CHAPTER 12: STRUCTURE AND PROPERTIES OF CERAMICS

ISSUES TO ADDRESS...

- **Structures of ceramic materials:**
  How do they differ from that 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?

CERAMIC BONDING

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

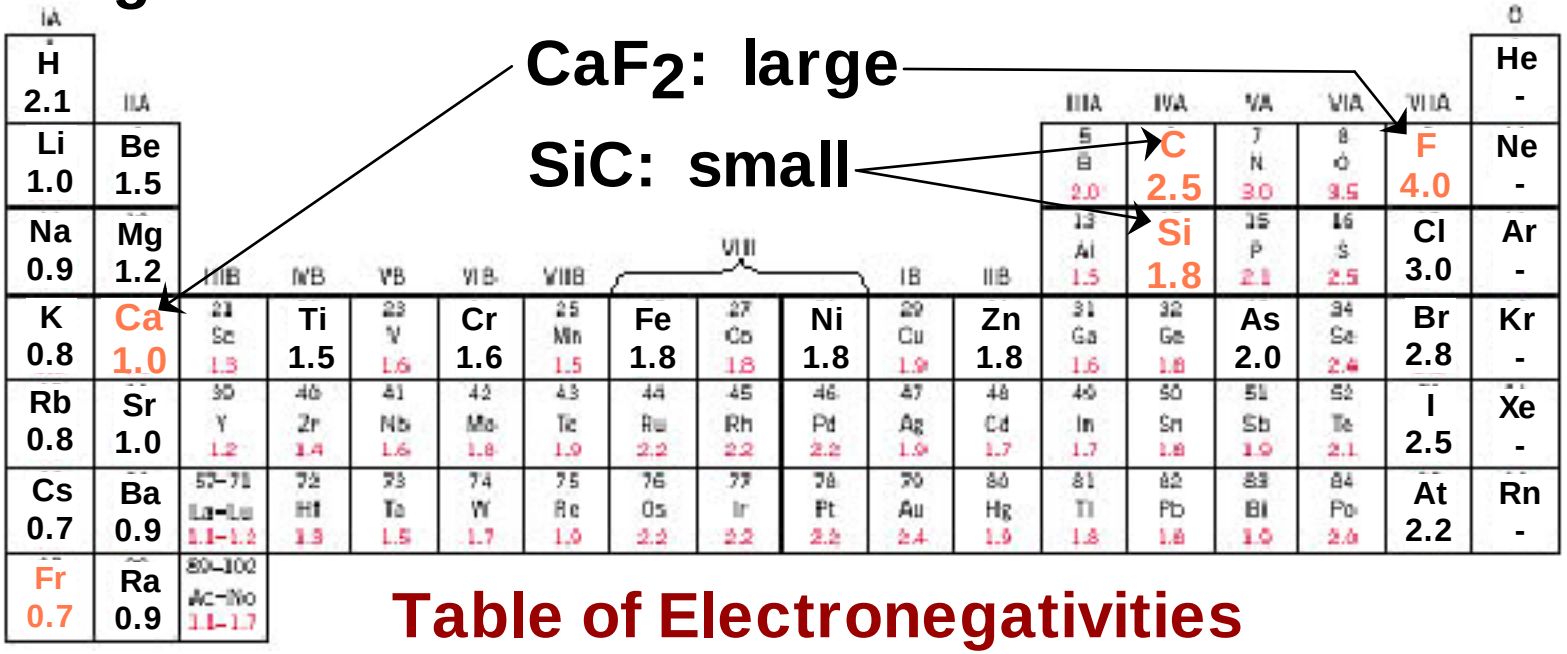
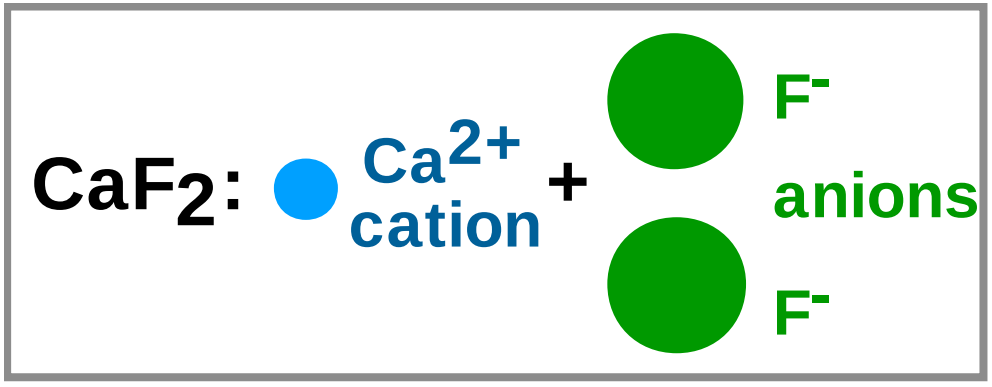


