Chapter 12: Structures & Properties of Ceramics

ISSUES TO ADDRESS...

- Review of structures for ceramics
- How are impurities accommodated in the ceramic lattice?
- In what ways are ceramic phase diagrams similar to phase diagrams for metals?
- How are the mechanical properties of ceramics measured, and how do they differ from those for metals?

Class Exercise

Given the unit cell structure on the right, please determine the followings

- Number of Si atoms in a unit cell

4

- Number of C atoms in a unit cell

4

- Chemical formula for this compound?

SiC

- Coordination number for Si atoms?

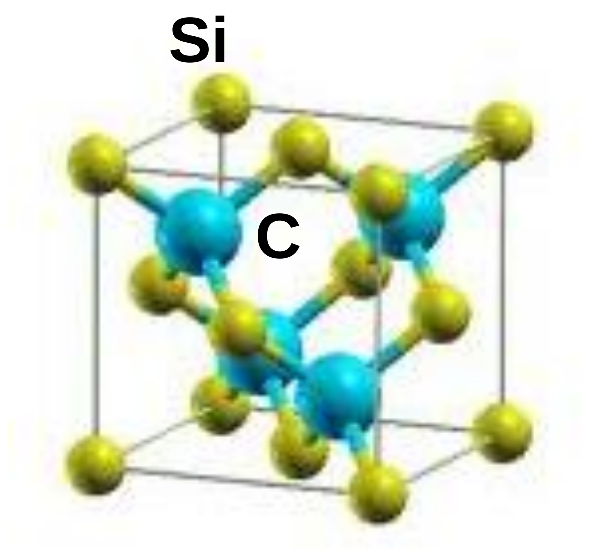
4

- Coordination number for C atoms?

4

- What is the predominating bond nature?

Covalent



http://www.theochem.unito.it/crystal_tuto/mssc2008_cd/tutorials/cphf/cphf.html

Class Exercise

Given the unit cell structure on the right, please determine the followings

- Number of Mg atoms in a unit cell

3

- Number of B atoms in a unit cell

6

- Chemical formula for this compound?

MgB2

- Is the position of Mg and B geometrically equivalent?

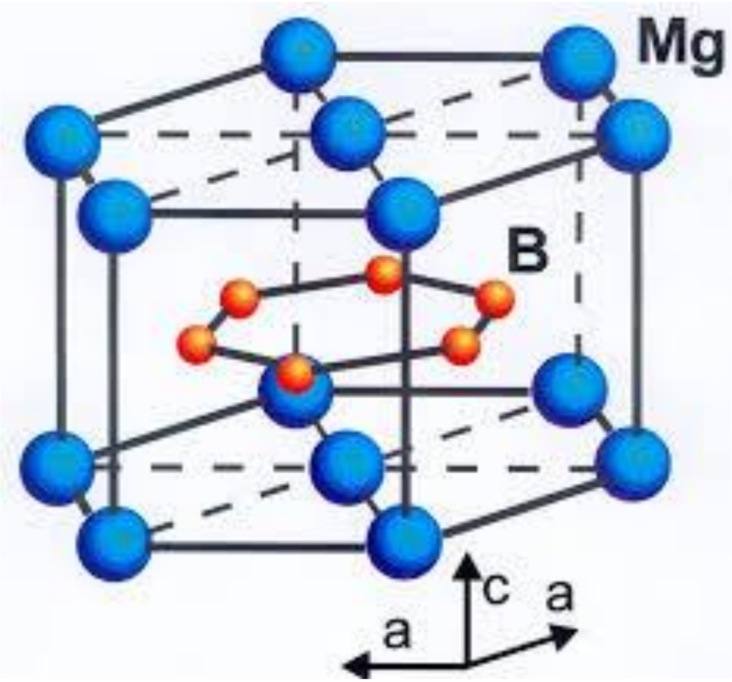
NO

- Coordination number for Mg atoms?

12

- Coordination number for B atoms?

