Mat E 272

Lectures 22-23: Introduction to Ceramic Materials

November 26 & 28, 2001

Introduction:

The primary emphasis of this class has previously been on the structure and properties of pure metals and metal alloys. At this point we turn our attention to another distinct class of materials called *ceramics*. Unlike metals, there is no single element that we classify as belonging to this category of materials. Ceramic materials consist of at least two elements (sometimes many more), which makes their crystal structures more complex than those of the comparatively simple metals we have have discussed previously. Ceramics are typically characterized as possessing a high melting temperature (i.e., "refractory"), low electrical conductivity (usually electrical insulators), low coefficients of thermal expansion, and are usually strong in compression, but brittle. There is essentially no dislocation motion in ceramics, which makes their mechanical behavior fundamentally different from that of metals; mechanical properties of ceramics are determined by crack initiation and propagation. Ceramics find extensive applications as insulators (electrical and thermal), building materials (bricks and tiles), cutting and forming tools (diamond, c-BN), pottery, crockery, and sanitary ware.

Ceramic Materials

Definition:

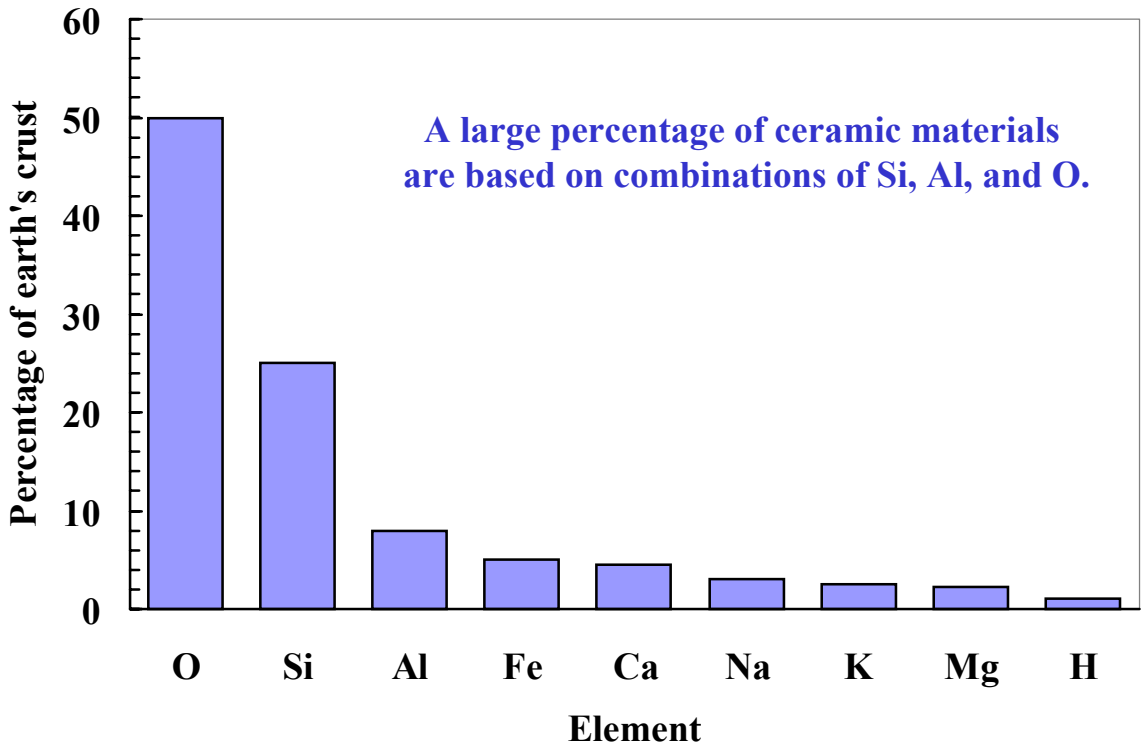
A ceramic material is usually defined as any **inorganic, nonmetallic, crystalline substance**. Glasses, while nonmetallic and inorganic, are amorphous and so do not fall in this category.

Bonding:

Ceramic materials exhibit **ionic** bonding (MgO), **covalent** bonding (SiC), or a **hybrid** of the two (Al_2O_3 - alumina).

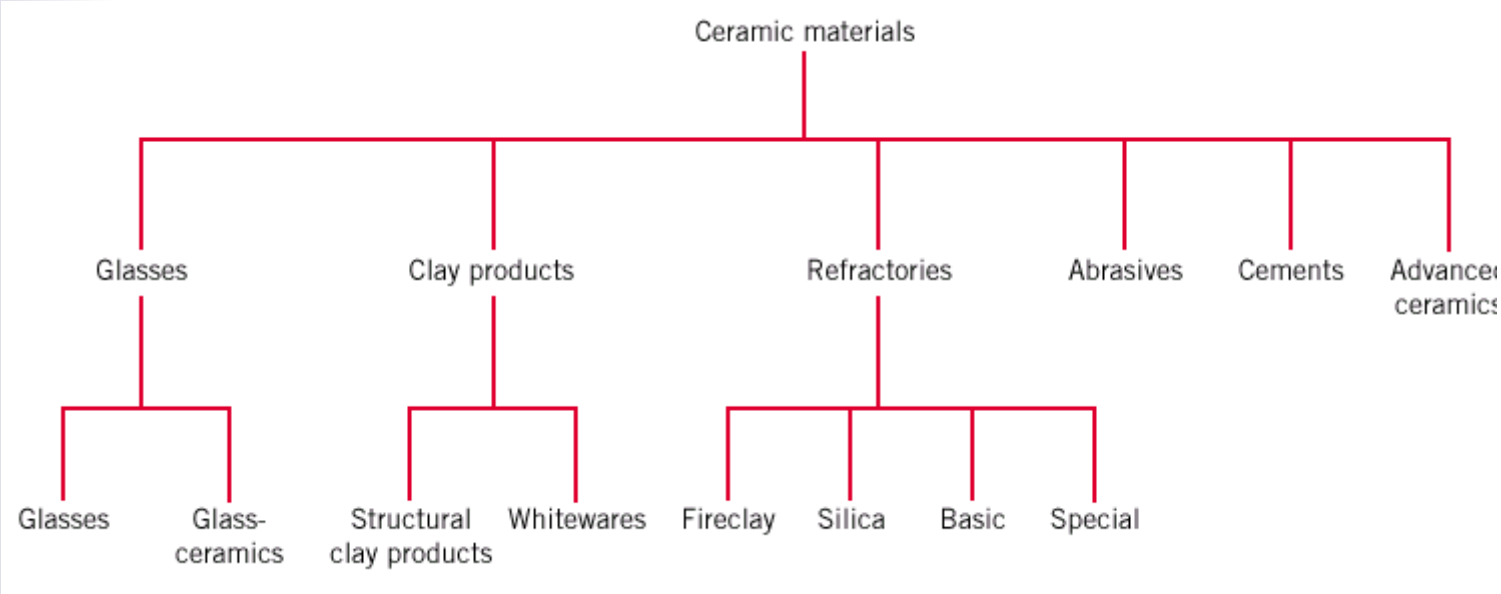
Structures:

Ceramic materials crystallize in a wide variety of structures. There are two main groups; those that possess relatively simple crystal structures such as SiC and MgO, and those based on a SiO_4 tetrahedron, otherwise known as silicates.



Ceramic Materials

How do we classify ceramic materials?



Common ceramic materials

Non-silicate ceramics

chemical formula	common name	chemical formula	common name
Al_2O_3	alumina		
MgO	magnesia	SiC	silicon carbide
$MgAl_2O_4$	spinel	Si_3N_4	silicon nitride
BeO	beryllia	TiC	titanium carbide
ThO_2	thoria	TaC	tantalum carbide
UO_2	uranium dioxide	WC	tungsten carbide
ZrO_2	zirconia	BN	boron nitride
$BaTiO_3$	barium titanate	C	graphite

Silicate ceramics

	composition (wt. %)					
Ceramic	SiO_2	Al_2O_3	K_2O	MgO	CaO	other
Silica	96					4
Firebrick	50-70	45-25				5
Mullite	28	72				-
Electrical porcelain	61	32	6			1
Steatite porcelain	64	5		30		1
Portland cement	25	9			64	2

Ceramic crystal structures

Similar to metal crystal structures but with one important difference…

In ceramics, the lattice sites are occupied by IONS

CATIONS: positively charged ions (usually the smaller of the two)

- electron loss TO the more electronegative atom
- cations are usually metals, from the left side of the periodic table

ANIONS: negatively charged ions (usually the larger of the two)

- electron gain FROM the more electropositive atom
- anions are usually non-metals, from the right side of the periodic table

The fact that the lattice sites are occupied by <u>charged ions</u> has a huge impact on what kind of arrangement the atoms assume, what kind of vacancies are possible, and why slip (plastic deformation) is essentially non-existent...