Table of Electronegativities

Adapted from Fig. 2.7, *Callister 6e.* (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

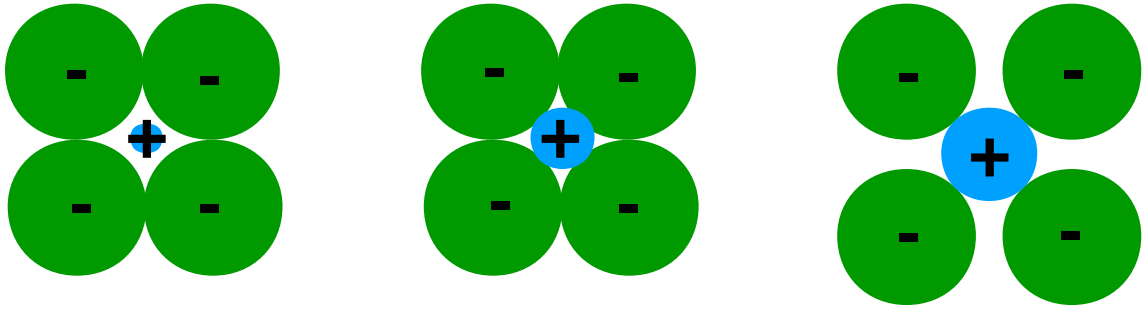
- **Charge Neutrality:**
  --Net charge in the structure should be zero.



--General form: A_mX_p

m, p determined by charge neutrality

- **Stable structures:**
  --maximize the # of nearest oppositely charged neighbors.



Adapted from Fig. 12.1, *Callister 6e.*

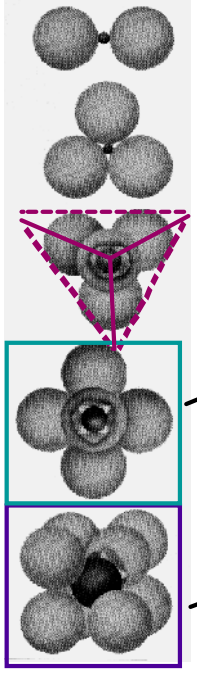
COORDINATION # AND IONIC RADII

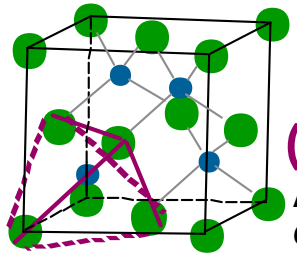
- **Coordination # increases with** $\frac{r_{cation}}{r_{anion}}$

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

$\frac{r_{cation}}{r_{anion}}$	Coord #
< .155	2
.155-.225	3
.225-.414	4
.414-.732	6
.732-1.0	8

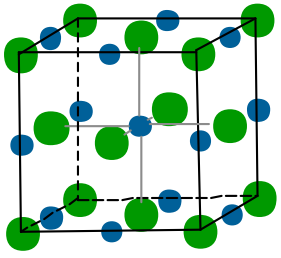
Adapted from Table 12.2, *Callister 6e.*





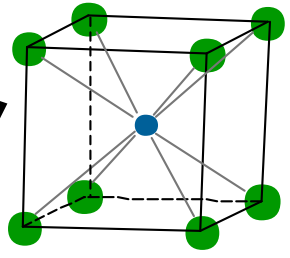
ZnS (zincblende)

Adapted from Fig. 12.4, *Callister 6e.*



NaCl (sodium chloride)

Adapted from Fig. 12.2, *Callister 6e.*



CsCl (cesium chloride)

Adapted from Fig. 12.3, *Callister 6e.*

EX: PREDICTING STRUCTURE OF FeO

- **On the basis of ionic radii, what crystal structure 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 6e.*

