

Chapter Outline: Ceramics

Chapter 13: Structure and Properties of Ceramics

- Crystal Structures
- Silicate Ceramics
- Carbon
- Imperfections in Ceramics

Optional reading: 13.6 – 13.10

Ceramics

- *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, can have combination of ionic and covalent bonding
- Generally hard and brittle
- Generally electrical and thermal insulators
- 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.

Bonding in Ceramics (Review of Chapter 2)

IA	I	IIA	III	IV	V	VI	VII	VIII	IX	X	XI	XII	IIIA	IVA	VA	VIA	VIIA	0																	
1	H	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																	
2.1	Li	1.5	1.0	1.5	1.3	1.5	1.6	1.5	1.8	1.8	1.9	1.6	1.5	1.8	2.1	2.5	3.0	4.0	-																
0.9	Na	1.2	0.8	1.0	1.3	1.5	1.6	1.5	1.8	1.8	1.9	1.6	1.5	1.8	2.1	2.5	3.0	-	2																
19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr
0.8	0.8	1.0	1.0	1.3	1.3	1.5	1.5	1.6	1.6	1.5	1.5	1.8	1.8	1.5	1.5	1.8	1.8	1.9	1.9	1.6	1.6	1.9	1.9	1.6	1.6	1.8	1.8	2.0	2.0	2.4	2.4	2.8	2.8	-	-
37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe
0.8	0.8	1.0	1.0	1.2	1.2	1.4	1.4	1.6	1.6	1.8	1.8	1.9	1.9	2.2	2.2	2.2	2.2	1.9	1.9	1.7	1.7	1.7	1.7	1.7	1.7	1.8	1.8	1.9	1.9	2.1	2.1	2.5	2.5	-	-
55	Cs	56	Ba	57-71	La-Lu	72	Hf	73	Ta	74	W	75	Re	76	Os	77	Ir	78	Pt	79	Au	80	Hg	81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn
0.7	0.7	0.9	0.9	1.1-1.2	1.1-1.2	1.3	1.3	1.5	1.5	1.7	1.7	1.9	1.9	2.2	2.2	2.2	2.2	2.4	2.4	1.9	1.9	1.8	1.8	1.8	1.8	1.8	1.8	1.9	1.9	2.0	2.0	2.2	2.2	-	-
87	Fr	88	Ra	89-102	Ac-No																														
0.7	0.7	0.9	0.9	1.1-1.7	1.1-1.7																														

Electronegativity - a measure of how willing atoms are to accept electrons (subshells with one electron - low electronegativity; subshells with one missing electron - high electronegativity). Electronegativity increases from left to right.

The atomic bonding in ceramics is mixed, ionic and covalent, the degree of ionic character depends on the difference of electronegativity between the cations (+) and anions (-).

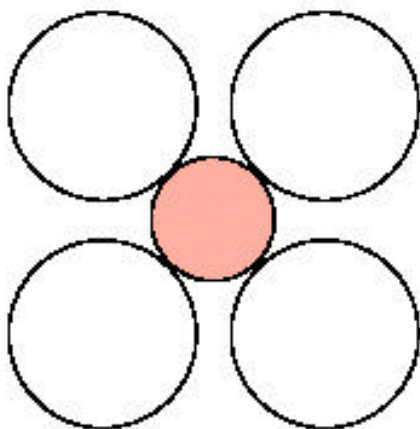
<i>Material</i>	<i>Percent Ionic Character</i>
CaF ₂	89
MgO	73
NaCl	67
Al ₂ O ₃	63
SiO ₂	51
Si ₃ N ₄	30
ZnS	18
SiC	12

Crystal Structures in Ceramics with predominantly ionic bonding

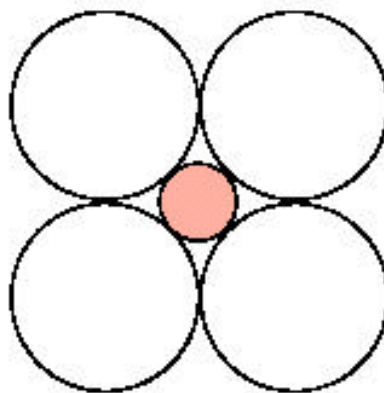
Crystal structure is defined by

- Magnitude of the electrical charge on each ion. Charge balance dictates chemical formula (Ca^{2+} and F^- form CaF_2).
- Relative sizes of the cations and anions. Cations want maximum possible number of anion nearest neighbors and vice-versa.

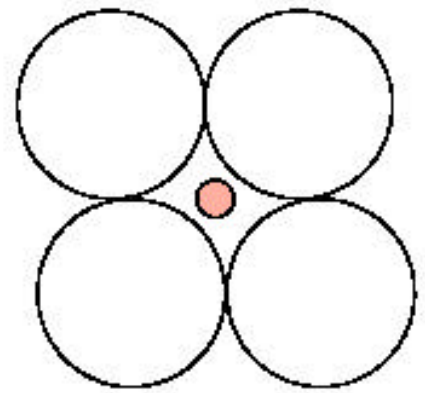
Stable ceramic crystal structures: anions surrounding a cation are all in contact with that cation. For a specific coordination number there is a critical or minimum cation-anion radius ratio r_C/r_A for which this contact can be maintained.



Stable

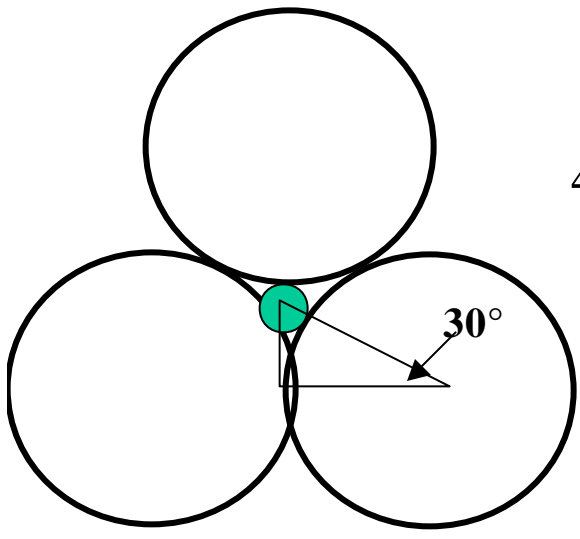


Stable



Unstable

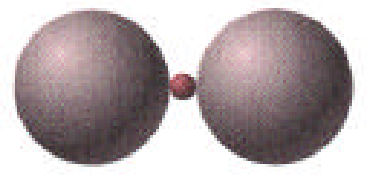
The critical ratio can be determined by simple geometrical analysis



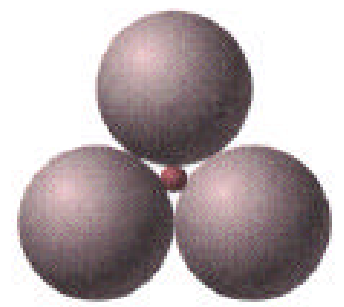
$$\begin{aligned} \cos 30^\circ &= 0.866 \\ &= R/(r+R) \\ &\downarrow \\ r/R &= 0.155 \end{aligned}$$