Ceramic crystal structures

Ceramic crystal structure considerations:

1) **charge neutrality**

the bulk ceramic <u>must</u> remain electrically neutral
this means the NET CHARGE must sum to ZERO

2) **coordination number (CN) depends on atomic size ratio**

CN ≡ number of nearest-neighbor atoms
as r_c/r_a increases,* the cation's CN also increases

What's so important about CN?
CN determines the possible crystal structures
since CN determines crystal structure,
and crystal structure determines physical properties,
therefore, <u>CN determines physical properties</u>

(*) r_c/r_a is simply the ratio of cation radius to anion radius

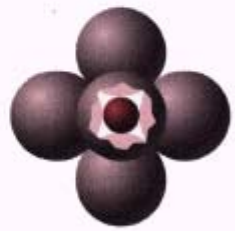
Coordination number

Note that larger coordination numbers correspond to larger cation ions. Rationale: as the atom size increases, it becomes possible to pack more and more atoms around it

crystal structure of the ceramic is determined by the CN:

Cation	*Ionic Radius (nm)*	*Anion*	*Ionic Radius (nm)*
Al^{3+}	0.053	Br^{-}	0.196
Ba^{2+}	0.136	Cl^{-}	0.181
Ca^{2+}	0.100	F^{-}	0.133
Cs^{+}	0.170	I^{-}	0.220
Fe^{2+}	0.077	O^{2-}	0.140
Fe^{3+}	0.069	S^{2-}	0.184
K^{+}	0.138		
Mg^{2+}	0.072		
Mn^{2+}	0.067		
Na^{+}	0.102		
Ni^{2+}	0.069		
Si^{4+}	0.040		
Ti^{4+}	0.061		

Ionic radii for several cations and anions for a coordination number of 6

CN	r_c/r_a	geometry
2	<0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	

Charge neutrality

Role of charge neutrality in determining allowable compositions:

Example: The compounds "MgO_2" or "Cs_2Cl" do not exist. Why not?

Consider the element's electronic valence states:

1) Mg: Mg^{2+} (divalent), O: O^{2-} (divalent)
   net charge per MgO_2 molecule = 1(2+) + 2(2-) = -2
   this is a net negative charge, which is not allowed

2) Cs: Cs^{1+} (monovalent), Cl: Cl^{1-} (monovalent)
   net charge per Cs_2Cl molecule = 2(1+) + 1(1-) = -1
   this is a net positive charge, which is not allowed.

In order to maintain charge neutrality, these elements combine to form MgO and CsCl. With a 1:1 cation to anion ratio, charge neutrality is preserved.

Charge neutrality

Examples of <u>allowable</u> ceramic stoichiometry:

Mn - O: $Mn^{2+}O^{2-}$ **net charge = 1(2+) + 1(2-) = 0**

Mn - F: $Mn^{2+}F_2^{-}$ **net charge = 1(2+) + 2(1-) = 0**

Fe - O: $Fe^{2+}O^{2-}$ **net charge = 1(2+) + 1(2-) = 0**

Fe - O: $Fe^{3+}{}_2O^{2-}{}_3$ **net charge = 2(3+) + 3(2-) = 0**

Ti - O: $Ti^{4+}O^{2-}{}_2$ **net charge = 1(4+) + 2(2-) = 0**

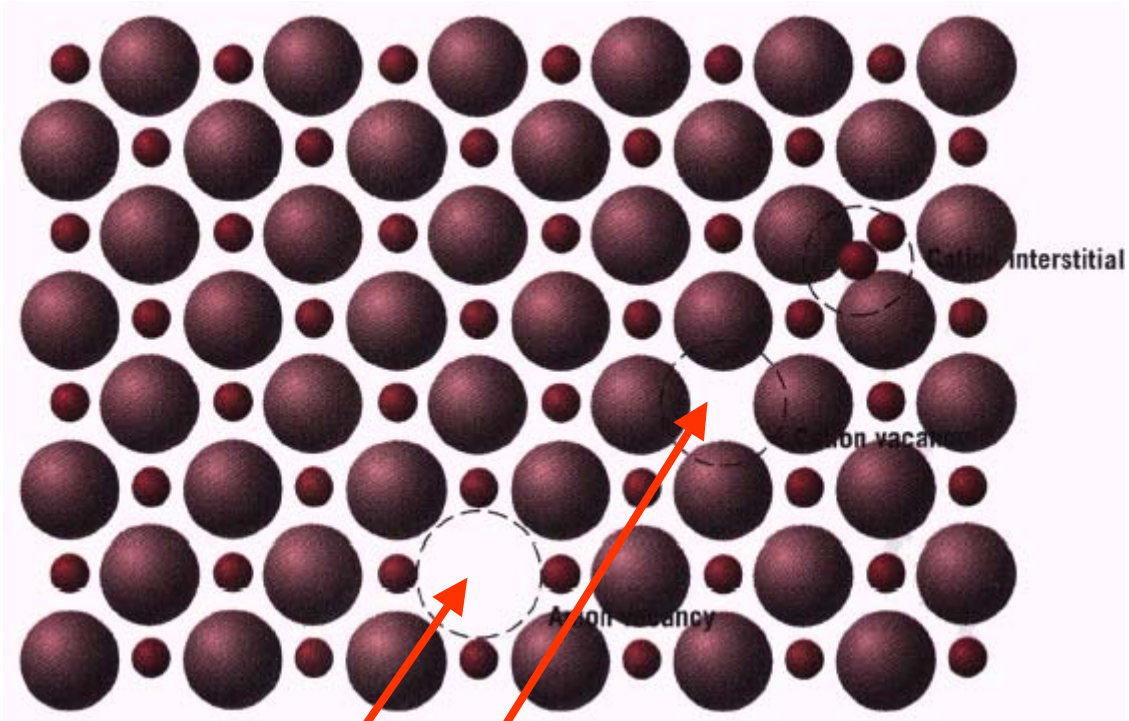
Si - O: $Si^{4+}O^{2-}{}_2$ **net charge = 1(4+) + 2(2-) = 0**

Al - O: $Al^{3+}{}_2O^{2-}{}_3$ **net charge = 2(3+) + 3(2-) = 0**

Defects in ceramic materials

Examples of cation and anion vacancies (and a cation interstitial):

In an ionic ceramic, a cation vacancy must be accompanied by a corresponding anion vacancy in order to maintain charge neutrality.



An anion vacancy

A cation vacancy

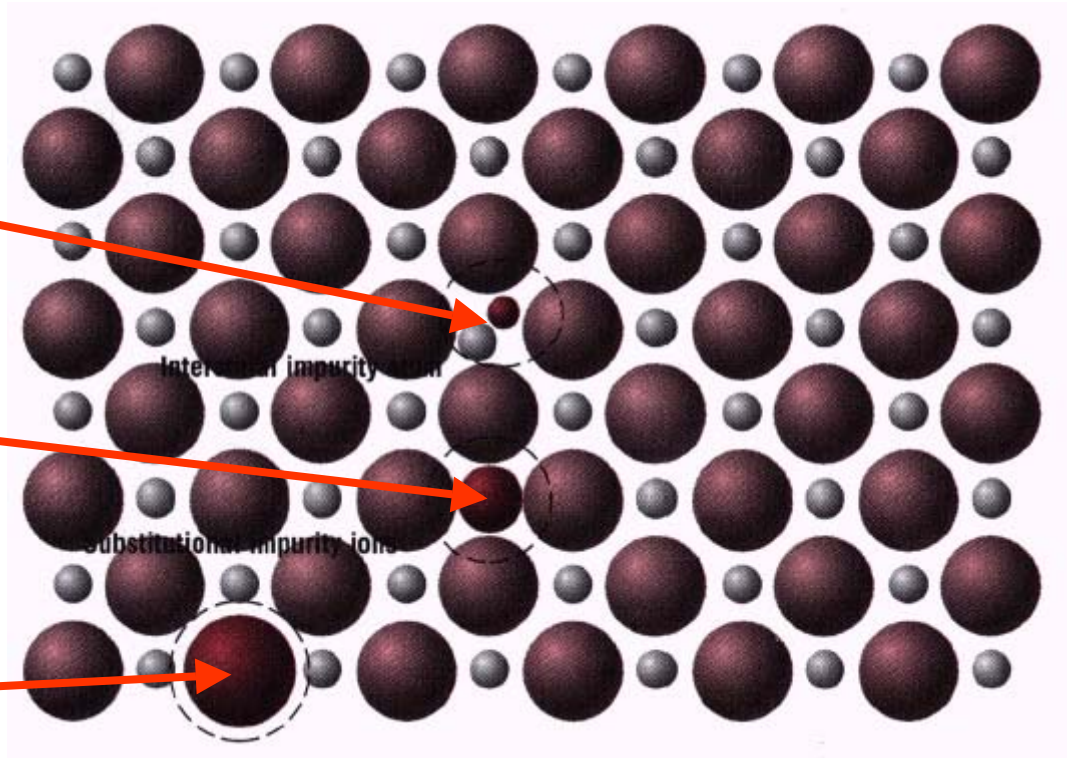
Defects in ceramic materials

Examples of interstitial, anion substitution, and cation substitution in an ionic ceramic compound:

Interstitial impurity ion

Substitutional cation impurity

Substitutional anion impurity

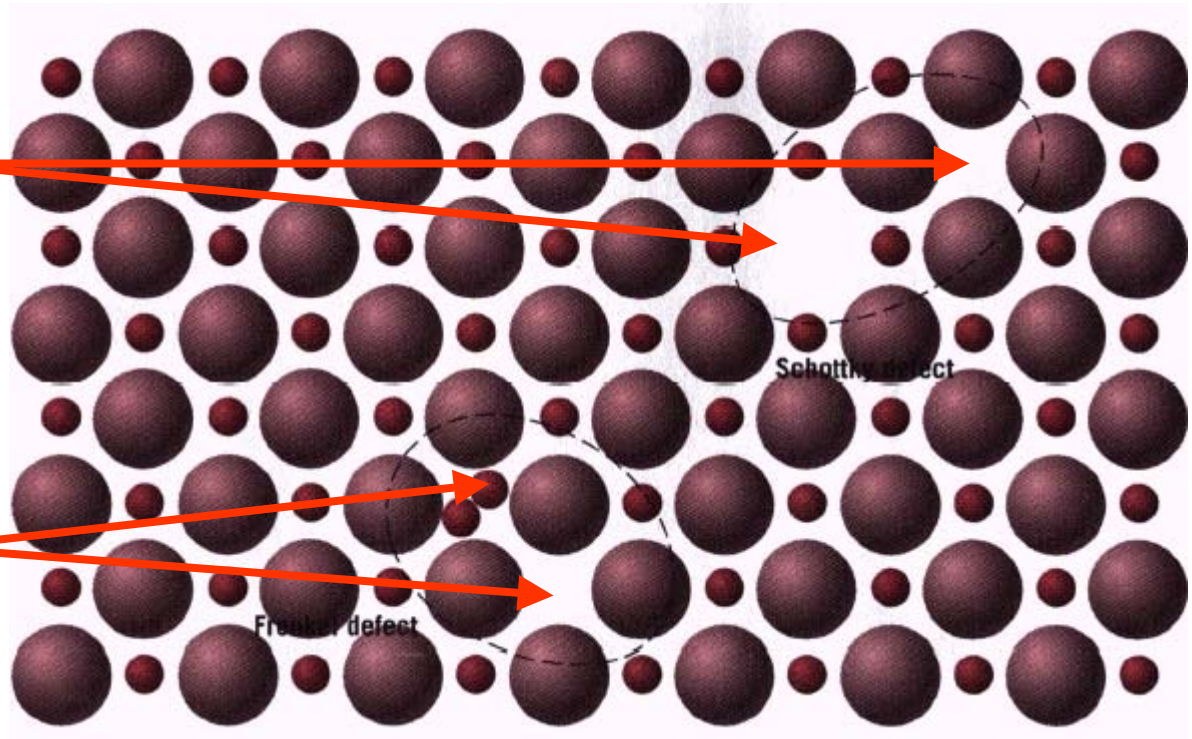


Defects in ceramic materials

<u>Frenkel and Schottky defects</u> are found in ceramics because defects occur in pairs (to maintain charge neutrality):

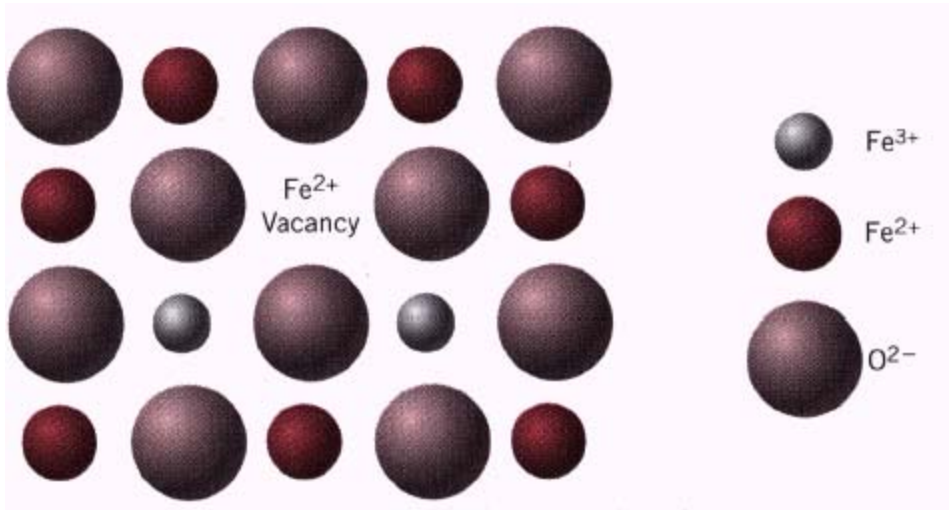
Cation-anion vacancy pair (Schottky defect)

Cation vacancy-cation interstitial pair (Frenkel defect)



Defects and charge neutrality

Sometimes, an ion can possess multiple valence states, such as iron. Consider the following schematic representation of an Fe^{2}+ vacancy in FeO that results from the formation of two trivalent (Fe^{3}+) ions:



The presence of 2 trivalent ions gives the material an excess charge of +2. Consequently, charge neutrality is maintained by forming a vacancy on a divalent cation site, thus reducing the net charge by this amount.

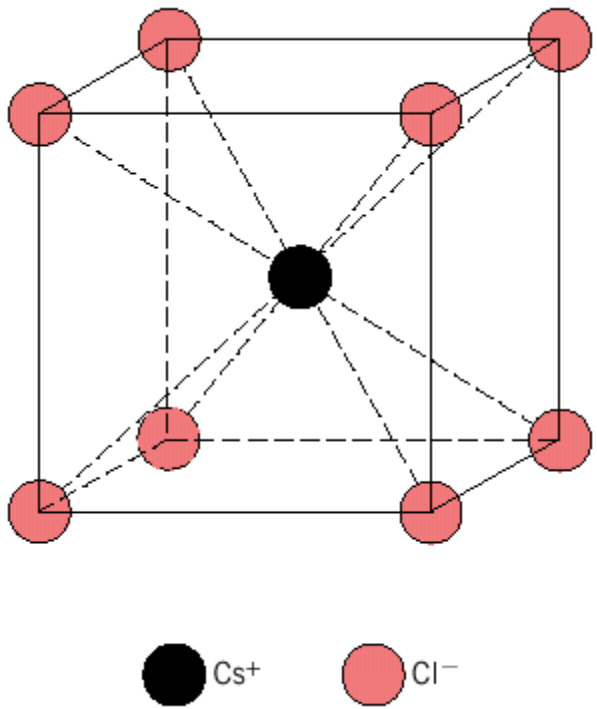
Ceramic crystal structures

A number of important crystal structures are associated with ceramic materials; our survey of the more common structure types begins with the A-X compounds (equal numbers of cations and anions) (note: this structure forms only in the case of equal charge on both species!)

1) Cesium Chloride (CsCl) structure

CN = 8
<u>NOT a BCC structure</u>
(2 interpenetrating simple cubics)
Cl^- anions at corners of unit cube
Cs^+ cations at centers of unit cube

(we can think of this as a simple cubic structure in which 2 atoms associated with each lattice point)



A-X ceramic crystal structures

2) Rock Salt (NaCl) structure

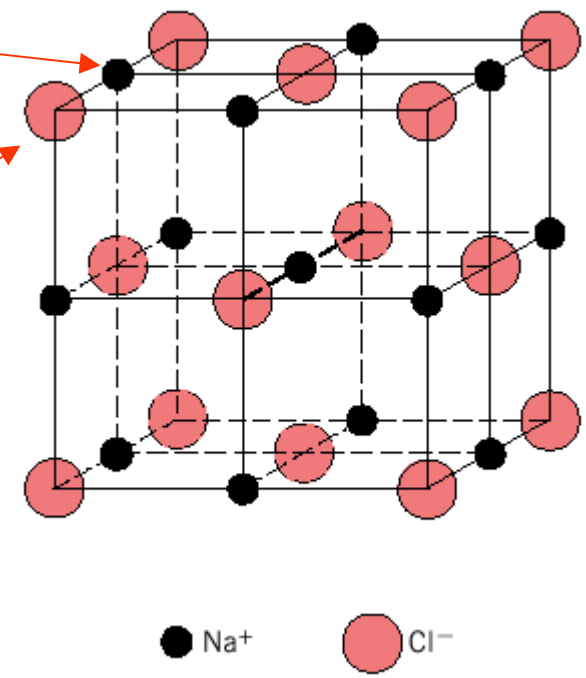
(most common A-X structure)

