



Ceramic Materials

Outline

Structure and Properties of Ceramics

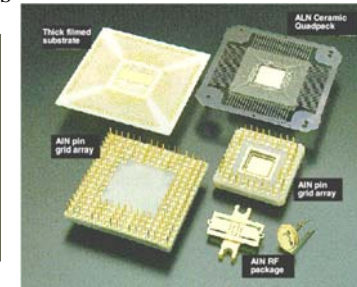
- Introduction
- Classifications of Ceramics
- Crystal Structures
- Silicate Ceramics
- Ceramic Phase Diagram
- Carbon based materials



Ceramics

- Why study ceramic materials?
 - Very “traditional” (*civil engineering material*)
 - **BUT** also new **high-tech** ceramics and applications.
 - **Optical** (*transparency*) opto-electronic.
 - **Electronic** (*piezoelectrics, sensors, superconductors*)
 - **Thermo-mechanical** (*engine materials*)
 - Cutting tools

In 1974, the U.S. market for the ceramic industry was estimated at **\$20 million**. Today, the U.S. market is estimated to be over **\$35 billion**.



Courtesy of NTK Technical Ceramics

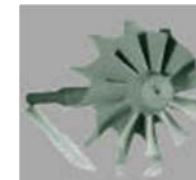
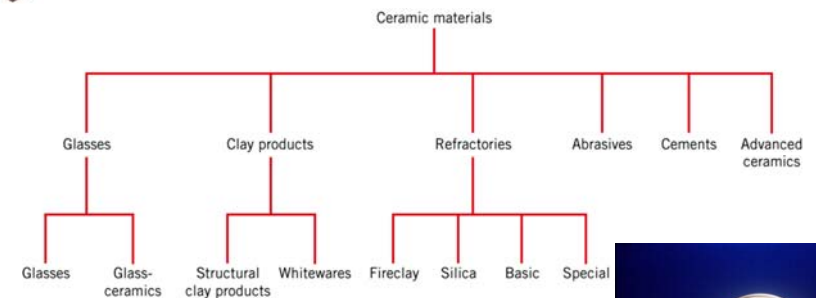


Ceramics / Introduction

- *keramikos* - burnt stuff in Greek → desirable properties of ceramics are normally achieved through a **high-temperature heat treatment process** (*firing*).
- Usually a compound between metallic and non-metallic elements.
- Always composed of more than one element (e.g., Al_2O_3 , NaCl, SiC, SiO_2)
- Bonds are partially or totally **ionic**, and can have **combination** of ionic and covalent bonding (*Chapter 2*)
- Ceramics are typically characterized as possessing a high melting temperature (i.e., “**refractory**”),
- Generally **hard** and **brittle**
- *Generally* electrical and thermal **insulators** (*exceptions: graphite, diamond, AlN... and others*)
- Can be optically opaque, semi-transparent, or transparent
- Traditional ceramics – based on clay (china, bricks, tiles, porcelain), glasses.
- **New ceramics** for electronic, computer, aerospace industries.



Classifications of Ceramics





CERAMIC CRYSTAL STRUCTURES

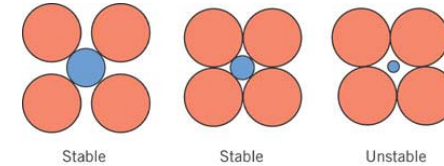
- ❖ Usually two types of atomic species (e.g. Na and Cl) so crystal structure is made up of both ions.
 - *Must satisfy charge neutrality PLUS size/coordination number requirements.*
- ❖ Usually compounds between metallic ions (e.g. Fe, Ni, Al) called **cations** and non-metallic ions (e.g. O, N, Cl) called **anions**.
- ❖ **Cations** (+ve) usually smaller than **anions** (-ve). Each tries to maximize number of opposite neighbors.
- ❖ **Coordination number** reflects
- ❖ **Standard** type of crystal structures
 - ✓ (AX) - NaCl, CsCl, ZnS etc.
 - ✓ Or (A_mX_p) - CaF₂, UO₂, Si₃N₄
 - ✓ Also, more complex: ($A_mB_nX_p$) - BaTiO₃



CERAMIC CRYSTAL STRUCTURES

Crystal structure is defined by:

- **Magnitude of the electrical charge on each ion.** Charge balance dictates chemical formula (Ca²⁺ and F⁻ form CaF₂).
- **Relative sizes of the cations and anions.** Cations want to maximum possible number of anion nearest neighbours and vice-versa. (i.e. *Crystal structure of the ceramic is determined by the coordination number*)

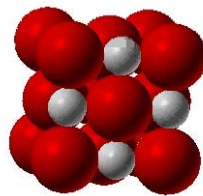


Stable ceramic crystal structures:

- Anions surrounding a cation are all **in contact** with that cation.
- For a specific **coordination number** there is a or cation-anion radius ratio r_C/r_A for which this contact can be maintained.
- This ratio can be determined by simple geometrical analysis (*Example 12.1*).