C.N. r_C/r_A Geometry

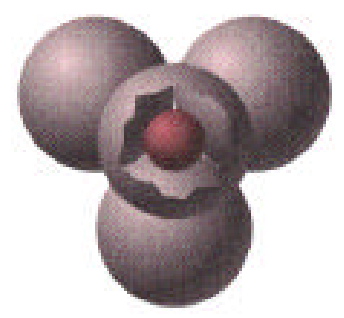
2 <0.155



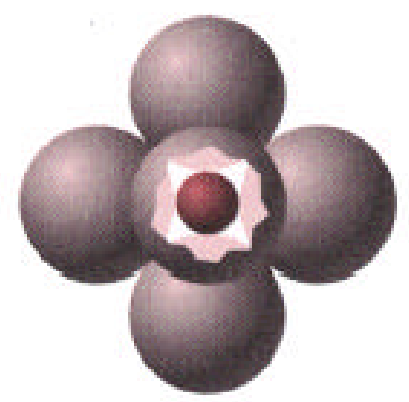
3 0.155-0.225



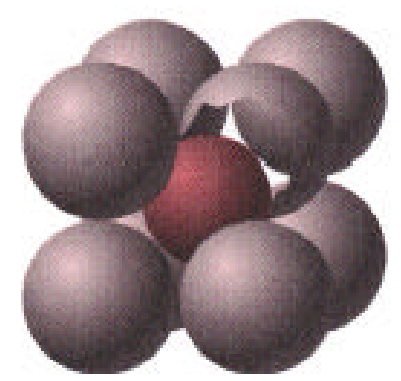
4 0.225-0.414



6 0.414-0.732



8 0.732-1.0

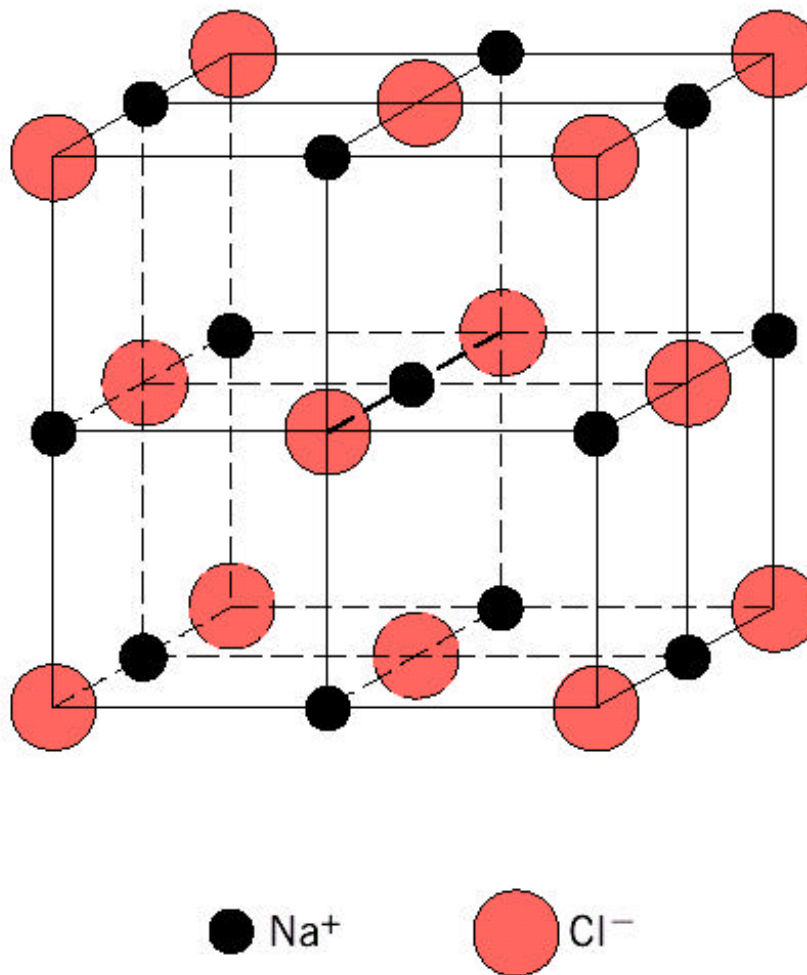


Crystal Structures in Ceramics

Example: Rock Salt Structure

NaCl structure: $r_C = r_{\text{Na}} = 0.102 \text{ nm}$, $r_A = r_{\text{Cl}} = 0.181 \text{ nm}$
 $\Rightarrow r_C/r_A = 0.56$

From the table for stable geometries we see that C.N. = 6



Two interpenetrating FCC lattices

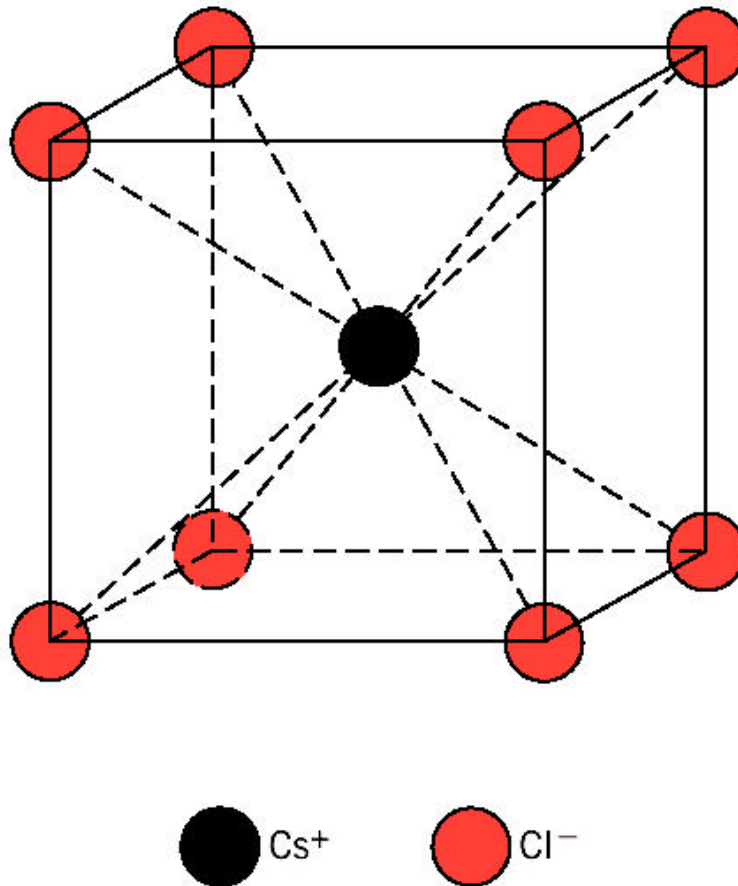
NaCl, MgO, LiF, FeO have this crystal structure

More examples of crystal structures in ceramics (will not be included in the test)

Cesium Chloride Structure: $r_C = r_{Cs} = 0.170 \text{ nm}$, $r_A = r_{Cl} = 0.181 \text{ nm}$

