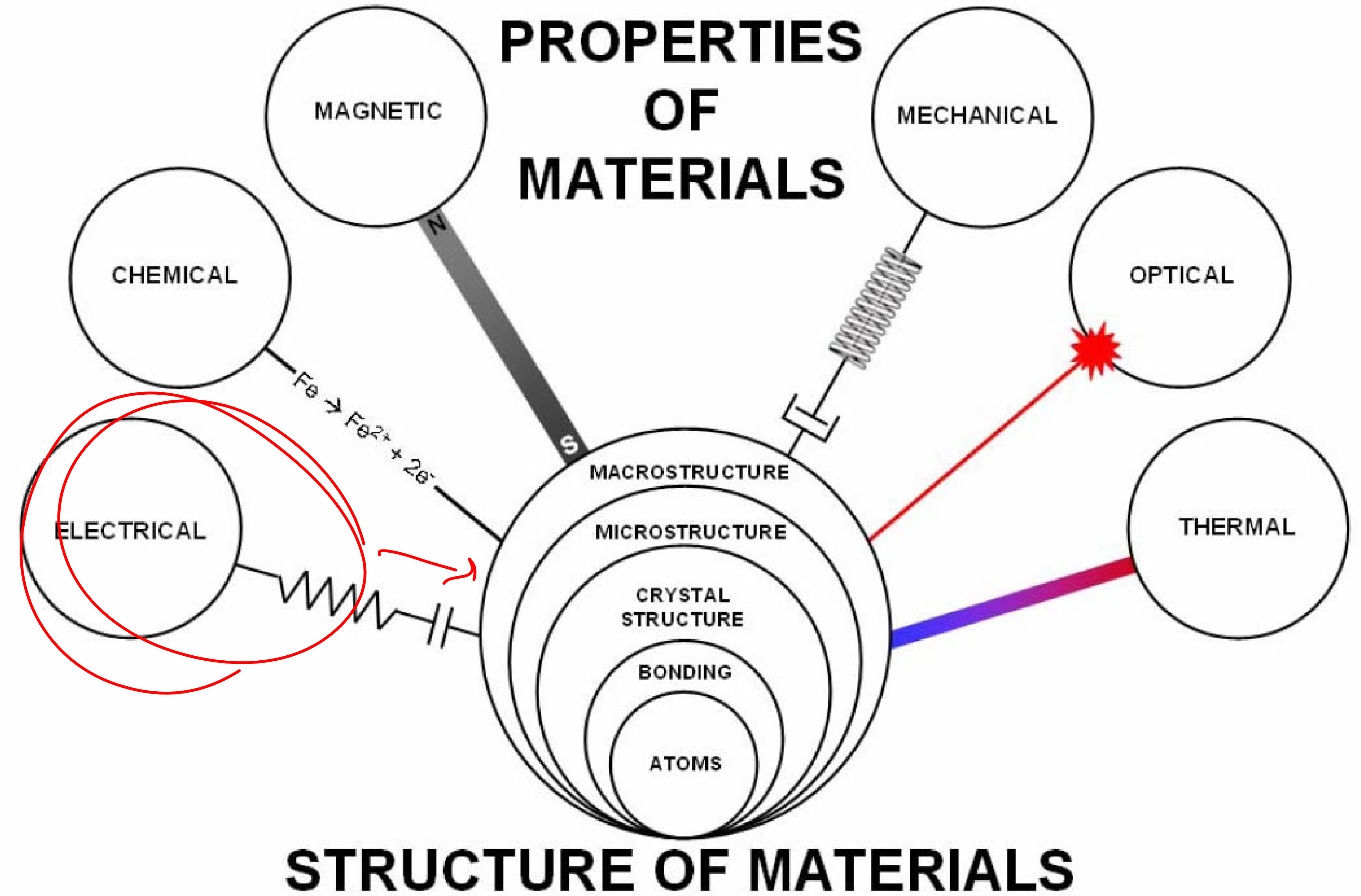
Announcement

- **Chapter 18**
  - **18.1 – 18.13, 18.15 – 18.23**
  - **Note – <u>Dielectric behavior</u> will not be covered in lecture and will have no assigned problems. Please read those sections and understand the concepts. Especially 18.20 and 18.21.**

- Recognize links between structure and properties for a variety of materials.


PROPERTIES
OF
MATERIALS
MAGNETIC
MECHANICAL
CHEMICAL
OPTICAL
ELECTRICAL
THERMAL
N
S
Fe → Fe^{2+} + $2e^-$
MACROSTRUCTURE
MICROSTRUCTURE
CRYSTAL
STRUCTURE
BONDING
ATOMS
STRUCTURE OF MATERIALS

Ohm's Law

- **Familiar form**
  - **$V = I R$**
  - **Geometry dependent**
- **"Materials" or "Physics" form**
  - **$J = \sigma \varepsilon$**
  - **Independent of geometry**

Conductivity (Table 18.6)

- **J – current density (Amps/metre²)**
- **q – charge (Coulombs = Amps * sec)**

- **J = n |q| v** $\quad \frac{A}{m^2} = \frac{\#\text{ charges}}{m^3}(A\cdot s)\,m/s$
- **σ ε = n |q| v** → "drift velocity"
- **σ = n |q| (v/ε)**

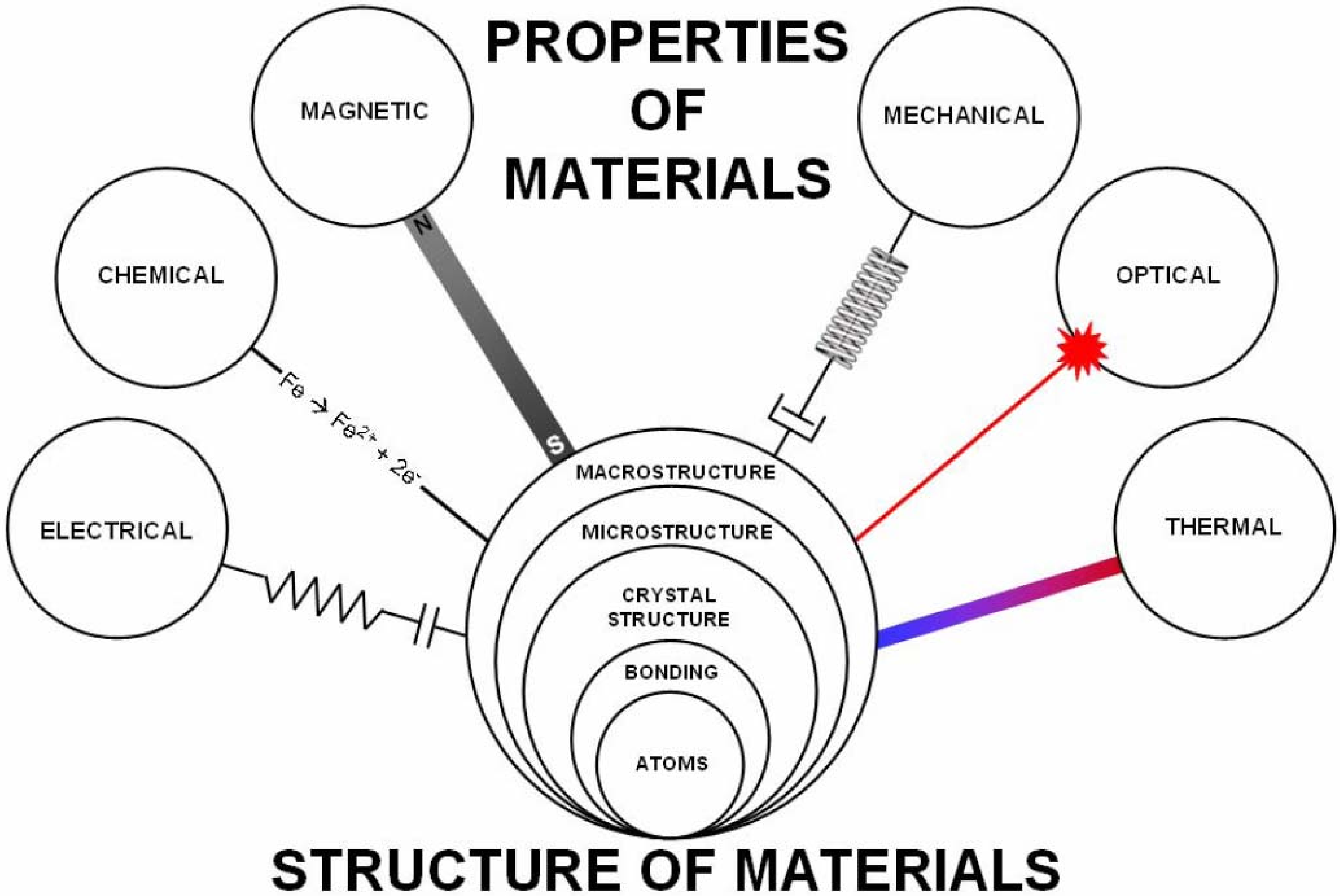
- **Finally, σ = n |q| μ** $\quad \frac{m/s}{V/m} \rightarrow \frac{m^2}{V\cdot s}$