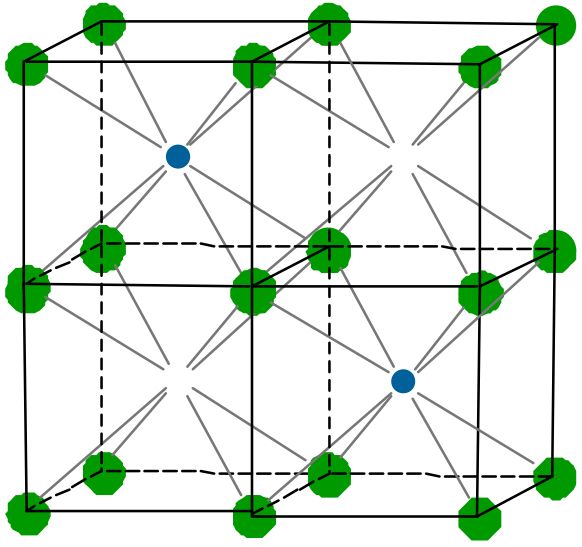
- **Answer:**

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

based on this ratio,
--coord # = 6
--structure = NaCl

A_mX_p STRUCTURES

- **Consider CaF_2 :** $\frac{r_{cation}}{r_{anion}} = \frac{0.100}{0.133} \approx 0.8$
- **Based on this ratio, coord # = 8 and structure = CsCl.**
- **Result: CsCl structure w/only half the cation sites occupied.**



- **Only half the cation sites are occupied since #Ca^{2+} ions = 1/2 # F^- ions.**

Adapted from Fig. 12.5, *Callister 6e.*

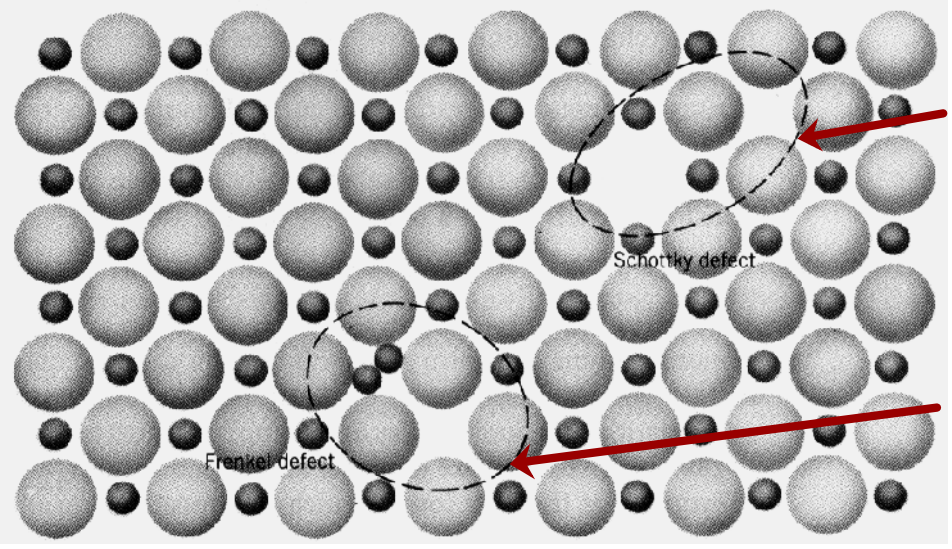
DEFECTS IN CERAMIC STRUCTURES

- **Frenkel Defect**

  --a cation is out of place.

- **Shottky Defect**

  --a paired set of cation and anion vacancies.



Shottky Defect:

Frenkel Defect

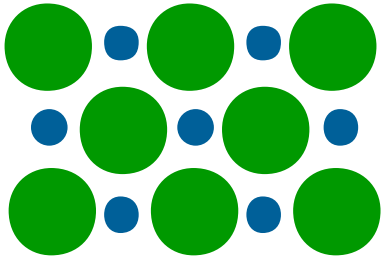
Adapted from Fig. 13.20, *Callister 5e.* (Fig. 13.20 is from W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, John Wiley and Sons, Inc., p. 78.) See Fig. 12.21, *Callister 6e*.