CN = 6

--> $0.414 < r_c/r_a < 0.732$

Cations (Na^+) and anions (Cl^-) each assume their own FCC lattice. Thus, the net structure can be thought of as 2 interpenetrating FCC lattices

common materials possessing this structure: NaCl, MgO, MnS, LiF, FeO



A-X ceramic crystal structures

3) Zinc Blende (ZnS) structure

CN = 4

---> $0.225 < r_c/r_a < 0.414$

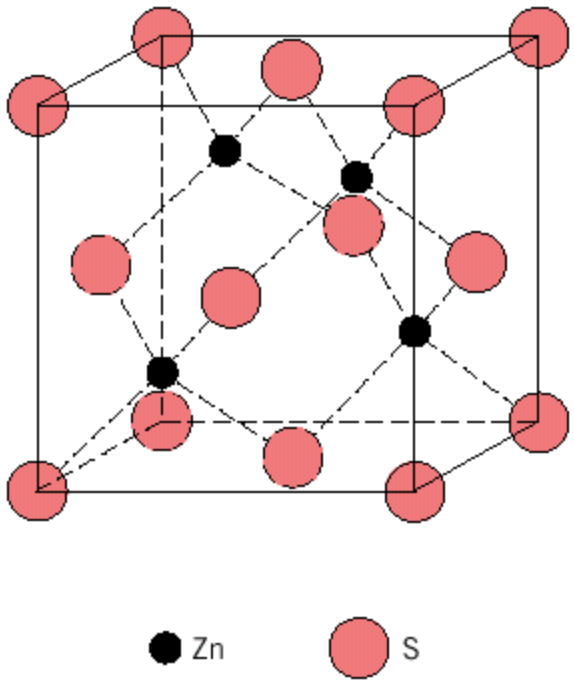
all ions are *tetrahedrally* coordinated

each atom is bonded to 4 atoms of the opposite type

corner and face sites are occupied by anions (S^-) interior tetrahedral sites are occupied by cations (Zn^+)

the bonding is mostly covalent

other compounds possessing this structure: ZnTe, SiC



A_m-X_p ceramic crystal structures

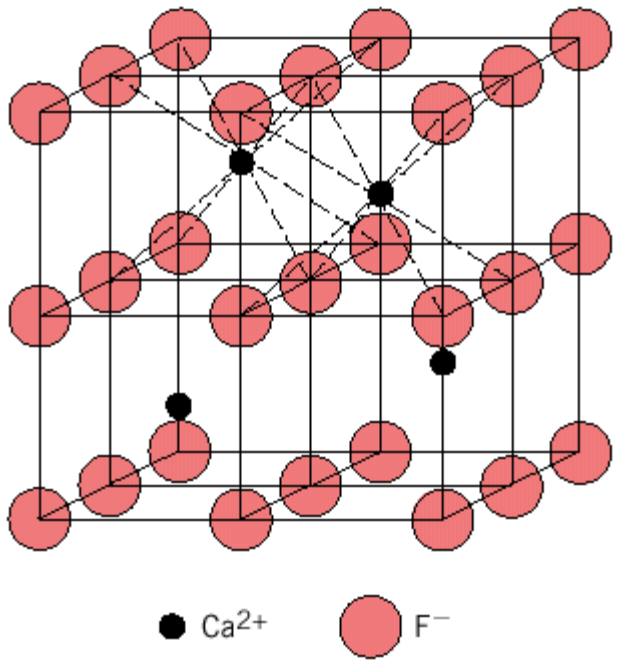
Suppose the electrical charge on the cation and ion is NOT the same. In this case, the stoichiometry of the crystal CANNOT be 1:1; in order to achieve charge neutrality, the ratio of cations to anions must ≠ 1. We classify these crystals A_mX_p, where m &/or p ≠ 1.

Example:

$AX_2 \Rightarrow CaF_2$
$r_c/r_a \cong 0.8 \rightarrow CN = 8$

cations (Ca^{2+}) are positioned at the centers of unit cubes while anions (F^-) occupy corner sites. Since there are half as many Ca^{2+} as there as F^-, only half the center cube positions are occupied.

A unit cell consists of 8 such cubes, shown at right. Other such compounds: UO_2, PuO_2, and ThO_2.



$A_mB_nX_p$ ceramic crystal structures

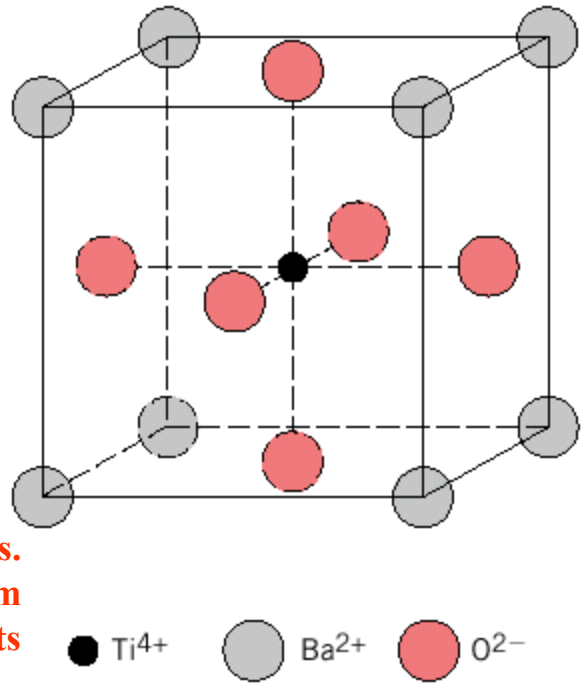
Many ceramic materials contain more than one type of cation; as long as charge neutrality is maintained, there is no absolute limit to the number of cations (or anions) that a crystal may possess. In the case of two cations (A and B) and one species of anion (X), the chemical formula is designated as $A_mB_nX_p$.

Example: Barium titanate ($BaTiO_3$)

"Perovskite" structure

one species of cation (Ba^{2+}) is positioned at the unit cube corners; a single second cation (Ti^{4+}) is located at the cube center. The anions (O^{2-}) occupy the face center positions.

CN (O^{2-}) = 6; CN (Ba^{2+}) = 12; CN (Ti^{4+}) = 6



Commonly employed as a piezoelectric material (literal trans. "pressure electricity"). Electric polarization results from application of external force. (also called a transducer - converts mechanical strain into electrical energy.)

Ceramic density calculations

We previously showed that the theoretical density of a metal could be calculated from the relationship

$$\rho = \frac{nA}{V_{uc} N_A}$$

where n is the # atoms per unit cell, A is the (average) atomic mass, V_c is the unit cell volume, and N_A is Avagadro's number.

In a similar manner, we can calculate the theoretical density for complex ceramic materials simply by replacing "A" in the above equation with an expression that accounts for the atomic weights of both the cations and anions:

$$\rho = \frac{n\left(\sum A_c + \sum A_A\right)}{V_c N_A}$$

In this expression, $\sum A_c$ and $\sum A_A$ are just the sums of atomic masses of all cations and anions, respectively, in the unit cell.

Ceramic density calculations

Example: ***calculate the density of FeO, given that it has the rock salt crystal structure.***

Solution: we use the equation $\rho = \frac{n\left(\sum A_c + \sum A_A\right)}{V_c N_A} = \frac{n\left(\sum A_{Fe} + \sum A_O\right)}{V_c N_A}$

Since the crystal structure is rock salt, n' = 4 formula units per unit cell, and

$$V_C = a^3 = (2r_{Fe^{2+}} + 2r_{O^{2-}})^3 = [2(0.077\ \text{nm}) + 2(0.140\ \text{nm})]^3$$

$$= 0.0817\ \frac{\text{nm}^3}{\text{unit cell}} = 8.17 \times 10^{-23}\ \frac{\text{cm}^3}{\text{unit cell}}$$

Thus,

$$\rho = \frac{(4\ \text{formula units/unit cell})(55.85\ \text{g/mol} + 16.00\ \text{g/mol})}{(8.17 \times 10^{-23}\ \text{cm}^3/\text{unit cell})(6.023 \times 10^{23}\ \text{formula units/mol})}$$

$$= 5.84\ \text{g/cm}^3$$

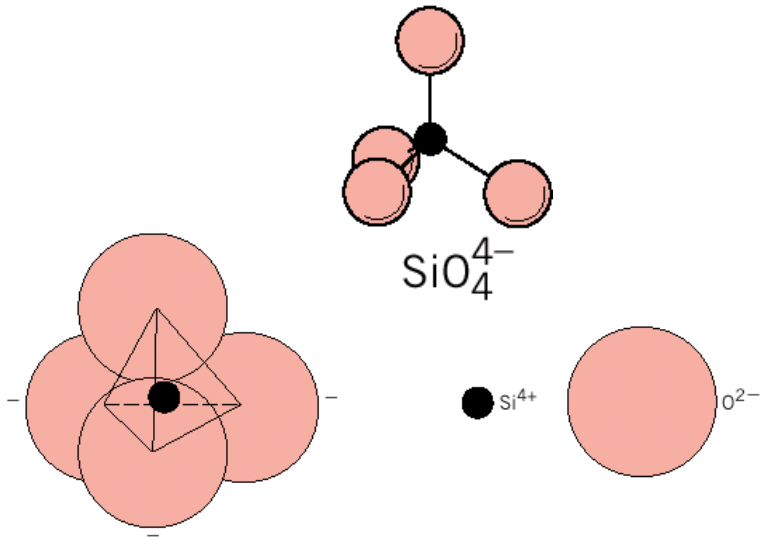
Silicates

Silicon and oxygen are the two most abundant elements in the earth's crust. Not surprisingly, most clays, soils, rocks and sand fall under the broad category of *silicates*, or ceramics composed primarily of Si and O.

The fundamental building block of all silicate materials is the SiO_4 tetrahedron. It consists of a single Si^{4+} ion at the center of a tetrahedron formed by 4 O^{2-} ions: Silicates are characterized by predominately covalent bonding*. As such, silicate bonding tends to be highly directional and relatively strong (high melting point).

*** Because covalent bonding is highly directional, silicates have a relatively open structure and thus a low density.**

Note: each SiO_4 sub-unit carries with it a net negative charge. This does not violate our previous rule about charge neutrality because isolated SiO_4 tetrahedra do not exist.