6



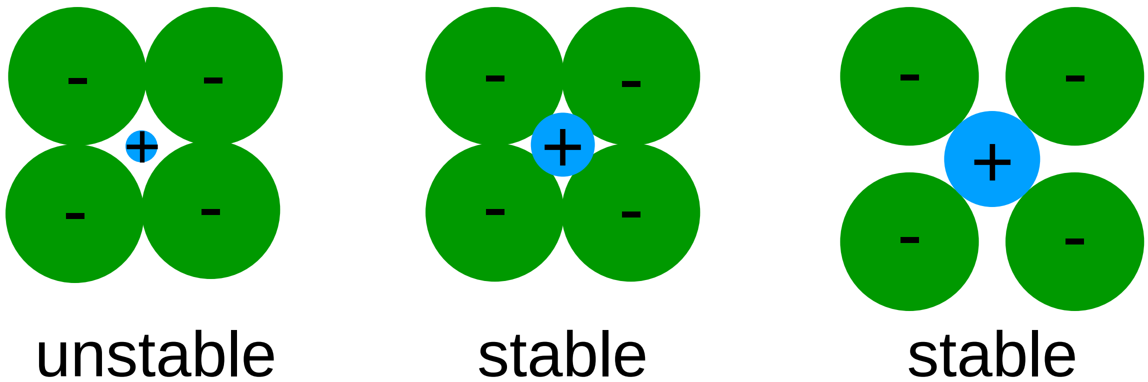
http://physics.aalto.fi/groups/nanospin/facilities/pulsed-laser-deposition/

Factors that Determine Crystal Structure

1. Maximize the # of oppositely charged ion neighbors (or CN)

- CN depends on **relative sizes of ions:**

--.

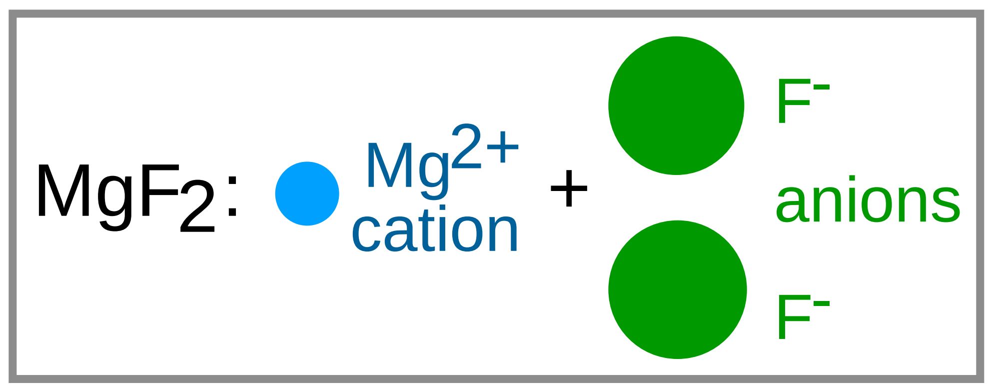


Adapted from Fig. 12.1, *Callister & Rethwisch 8e.*

2. Maintenance of **charge neutrality** :

--Net charge in a ceramics should be zero.

--Reflected in chemical formula:



$A_m X_p$

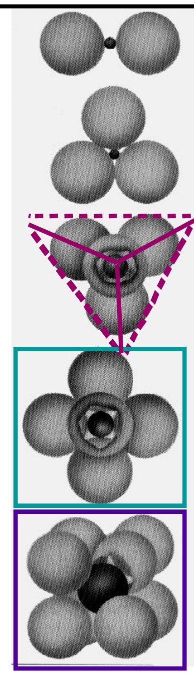
m, p values to achieve charge neutrality

Coordination # and Ionic Radii Ratio

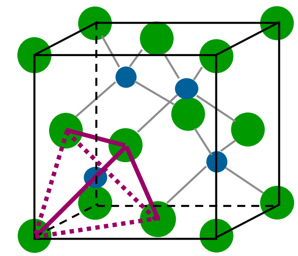
- Coordination # (CN) for cation increases with size ratio of $\frac{r_{cation}}{r_{anion}}$

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

$\frac{r_{cation}}{r_{anion}}$	CN	
< 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
> 1.0	12	

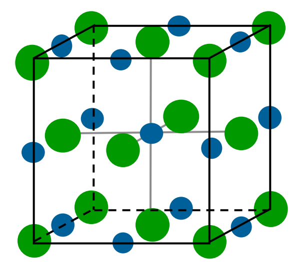


Adapted from Table 12.2, *Callister & Rethwisch 8e.*



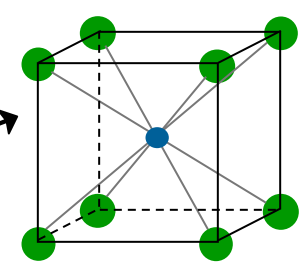
e.g.: ZnS (zinc blende)