CERAMIC CRYSTAL STRUCTURES



Coordination Number

- **Recall**, CN is the number of adjacent atoms (**ions**) surrounding a reference atom (**ion**) without overlap of electron orbitals.
- Note that **larger** coordination numbers correspond to cation ions.
- *Rationale: as the atom size increases, it becomes possible to pack more and more atoms around it.*
- **Ideal:** Like-sized atoms, CN = ...

Example: KCl

$K^+ r_C = 0.133 \text{ nm}$, $Cl^- r_A = 0.188 \text{ nm}$,

$r_C / r_A = \dots\dots\dots$

$\Rightarrow \dots\dots\dots$

Coordination Number	Cation-Anion Radius Ratio	Coordination Geometry
2	< 0.155	
3	0.155-0.225	
4	0.225-0.414	
6	0.414-0.732	
8	0.732-1.0	



Crystal Structures in Ceramics

Example: Rock Salt Structure

NaCl structure:

$$r_C = r_{Na} = 0.102 \text{ nm}$$

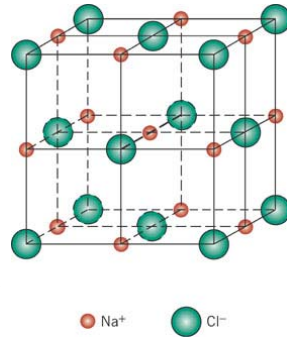
$$r_A = r_{Cl} = 0.181 \text{ nm}$$

$$\Rightarrow r_C / r_A = \dots\dots$$

From the table for stable geometries we see that

$$\text{C.N.} = \dots\dots$$

NaCl, MgO, LiF, FeO have this crystal structure



Crystal Structures in Ceramics

Example: Cesium Chloride Structure

CsCl Structure:

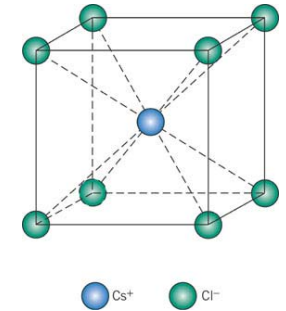
$$r_C = r_{Cs} = 0.170 \text{ nm}$$

$$r_A = r_{Cl} = 0.181 \text{ nm}$$

$$\Rightarrow r_C / r_A = \dots\dots$$

From the table for stable geometries we see that

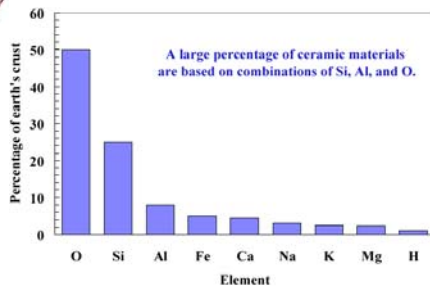
$$\text{C.N.} = \dots\dots$$



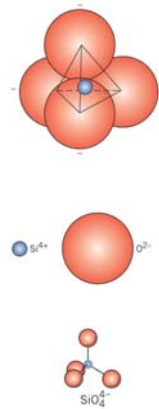
Conclusion: It is not only the **chemical formula** which determines the crystal structure but also the **relative sizes** of the cations and anions.



