Aalto University
School of Engineering

# COE-C2004 - Materials Science and Engineering

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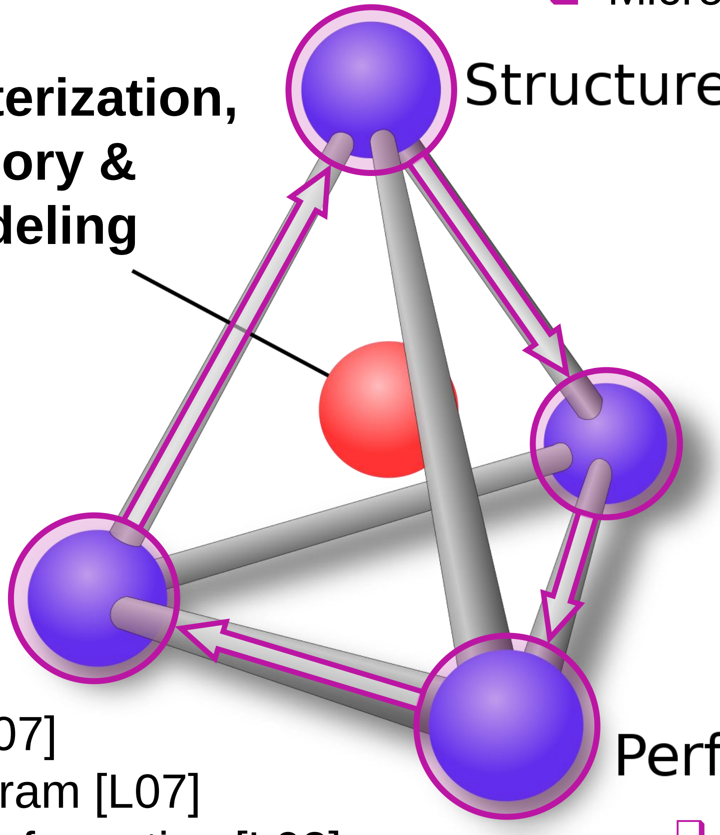
# Lecture flow

- Atomic structure [L01]
- Crystal structure [L02]
- Microstructure (phases) [L08]




- Elasticity [L03]
- Plasticity [L03 & L04]
- Hardness [L03]
- Failure [L05 & 06]
- Physical properties [L11]

- Diffusion [L07]
- Phase Diagram [L07]
- Phase Transformation [L08]
- Processes [L09]

- Elasticity and plasticity [L03 & L04]
- Failure [L05 & 06]

# Learning Objectives

After studying this chapter you should be able to do the following:

- Name the types of ceramics and describe their basic applications.
- Sketch/describe unit cells for sodium chloride, cesium chloride, zinc blende, diamond cubic crystal structures. Do likewise for the atomic structures of graphite and a silica glass.
- Given the chemical formula for a ceramic compound and the ionic radii of its component ions, predict the crystal structure.
- Name and describe different ionic point defects that are found in ceramic compounds.
- On the basis of slip considerations, explain why crystalline ceramic materials are normally brittle.

# Ceramics – Applications

# Ceramic and its types

A **ceramic** is any of the various hard, brittle, heat-resistant and corrosion-resistant materials made by shaping and then firing a nonmetallic mineral, such as clay, at a high temperature.

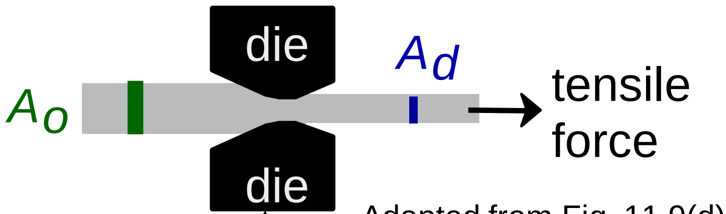
## Ceramic Materials

- **Glasses**
  - -optical
  - -composite reinforce
  - -containers/ household
- **Clay products**
  - -whiteware
  - -structural
- **Refractories**
  - -bricks for high *T* (furnaces)
- **Abrasives**
  - -sandpaper
  - -cutting
  - -polishing
- **Cements**
  - -composites
  - -structural
- **Ceramic biomaterials**
  - -implants
- **Carbon**
  - -composites
  - -abrasives
- **Advanced ceramics**
  - -engine rotors valves bearings
  - -sensors

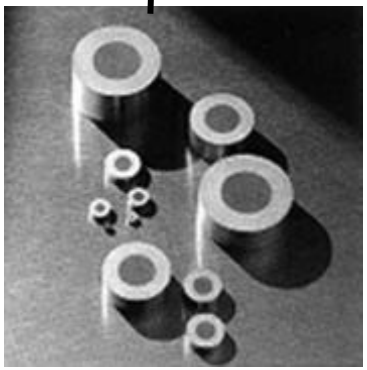
Adapted from Fig. 13.1 and discussion in Sections 13.2-10, *Callister & Rethwisch 10e.*

# Ceramics Application: Die Blanks

- Die blanks:
  -- Need wear resistant properties!
- Die surface:
  -- 4 μm polycrystalline diamond particles that are sintered onto a cemented tungsten carbide substrate.
  -- polycrystalline diamond gives uniform hardness in all directions to reduce wear.




Adapted from Fig. 11.9(d), *Callister & Rethwisch 10e.*

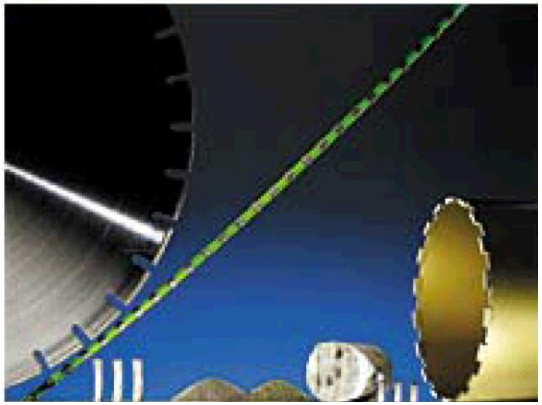


Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.