Modify Electrical Properties

- $\sigma = n\,|q|\,\mu$
- Options are modify #charges or mobility

- Modify n
  - Doping
  - Change temperature → $e^{\left(-\frac{E_g}{kT}\right)}$

- Modify μ
  - Bonding
  - Defects
  - Microstructure
  - Diffusion (ionic conductors)


PROPERTIES
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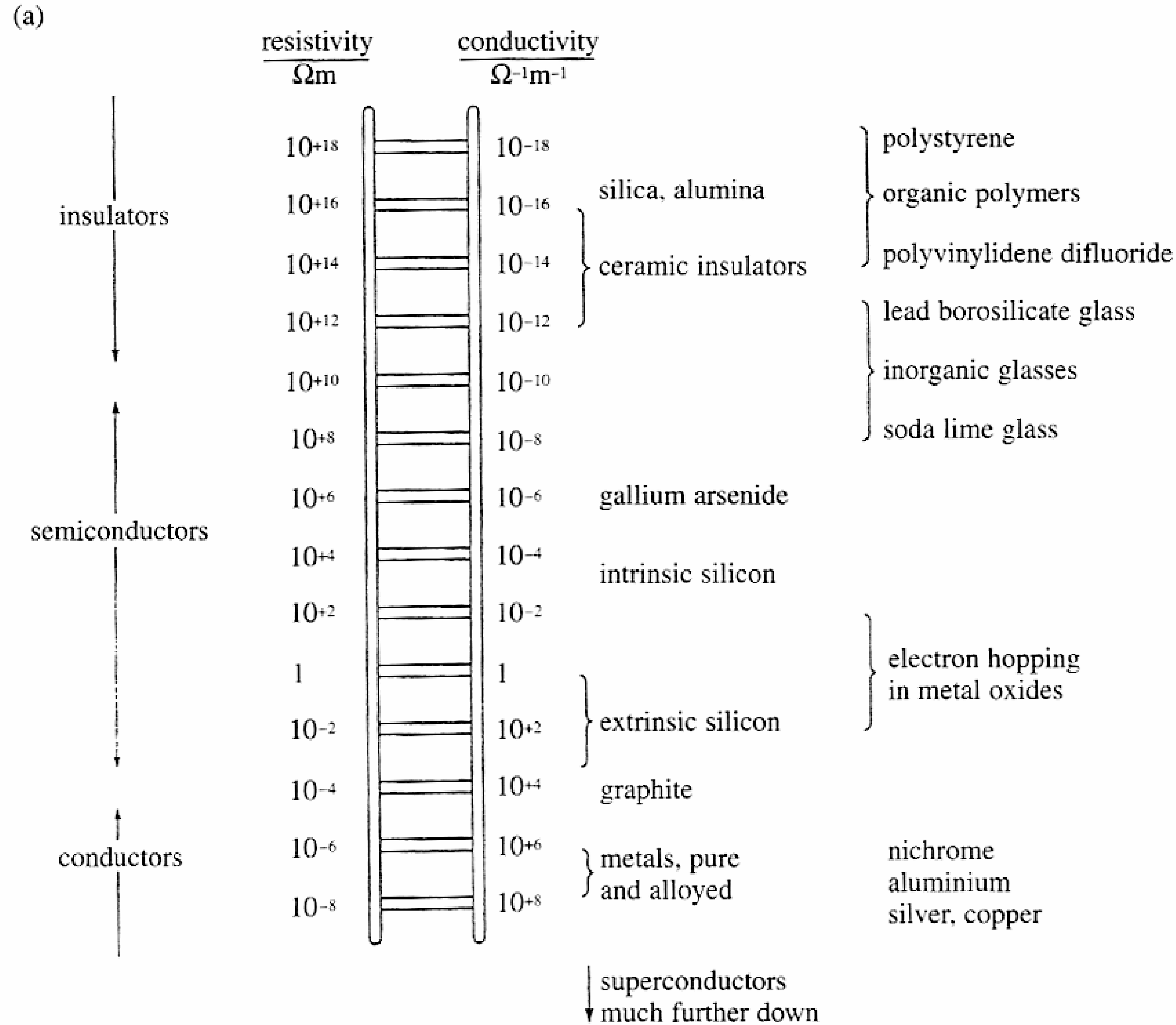
Ceramics in EE
"Electroceramics"

- **Electroceramics by A.J. Moulsen and J.M. Herbert**
- **http://www3.interscience.wiley.com/cgi-bin/booktoc/104557643**


(a)
resistivity
Ωm
conductivity
Ω-1m-1
insulators
semiconductors
conductors
10+18
10+16
10+14
10+12
10+10
10+8
10+6
10+4
10+2
1
10-2
10-4
10-6
10-8
10-18
10-16
10-14
10-12
10-10
10-8
10-6
10-4
10-2
1
10+2
10+4
10+6
10+8
silica, alumina
ceramic insulators
gallium arsenide
intrinsic silicon
extrinsic silicon
graphite
metals, pure
and alloyed
superconductors
much further down
polystyrene
organic polymers
polyvinylidene difluoride
lead borosilicate glass
inorganic glasses
soda lime glass
electron hopping
in metal oxides
nichrome
aluminium
silver, copper

What good are ceramics for an electrical application?