Silicate Ceramics



Composed mainly of **silicon** and **oxygen**, the two **most abundant** elements in earth's crust (rocks, soils, clays, sand)



- Basic **building block**: SiO₄⁴⁻ **tetrahedron**.
- Si-O bonding is largely **covalent**, but overall SiO₄ block has charge of -4.
- **Note**: each SiO₄ unit carries with it a net negative charge.
 - *This does not violate our previous rule about charge neutrality because isolated SiO₄ tetrahedra do not exist.*
- different ways to arrange SiO₄⁴⁻ blocks
 \Rightarrow **Various silicate structures**



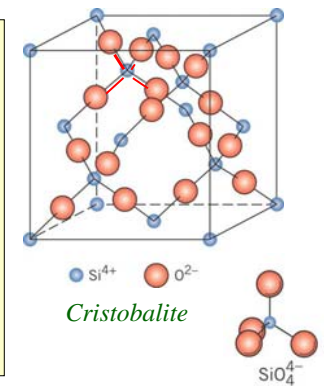
Silicon Oxide (Silica)

- The most simple silicate structure is silicon dioxide, SiO₂. 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 SiO₂ unit cell is

• Silica can assume various polymorphs depending on temperature:

- **quartz** (< 870°C: trigonal)
- **tridymite** (870°C – 1470°C: hexagonal)
- **crystalite** (> 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**.

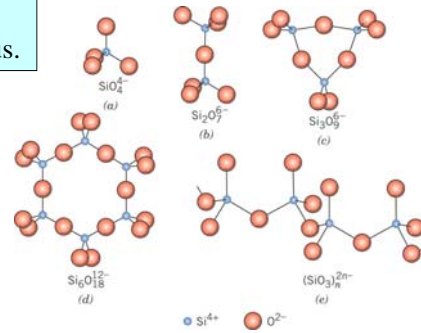




Silica Glasses

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

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



Silica Glasses

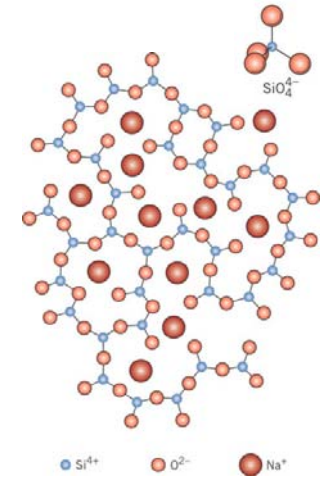
Most of our common commercial glasses consist of a silica network, to which various **other oxide ceramics** such as CaO and Na_2O have been added.

These oxides themselves do not form networks, but rather modify the networks.

- *Consequently, such additives are called*

For example, the accompanied schematic 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.



Ceramic Phase Diagrams

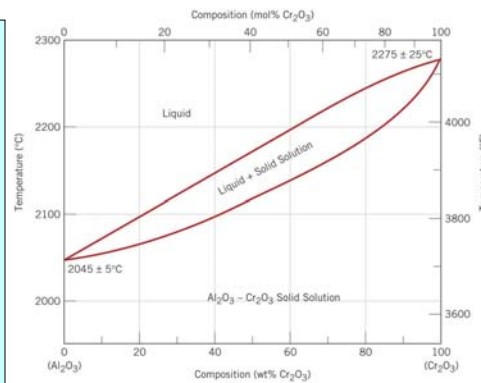
Phase diagrams for **ceramic materials** obey the same rules as for **metal systems**. An important difference is that the components are usually themselves **binary compounds**, rather than pure elements.

$\text{Cr}_2\text{O}_3 - \text{Al}_2\text{O}_3$

➤ One of the simplest ceramic binary phase diagrams.

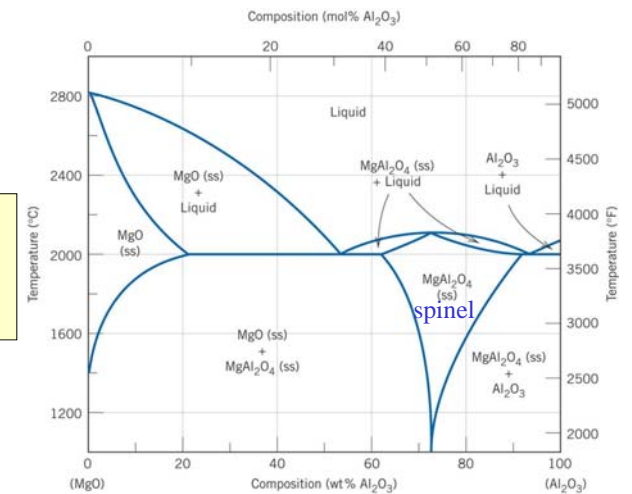
Complete solubility:

- ✓ 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)



