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:

CaF_2: large

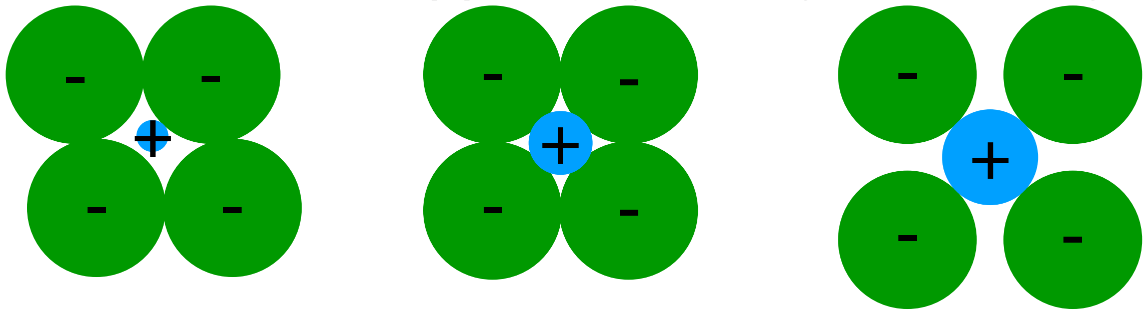
SiC: small

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	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															

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.)

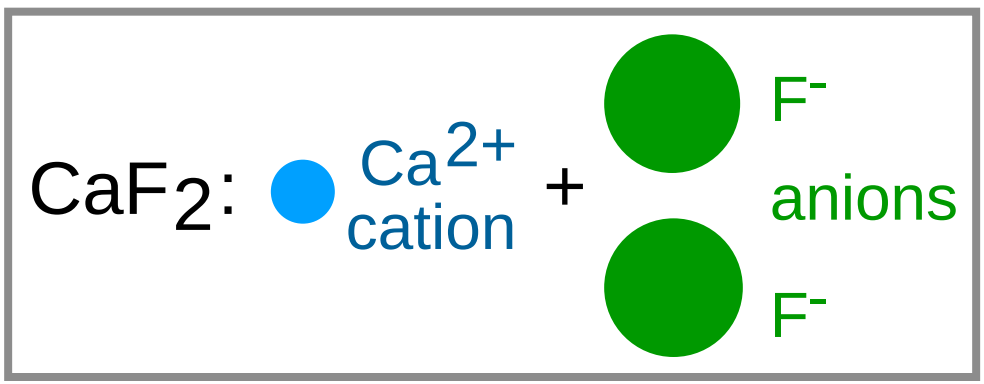
Factors that Determine Crystal Structure

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



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

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

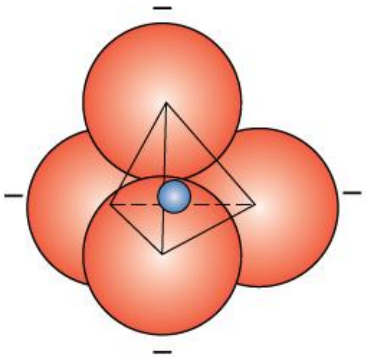


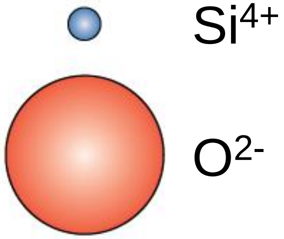
$A_m X_p$

m, p values to achieve charge neutrality

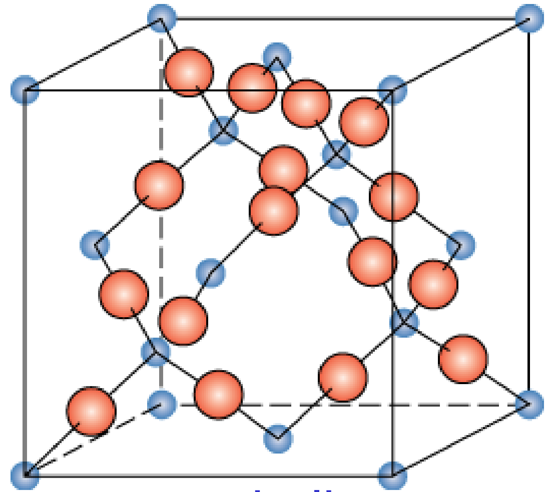
Silicate Ceramics

Most common elements on earth are Si & O





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



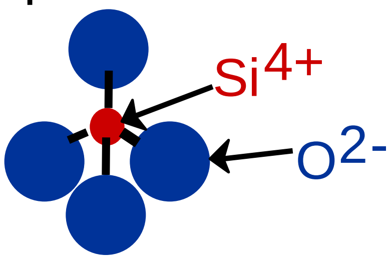
crystobalite

- 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:

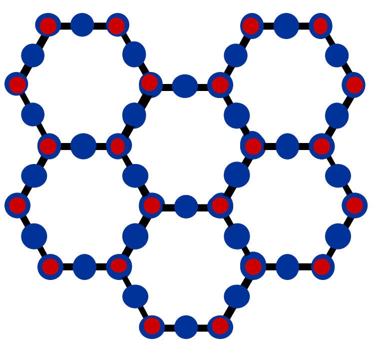
SiO_4^{4-} tetrahedron

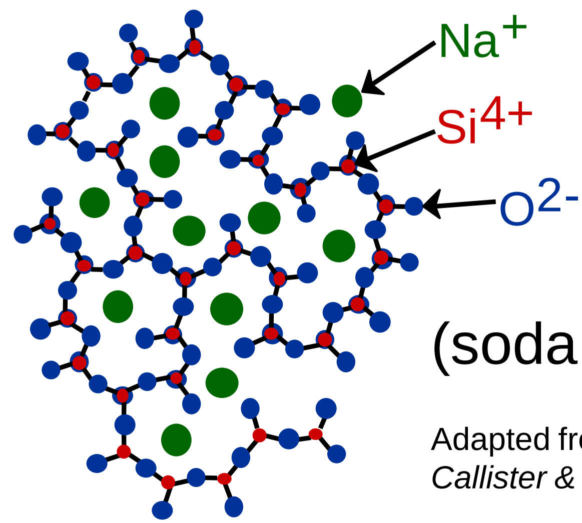


Glass is noncrystalline (amorphous)

- 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:





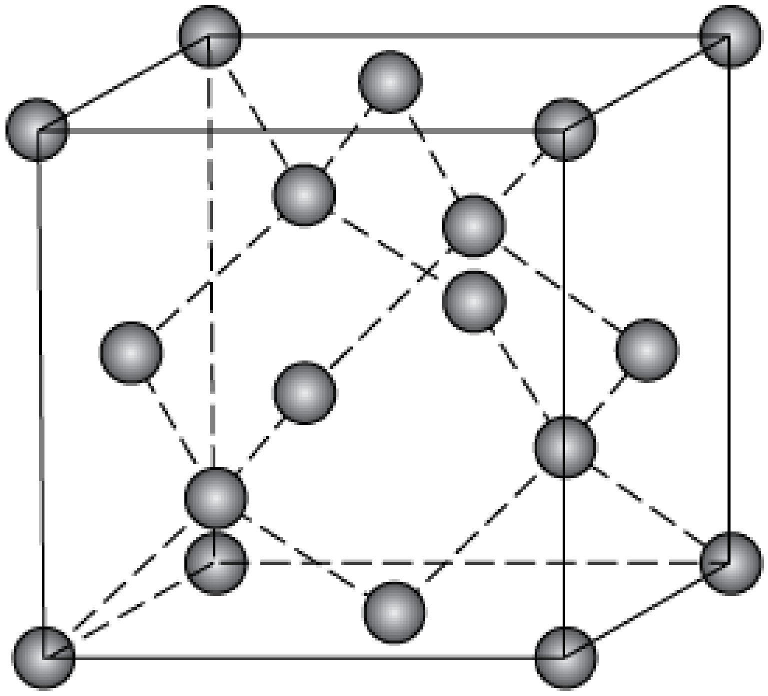
(soda glass)

Adapted from Fig. 12.11, *Callister & Rethwisch 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.