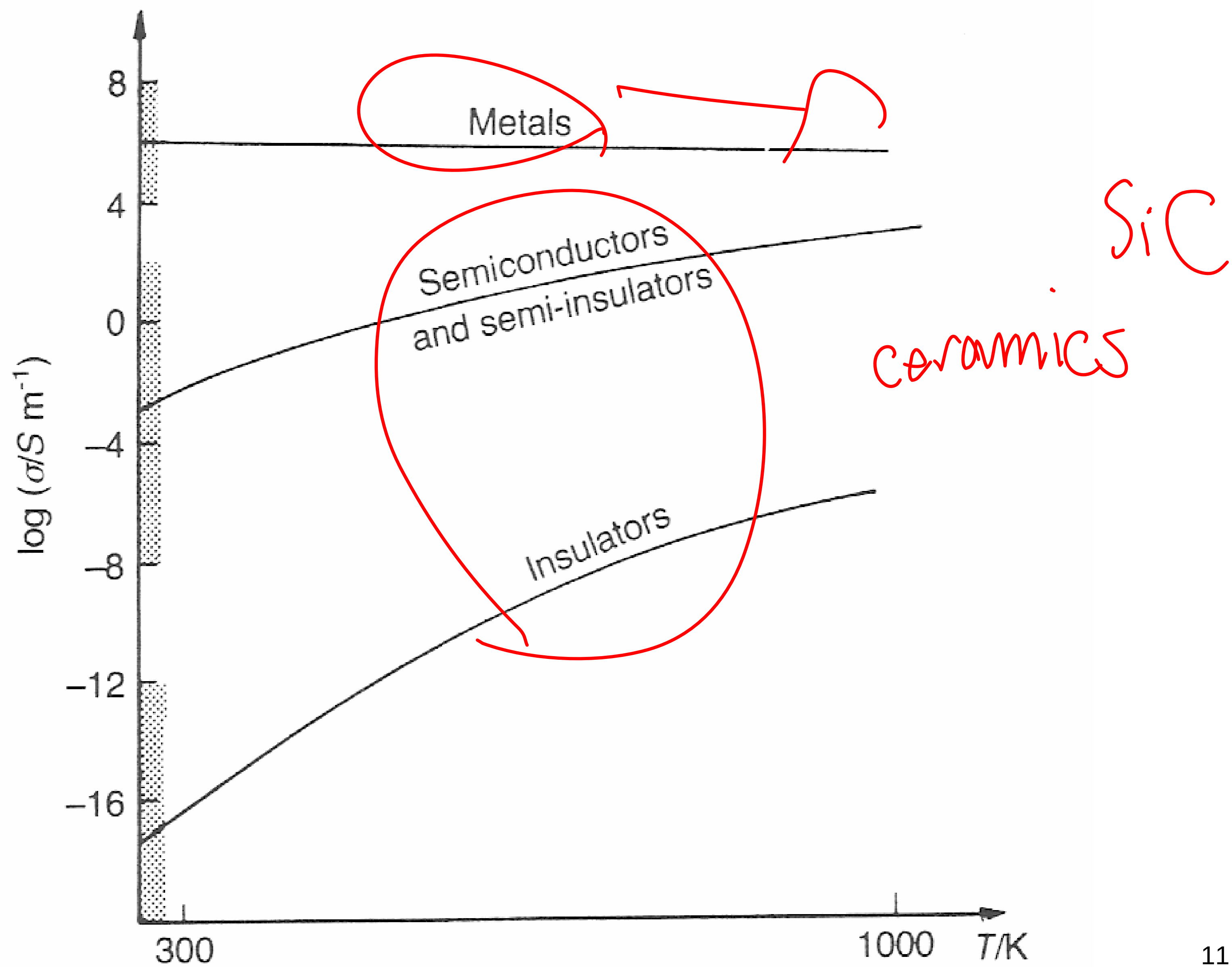
- **Insulator**

- **Store electric charge (dielectric)**

- **Conductor!?!?!?** SiC

Resistor → Heating element

Conduction in an ionic material



Conduction in an ionic material

- $\sigma_T = \sigma_{electronic} + \sigma_{ionic}$

small

units

$$\mu_I = \frac{n_I e D_I}{k_b T}$$

Na^+

Mg^{2+}

$$\frac{m^2}{V \cdot S}$$

$$\frac{\frac{\#\ charges}{ion}\ (C)\ (m^2/s)}{\frac{J}{atom\ K}\ K}$$

atom

$$J/C \cdot S$$

- **Problem 18.48**
  - **At temperatures between 540ºC(813 K) and 727ºC(1000 K), the activation energy and pre-exponential for the diffusion coefficient of Na^+ in NaCl are 173,000 J/mol and 4.0×10^{-4} m^2/s, respectively. Compute the mobility for an Na^+ ion at 600ºC**

Ceramics are everywhere…

- High temperature heating elements
- Gas sensors
- Microelectronics
- Fuel cells S.O.F.C.
- Batteries
- Dielectrics
- Thick and thin film resistors ~ ohmic
- Specialized devices
  - Piezoelectrics
  - Pyroelectrics

Table 7.1 Some common electrical ceramics.

Ceramic		Crystalline phases	Glassy phase = SiO_2+	Made from
Porcelain	Triaxial	Quartz (SiO_2) Mullite $(Al_2O_3)_2(SiO_2)_3$	Al, K	45% clay e.g. kaolin (China clay) $Al_2(Si_2O_5)(OH)_4$ 35% flux e.g. feldspar $KAlSi_3O_8$ 20% filler e.g. quartz: flint or sand SiO_2
	Aluminous	Al_2O_3	Al, Mg	95% alumina Al_2O_3 5% talc (steatite) $Mg_3(Si_2O_5)_2(OH)_2$ (very similar to clay) or as for triaxial porcelain with flint replaced by alumina
Steatite		Enstatite $(MgO)(SiO_2)$ (mainly)	Mg	15% clay 83% talc 2% chalk ($CaCO_3$)
Cordierite		Cordierite $(MgO)_2(Al_2O_3)_2(SiO_2)_5$	Mg	80% clay 20% talc
Alumina		Alumina (Al_2O_3)	—	Bauxite $(Al_2O_3)(H_2O)_2$
Barium titanate		$BaTiO_3$ (= BaO-TiO_2)	—	Barium carbonate ($BaCO_3$) and rutile (TiO_2)

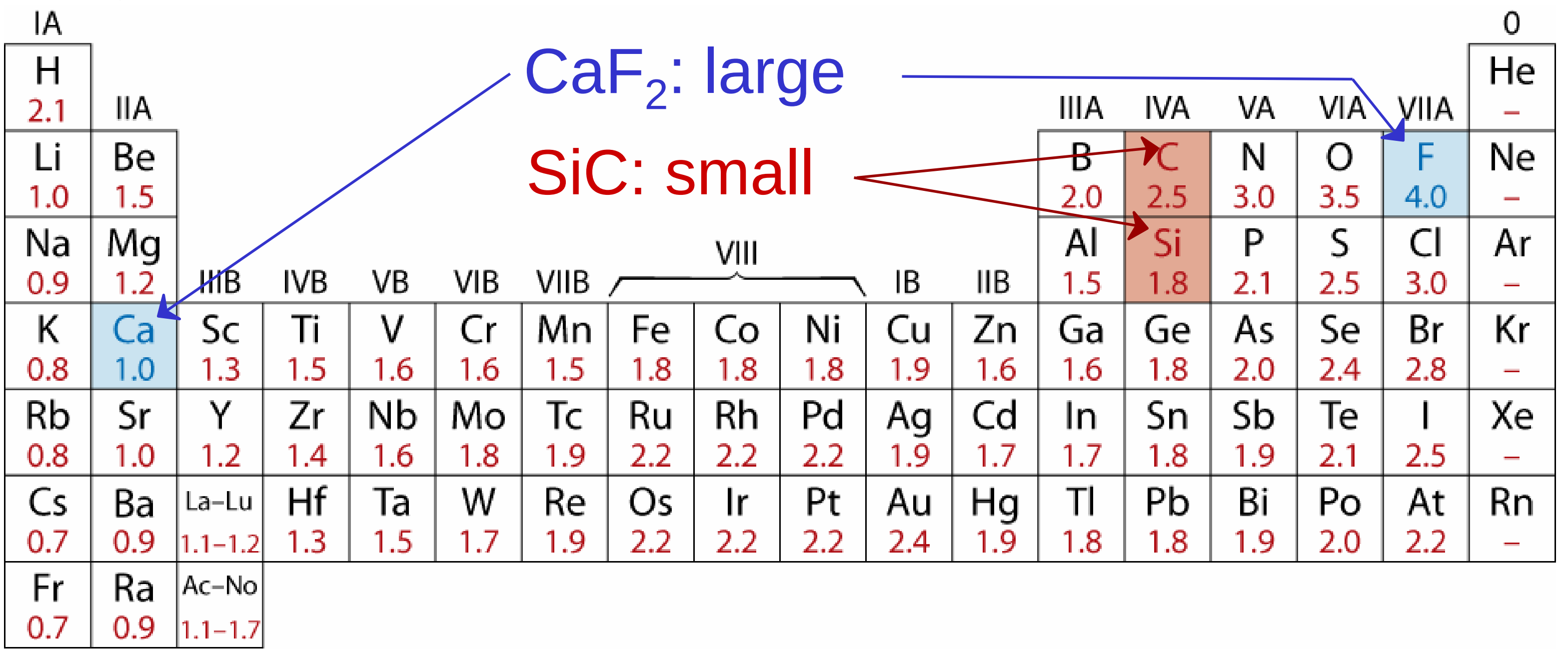
Table 18.5 Dielectric Constants and Strengths for Some Dielectric Materials

