

## Chapter 12 Structures and properties of ceramics

- ☐ Bonding in ceramics
- ☐ Imperfection in ceramics
- ☐ Electric properties of ceramics
- ☐ Ceramic phase diagrams
- ☐ Brittle fracture of ceramics
- ☐ Stress-strain behavior
- ☐ Mechanisms of plastic deformation

## Ceramic bonding

**□ Bonding:**

--Mostly ionic, some covalent.

--% ionic character increases with difference in electronegativity.

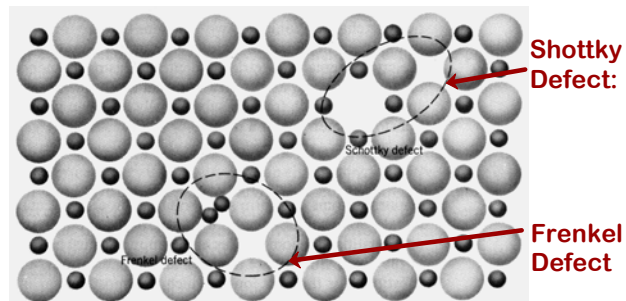
Table of Electronegativities

IA		IIA		IIIA		IVA		VA		VIA		VIIA		VIIIA	
H 2.1															
Li 1.0	Be 1.5														
Na 0.9	Mg 1.2														
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Ni 1.8	Cu 1.9	Zn 1.8	Ga 1.6	As 2.0	Br 2.8	Kr 3.0	
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.9	Tc 2.2	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	Sn 1.8	Sb 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	La-Lu 1.1-1.3	Hf 1.3	Ta 1.5	W 1.9	Re 2.2	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
Fr 0.7	Ra 0.9	89-102 Ac-Lr 1.1-1.7													

CaF<sub>2</sub>: large  
SiC: small

## Imperfections in ceramics

- Schottky defects: --a paired set of cation and anion vacancies.
- Frenkel defects: an atom from a lattice site to an interstitial position

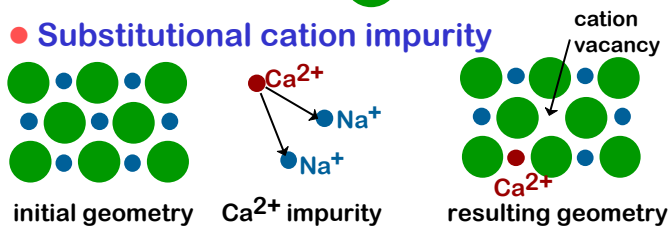


## Point defects in Ionic Crystals

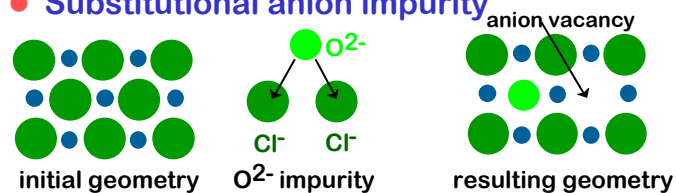
- Impurities must also satisfy charge balance

• Ex: NaCl  $\text{Na}^+$  (blue dot)  $\text{Cl}^-$  (green circle)

### • Substitutional cation impurity



### • Substitutional anion impurity



## Point Defects in Ionic Crystals

### □ Defect examples for other ionic crystal systems

☑ In simple ionic crystals, both Schottky and Frenkel defects occur, but the concentration of one type generally exceeds that of the other

- Schottky defects dominate in alkali halides
- Cation Frenkel defects dominate in AgCl and AgBr
- Anion Frenkel defects dominate in CaF<sub>2</sub> and fluorites