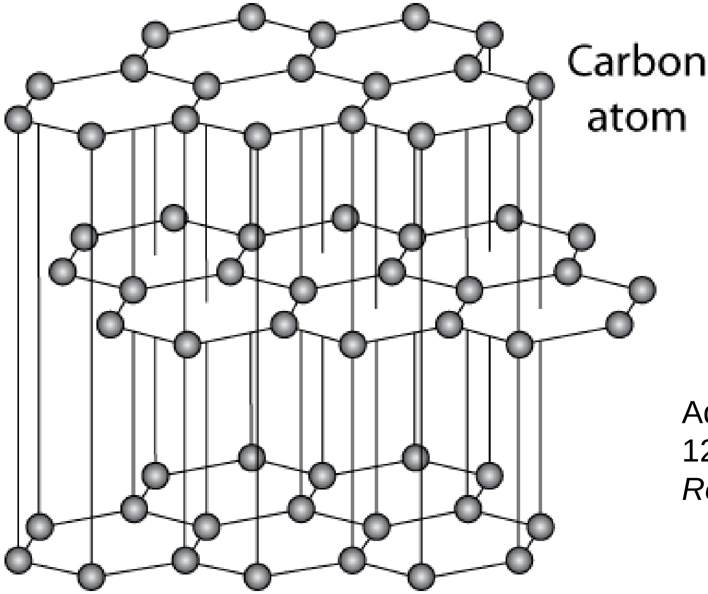


Adapted from Fig. 12.15, *Callister & Rethwisch 8e.*

Polymorphic Forms of Carbon (cont)

Graphite

– layered structure – parallel hexagonal arrays of carbon atoms



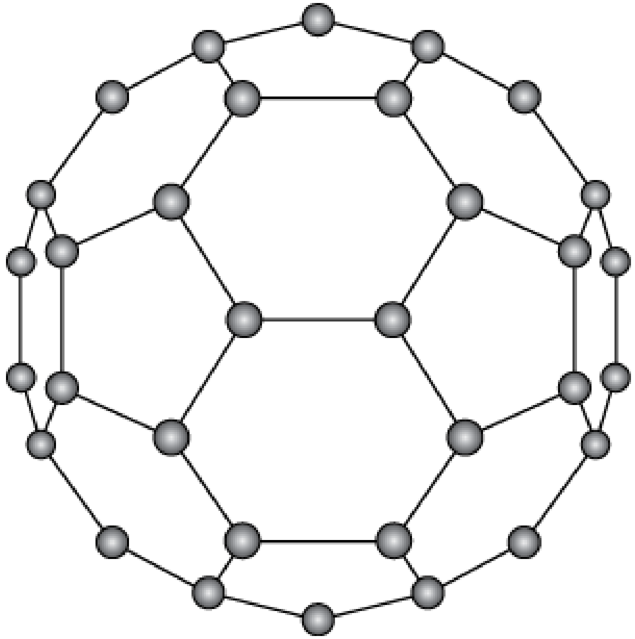
Adapted from Fig. 12.17, *Callister & Rethwisch 8e.*

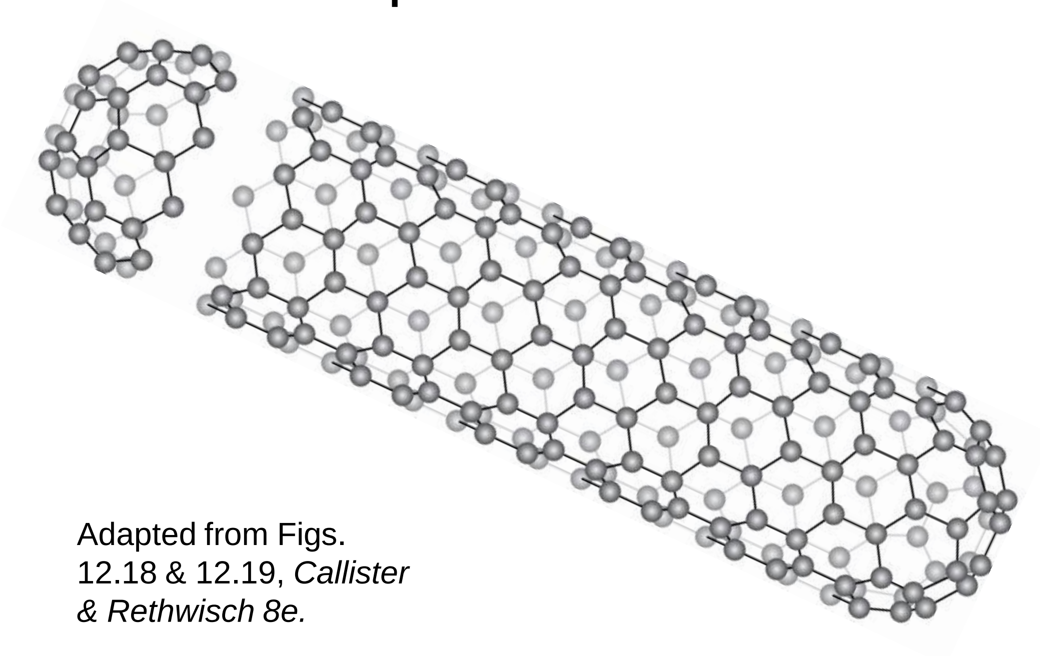
– weak van der Waal's forces between layers