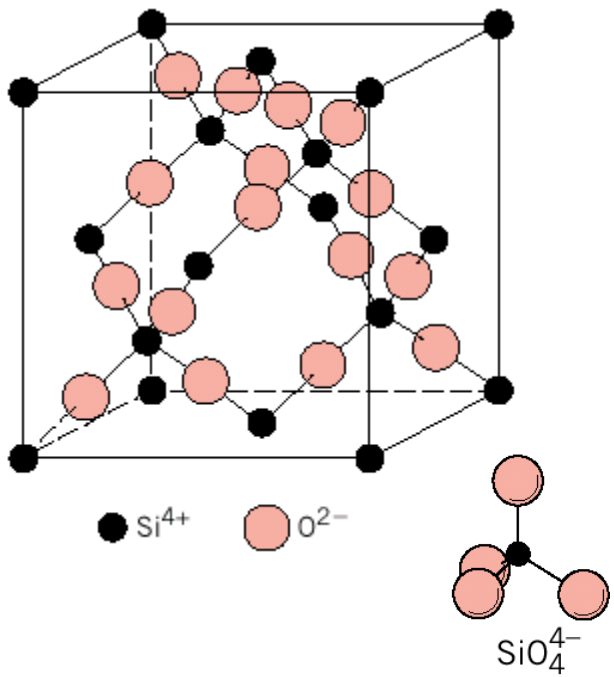


Silicon oxide (silica)

The most simple silicate structure is silicon dioxide, SiO_2
This structure results when each corner oxygen ion is shared by adjacent tetrahedra. As a consequence of the anion sharing, the net ratio of cation to anion in a unit cell is 1:2. Since silicon and oxygen have valence states of 4+ and 2-, respectively, the SiO_2 unit cell is electrically neutral.

Silica can assume various polymorphs depending on temperature:

quartz (< 870°C: trigonal)
tridymite (870°C - 1470°C: hexagonal)
cristobalite (> 1470°C: tetragonal)

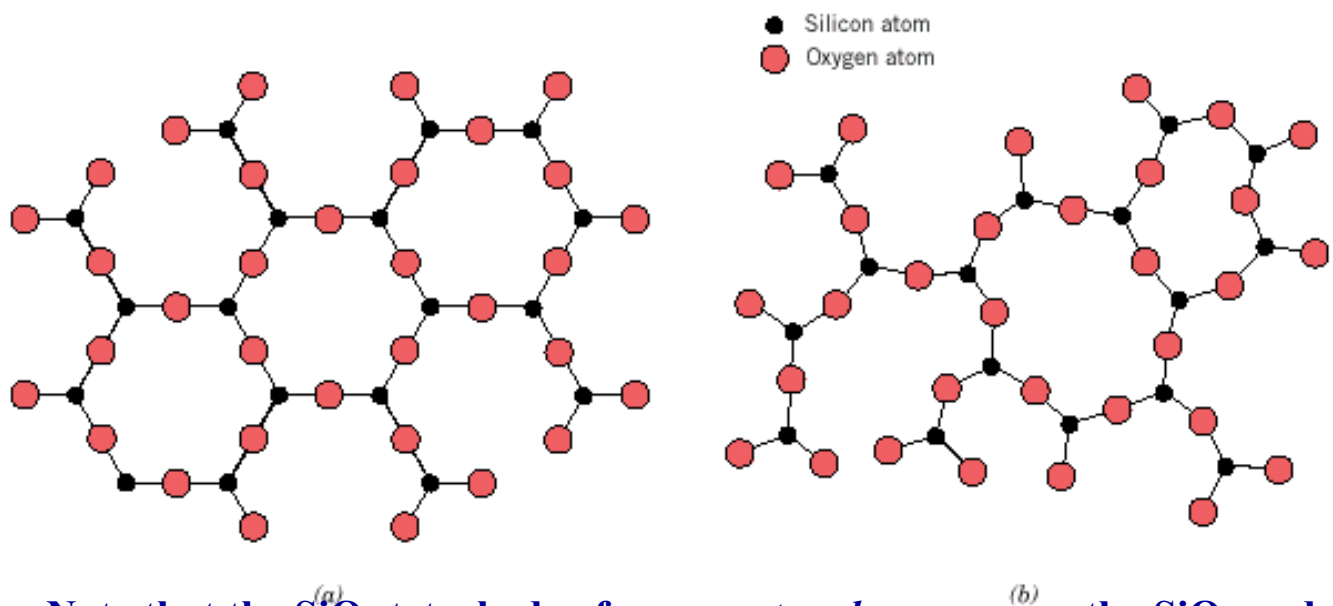


When pure, silica is colorless to white.
Silica is insoluble in water and also in most acids, except HF.
Pure fused silica melts at 1750°C but softens at 1400°C.

Silica glasses

Silica exists in either a crystalline state (discussed previously) or in a disordered (amorphous or glassy) state. Another term synonymous with glassy is vitreous.

Examples of devitrified (left) and vitreous silica (right) are shown below:

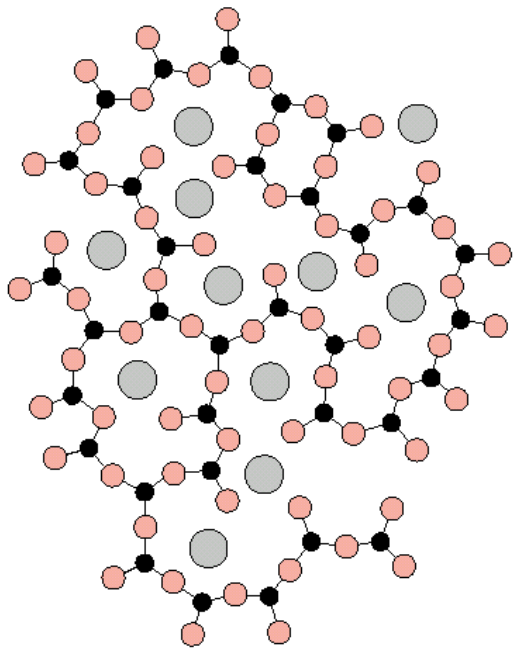


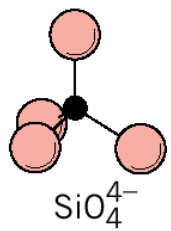
Note that the SiO_4 tetrahedra form a *network*; consequently, SiO_2 and related ceramics are called "network formers."

Silica glasses

Most of our common commercial glasses consist of a silica network, to which various other oxide ceramics such as CaO and Na2O have been added. These oxides themselves do not form networks, but rather, modify them. Consequently, such additives are called network modifiers. For example, the schematic below represents the general structure of a sodium silica glass, where the sodium ions become incorporated within the silica network.

Network modifiers are added to silica glasses in order to impart specific properties, such as a reduced softening or vitrification temperature, a different viscosity, or a particular color or tint.





Carbon-based materials

Since graphite is often considered a ceramic, and since the crystal structure of diamond is related to the zinc blende structure, discussion of carbon-based materials typically accompanies ceramics.

We will review the crystal structure and salient properties of the three known polymorphs of carbon:

diamond (metastable)

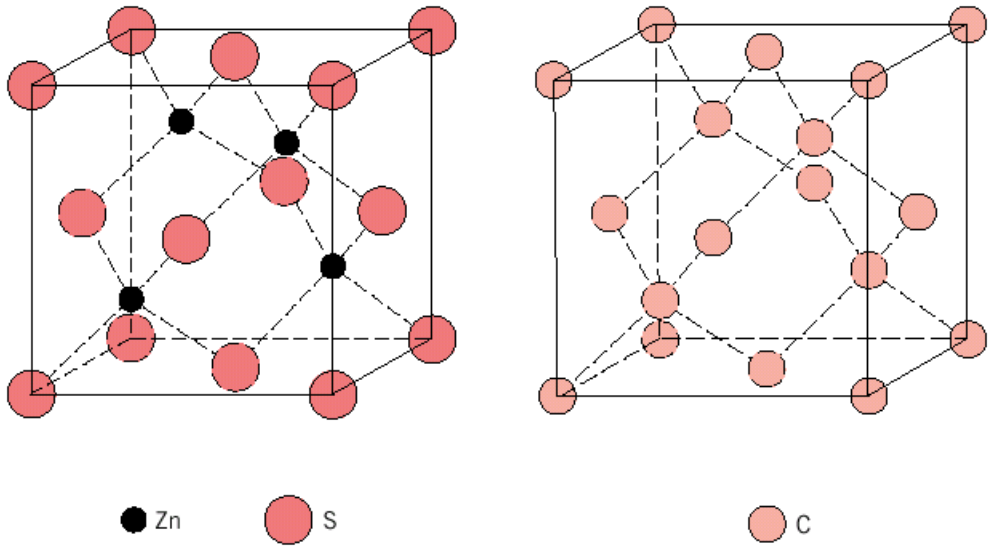
graphite (stable)

fullerene (stable)

Carbon-based materials

1) diamond

same crystal structure as ZnS but with carbon atoms exclusively:



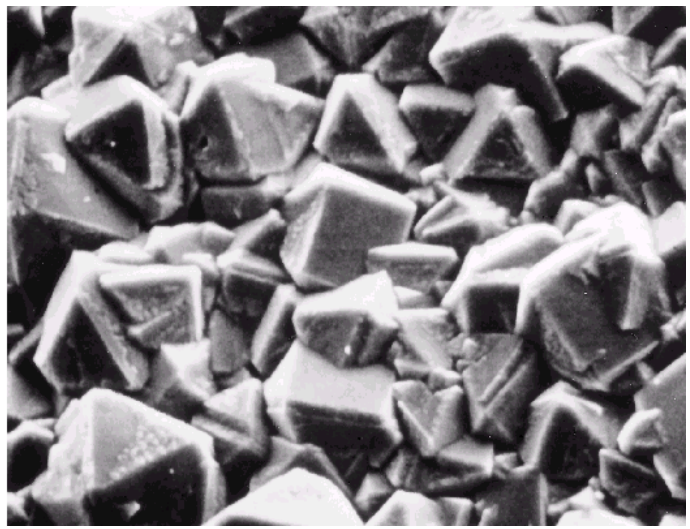
ZnS (left) and diamond cubic (right)