# Ceramics Application: Cutting Tools

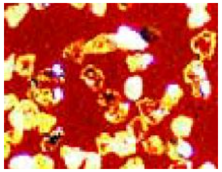
- Tools:
  - -- for grinding glass, tungsten, carbide, ceramics
  - -- for cutting Si wafers
  - -- for oil drilling
- Materials:
  - -- manufactured single crystal or polycrystalline diamonds in a metal or resin matrix.
  - -- polycrystalline diamonds resharpen by microfracturing along cleavage planes.

oil drill bits



blades

Single crystal diamonds



polycrystalline diamonds in a resin matrix.

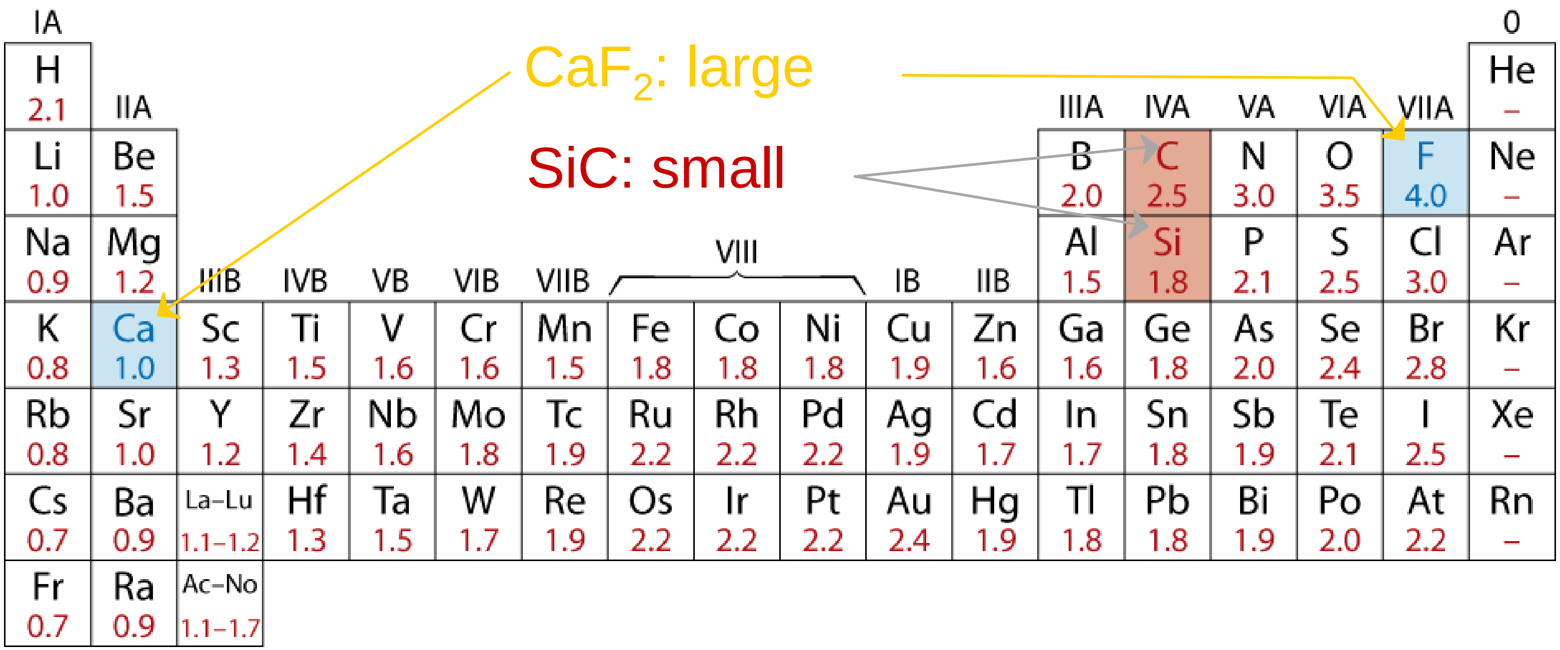
Photos courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.

# Ceramics – Structure

# 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:



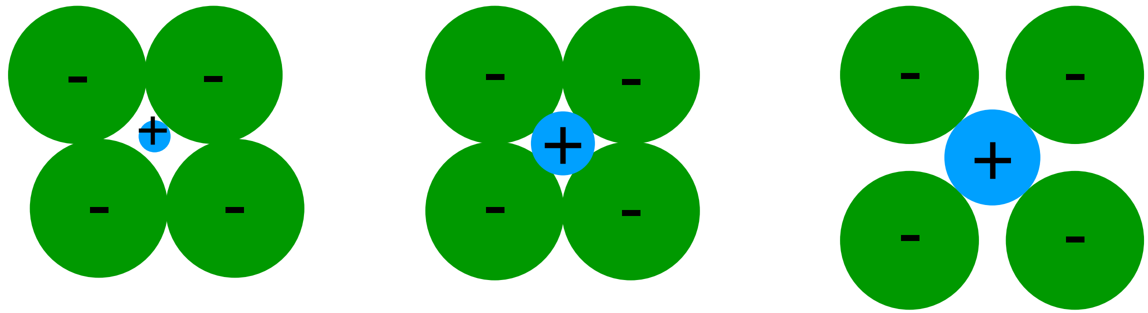
# Ceramic Crystal Structures

Oxide structures

- oxygen anions larger than metal cations
- close packed oxygen in a lattice (usually FCC)
- cations fit into interstitial sites among oxygen ions