– 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

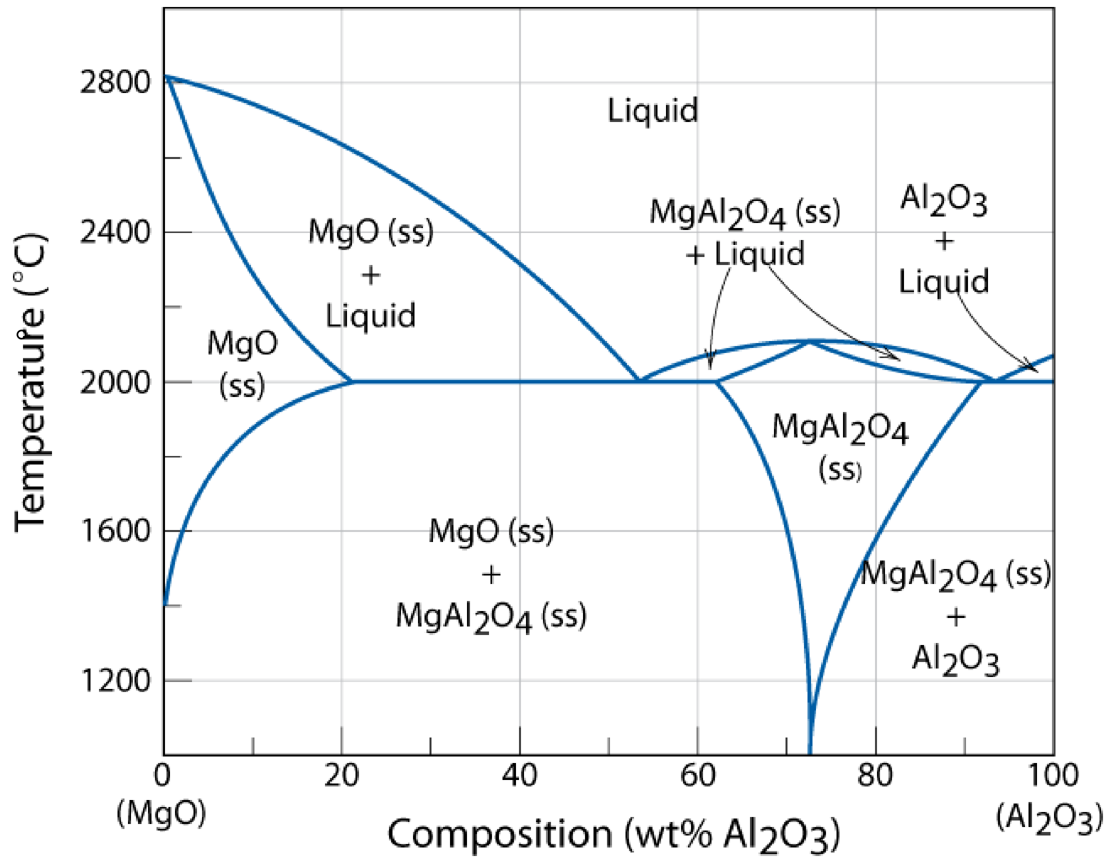




Adapted from Figs. 12.18 & 12.19, *Callister & Rethwisch 8e.*

Ceramic Phase Diagrams

$MgO-Al_2O_3$ diagram:



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

Mechanical Properties

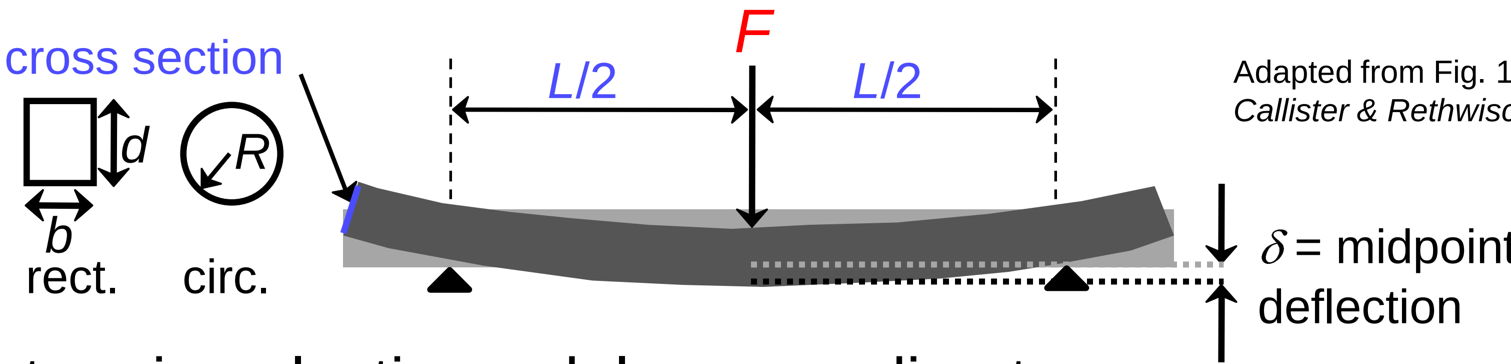
Ceramic materials are more brittle than metals.

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

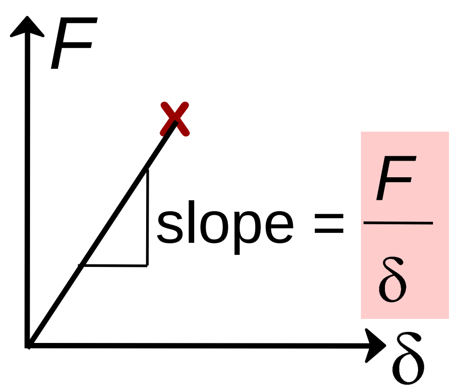
Flexural Tests – Measurement of Elastic Modulus

- 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:



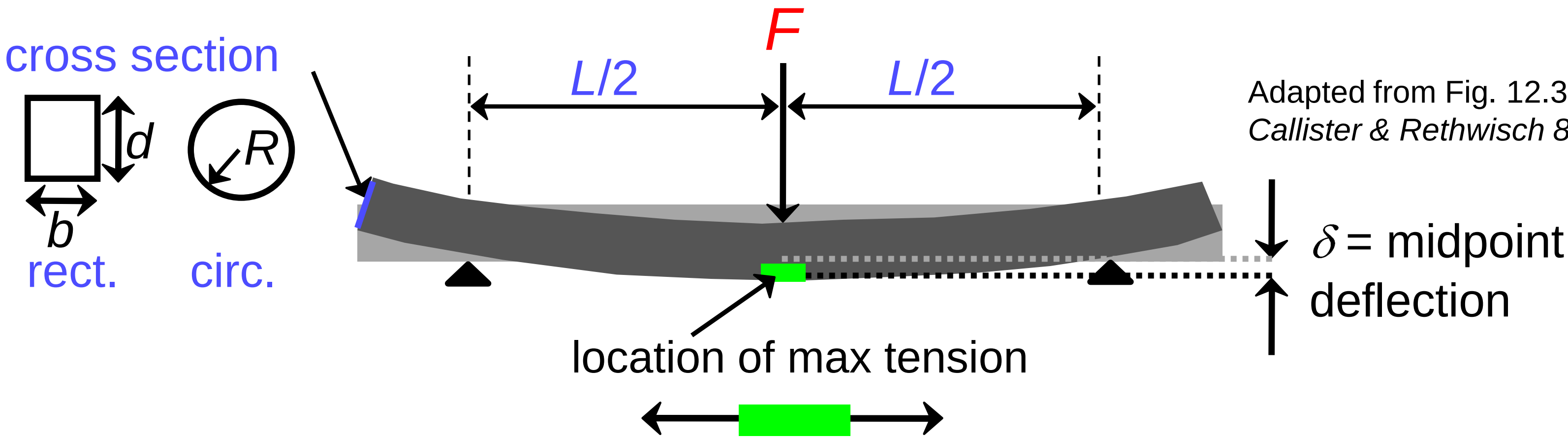
linear-elastic behavior

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

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

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