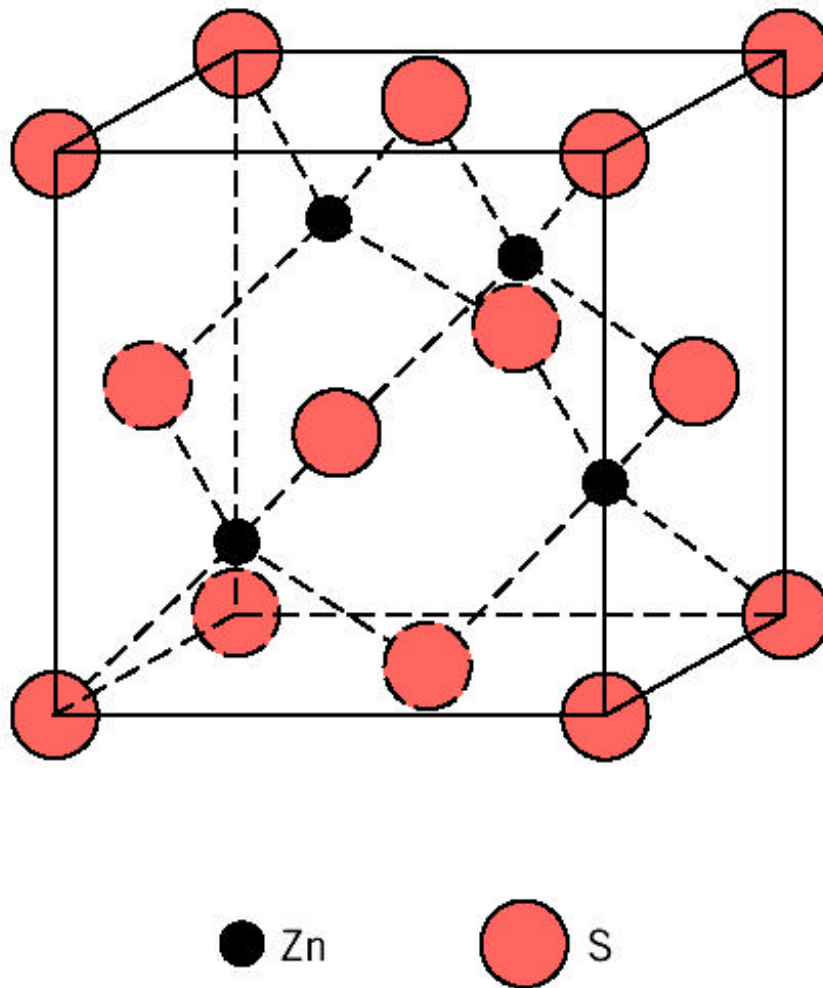
$$\Rightarrow r_C/r_A = 0.94$$

From the table for stable geometries we see that C.N. = 8



More examples of crystal structures in ceramics (will not be included in the test)

Zinc Blende Structure: typical for compounds where covalent bonding dominates. C.N. = 4

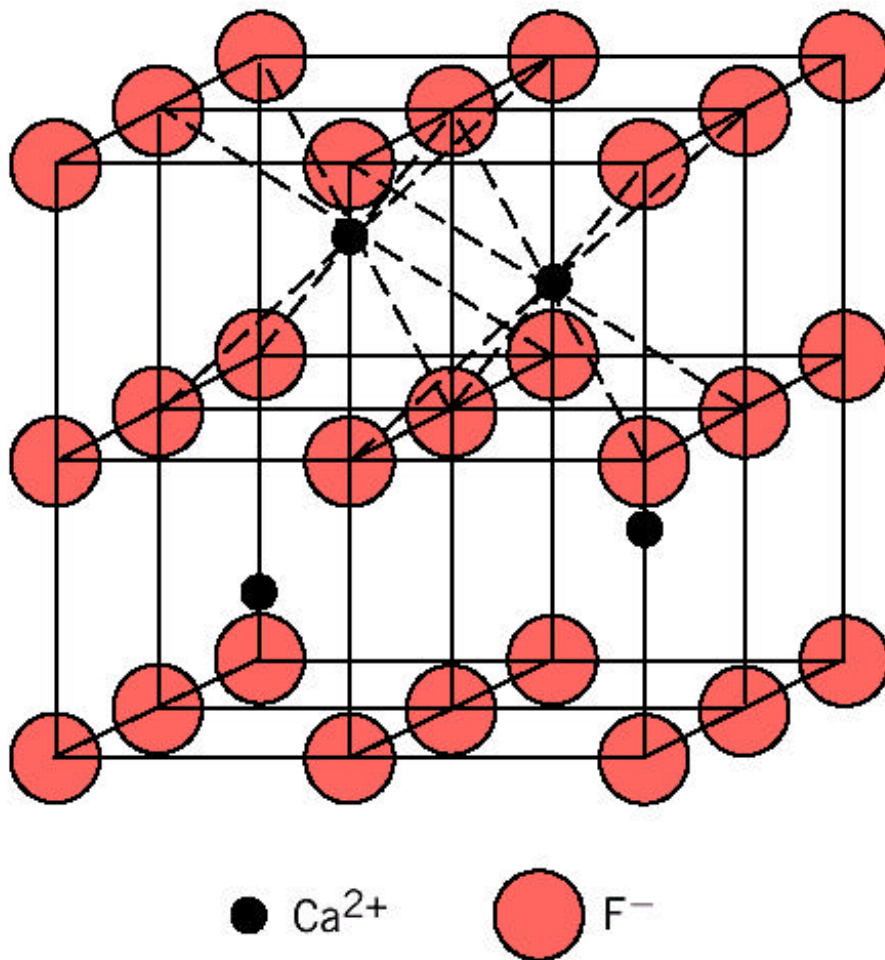


ZnS, ZnTe, SiC have this crystal structure

More examples of crystal structures in ceramics (will not be included in the test)

Fluorite (CaF_2): $r_{\text{C}} = r_{\text{Ca}} = 0.100 \text{ nm}$, $r_{\text{A}} = r_{\text{F}} = 0.133 \text{ nm}$
 $\Rightarrow r_{\text{C}}/r_{\text{A}} = 0.75$

From the table for stable geometries we see that C.N. = 8



FCC structure with 3 atoms per lattice point

Density computation (similar to Chapter 3.5 for metals)

$$\rho = n'(SA_C + SA_A) / (V_c N_A)$$

n' : number of formula units in unit cell (all ions that are included in the chemical formula of the compound = formula unit)