# Factors that Determine Crystal Structure

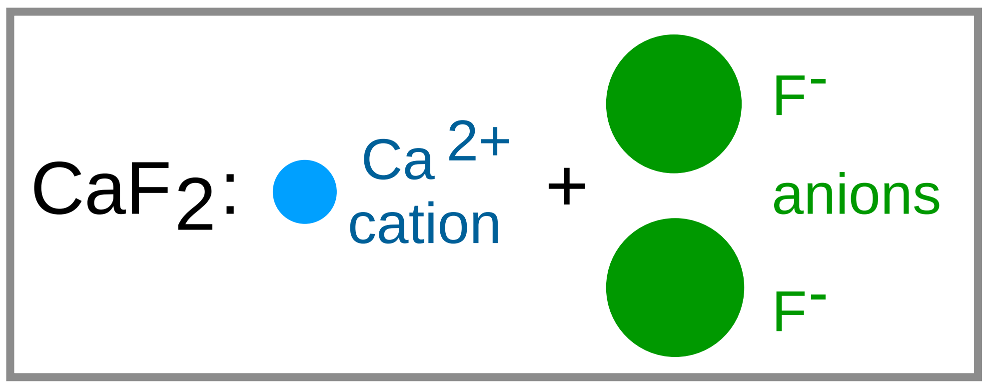
1. Relative sizes of ions – Formation of stable structures:
   --maximize the # of oppositely charged ion neighbors.




unstable stable stable

Adapted from Fig. 12.1, *Callister & Rethwisch 10e.*

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

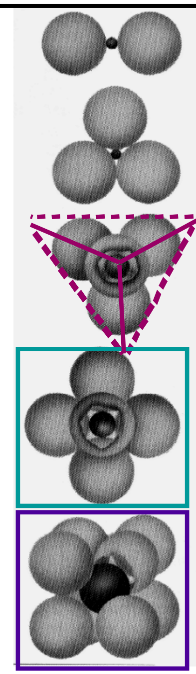
# Coordination Number and Ionic Radii

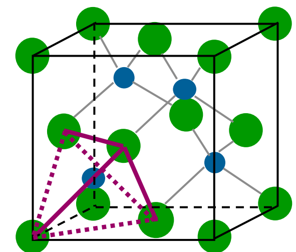
- Coordination Number increases with $\dfrac{r_{cation}}{r_{anion}}$

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

| $\dfrac{r_{cation}}{r_{anion}}$ | Coord. Number | |
|---|---|---|
| < 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 |

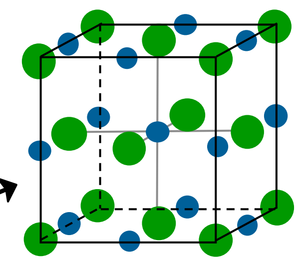
Adapted from Table 12.2, *Callister & Rethwisch 10e.*





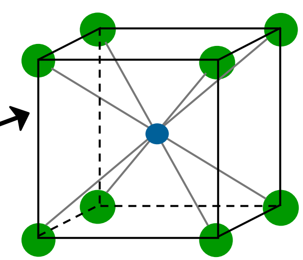
ZnS (zinc blende)

Adapted from Fig. 12.4, *Callister & Rethwisch 10e.*



NaCl (sodium chloride)

Adapted from Fig. 12.2, *Callister & Rethwisch 10e.*

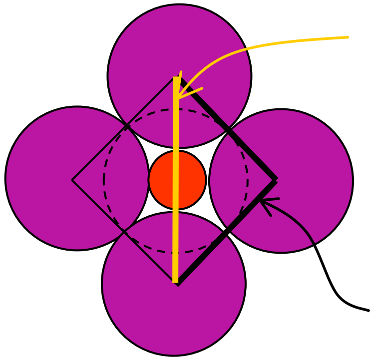


CsCl (cesium chloride)

Adapted from Fig. 12.3, *Callister & Rethwisch 10e.*

# Computation of Minimum Cation-Anion Radius Ratio

- Determine minimum $r_{cation}/r_{anion}$ for an octahedral site (C.N. = 6)



$$2r_{anion} + 2r_{cation} = \sqrt{2}a$$

$$a = 2r_{anion}$$

$$2r_{anion} + 2r_{cation} = 2\sqrt{2}r_{anion}$$

$$r_{anion} + r_{cation} = \sqrt{2}r_{anion} \qquad r_{cation} = (\sqrt{2} - 1)r_{anion}$$

$$\frac{r_{cation}}{r_{anion}} = \sqrt{2} - 1 = 0.414$$

# Predicting the Crystal 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 & Rethwisch 10e.*

- Answer:

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

$$= 0.550$$

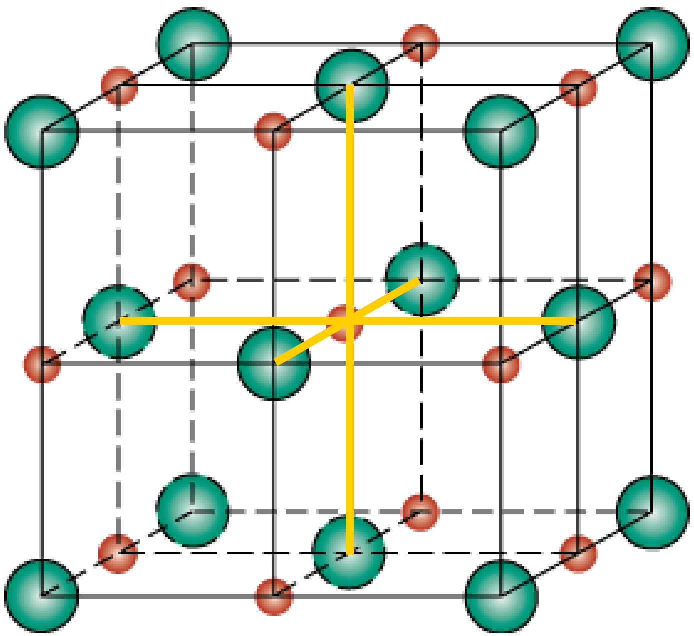
based on this ratio,
-- coord # = 6 because

$0.414 < 0.550 < 0.732$

-- crystal structure is NaCl

# Rock Salt Structure

Same concepts can be applied to ionic solids in general.
Example: NaCl (rock salt) structure