Adapted from Fig. 12.4, *Callister & Rethwisch 8e.*



e.g.: NaCl (sodium chloride)

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

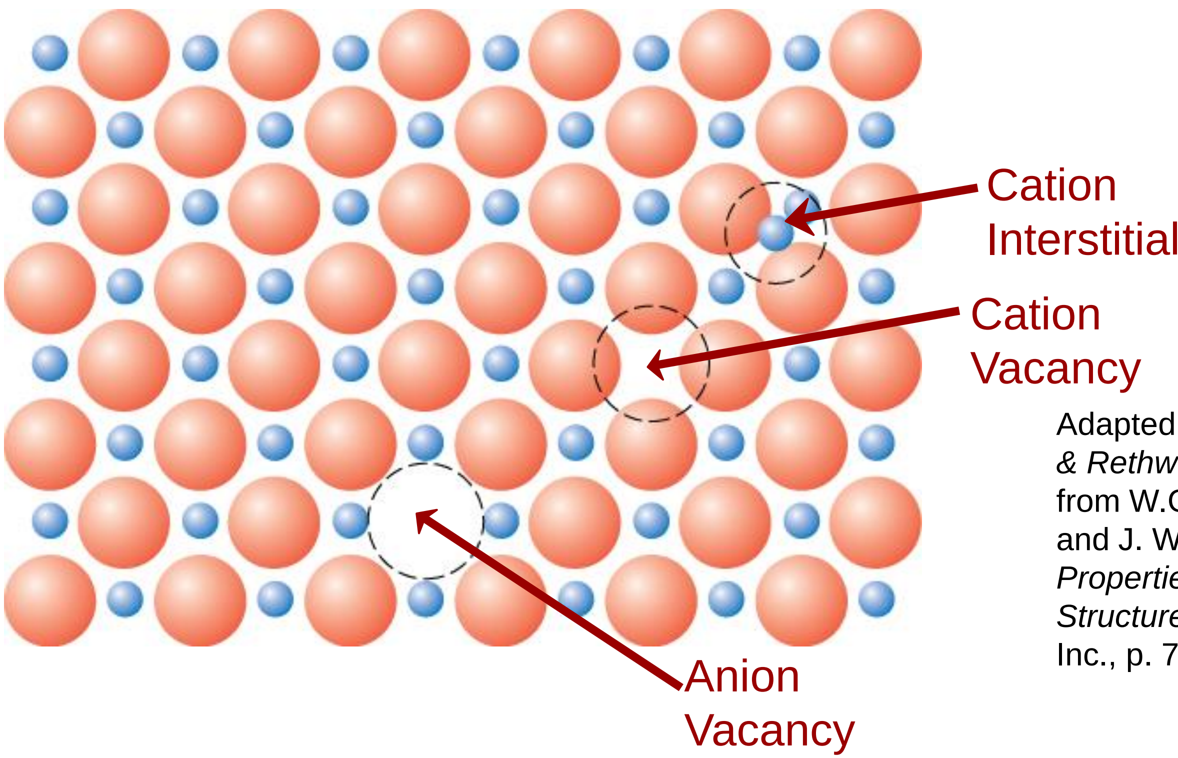


e.g.: CsCl (cesium chloride)

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

Vacancy & Interstitials in Ceramics (i)

- Vacancies
  -- vacancies exist in ceramics for both cations and anions
- Interstitials
  -- interstitials exist for cations
  -- interstitials are normally NOT observed for anions because anions are usually too large to fit in 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.)