Material	*Dielectric Constant* 60 Hz	*Dielectric Constant* 1 MHz	*Dielectric Strength (V/mil)*[a]
	Ceramics		
Titanate ceramics	—	15–10,000	50–300
Mica	—	5.4–8.7	1000–2000
Steatite (MgO–SiO_2)	—	5.5–7.5	200–350
Soda–lime glass	6.9	6.9	250
Porcelain	6.0	6.0	40–400
Fused silica	4.0	3.8	250
	Polymers		
Phenol-formaldehyde	5.3	4.8	300–400
Nylon 6,6	4.0	3.6	400
Polystyrene	2.6	2.6	500–700
Polyethylene	2.3	2.3	450–500
Polytetrafluoroethylene	2.1	2.1	400–500

[a] One mil = 0.001 in. These values of dielectric strength are average ones, the magnitude being dependent on specimen thickness and geometry, as well as the rate of application and duration of the applied electric field.

Ceramic Bonding

- 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.

Ceramic Crystal Structures

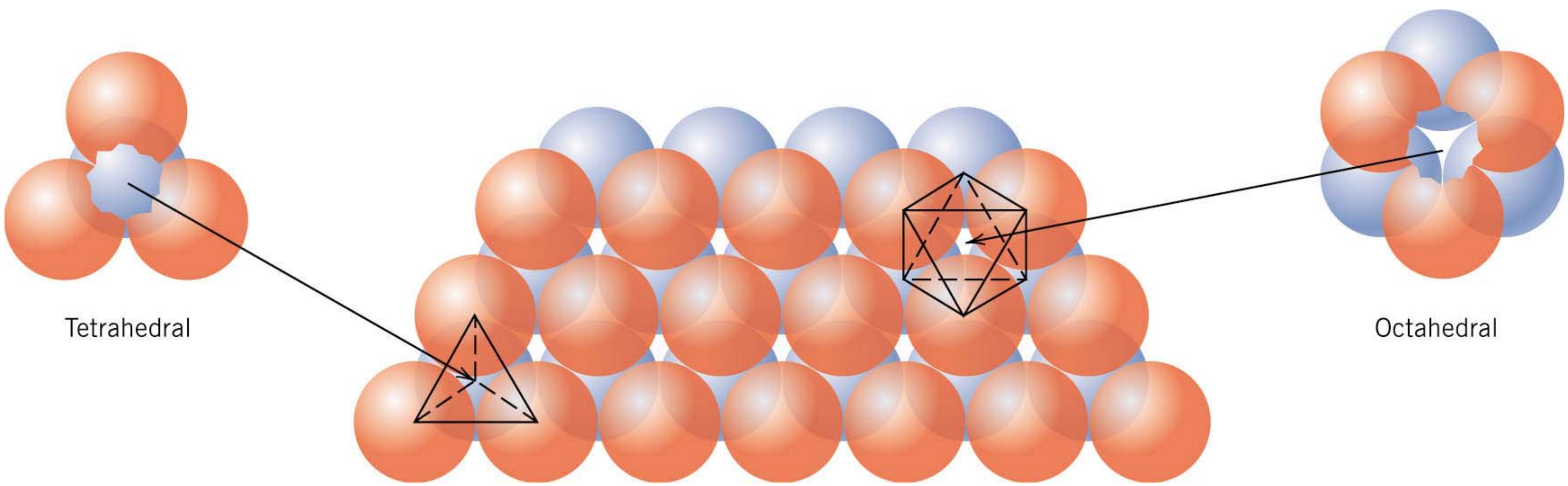
Al_2O_3 O^{2-}

Oxide structures

– oxygen anions much larger than metal cations

– close packed oxygen in a lattice (usually FCC)