Adapted from Fig. 12.2, *Callister & Rethwisch 10e.*

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

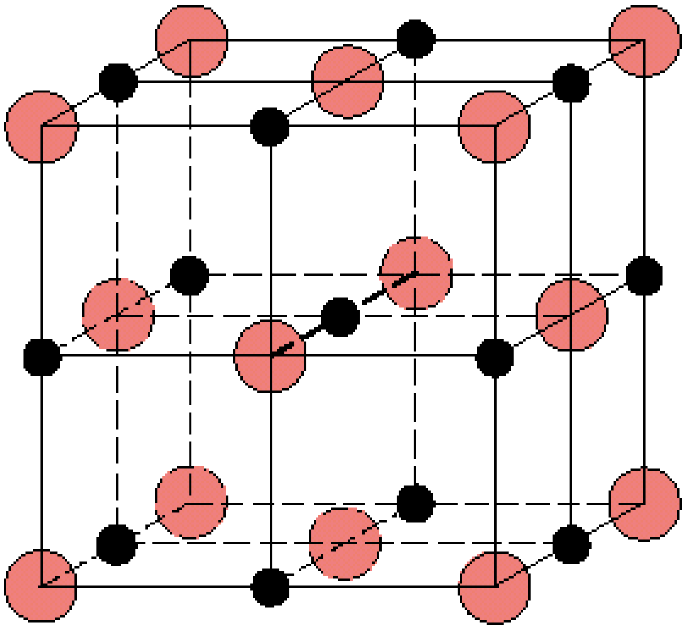
$Cl^-$ $r_{Cl} = 0.181$ nm

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

$\therefore$ cations ($Na^+$) prefer octahedral sites

# MgO and FeO

MgO and FeO also have the NaCl structure



$O^{2-}$ $r_O = 0.140$ nm

$Mg^{2+}$ $r_{Mg} = 0.072$ nm

$r_{Mg}/r_O = 0.514$

$\therefore$ cations prefer octahedral sites

Adapted from Fig. 12.2,
*Callister & Rethwisch 10e.*

So each $Mg^{2+}$ (or $Fe^{2+}$) has 6 neighbor oxygen atoms

# AX Crystal Structures

AX–Type Crystal Structures include NaCl, CsCl, and zinc blende

Cesium Chloride structure:

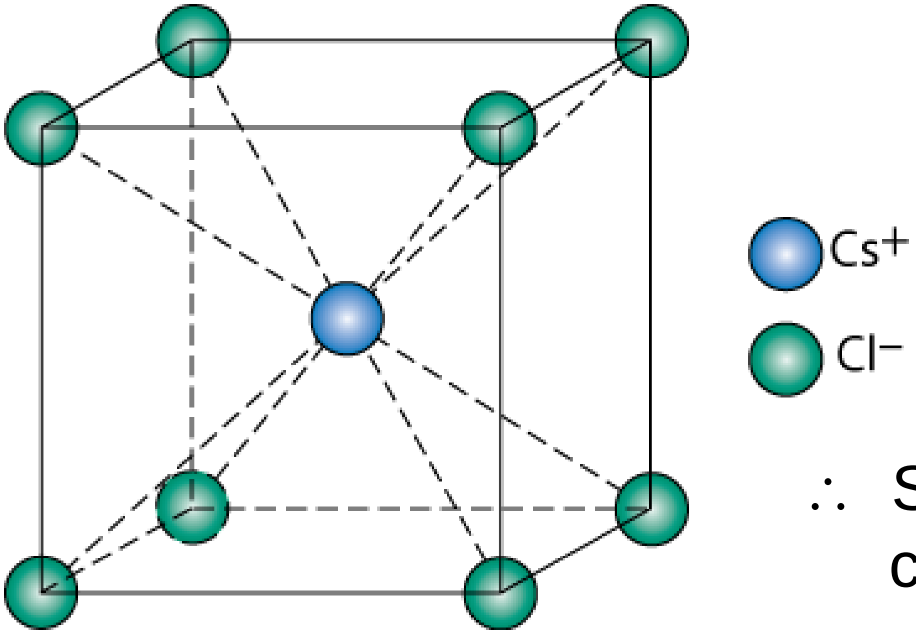



Fig. 12.3, *Callister & Rethwisch 10e.*

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

$\therefore$ Since $0.732 < 0.939 < 1.0$, cubic sites preferred

So each $Cs^+$ has 8 neighbor $Cl^-$

# $AX_2$ Crystal Structures

Fluorite structure

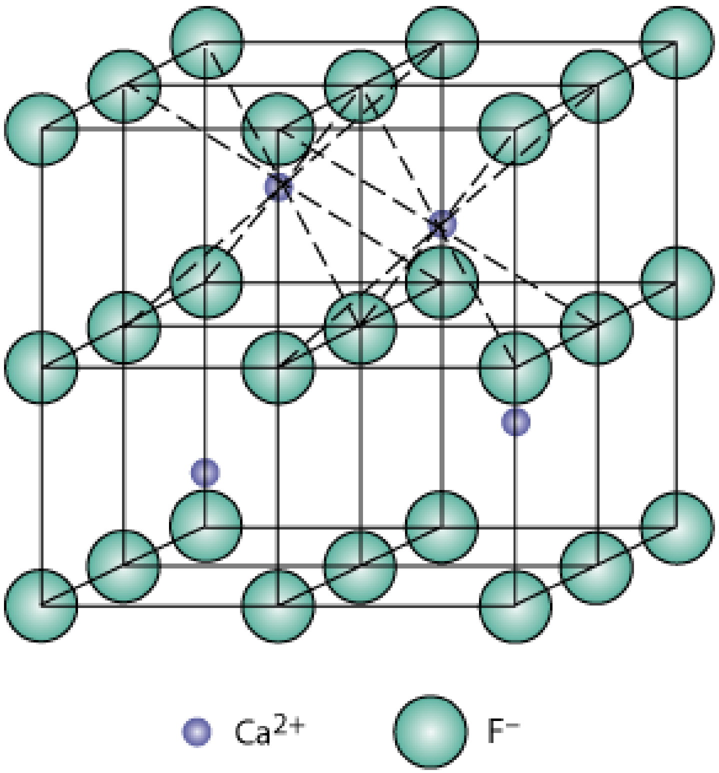



Fig. 12.5, *Callister & Rethwisch 10e.*

- Calcium Fluorite ($CaF_2$)
- Cations in cubic sites

- $UO_2$, $ThO_2$, $ZrO_2$, $CeO_2$

- Antifluorite structure – positions of cations and anions reversed

# $ABX_3$ Crystal Structures

- Perovskite structure

Ex: complex oxide

$BaTiO_3$

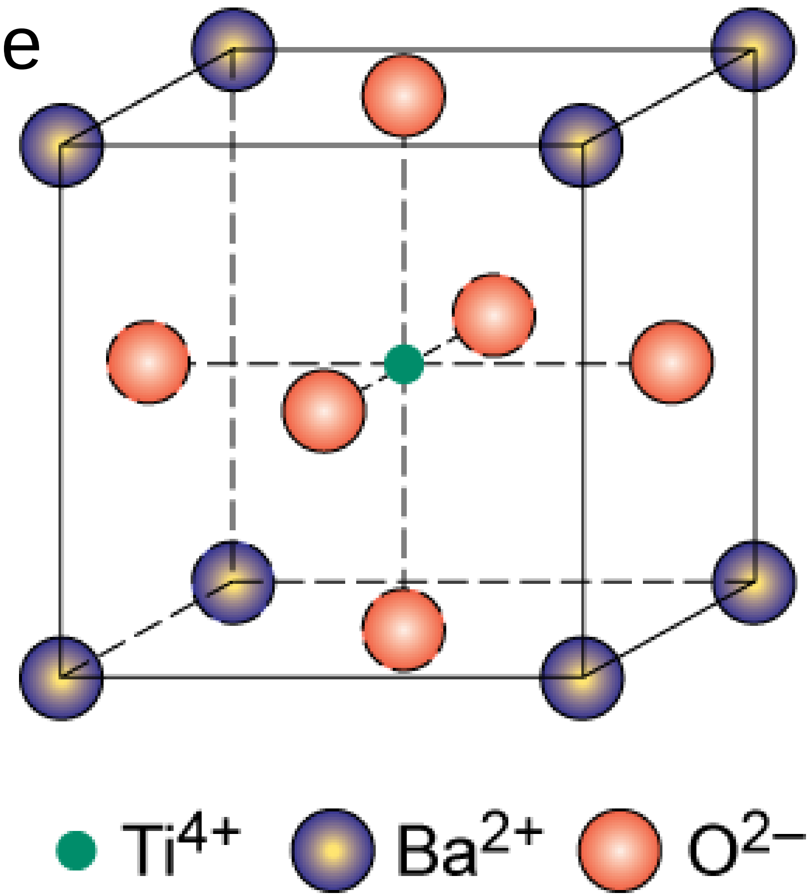
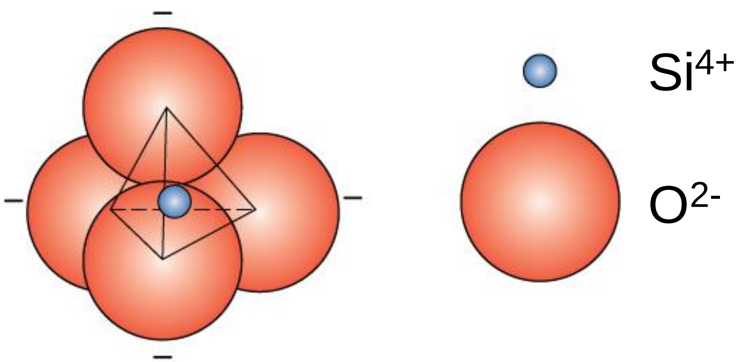


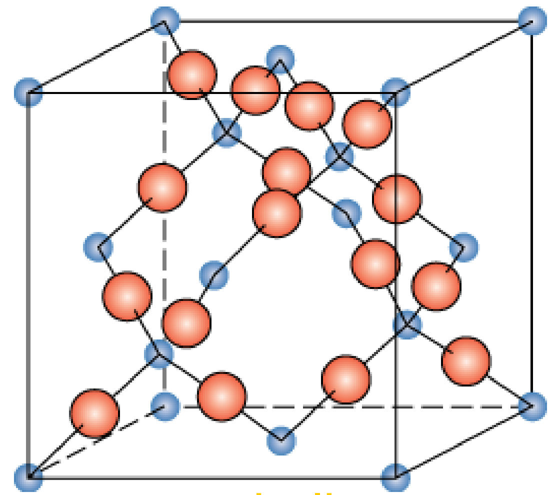

Fig. 12.6, *Callister & Rethwisch 10e.*

# Silicate Ceramics

Most common elements on earth are Si & O




Figs. 12.9 & 12.10, *Callister & Rethwisch 10e*



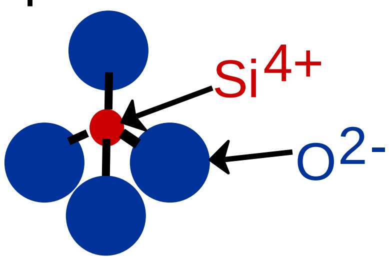
crystobalite

- $SiO_2$ (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:

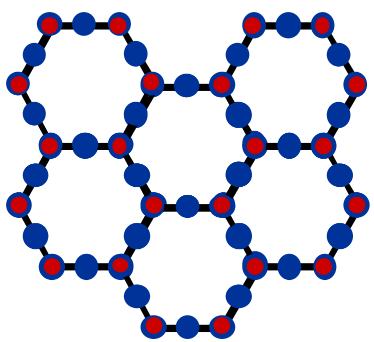
$Si0_4^{4-}$ tetrahedron

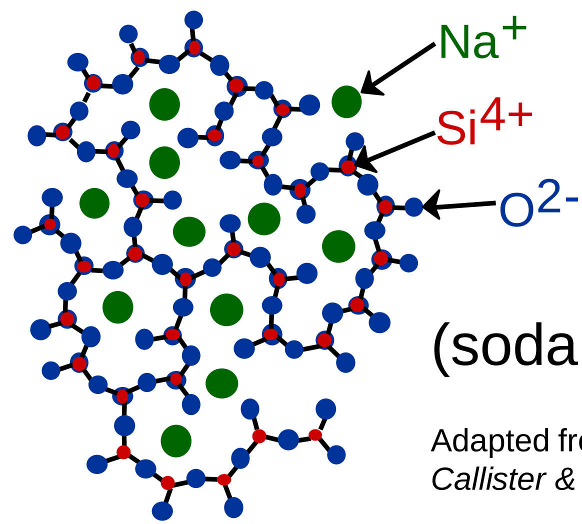



Glass is noncrystalline (amorphous)

- 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 10e*.