## Electric Properties

### □ Electrical conductivity: the mobility of charged point defects

$$\sigma = n(\mu^+ + \mu^-)e$$

$$\approx n\mu^+e \approx \exp\left(-\frac{E_a}{KT}\right)$$

Since the cation vacancy is more mobile than anion vacancy

$n$ -- defect concentration

$e$ -- charge

$\mu$ -- mobility

## Electric Properties (continue)

### □ Electrical conductivity

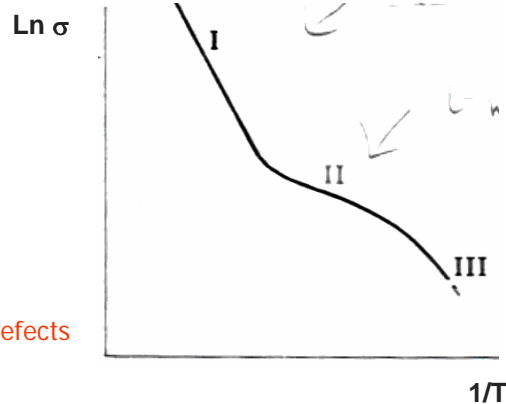
- Region I: Schottky defects

$$E_a = E_m + 1/2(E_+ + E_-)$$

- Region II: Cation vacancies

$$E_a = E_m$$

- Region III: cation vacancies, impurity ions, clustering of defects

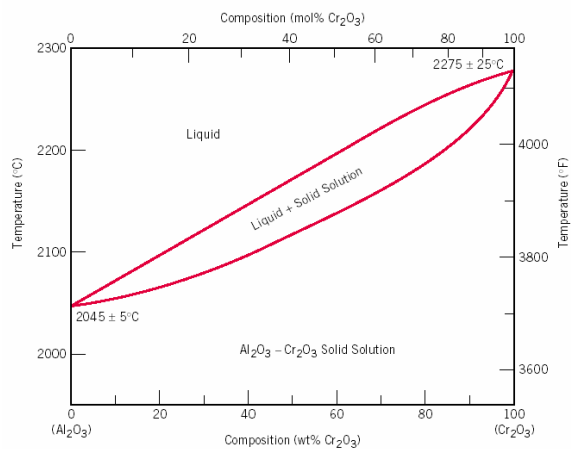


Effect of temperature on electrical conductivity of a NaCl crystal containing a small conc. of a divalent cation

## Ceramic phase diagram

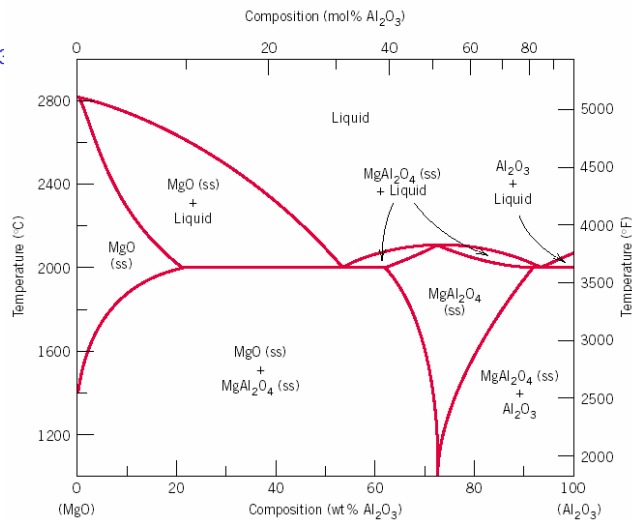
### □ The $\text{Al}_2\text{O}_3$ - $\text{Cr}_2\text{O}_3$ system

- Isomorphous
- In solid solution  $\text{Al}^{3+}$  substitute  $\text{Cr}^{3+}$
- Al and Cr should have similar radius and same charge
- Both  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  have the same crystal structure



## Ceramic phase diagram

- The  $\text{Mg}_2\text{O}-\text{Al}_2\text{O}_3$  system
- Intermediate phase -- spinel compound

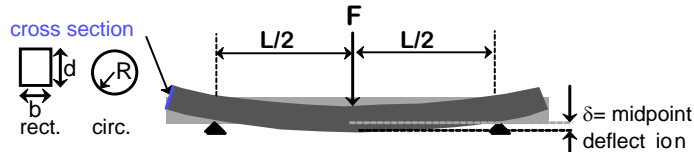


## Stress-strain behavior

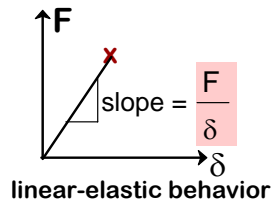
- Flexural testing replace tensile testing
- Reasons for not a standard tension test
  - difficult to prepare and test specimens having a required geometry
  - difficult to grip brittle materials without fracturing them
  - ceramics fail after only about 0.1% strain and samples are difficult to align without experiencing bending stress

## 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.



- Determine elastic modulus according to:

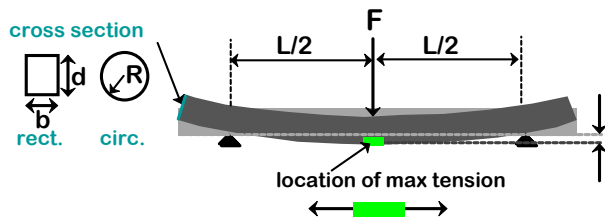


$$E = \frac{F}{\delta} \frac{L^3}{4bd^3} = \frac{F}{\delta} \frac{L^3}{12\pi R^4}$$

rect. cross section      circ. cross section

## Measuring strength

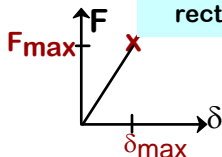
- 3-point bend test to measure room T strength.