SA_C : sum of atomic weights of cations in the formula unit

SA_A : sum of atomic weights of anions in the formula unit

V_c : volume of the unit cell

N_A : Avogadro's number, 6.023×10^{23} (formula units)/mol

Example: NaCl

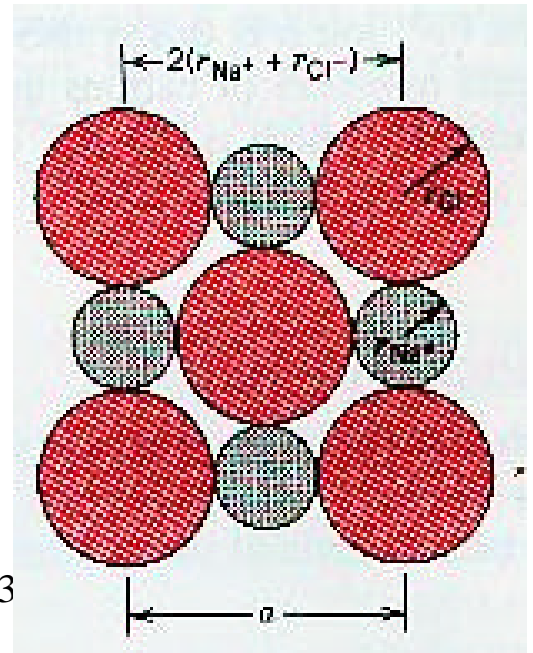
$n' = 4$ in FCC lattice

$$SA_C = A_{Na} = 22.99 \text{ g/mol}$$

$$SA_A = A_{Cl} = 35.45 \text{ g/mol}$$

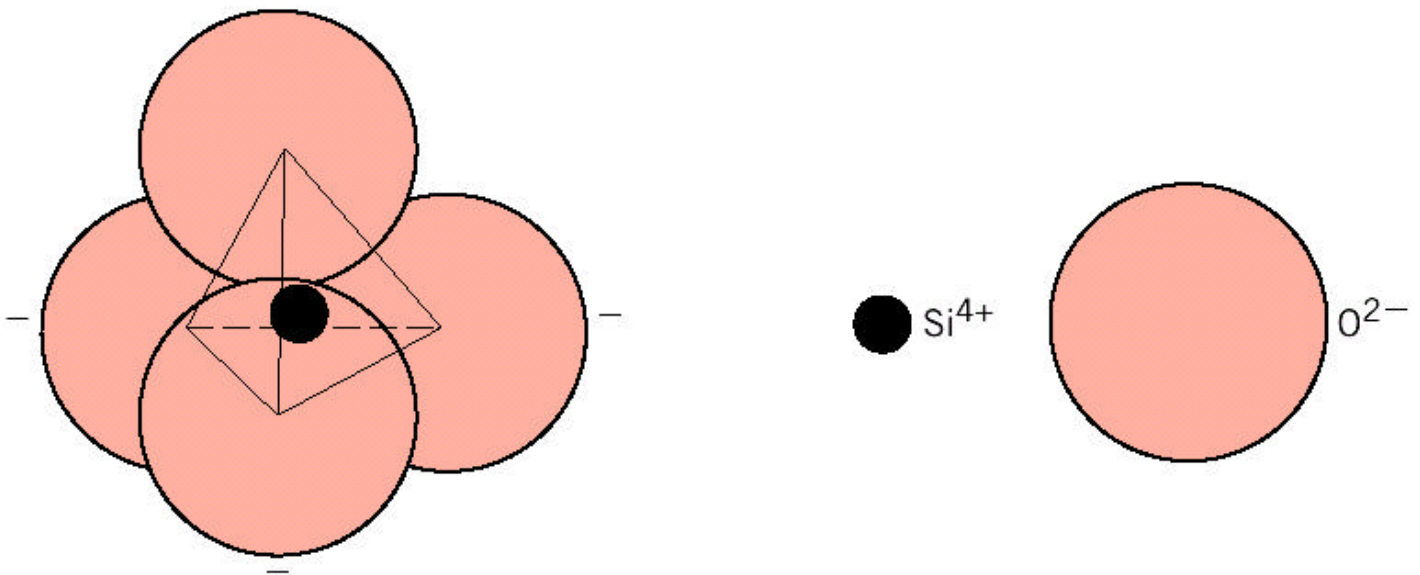
$$V_c = a^3 = (2r_{Na} + 2r_{Cl})^3 =$$

$$= (2 \times 0.102 \times 10^{-7} + 2 \times 0.181 \times 10^{-7})^3 \text{ cm}^3$$



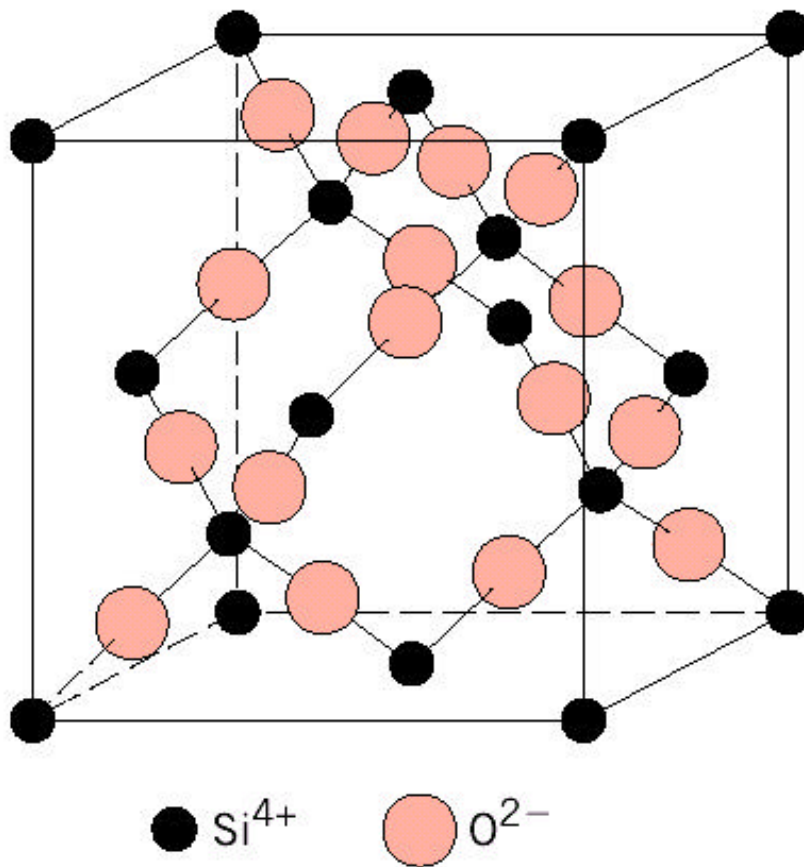
Silicate Ceramics

- Composed mainly of silicon and oxygen, the two most abundant elements in earth's crust (rocks, soils, clays, sand)
- Basic building block: SiO_4^{4-} tetrahedron
- Si-O bonding is largely covalent, but overall SiO_4 block has charge of -4
- Various silicate structures – different ways to arrange SiO_4^{4-} blocks



Silica = silicon dioxide = SiO_2

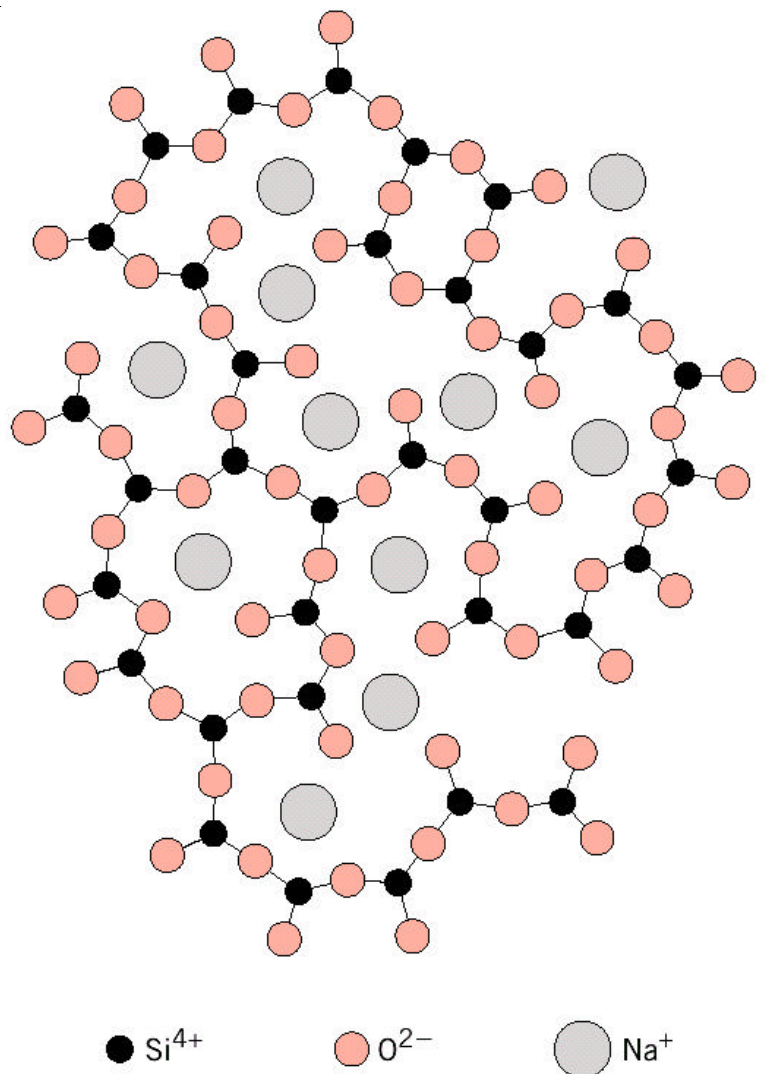
- Every oxygen atom is shared by adjacent tetrahedra
- Silica can be crystalline (e.g., quartz) or amorphous, as in glass (fused or vitreous silica)