Carbon-based materials

1) diamond (cont'd)

- chemical bonding is purely covalent
- highly symmetrical unit cell
- extremely hard (hardest known bulk solid)
- low electrical conductivity
- high thermal conductivity
- optically transparent (visible and IR)
- used as gemstones and industrial grinding/machining/cutting materials (not suitable for high speed machining of steels

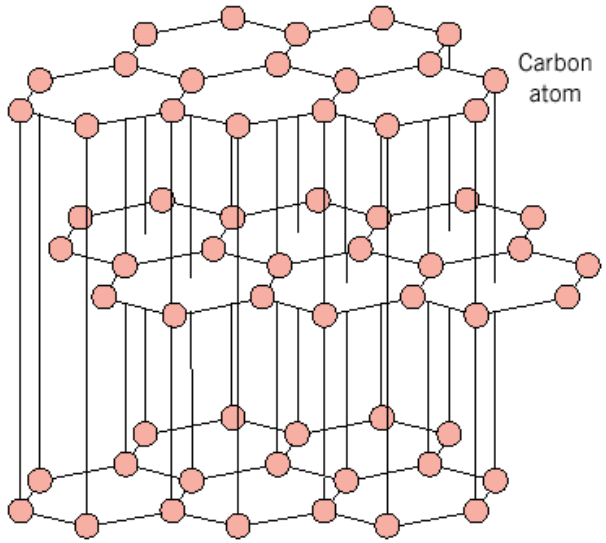
has been prepared in the form of thin films (CVD - chemical vapor deposition) for coating applications (drills, dies, bearings, knives)



Carbon-based materials

2) graphite

- carbon atoms assume a hexagonal, layered configuration
- strong covalent bonding within the layers
- weak van der Waals bonding between layers
  - this give graphite its excellent lubrication properties (since the layers easily slide across one another
- high electrical conductivity within the layers
- good compressive strength
- excellent thermal shock resistance



Commonly used as heater elements (in non-oxidizing atmospheres), metallurgical crucibles, casting molds, electrical contacts, brushes and resistors, high temperature refractories, air purification systems, and in rocket nozzles.

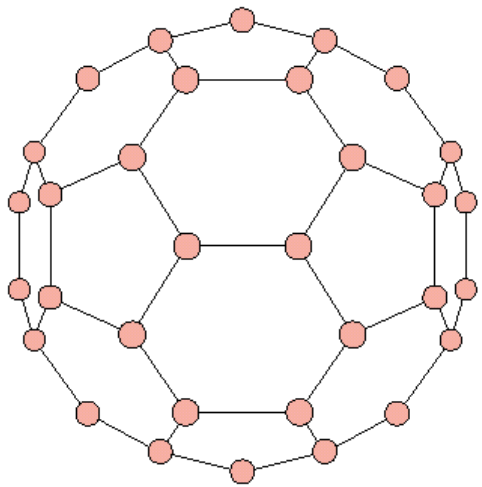
Carbon-based materials

3) Fullerene

- discovered in 1985 by spark synthesis
- carbon bond to form a hollow spherical molecule, each consisting of 60 carbon atoms
- commonly called "*Buckminsterfullerene*" after R. Buckminster Fuller, original designer of the geodesic dome.
- The highly symmetrical nature of the bonding gives rise to a highly stable molecule.
- Individual C60 molecules bond together to form a FCC lattice
- other forms have recently been discovered including tubes and rods (*buckytubes*)
  - reported to possess the highest strength-to-weight ratio of any known material!

Possible applications:

drug delivery
low mass structural members
?



Ceramic phase diagrams

Phase diagrams for ceramic materials obey the same rules as for metal systems. An important difference is that the terminal end phases are usually themselves binary compounds, rather than pure elements. A number of binary systems contain oxygen as a common element.

We will now look at a few of the more important pseudo-binary systems as examples:

Cr_2O_3 - Al_2O_3

SiO_2 - Al_2O_3

MgO - Al_2O_3

$CaZrO_3$ - ZrO_2

Ceramic phase diagrams

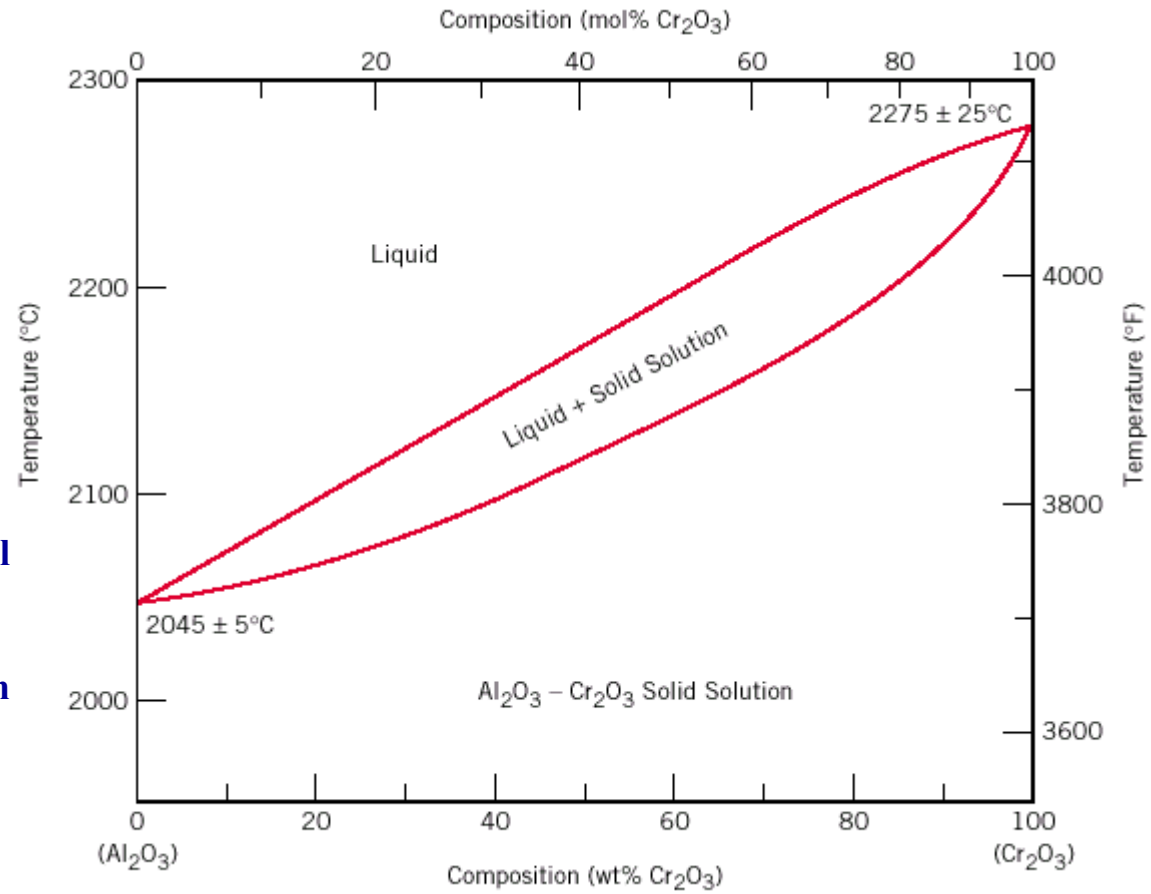
Cr_2O_3 - Al_2O_3

One of the simplest pseudo-binary phase diagrams.