– cations in the holes of the oxygen lattice



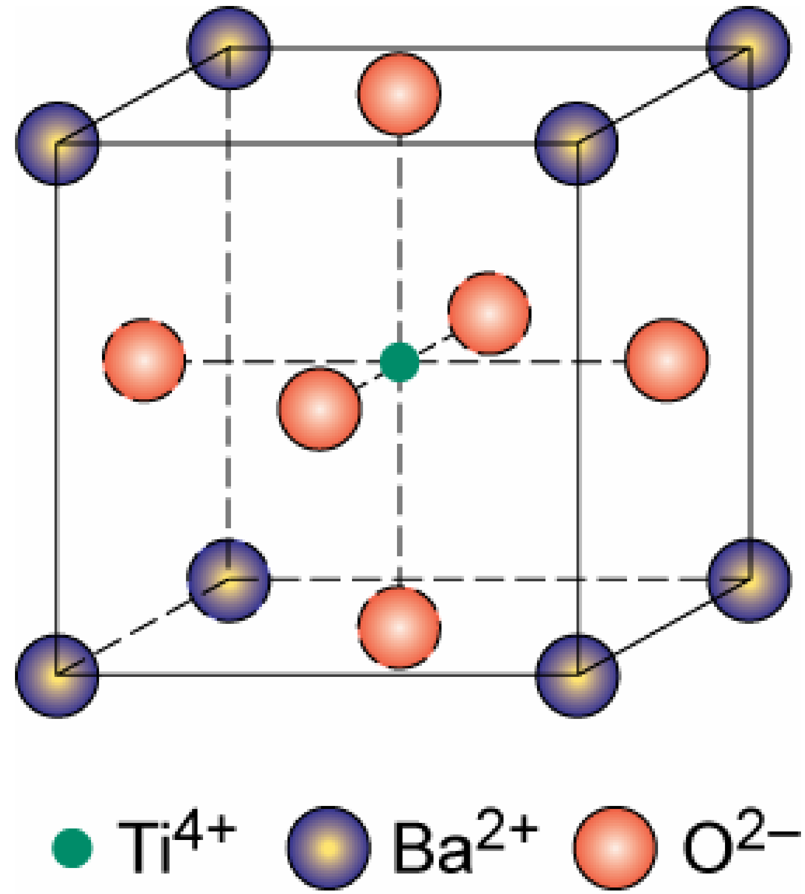
ABX_3 Crystal Structures

- Perovskite

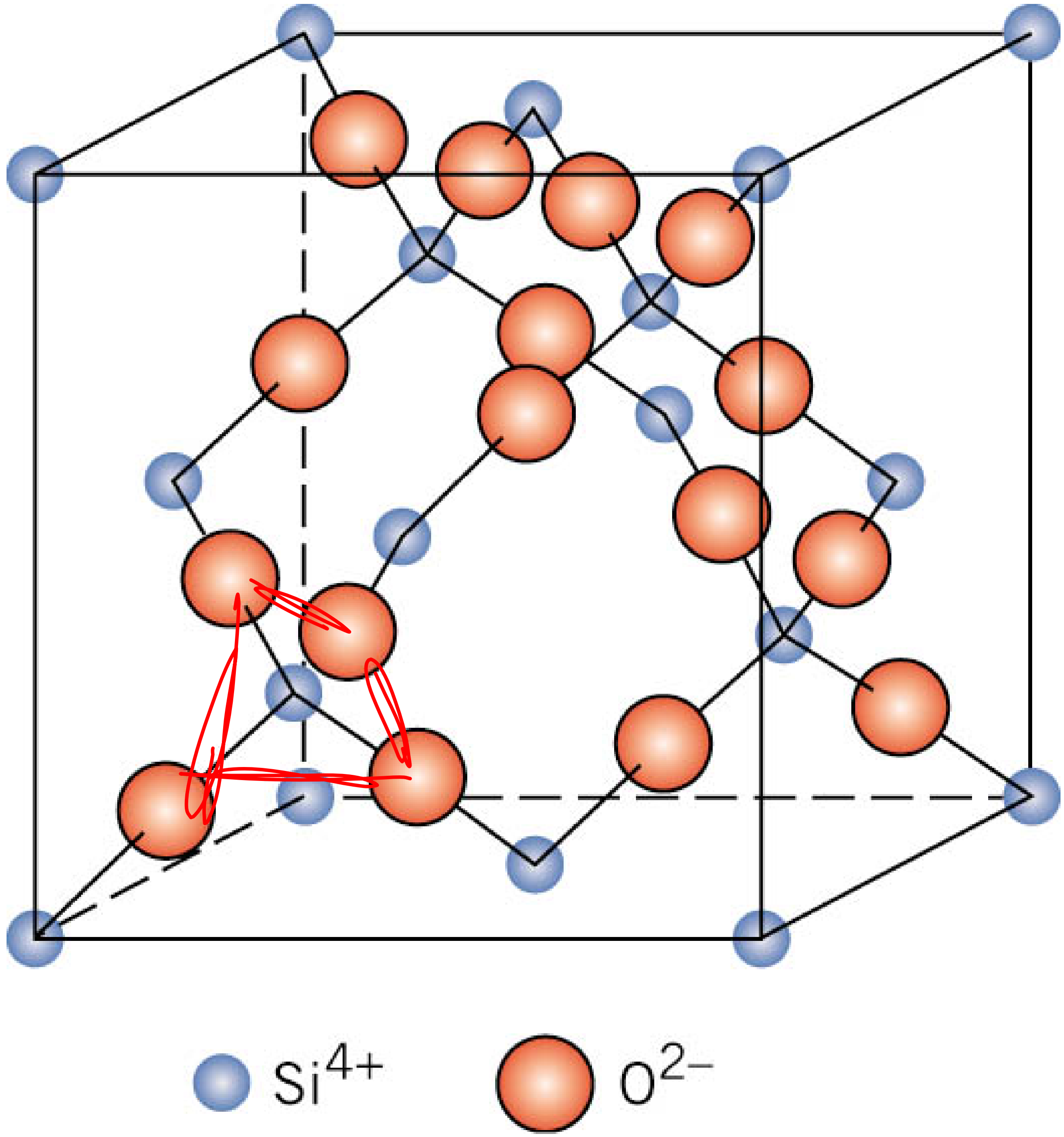
Ex: complex oxide

$BaTiO_3$

percent ionic



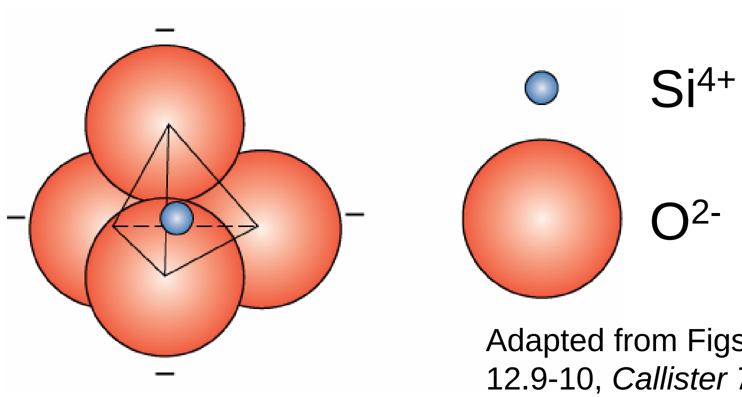
Adapted from Fig. 12.6, *Callister 7e.*



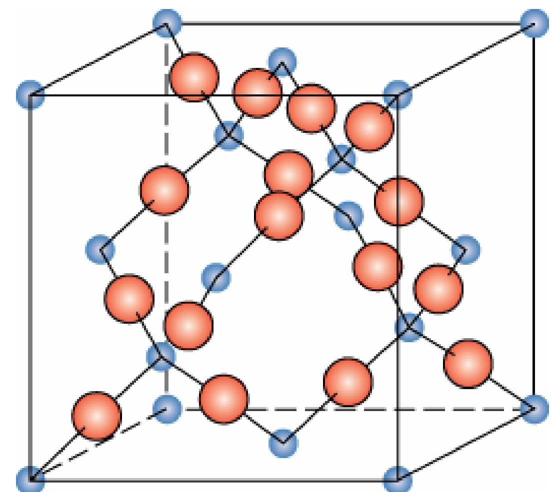
Si4+
O2−

Silicate Ceramics

Most common elements on earth are Si & O



Adapted from Figs. 12.9-10, *Callister 7e.*

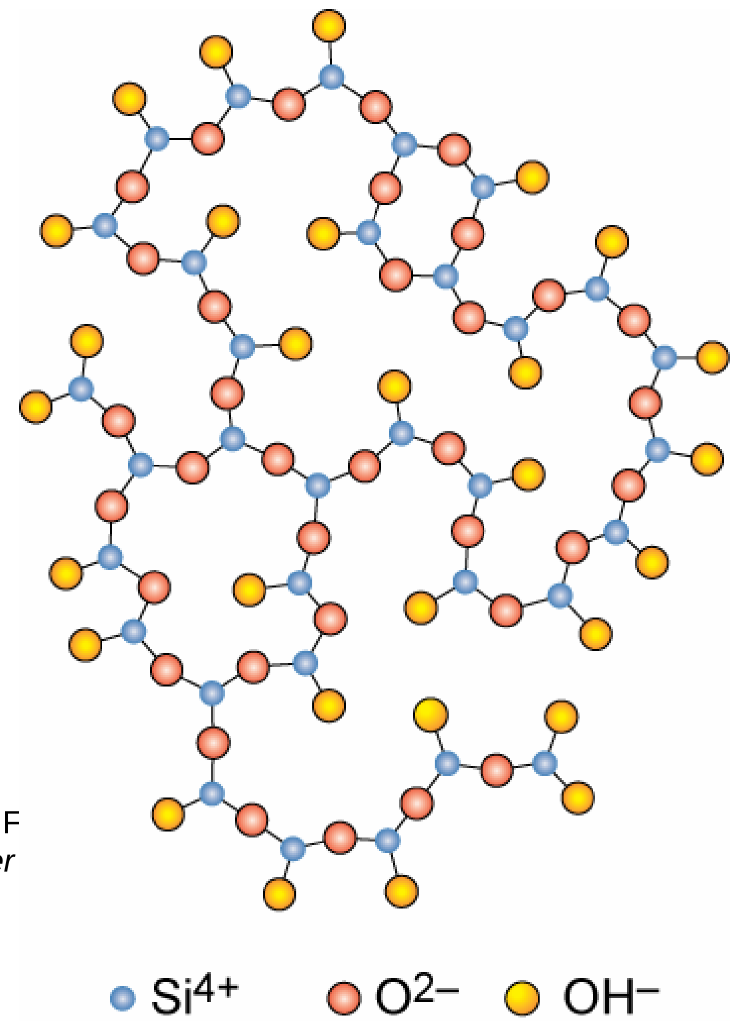


crystobalite

- SiO_2 (silica) structures are quartz, crystobalite, & tridymite
- The strong Si-O bond leads to a strong, high melting material (1710ºC)

Amorphous Silica

- Silica gels - amorphous SiO_2
  - Si^{4+} and O^{2-} not in well-ordered lattice
  - Charge balanced by H^+ (to form OH^-) at "dangling" bonds
    - very high surface area > 200 m^2/g
  - SiO_2 is quite stable, therefore unreactive
    - makes good catalyst support



Adapted from F 12.11, *Callister*

Integrated Circuit Devices

thermally grown
CVD chemical vapor deposition

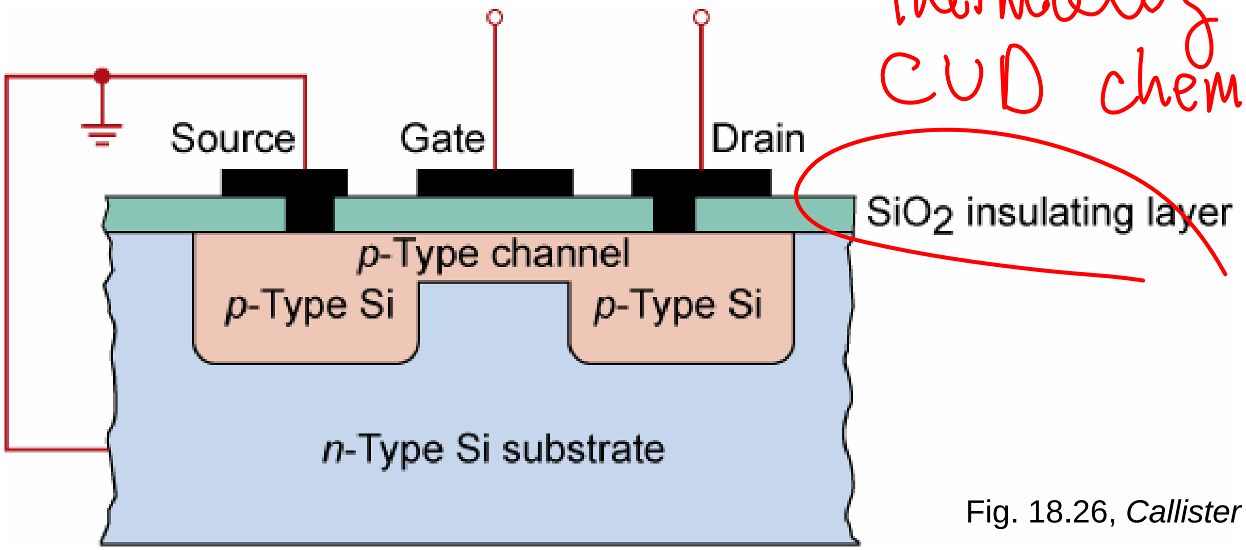


Fig. 18.26, *Callister 6e*.

Ceramics

- **Bonding ranges from ionic to covalent**
  - **Electrons are localized; leads to insulating or semiconducting properties**