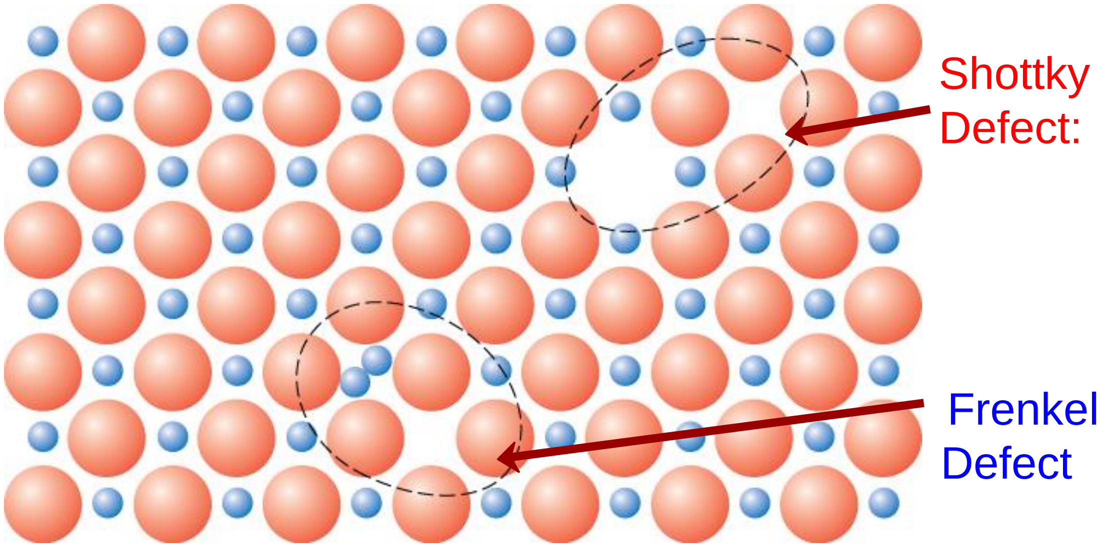
Vacancy & Interstitials in Ceramics (ii)

- Frenkel Defect

  -- a cation vacancy-cation interstitial pair.

- Shottky Defect

  -- a paired set of cation and anion vacancies.

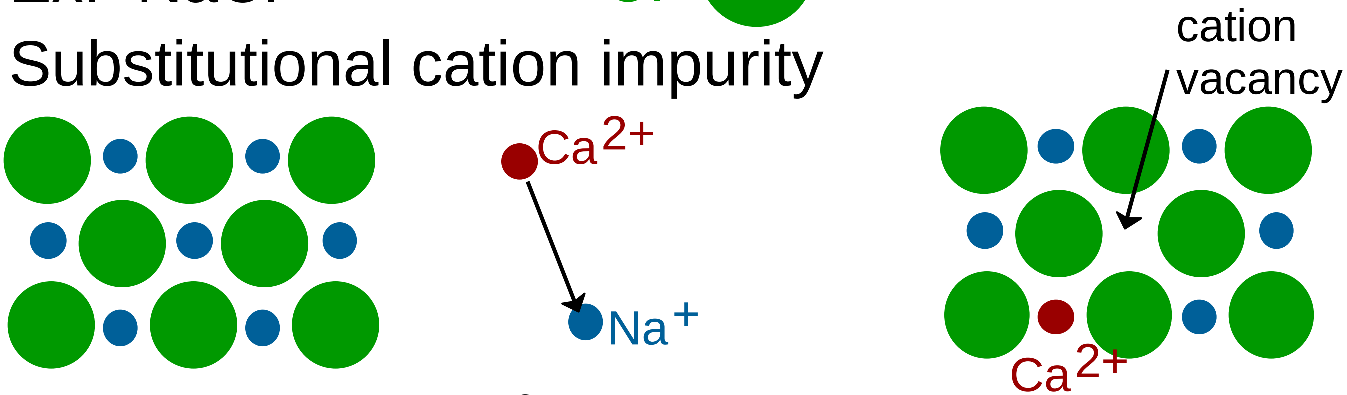


Adapted from Fig.12.21, *Callister & Rethwisch 8e.* (Fig. 12.21 is from W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, John Wiley and Sons, Inc., p. 78.)