Complete solubility: Al, Cr atoms possess similar size and chemical valence

Both oxides have the same crystal structure

Al^{3+} substitutes for the Cr^{3+} ion in Cr_2O_3 (and vice versa)



Ceramic phase diagrams

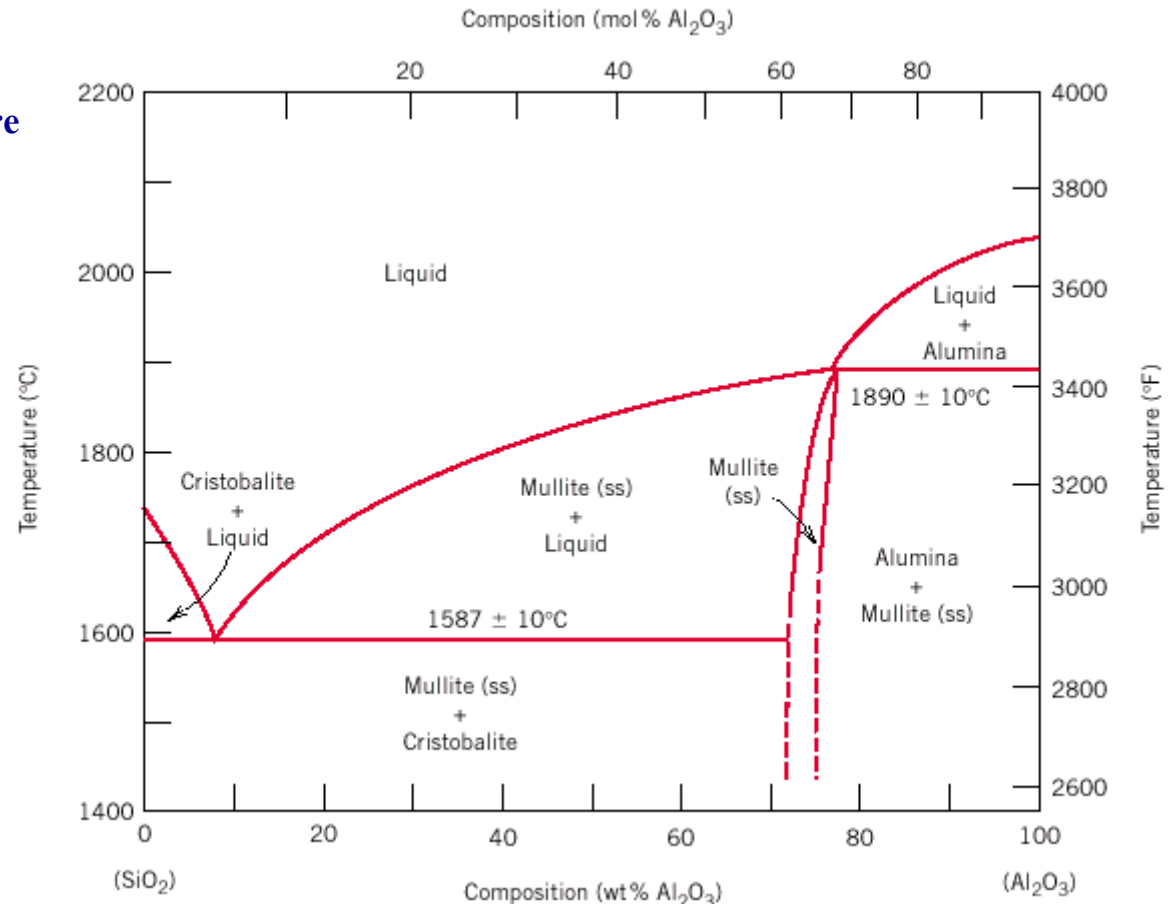
SiO_2 - Al_2O_3

Most commercial refractories are based on the silica - alumina system

fireclay refractories contain 25 - 45 wt. % Al_2O_3
typically used in furnace construction (insulation)
silica refractories (< 7 wt. % Al_2O_3) are used as load-bearing supports for large industrial furnaces

note the absence of solubility on either endpoint

one intermediate compound exists: mullite ($3Al_2O_3$ - $2SiO_2$)



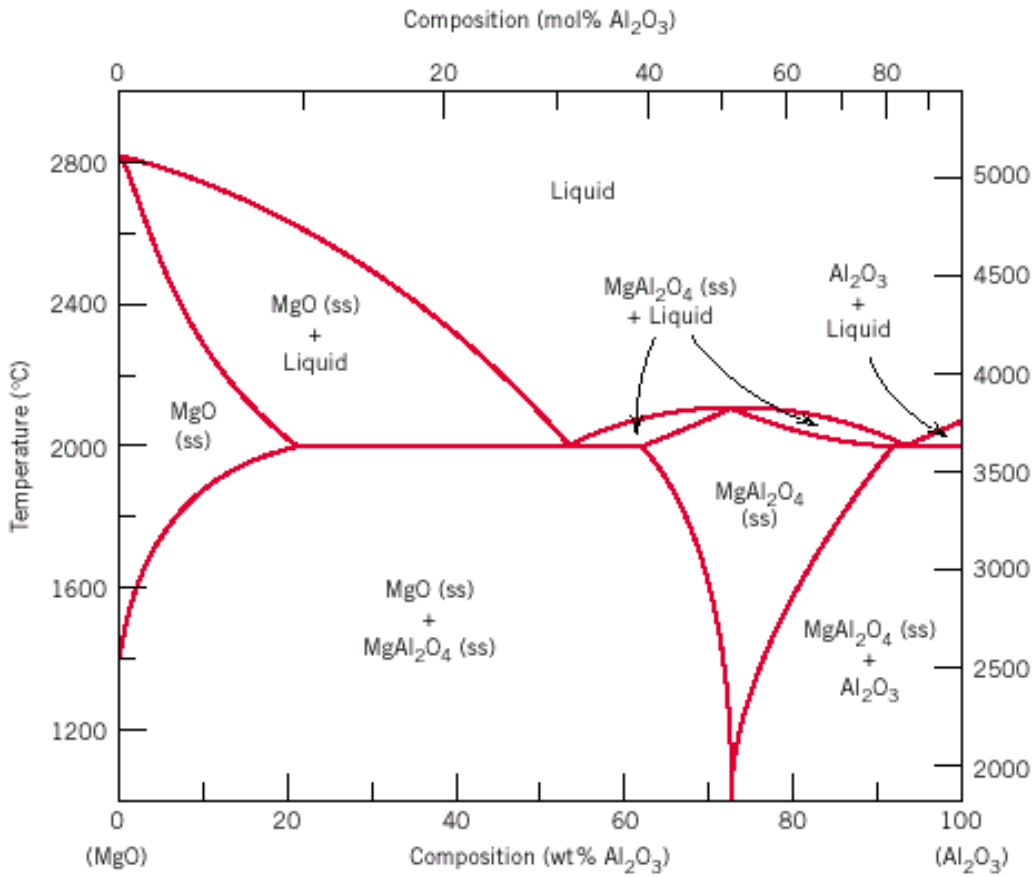
Ceramic phase diagrams

$MgO - Al_2O_3$

The phase diagram is similar to the Pb-Mg, except that the intermediate phase ($MgAl_2O_4$ or "spinel") remains stable over a range of compositions.

Solubility of either terminal end component is negligible in the other.

This system contains two eutectics, one on either side of the spinel phase.



Ceramic phase diagrams

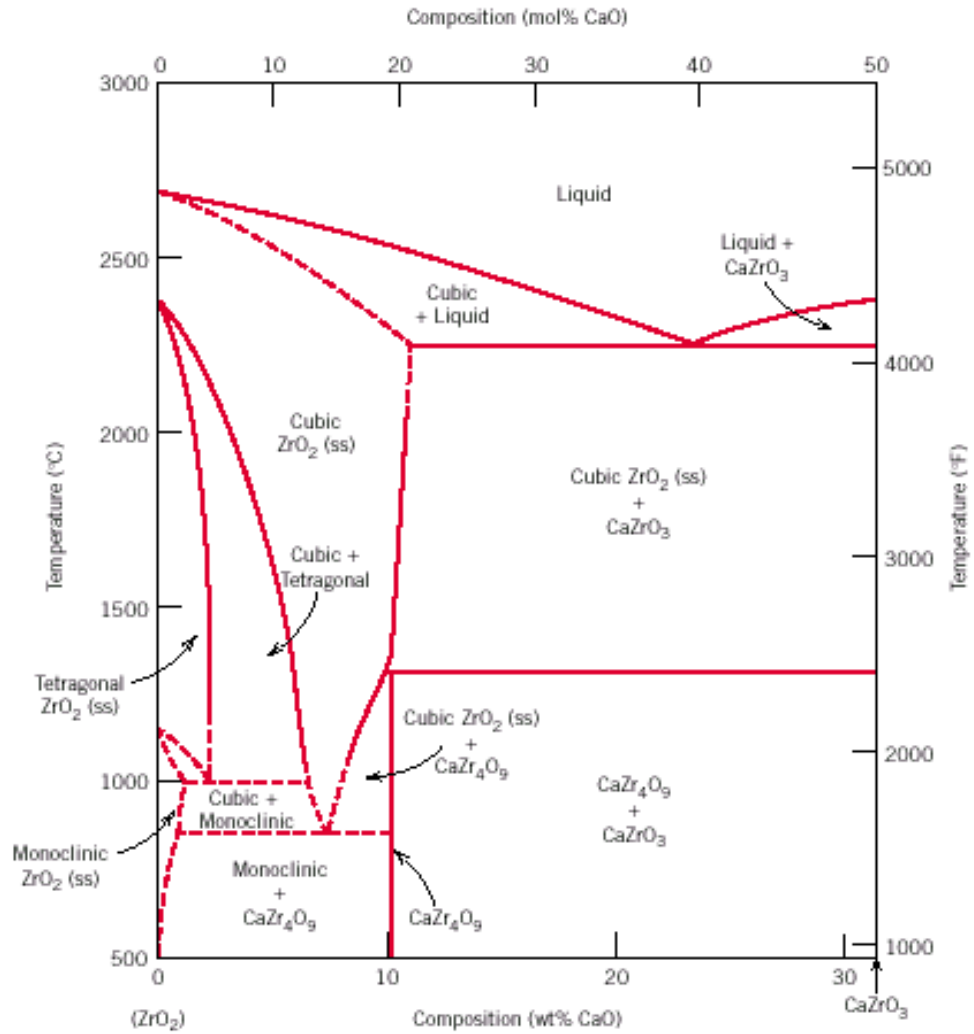
$CaZrO_3$ - ZrO_2

Only a partial phase diagram is shown; out to 31 wt. % CaO ($CaZrO_3$)

One eutectic and two eutectoid invariants are shown; can you identify them?