electronic

- **Bonding is constrained**
  - **Slip does not occur readily**
  - **Plasticity is very minimal, materials are often brittle**

Taxonomy of Ceramics

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

Adapted from Fig. 13.1 and discussion in Section 13.2-6, *Callister 7e.*

- Properties:
  - -- T_m for glass is moderate, but large for other ceramics.
  - -- Small toughness, ductility; large moduli & creep resist.

$0.4 T_m$

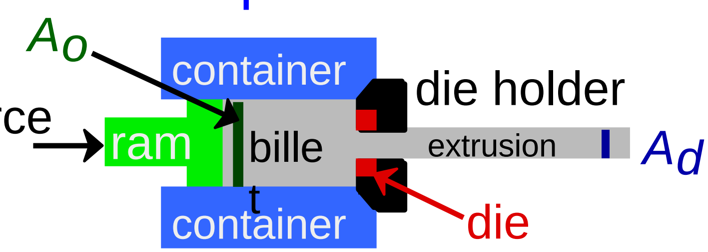
- Applications:
  - -- High *T*, wear resistant, novel uses from charge neutrality.
- Fabrication
  - -- some glasses can be easily formed
  - -- other ceramics can not be formed or cast.

Ceramic Fabrication Methods-IIA

GLASS FORMING | **PARTICULATE FORMING** | CEMENTATION

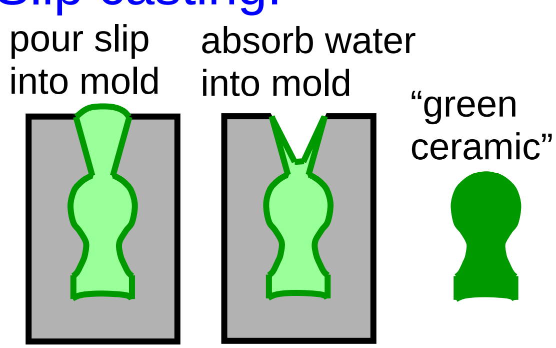
- Milling and screening: desired particle size
- Mixing particles & water: produces a "slip"
- Form a "green" component

  --Hydroplastic forming:
  extrude the slip (e.g., into a pipe)

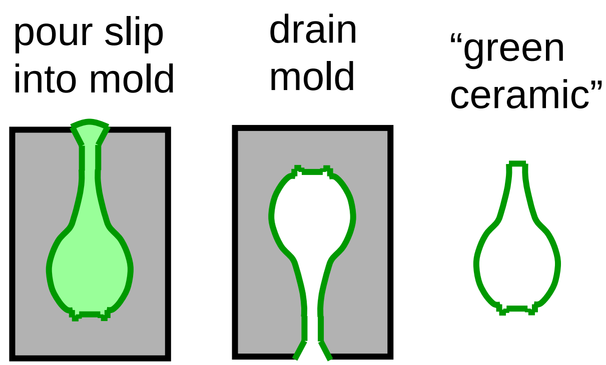


Adapted from Fig. 11.8 (c), *Callister 7e*.

  --Slip casting:



solid component



hollow component

Adapted from Fig. 13.12, *Callister 7e*. (Fig. 13.12 is from W.D. Kingery, *Introduction to Ceramics*, John Wiley and Sons, Inc., 1960.)