3D network of SiO_4 tetrahedra in cristobalite
High melting temperature of $1710\text{ }^\circ\text{C}$

Window glasses

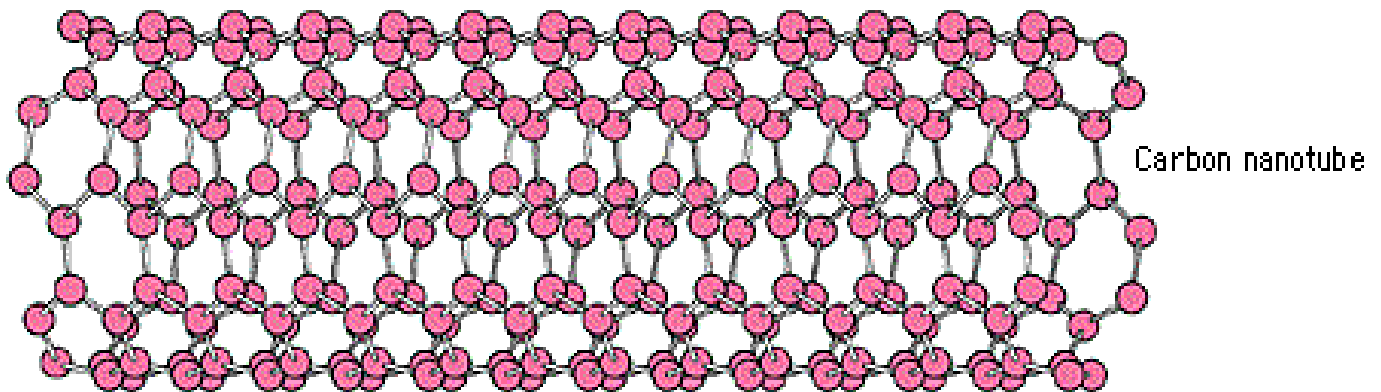
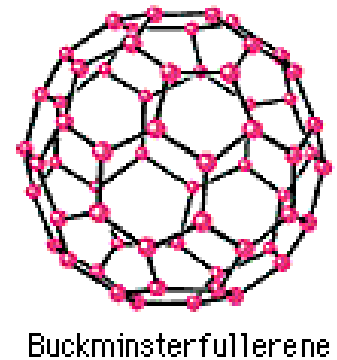
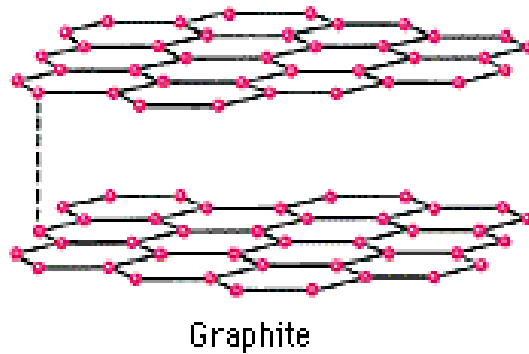
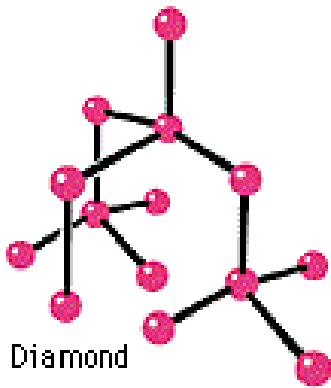
Most common window glasses are produced by adding other oxides (e.g. CaO , Na_2O) whose cations are incorporated within SiO_4 network. The cations break the tetrahedral network and glasses melt at lower temperature than pure amorphous SiO_2 because. A lower melting point makes it easy to form glass to make, for instance, bottles. Some other oxides (TiO_2 , Al_2O_3) substitute for silicon and become part of the network



Carbon

Carbon is **not a ceramic**

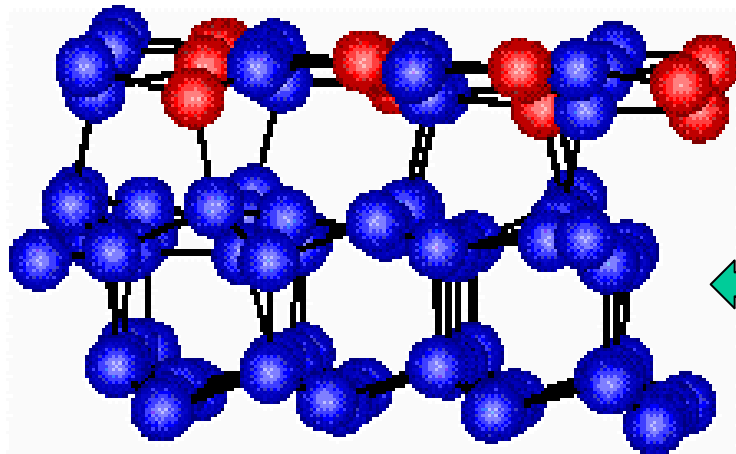
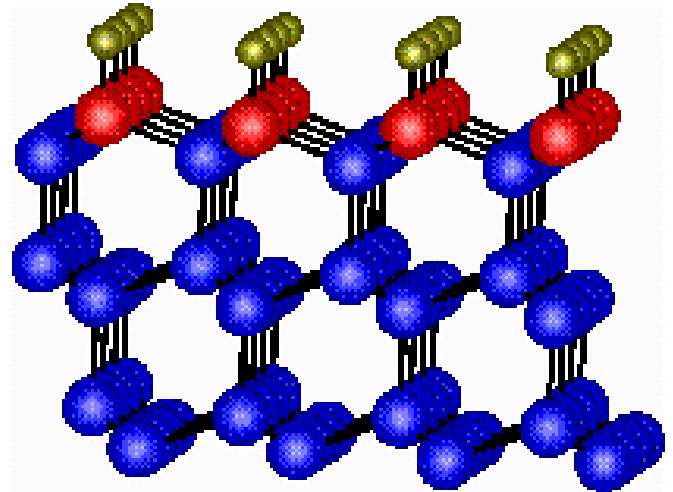
Carbon exists in various polymorphic forms: sp^3 diamond and amorphous carbon, sp^2 graphite and fullerenes/nanotubes, one dimensional sp carbon...



Carbon: Diamond

- Has diamond-cubic structure (like Si, Ge)
- One of the strongest/hardest material known
- High thermal conductivity (unlike ceramics)
- Transparent in the visible and infrared, with high index of refraction, looks nice, costs \$\$\$
- Semiconductor (can be doped to make electronic devices)
- Metastable (transforms to carbon when heated)