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

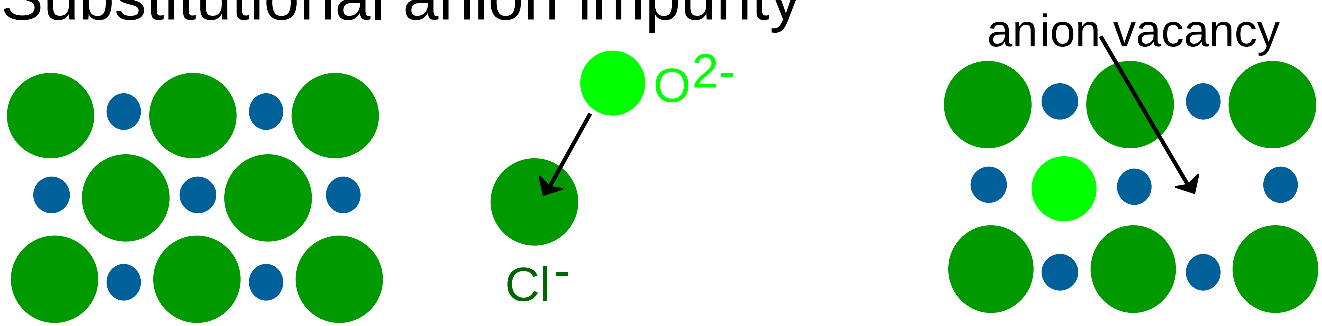
Substitution Atoms in Ceramics

- 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

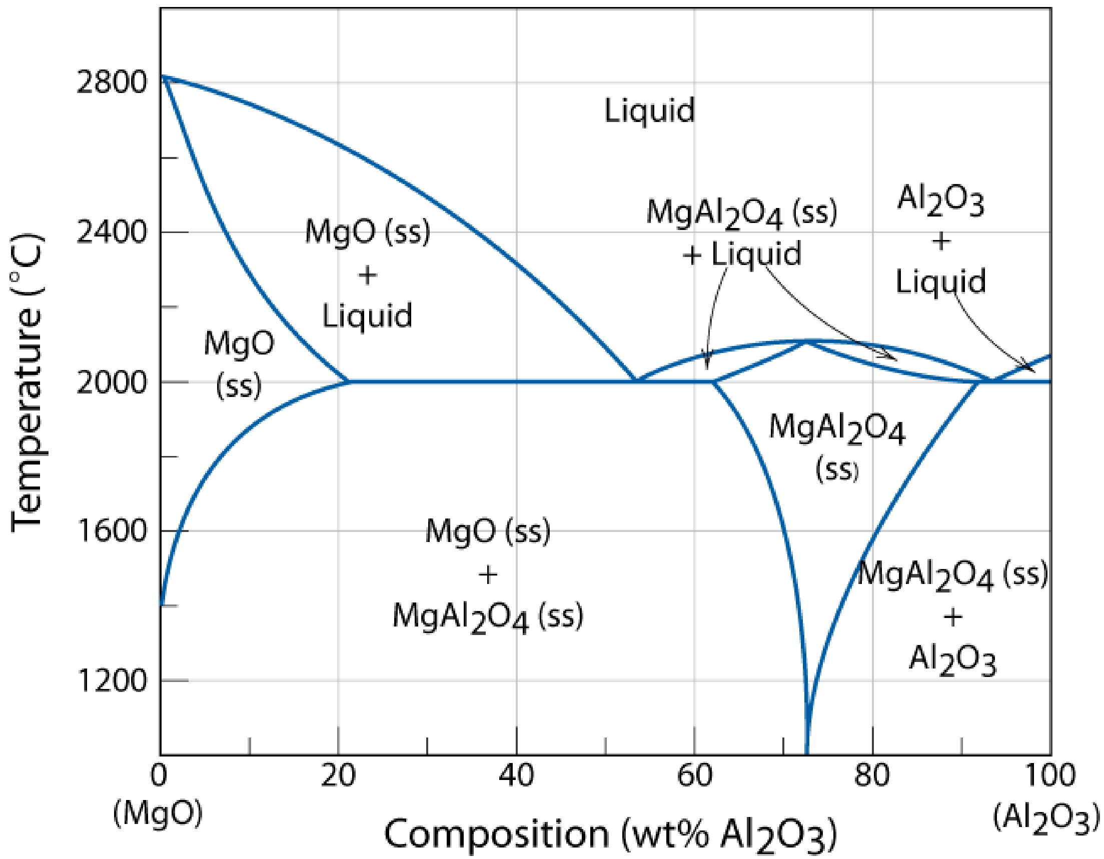
Ceramic Phase Diagrams

Same principles apply with respect to phases present, composition of each phase, and their relative amount

$MgO-Al_2O_3$ diagram:

Q:

- How many components and what are they?
- What are the single phases possible?
- What are the two-phase regions?
- For a 40wt% Al2O3 at 2200C, what are the phases, the composition (in terms of wt% Al2O3) for each phase, and the relative amount for each phase?



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

Mechanical Properties

Ceramic materials are more brittle than metals.