- Dry and fire the component

Clay Composition

A mixture of components used

(50%) 1. Clay

(25%) 2. Filler – e.g. quartz (finely ground)

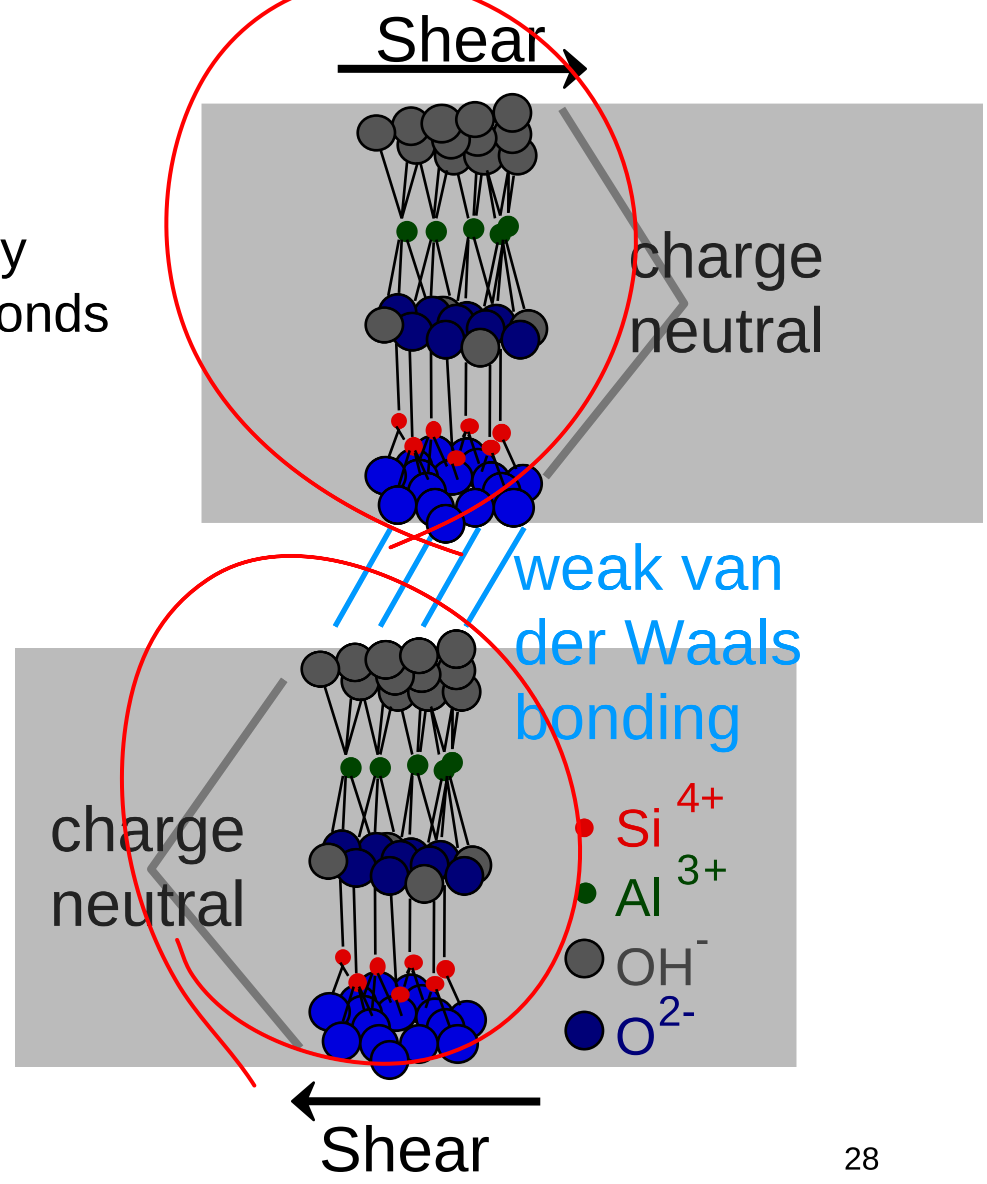
(25%) 3. Fluxing agent (Feldspar)

binds it together

aluminosilicates + K^+, Na^+, Ca^+

Features of a Slip

- Clay is inexpensive
- Adding water to clay
  - -- allows material to shear easily along weak van der Waals bonds
  - -- enables extrusion
  - -- enables slip casting

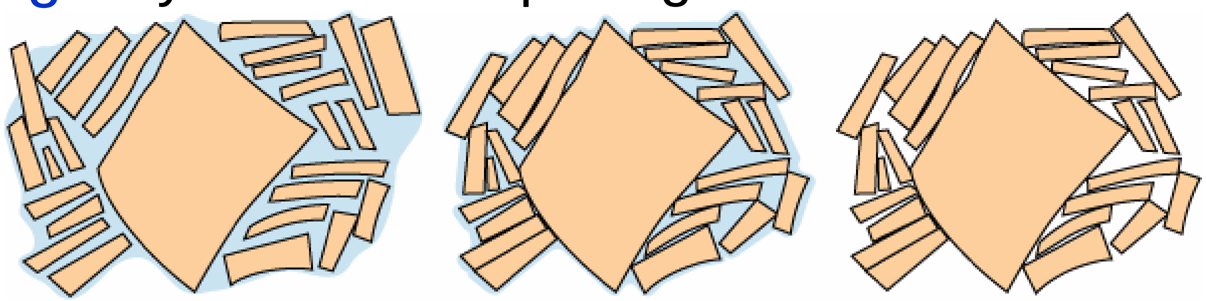


- Structure of Kaolinite Clay:

Adapted from Fig. 12.14, *Callister 7e*. (Fig. 12.14 is adapted from W.E. Hauth, "Crystal Chemistry of Ceramics", *American Ceramic Society Bulletin*, Vol. 30 (4), 1951, p. 140.)

Drying and Firing

- Drying: layer size and spacing decrease.



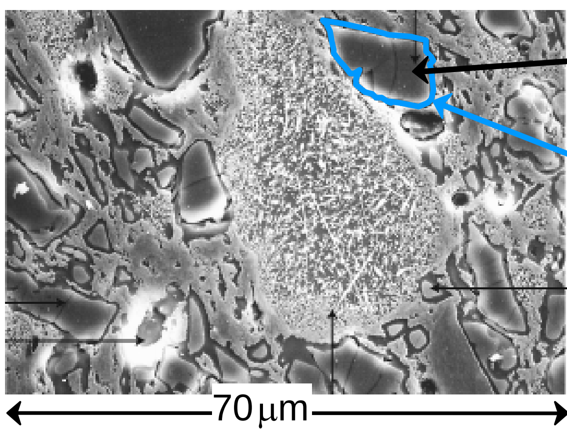
Adapted from Fig. 13.13, *Callister 7e*. (Fig. 13.13 is from W.D. Kingery, *Introduction to Ceramics*, John Wiley and Sons, Inc., 1960.)

wet slip   partially dry   "green" ceramic

Drying too fast causes sample to warp or crack due to non-uniform shrinkage

- Firing:
  --*T* raised to (900-1400°C)
  --vitrification: liquid glass forms from clay and flows between SiO_2 particles. Flux melts at lower *T*.

micrograph of porcelain



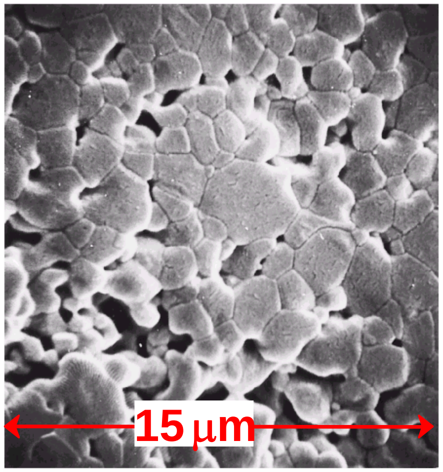
Adapted from Fig. 13.14, *Callister 7e*.
(Fig. 13.14 is courtesy H.G. Brinkies, Swinburne University of Technology, Hawthorn Campus, Hawthorn, Victoria, Australia.)

