not occur by dislocation motion for noncrystalline ceramics
  - Viscosity is a measure of of non-crystalline material's resistance to deformation



Hardness

Table 13.6 Approximate Knoop Hardness (100 g load) for Seven Ceramic Materials

Material	*Approximate Knoop Hardness*
Diamond (carbon)	7000
Boron carbide (B_4C)	2800
Silicon carbide (SiC)	2500
Tungsten carbide (WC)	2100
Aluminum oxide (Al_2O_3)	2100
Quartz (SiO_2)	800
Glass	550

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.