# 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.

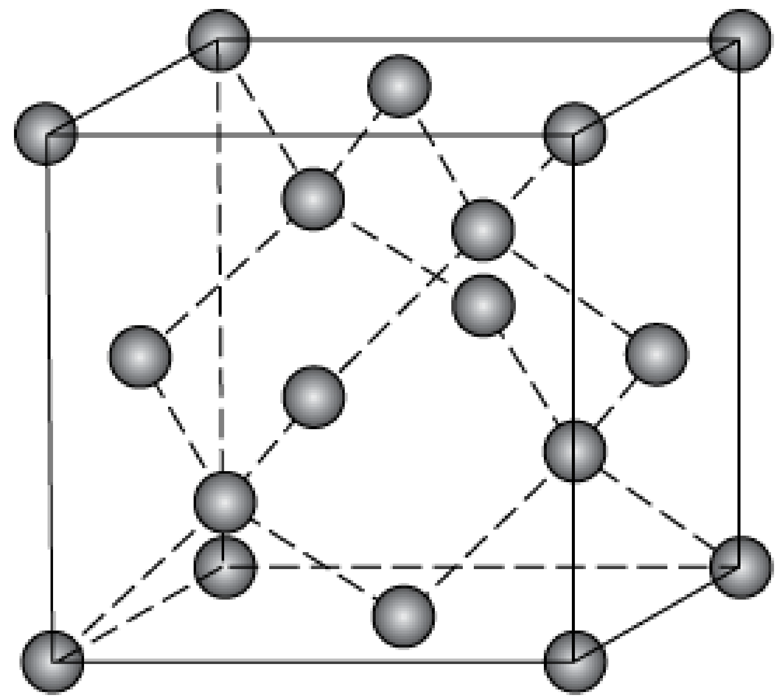


Fig. 12.16, *Callister & Rethwisch 10e.*

# Polymorphic Forms of Carbon (cont)

## Graphite

- layered structure – parallel hexagonal arrays of carbon atoms

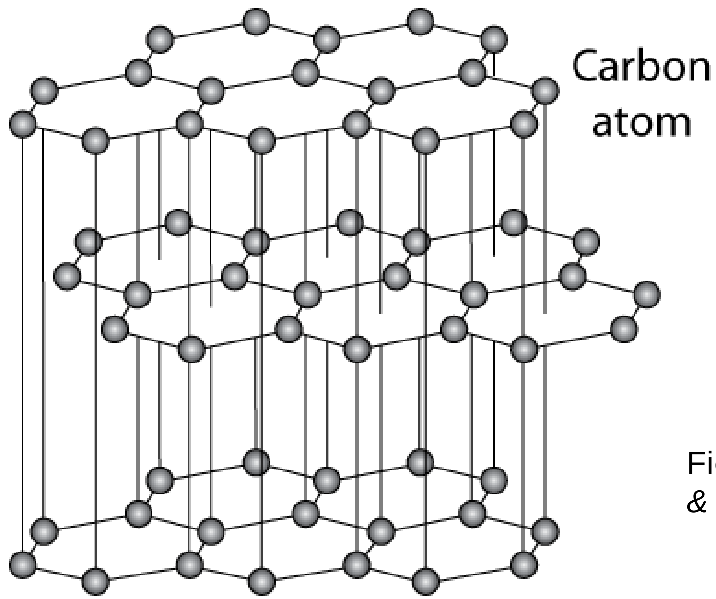



Fig. 12.17, *Callister & Rethwisch 10e.*

- weak van der Waal's forces between layers
- planes slide easily over one another -- good lubricant

# Ceramics – Defects

# 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

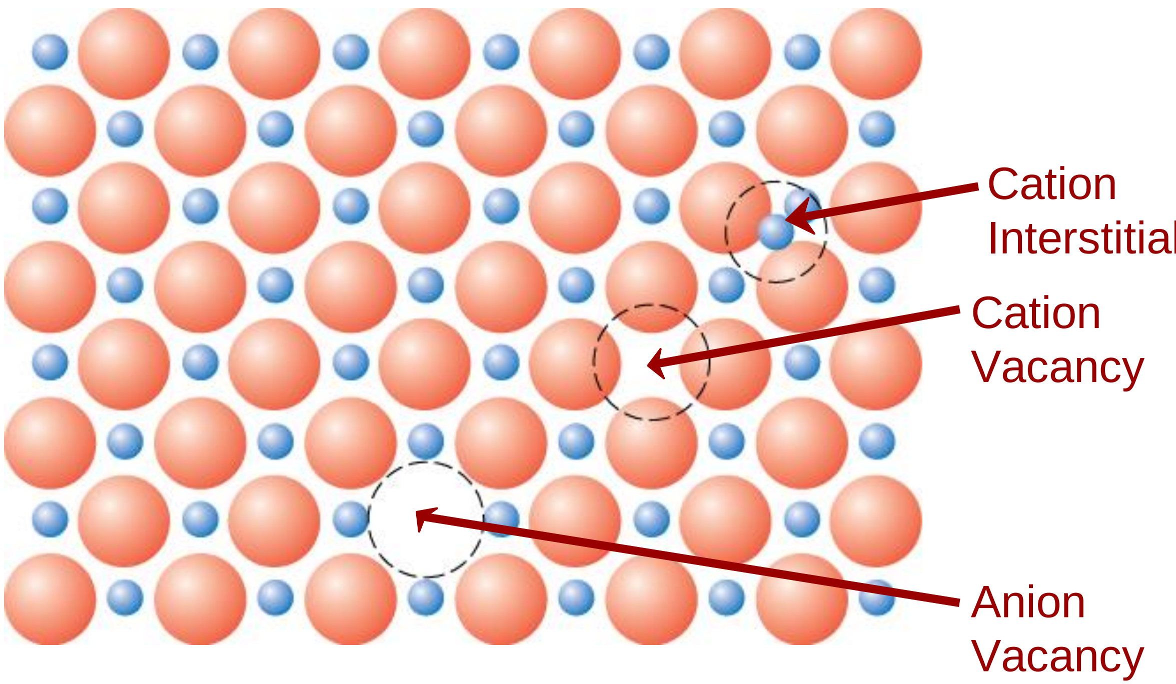



Fig. 12.18, *Callister & Rethwisch 10e.* (From W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, John Wiley & Sons, 1964. Reproduced with permission of Janet M. Moffatt.)