Ceramic Fabrication Methods-IIB

GLASS FORMING | PARTICULATE FORMING | CEMENTATION

Sintering: useful for both clay and non-clay compositions.

- Procedure:
  -- produce ceramic and/or glass particles by grinding
  -- place particles in mold
  -- press at elevated *T* to reduce pore size.
- Aluminum oxide powder:
  -- sintered at 1700°C
  for 6 minutes.



Adapted from Fig. 13.17, *Callister 7e*. (Fig. 13.17 is from W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, *Introduction to Ceramics*, 2nd ed., John Wiley and Sons, Inc., 1976, p. 483.)

Powder Pressing

Sintering - powder touches - forms neck & gradually neck thickens

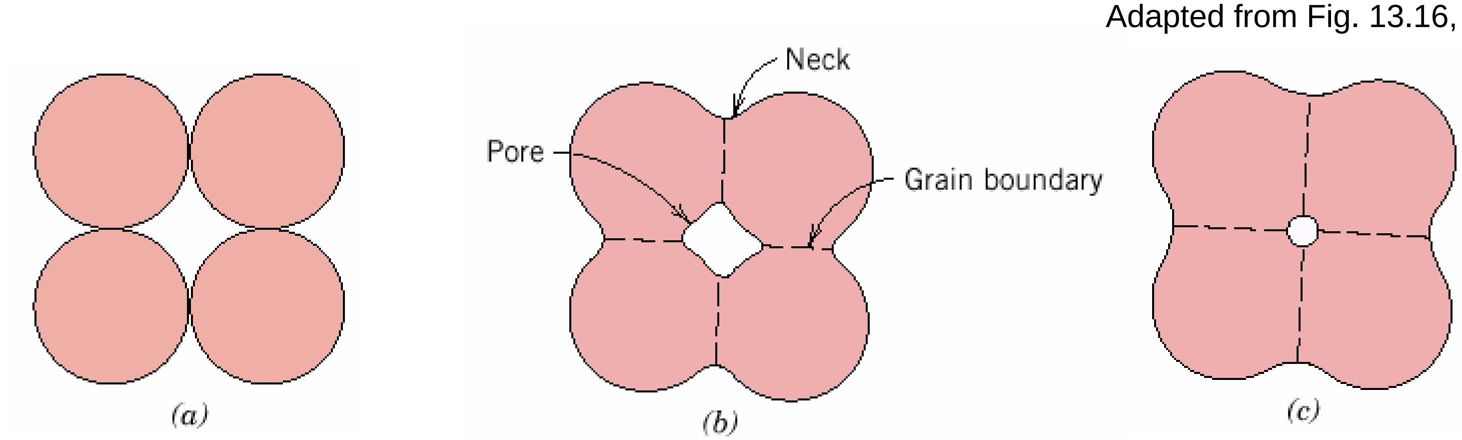
– add processing aids to help form neck
– little or no plastic deformation

Uniaxial compression - compacted in single direction

Isostatic (hydrostatic) compression - pressure applied by fluid - powder in rubber envelope

Hot pressing - pressure + heat

Adapted from Fig. 13.16, *Callister 7e*.



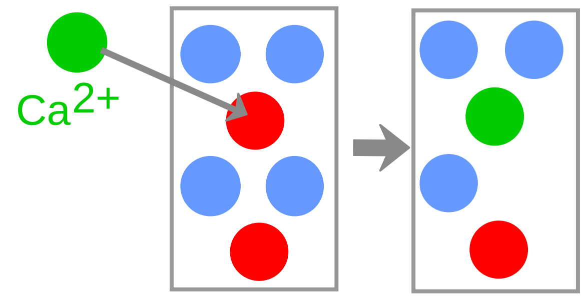
Ceramic Fabrication Methods-III

GLASS FORMING | PARTICULATE FORMING | **CEMENTATION**

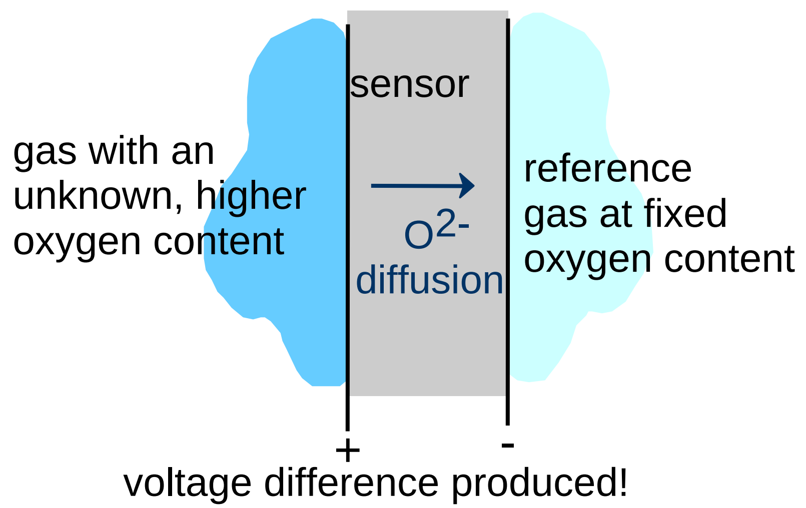
- Produced in extremely large quantities.
- Portland cement:
  -- mix clay and lime bearing materials
  -- calcinate (heat to 1400°C)
  -- primary constituents:
     tri-calcium silicate
     di-calcium silicate
- Adding water
  -- produces a paste which hardens
  -- hardening occurs due to hydration (chemical reactions with the water).
- Forming: done usually minutes after hydration begins.

Application: Sensors

- Example: Oxygen sensor ZrO_2
- Principle: Make diffusion of ions fast for rapid response.
- Approach:
  Add Ca impurity to ZrO_2:
  -- increases O^{2-} vacancies
  -- increases O^{2-} diffusion rate
- Operation:
  -- voltage difference produced when O^{2-} ions diffuse from the external surface of the sensor to the reference gas.



A Ca^{2+} impurity removes a Zr^{4+} and a O^{2-} ion.



Applications: Advanced Ceramics

Electronic Packaging

- Chosen to securely hold microelectronics & provide heat transfer
- Must match the thermal expansion coefficient of the microelectronic chip & the electronic packaging material. Additional requirements include:
  - good heat transfer coefficient
  - poor electrical conductivity
- Materials currently used include:
    - Boron nitride (BN)
    - Silicon Carbide (SiC)
    - Aluminum nitride (AlN)
      - thermal conductivity 10x that for Alumina
      - good expansion match with Si

Next time…

- More on ceramics in electrical engineering (based on the Electroceramics by A.J. Moulsen and J.M. Herbert)
  - High temperature heating elements
  - Gas sensors
  - Microelectronics
  - Fuel cells
  - Batteries
  - Dielectrics
  - Thick and thin film resistors
  - Piezoelectrics
  - Pyroelectrics
- Polymers