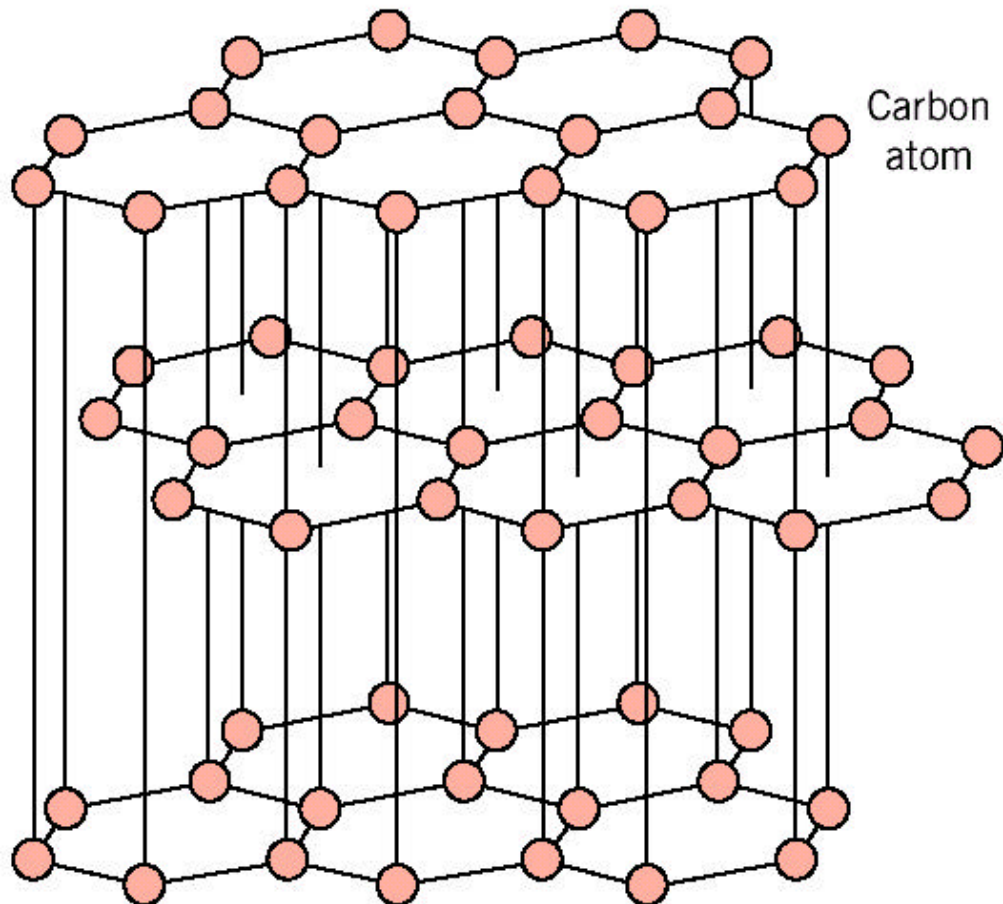
Hydrogenated diamond {111} surface with the dangling bonds or radicals terminated by hydrogen atoms



Diamond turning into graphite at elevated temperature

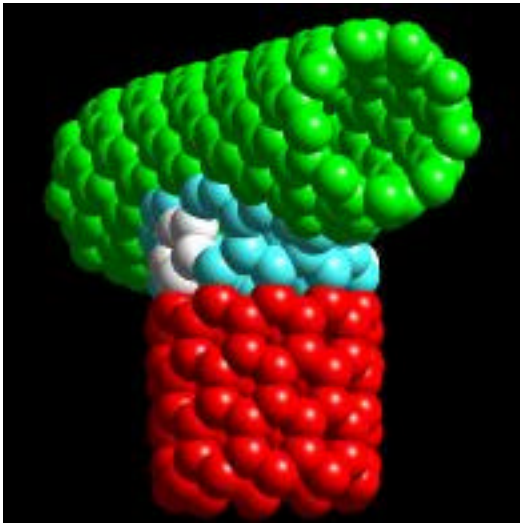
Carbon: Graphite

- 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
- Applications include furnaces, rocket nozzles, welding electrodes

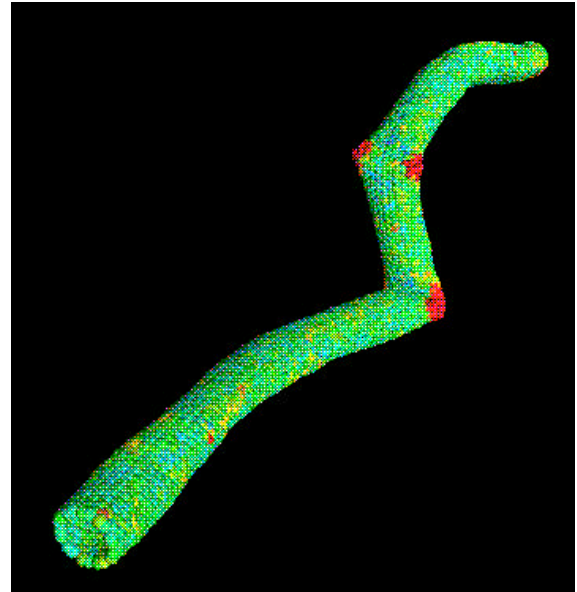


Carbon: buckyballs and nanotubes

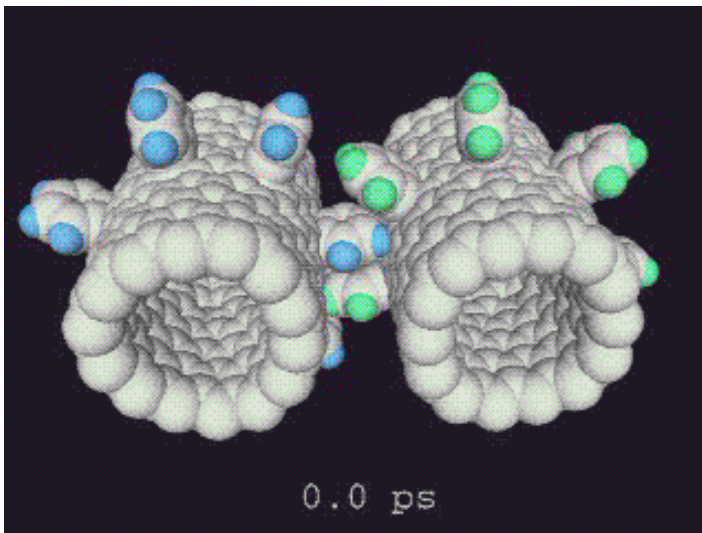
Buckminsterfullerenes (buckyballs) and carbon nanotubes are expected to play an important role in future nanotechnology applications (nanoscale materials, sensors, machines, and computers).