# Point Defects in Ceramics (ii)

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

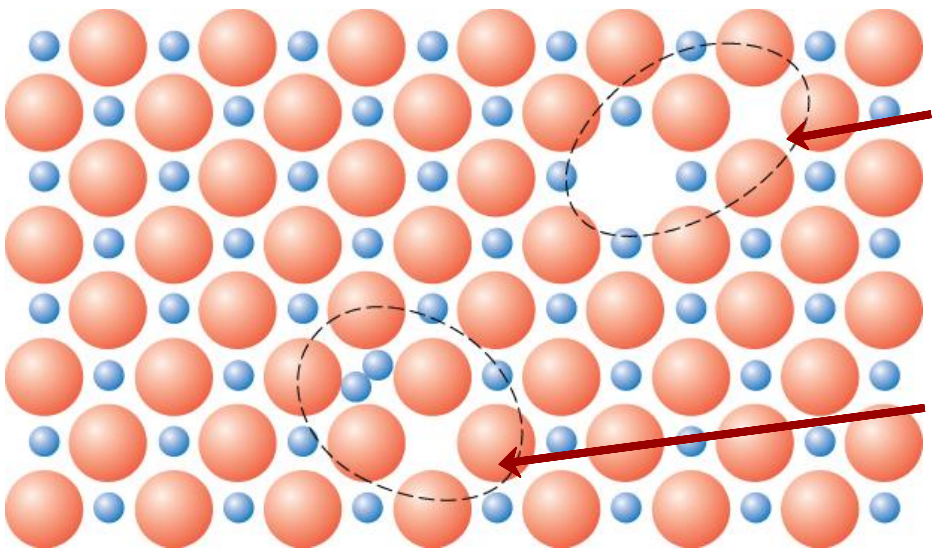
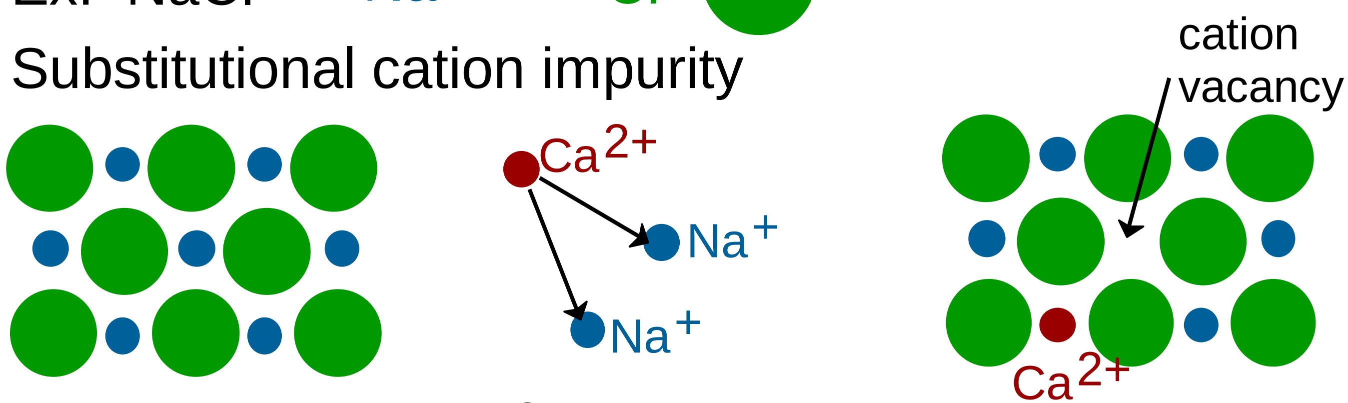



Fig. 12.19, *Callister & Rethwisch 10e.* (From W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, John Wiley & Sons, 1964. Reproduced with permission of Janet M. Moffatt.)

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

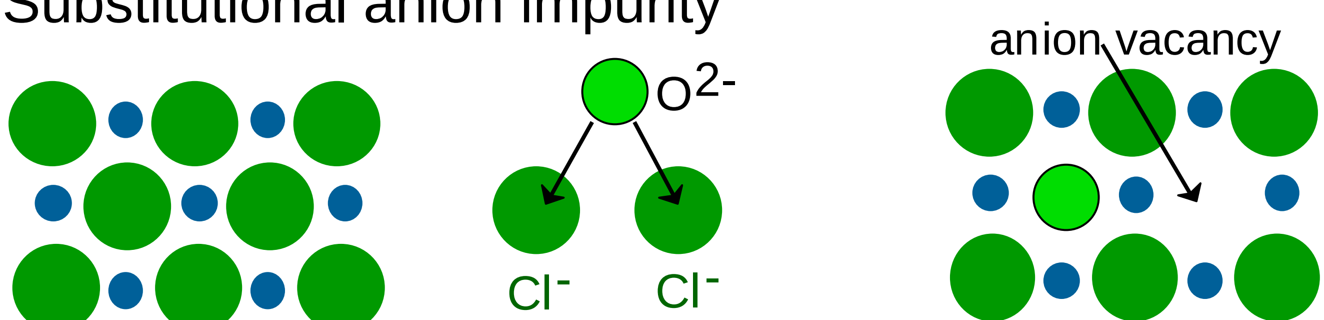
# Imperfections in Ceramics

- 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:

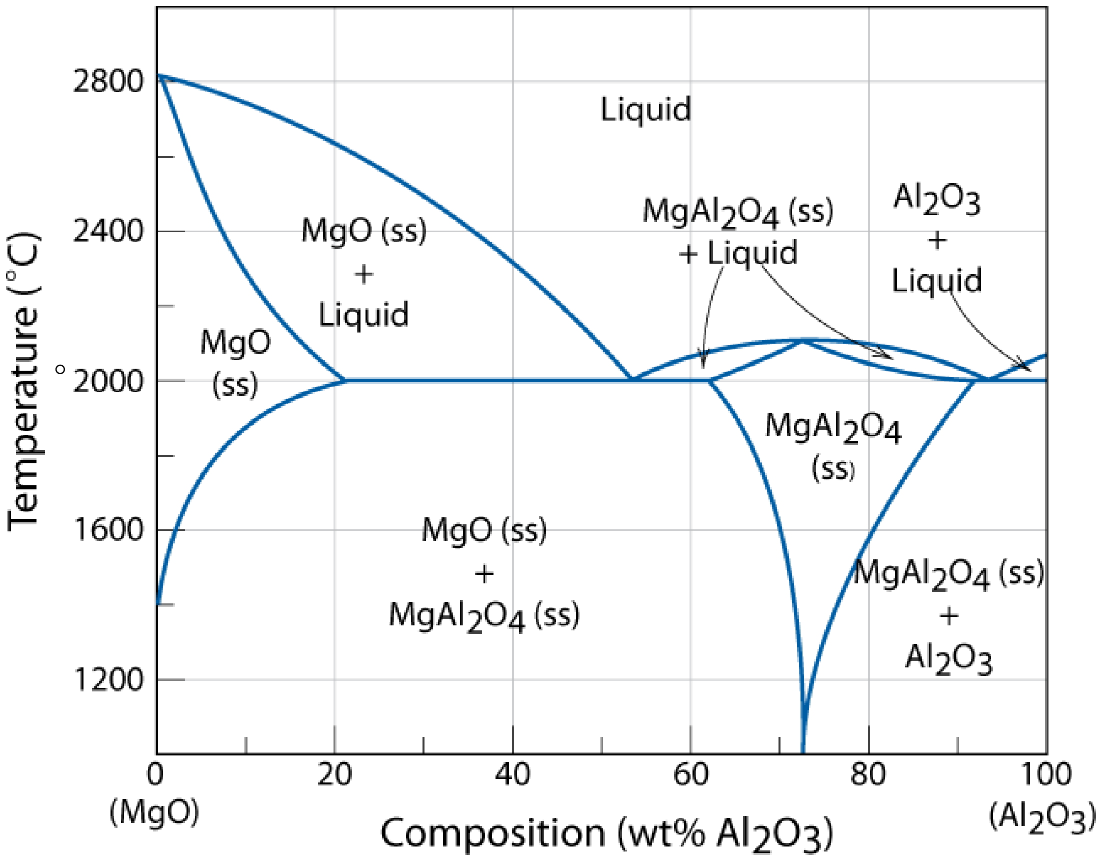



Fig. 12.23, Callister & Rethwisch 10e.
[Adapted from B. Hallstedt, "Thermodynamic Assessment of the System MgO–$Al_2O_3$," *J. Am. Ceram. Soc.*, 75[6], 1992, p.1502. Reprinted by permission of the American Ceramic Society.]

# Ceramics – Properties

# Mechanical Properties

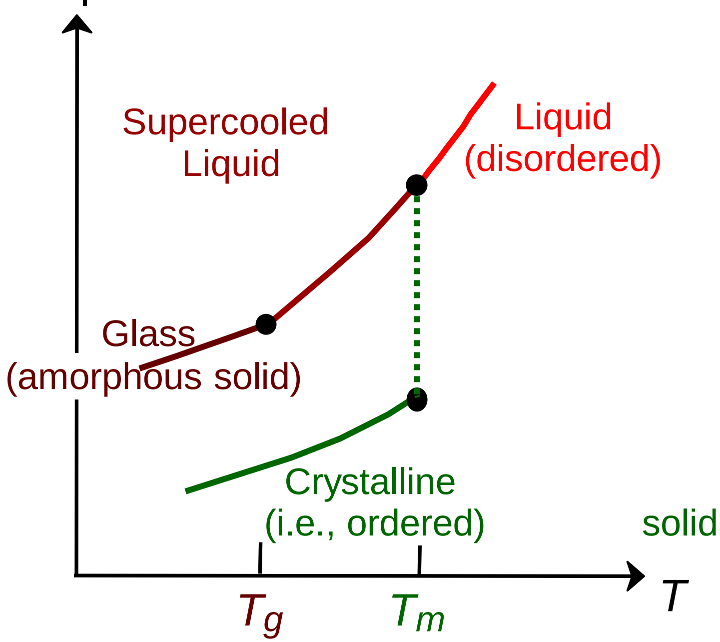
Ceramic materials are more brittle than metals.

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

# Glass Properties

- Specific volume ($1/\rho$) vs Temperature ($T$):




Adapted from Fig. 13.13, *Callister & Rethwisch 10e*.

- Crystalline materials:
  -- crystallize at melting temp, $T_m$
  -- have abrupt change in spec. vol. at $T_m$

- Glasses:
  -- do not crystallize
  -- change in slope in spec. vol. curve at glass transition temperature, $T_g$
  -- transparent - no grain boundaries to scatter light

# Summary

- Ceramics and their types.
- Interatomic bonding in ceramics is ionic and/or covalent.
- Ceramic crystal structures are based on:
  - maintaining charge neutrality
  - cation-anion radii ratios.
- Imperfections include:
  - Atomic point: vacancy, interstitial (cation), Frenkel, Schottky
  - Impurities: substitutional, interstitial
  - Maintenance of charge neutrality
- The ceramic materials are having high strength and more brittle than metals.

# Announcements

Next Monday (Dec 6) is a national holiday. The last lecture will take place via a recorded lecture.

Reading: Textbook **Ch. 11, 12 and further reading (Ch. 13, 14, 15, 16)**

Assignment: Open; DL: **18:00 Sunday**

~~Q&A time: **Tuesday 16:30**~~ **(merged w/ Exercise)**

Exercise: **Thursday 10:15 – 12:00**

# Questions?