- Flexural strength:

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

rect.      circ.



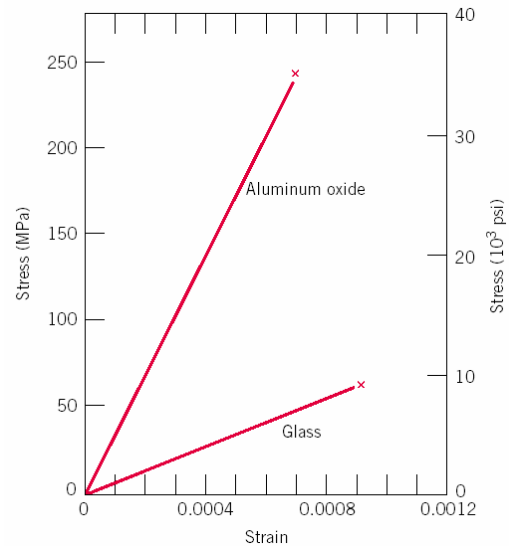
- Typ. values:

Material	$\sigma_{fs}$ (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 12.3, Callister 6e.

## Elastic behavior

- Typical stress-strain behavior to fracture for aluminum oxide and glass



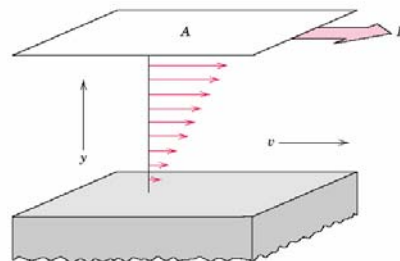
## Mechanisms of plastic deformation

- Crystalline ceramics are brittle

- Covalent bonds are relatively strong
- There are limited numbers of slip systems
- Dislocation structures are complex

- Noncrystalline ceramics

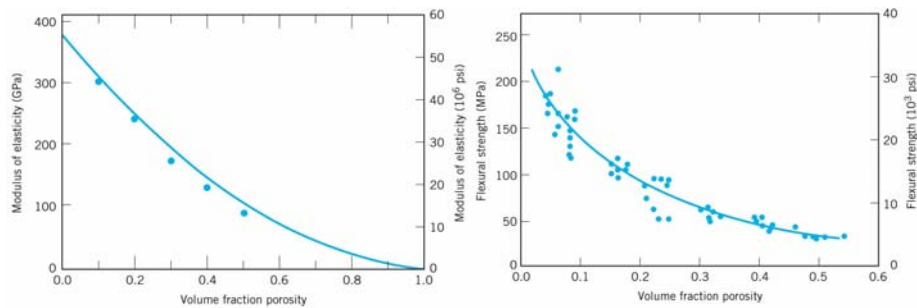
- Plastic deformation does not occur by dislocation motion for noncrystalline ceramics
- Viscosity is a measure of non-crystalline material's resistance to deformation



## Influence of porosity on mechanical behavior

□  $E = E_0(1 - 1.9P + 0.9P^2)$

□  $\sigma_{fs} = \sigma_0 \exp(-nP)$



## Hardness

**Table 13.6** Approximate Knoop Hardness (100 g load) for Seven Ceramic Materials

<i>Material</i>	<i>Approximate Knoop Hardness</i>
Diamond (carbon)	7000
Boron carbide (B <sub>4</sub> C)	2800
Silicon carbide (SiC)	2500
Tungsten carbide (WC)	2100
Aluminum oxide (Al <sub>2</sub> O <sub>3</sub> )	2100
Quartz (SiO <sub>2</sub> )	800
Glass	550



## Summary

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- Ceramic materials have mostly ionic bonding & some covalent bonding.
- Defects
  - must preserve charge neutrality
  - have a concentration that varies exponentially w/T.
- Room T mechanical response is elastic, but fracture is brittle, with negligible ductility.
- Elevated T creep properties are generally superior to those of metals (and polymers).