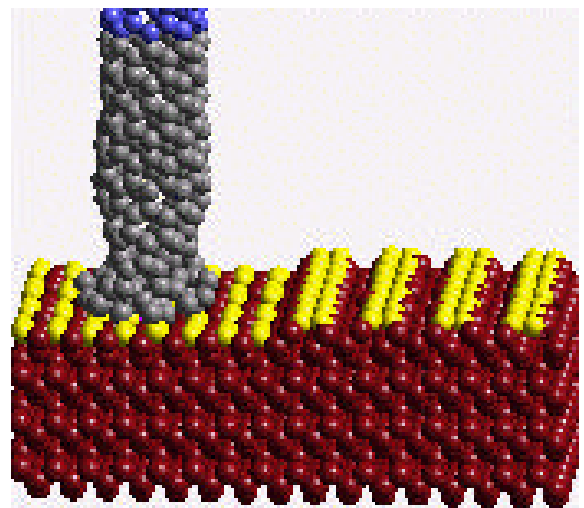
Carbon nanotube T-junction



Nanotubes as reinforcing fibers in nanocomposites



Nano-gear



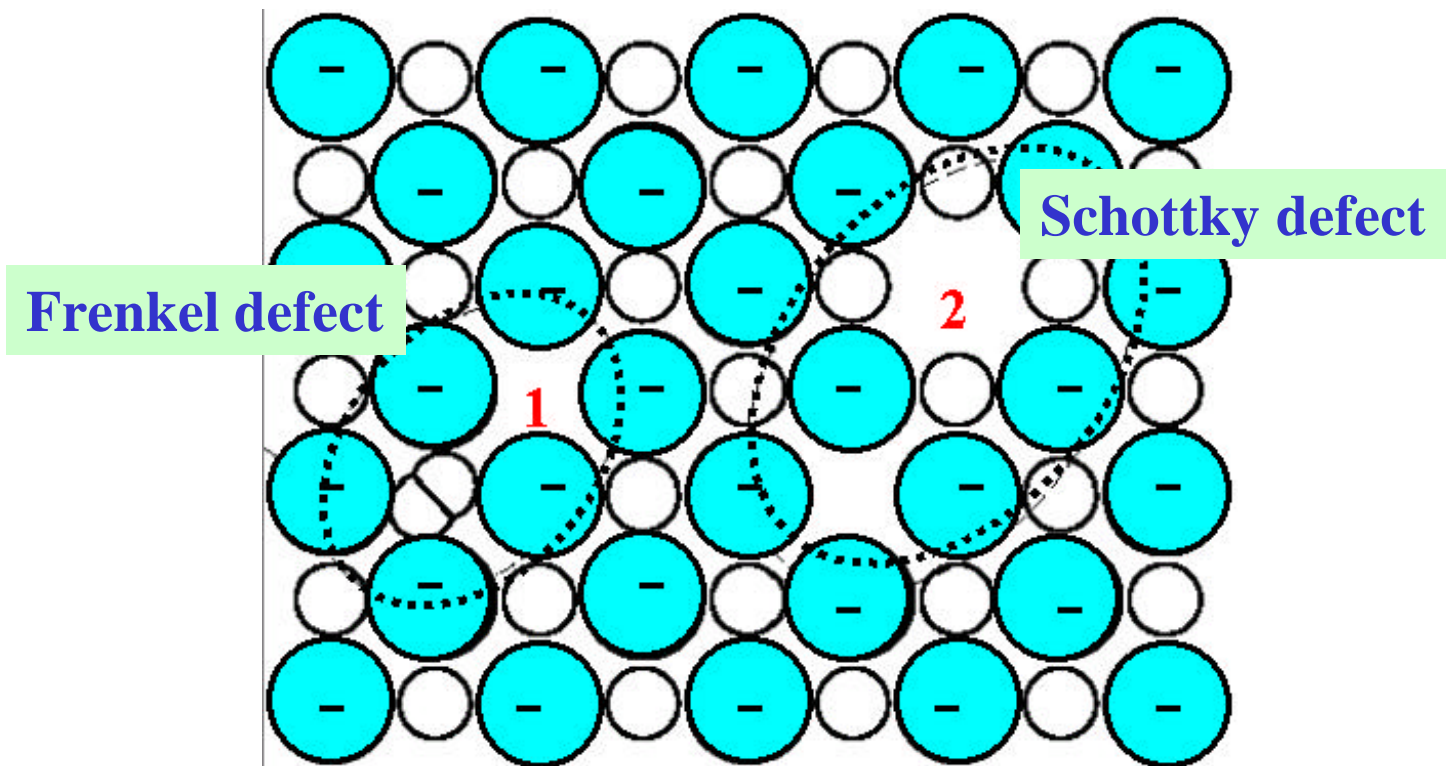
Nanotube holepunching/etching

Imperfections in Ceramics (I)

Point defects in ionic crystals are charged. The Coulombic forces are very large and any charge imbalance has a strong tendency to balance itself. To maintain charge neutrality several point defects can be created:

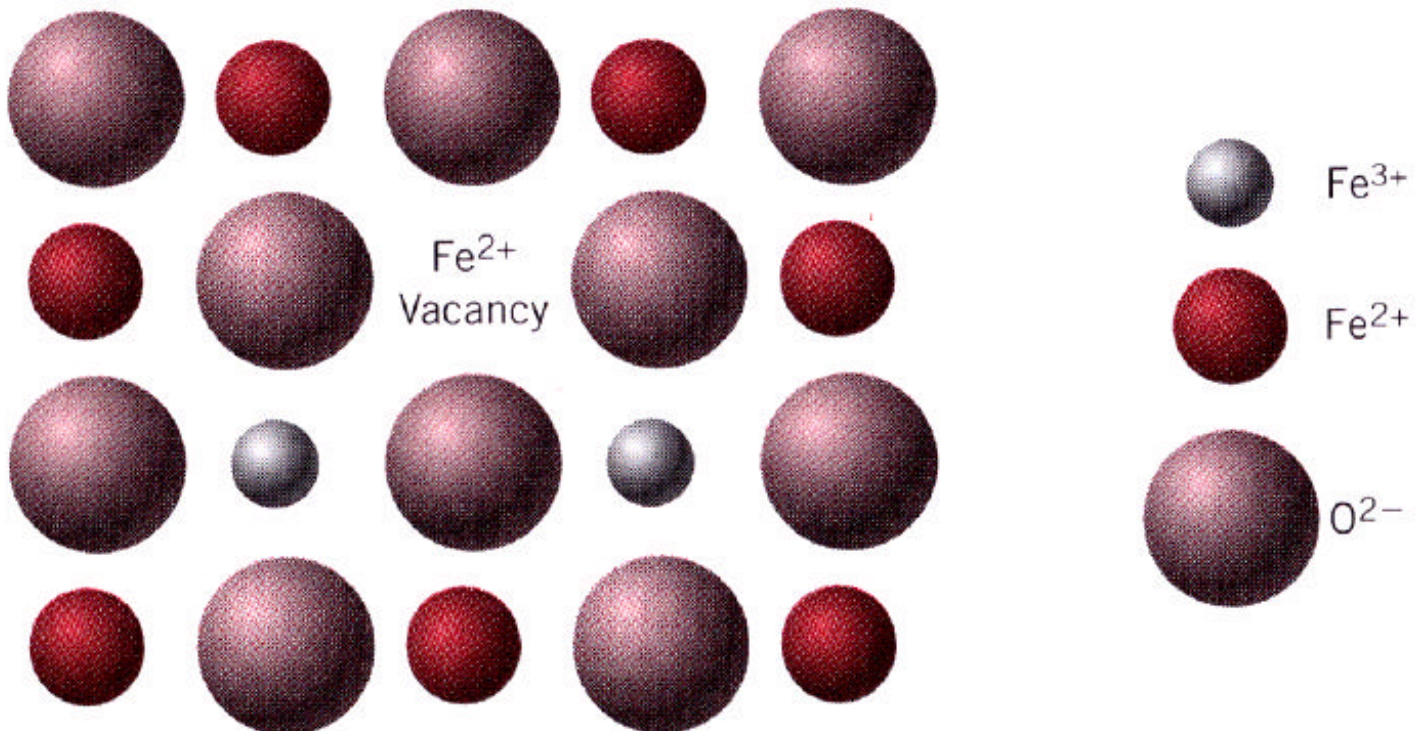
Frenkel defect is a pair of cation (positive ion) vacancy and a cation interstitial. It may also be an anion (negative ion) vacancy and anion interstitial. However anions are larger than cations and it is not easy for an anion interstitial to form.