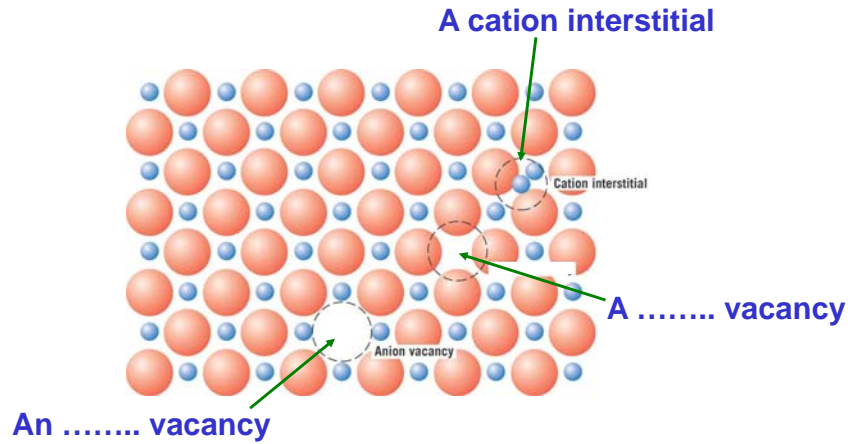
Ceramic Phase Diagrams

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





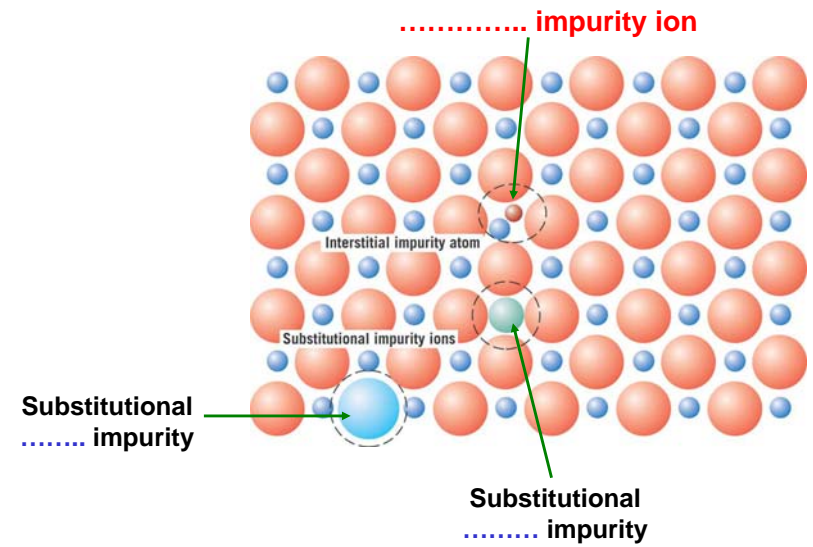
Defects in Ceramic Materials



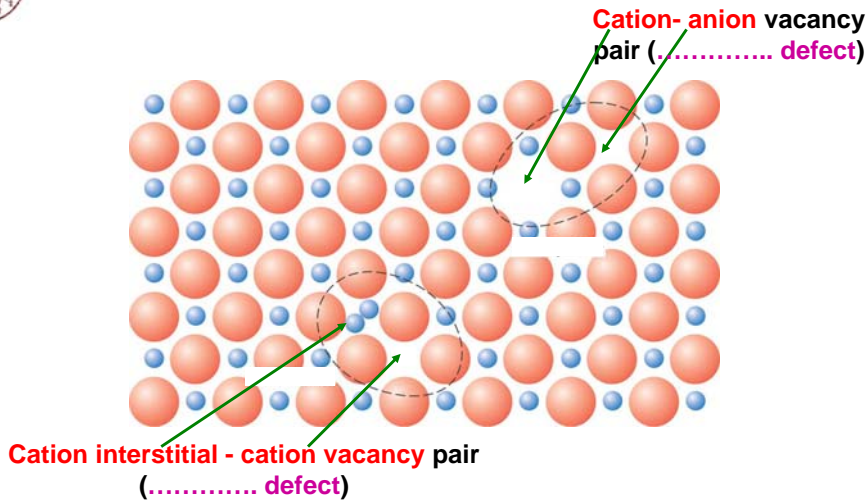
In an ionic ceramic, a *cation* vacancy must be accompanied by a corresponding *anion* vacancy in order to maintain **charge neutrality**.