Note that ZrO_2 displays three polymorphs; monoclinic, tetragonal, and cubic. (t→m) transformation is accompanied by a large volume change ⇒ crack formation.

Addition of 3 - 7 % CaO prevents transformation to the monoclinic phase (PSZ)



Mechanical properties of ceramics

Ceramic materials are notorious for their lack of ductility. In general, they are strong, but brittle; plastic deformation (slip) is essentially non-existent. Mechanical behavior is dictated by the Griffith theory of brittle fracture:

All ceramics are assumed to contain pre-existing microscopic defects (voids, cracks, grain corners) that act as stress concentrators. The local stress at the tip of a pre-existing flaw increases with decreasing tip radius of curvature and with increasing crack length according to

$$\sigma_m = 2\sigma_o \left(\frac{a}{\rho_t} \right)^{\frac{1}{2}}$$

Crack propagation occurs when σ_m exceeds the local tensile strength. Plane strain fracture toughness, K_{ic}, is a measure of a material's ability to resist fracture when a crack is present. Recall, $K_{Ic} = Y\sigma\sqrt{\pi a}$

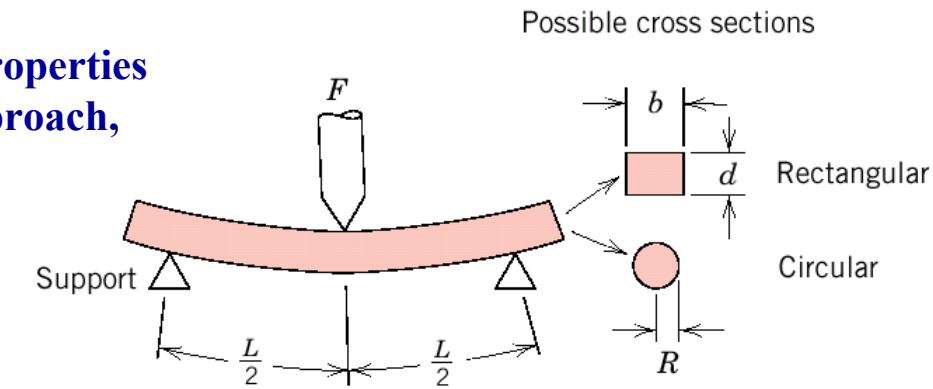
Values for K_{ic} for ceramic materials are usually (at least) an order of magnitude less than that for metals. Since there is no stress amplification under compression, ceramics are usually used under compressive loading.

Mechanical properties of ceramics

Recall in the case of metals, mechanical properties were determined from tensile tests, in which a stress-strain curve is generated. Ceramics are not normally tested in tension because:

- **it is difficult to machine to the required geometry**
- **it is difficult to grip brittle materials without inducing fracture**
- **ceramics typically fail after only ~ 0.1% strain**

For these reasons, the mechanical properties are determined using a different approach, the three point bend test:



	M	c	I	σ
Rectangular	$\frac{FL}{4}$	$\frac{d}{2}$	$\frac{bd^3}{12}$	$\frac{3FL}{2bd^2}$
Circular	$\frac{FL}{4}$	R	$\frac{\pi R^4}{4}$	$\frac{FL}{\pi R^3}$

σ = stress = $\frac{Mc}{I}$

where M = maximum bending moment
c = distance from center of specimen to outer fibers
I = moment of inertia of cross section
F = applied load

Mechanical properties of ceramics

Three point bend test:

- **specimen geometry is circular or rectangular cross section**
- **during the test, the top surface is under compression while the bottom surface is under tension**
- **maximum tensile stress occurs on the bottom surface, just below the top loading point**
- **the stress at fracture, σ_{fs}, (a.k.a. *flexural strength, modulus of rupture, fracture strength, or bend strength*) is given by**

$$\sigma_{fs} = \frac{3F_f L}{2bd^2}$$ **for samples with rectangular cross sections, and**

F_f is the load at fracture, L the distance between lower supports, b and d are the width and thickness.

$$\sigma_{fs} = \frac{F_f L}{\pi R^3}$$ **for samples with circular cross sections**

F_f is the load at fracture, L the distance between lower supports, R is the radius of the specimen.

Example - solved problem

A three-point transverse bend test is applied to an alumina cylinder with a reported flexural strength of 390 MPa (56 ksi). If the specimen radius is 2.5 mm (0.10") and the support point separation distance is 30 mm (1.2"), estimate whether or not the specimen would fracture when a load of 620 N (140 lb_f) is applied.

Solution:

Using Equation (**13.3b**), one can calculate the value of **σ;** if this value is greater than σ_{fs} (390 MPa), then fracture is expected.

$$\sigma_{fs} = \frac{F_f L}{\pi R^3}$$

for samples with circular cross sections

Where F_f is the load, L the distance between lower supports, and R is the radius of the specimen.

$$\sigma = \frac{FL}{\pi R^3} = \frac{(620N)(30\times10^{-3}m)}{\pi(2.5\times10^{-3}m)}$$

= 379 x 10^6 N/m^2 = 379 MPa (53.5ksi)

Since this value is less than the given value of σ_{fs} (390 MPa), fracture is **not** predicted.

Mechanical properties of ceramics

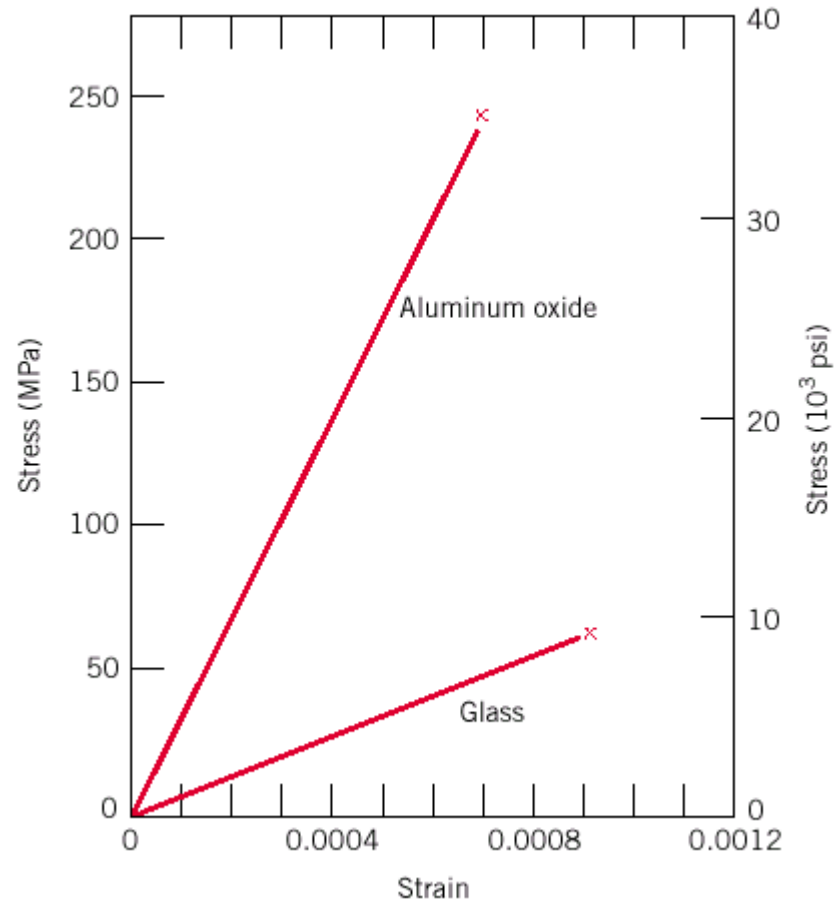
Typical results for three point bend test:

note the complete absence of plastic deformation

why...?

...because slip is more difficult in ceramic materials than in metals. For slip to occur, the atoms in one plane must "slide" over the atoms in an adjoining plane. In the case of ceramic materials, the atoms are charged ions, and a strong electrostatic repulsion prevents ions of the same charge from coming in close proximity to one another.

Al_2O_3 and glass



Mechanical properties of ceramics

A word about hardness of ceramic materials:

ceramic materials can exhibit much higher hardness values than metals; this property gives rise to a significant number of abrasion-related applications (sanding, cutting, grinding, finishing)

Chemically-modified $AlMgB_{14}$ has been shown to possess a hardness as high as 4600 on this scale.

Materials

Material	*Approximate Knoop Hardness*
Diamond (carbon)	7000
Boron carbide (B_4C)	2800
Silicon carbide (SiC)	2500
Tungsten carbide (WC)	2100
Aluminum oxide (Al_2O_3)	2100
Quartz (SiO_2)	800

Want more information?

Suggested references on ceramic materials and processing:

Introduction to the Principles of Ceramic Processing, J.S. Reed, John Wiley & Sons, NY, 1989.

Introduction to Ceramics, W.D. Kingery, H.K. Bowen and D.R. Uhlmann. 2nd Edition, John Wiley & Sons, NY,1976.

Clay and Ceramic Raw Materials, W.E. Worrall, Applied Science Publishers, London, 1975.

Fine Ceramics, F.H. Norton, Krieger, Malabar, FL, 1978.

Ceramic Processing Before Firing, G.Y. Onoda Jr and L.L. Hench, Wiley-Interscience, NY, 1978.