Schottky defect is a pair of anion and cation vacancies



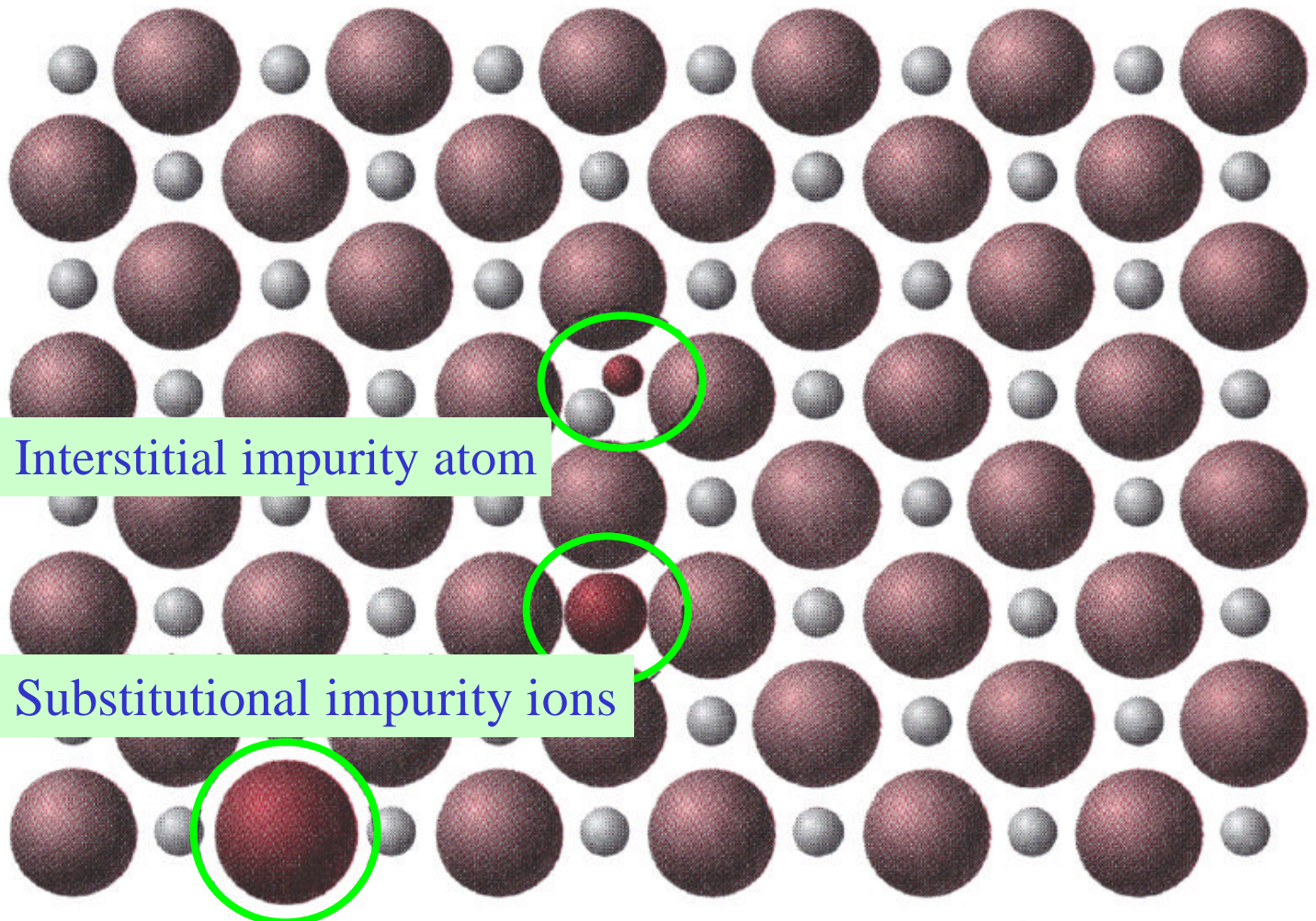
Imperfections in Ceramics (II)

- Frenkel and Schottky defects do not change ratio of cations to anions → the compound is **stoichiometric**
- **Non-stoichiometry** (composition deviates from the one predicted by chemical formula) may occur when one ion type can exist in two valence states, e.g. Fe^{2+} , Fe^{3+}
- For example, in FeO , usual Fe valence state is 2+. If two Fe ions are in 3+ state, then a Fe vacancy is required to maintain charge neutrality → fewer Fe ions → non-stoichiometry



Impurities in Ceramics

- Impurity atoms can exist as either substitutional or interstitial solid solutions
- Substitutional ions substitute for ions of like type
- Interstitial ions are small compared to host structure – formation of anion interstitials is unlikely
- Solubilities higher if ion radii and charges match closely
- Incorporation of ion with different charge state requires compensation by point defects



Mechanical Properties of Ceramics

- Ceramics are brittle. For brittle fracture stress concentrators are very important. (Chapter 8: measured fracture strengths are significantly smaller than theoretical predictions for perfect materials due to the stress risers)
- Fracture strength of ceramic may be greatly enhanced by creating compressive stresses in the surface region (similar to shot peening, case hardening in metals, chapter 8)
- The compressive strength is typically ten times the tensile strength. This makes ceramics good structural materials under compression (e.g., bricks in houses, stone blocks in the pyramids).

Plastic Deformation in Ceramics

- **Crystalline ceramics:** Slip (dislocation motion) is very difficult. This is because ions of like charge have to be brought into close proximity of each other → large barrier for dislocation motion. In ceramics with covalent bonding slip is not easy as well (covalent bonds are strong) ⇒ ceramics are brittle.
- **Non-crystalline ceramic:** there is no regular crystalline structure → no dislocations. Materials deform by **viscous flow**, i.e. by breaking and reforming atomic bonds, allowing ions/atoms to slide past each other (like in a liquid).
Viscosity is a measure of glassy material's resistance to deformation.

Viscosity

Viscosity is a measure of a non-crystalline (glass or liquid) material's resistance to deformation. High-viscosity fluids resist flow; low-viscosity fluids flow easily.

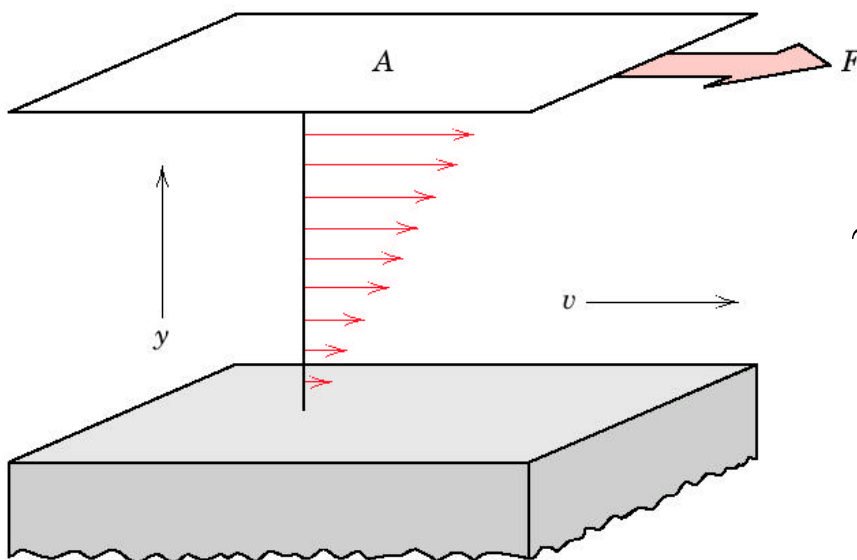
How readily a moving layer of fluid molecules drags adjacent layers of molecules along with it determines its viscosity.

Units are Pa-s, or Poises (P)

$$1 \text{ P} = 0.1 \text{ Pa-s}$$

Viscosity of water at room temp is $\sim 10^{-3} \text{ P}$

Viscosity of typical glass at room temp $\gg 10^{16} \text{ P}$



$$\eta = \frac{\tau}{dv/dy} = \frac{F/A}{dv/dy}$$

Summary

Make sure you understand language and concepts:

- Anion
- Cation
- Defect structure
- Frenkel defect
- Electroneutrality
- Schottky defect
- Stoichiometry
- Viscosity

Reading for next class:

Chapter 14: Applications and Processing of Ceramics

- Short review of glass/ceramics applications and processing (14.1 - 14.4)

Optional reading: 14.3, 14.5 – 14.18