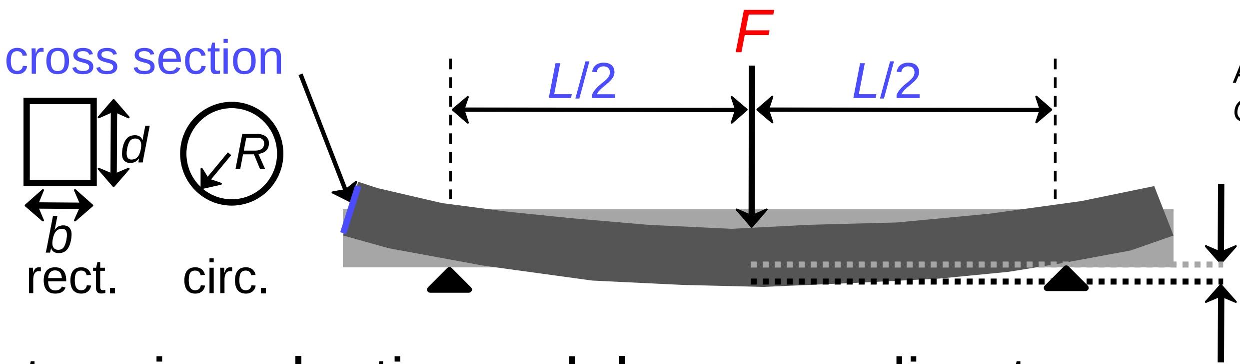
Why is this so?

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

Mechanical properties of ceramics measured often by bending or flexural tests instead of tensile test due, partly, to difficulty with tight clamping required for tensile tests

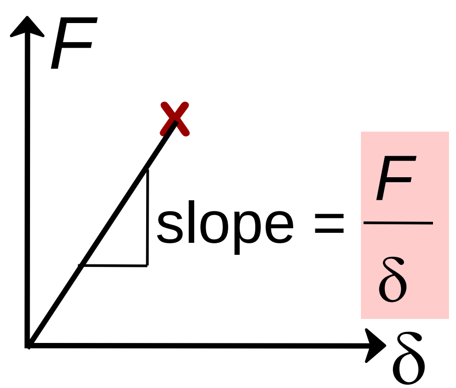
Flexural Tests – Measurement of Elastic Modulus for Ceramics

- Ceramics room *T* 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:



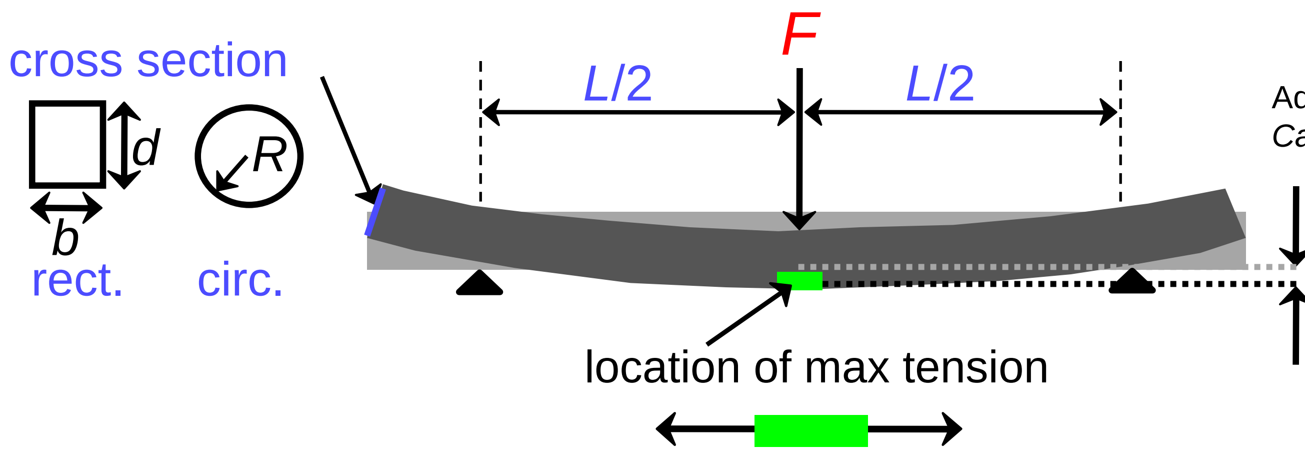
slope = $\frac{F}{\delta}$

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

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

Flexural Tests – Measurement of Flexural Strength for Ceramics

- 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 size ratios
- Imperfections
  -- Vacancy, interstitial (cation), Frenkel, Schottky
  -- Substitutional
  -- Maintenance of charge neutrality
- Room-temperature mechanical behavior – flexural tests
  -- linear-elastic region: measurement of elastic modulus
  -- brittle fracture: measurement of flexural strength