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

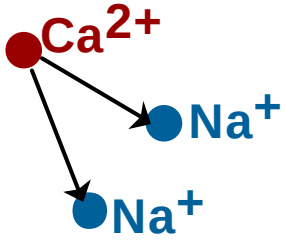
IMPURITIES

- Impurities must also satisfy charge balance
- Ex: NaCl 

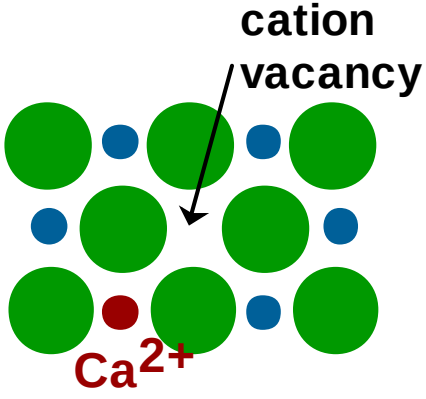
- Substitutional cation impurity



initial geometry

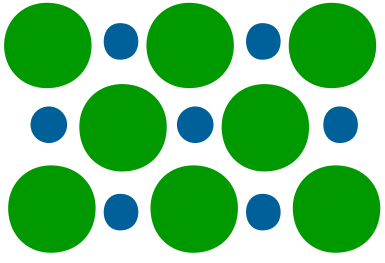


Ca^{2+} impurity

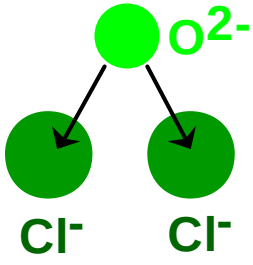


resulting geometry

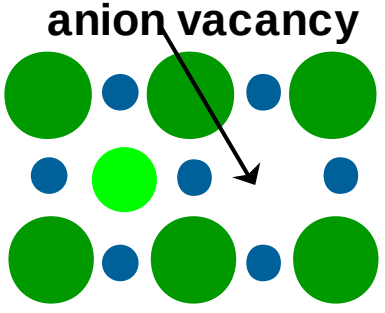
- Substitutional anion impurity



initial geometry



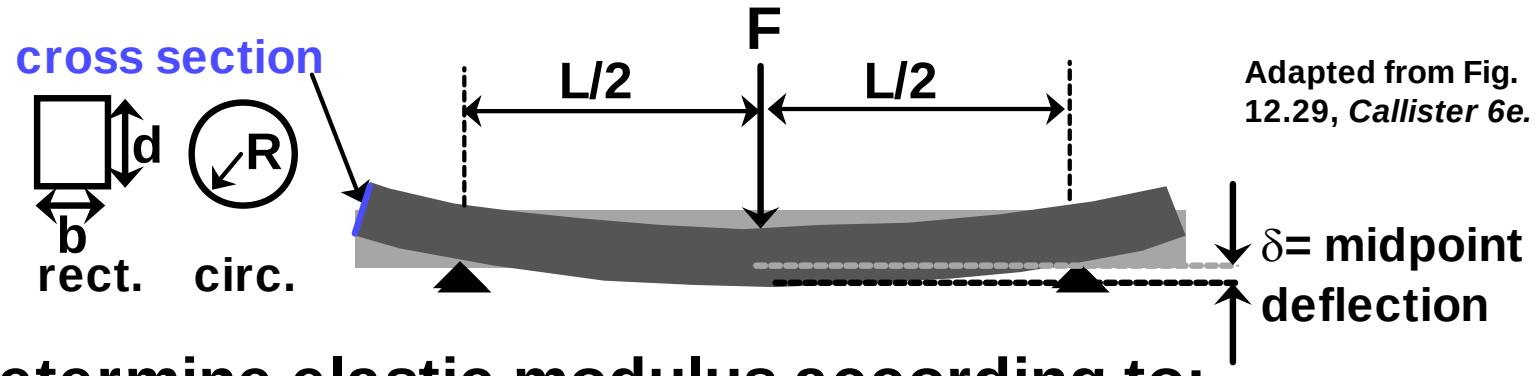
O^{2-} impurity



resulting geometry

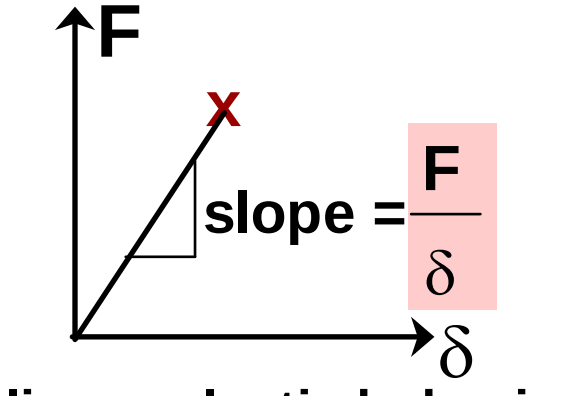
MEASURING ELASTIC MODULUS

- 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. 12.29, *Callister 6e.*

- Determine elastic modulus according to:



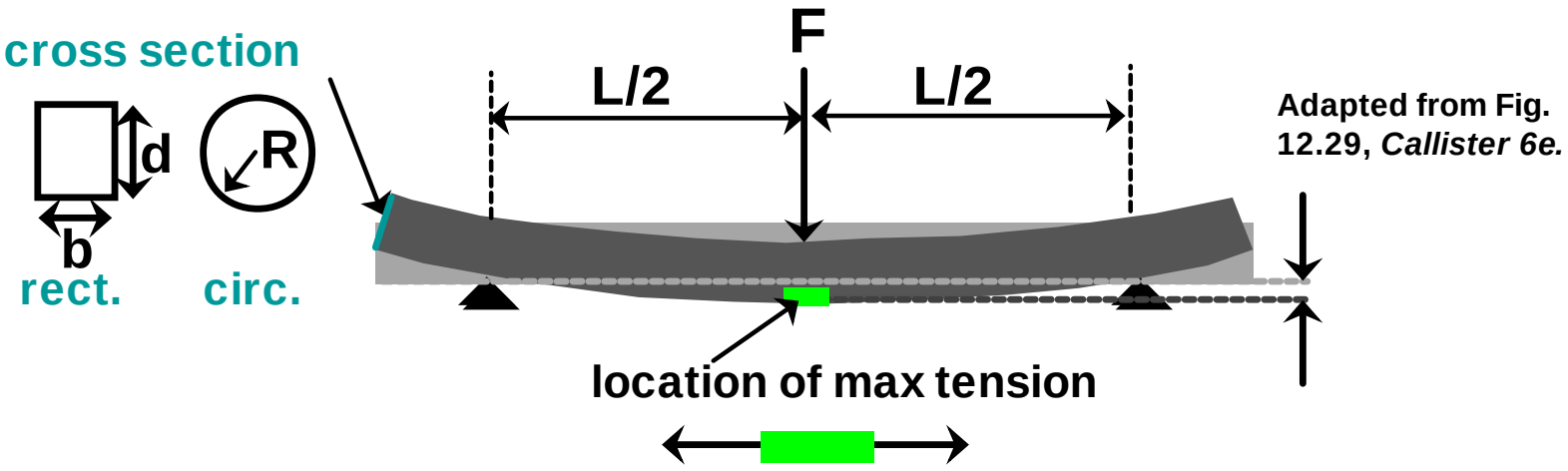
linear-elastic behavior

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

rect. cross section | circ. cross section

MEASURING STRENGTH

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

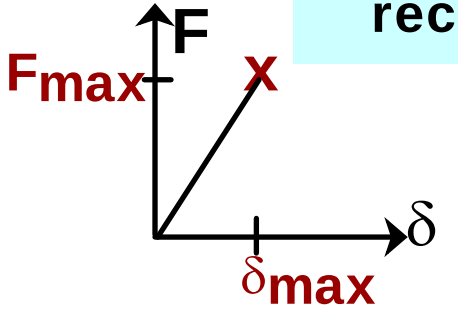


Adapted from Fig. 12.29, *Callister 6e.*

- Flexural strength:

$$\sigma_{fs} = \sigma_m^{fail} = \frac{1.5F_{max}L}{bd^2} = \frac{F_{max}L}{\pi R^3}$$

rect.



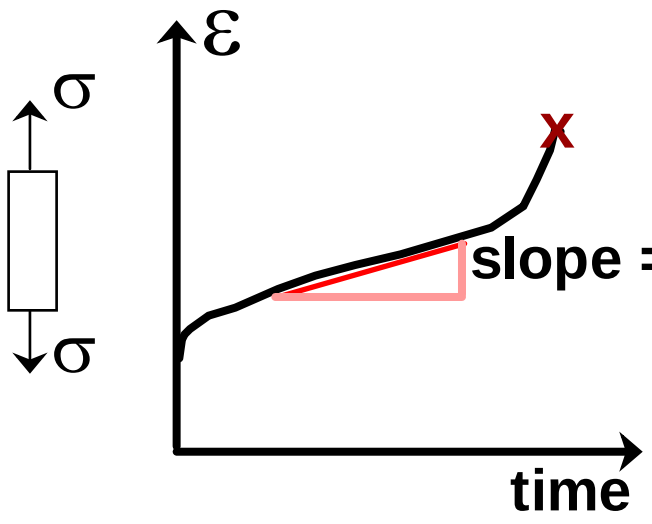
- Typ. values:

Material	σ_{fs}(MPa)	E(GPa)
Si nitride	700-1000	300
Si carbide	550-860	430
Al oxide	275-550	390
glass (soda)	69	69

Data from Table 12.5, *Callister 6e.*

MEASURING ELEVATED T RESPONSE

- **Elevated Temperature Tensile Test ($T > 0.4\ T_{melt}$).**
  creep test



slope = $\dot{\varepsilon}_{ss}$ = steady-state creep rate

- **Generally,**

$$\dot{\varepsilon}_{ss}^{ceramics} < \dot{\varepsilon}_{ss}^{metals} << \dot{\varepsilon}_{ss}^{polymers}$$

SUMMARY

- Ceramic materials have mostly covalent & some 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 brittle, with negligible ductility.
- Elevated T creep properties are generally superior to those of metals (and polymers).