Defects in Ceramic Materials



Defects in Ceramic Materials



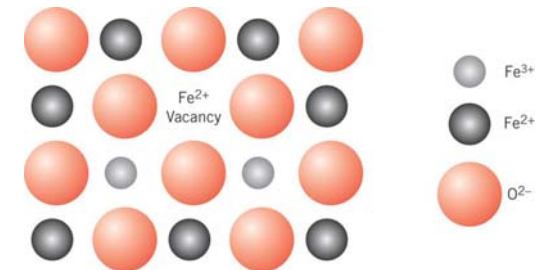
Frenkel and Schottky defects are found in ceramics because defects occur in **pairs** to maintain **charge neutrality**



Defects in ceramic materials

Sometimes, an ion can possess multiple valence states, such as iron (Fe^{2+} , Fe^{3+}).

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 the same amount.



Carbon- based materials

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

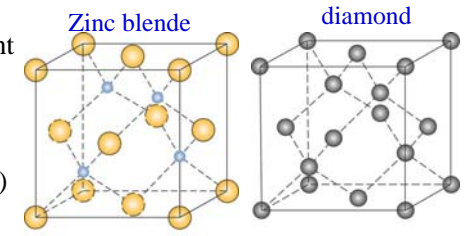
We will review the **crystal structure** and major **properties** of the three known polymorphs of carbon:

- **diamond (metastable)**
- **graphite (stable)**
- **fullerene (stable)**

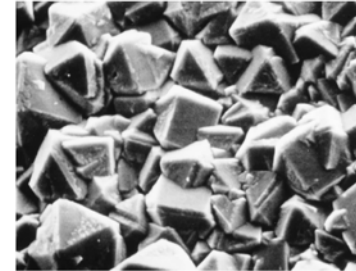


DIAMOND

- chemical bonding is purely covalent
- highly symmetrical unit cell
- extremely hard (..... known)
- electrical conductivity
- high thermal conductivity (.....)
- optically transparent
- used as **gemstones** and industrial Grinding, machining and cutting



same crystal structure as ZnS but with carbon atoms exclusively



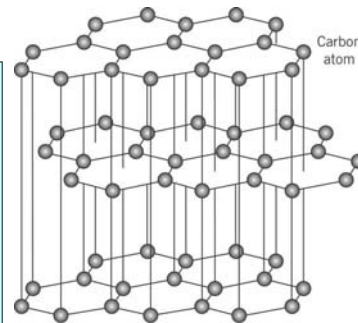
- Chemical vapor deposition (CVD)
- Thin films up to a few hundred microns Polycrystalline
- Applications: hard coatings (tool bits etc), machine components, "heat sinks" for **high power semiconductor devices**



GRAPHITE

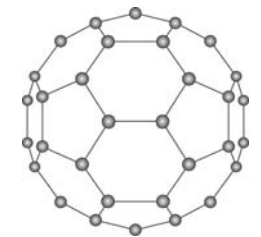
- Layered structure with **strong bonding** within the planar layers and **weak, van der Waals bonding** between layers
- Easy interplanar cleavage, applications as a lubricant and for writing (*pencils*)
- Good electrical conductor
- Chemically stable even at high temperatures
- excellent thermal shock resistance

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



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 **strength** to weight ratio of any known material!



Buckminsterfullerenes (buckyballs)

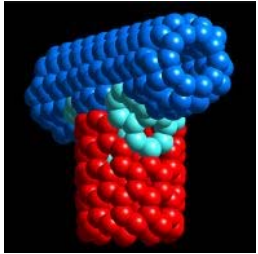
Possible applications:

- drug delivery
- low mass structural members
- ?

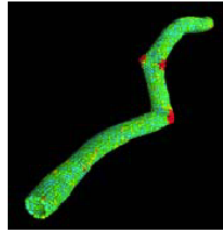


Carbon Nanotubes

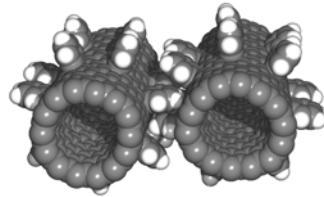
carbon nanotubes are expected to play an important role in future *nanotechnology* applications (nanoscale materials, sensors, machines, and computers)



Carbon nanotube T-junction



Nanotubes as reinforcing fibers in nanocomposites



carbon nanotube gear

<http://www.nas.nasa.gov/Groups/SciTech/nano/>



Next time:
Mechanical Properties and Processing of Ceramics