Chapter 12: Structures of Ceramics

Outline

- Introduction
- Crystal structures
  - Ceramic structure
  - AX-type crystal structures
  - AmXp-type
  - AmBnXp- type
- Silicate ceramics
- Carbon

Ceramic structures

- Two or more different elements
- More complex than metal structures
- Ionic and/or covalent bonds
- A mix of ionic and covalent bonds -- electronegativity
- Ionic bonds form ions
  - Metals give up electrons --metallic ions--cations--positively charged
  - Non-metals gain electrons --nonmetallic ions--anions--negatively charged
- Crystals must be electrically neutral, e.g. CaF_2

Ceramic structures (*continue*)

- Factors influence crystal structure
  - **Magnitude of electrical charge of ions**
  - **Relative size of ions (Non-metal > metal ions Rc/Ra<1)**
    - **Cations must be next to anions--maximize # of nearest neighbors that are anions**
    - **Stable structure--anions and cations must contact each other**

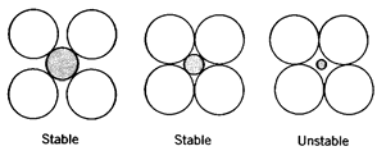
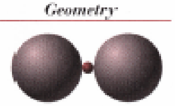
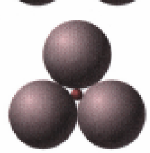
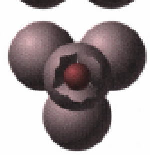
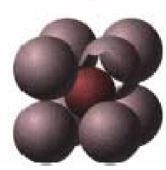


FIGURE 13.1 Stable and unstable anion–cation coordination configurations. Open circles represent anions; colored circles denote cations.

- **The # of anions depends on ratio of Rc/Ra**

Coordination numbers and geometries for various cation-anion radius ratios (R_c/R_a)

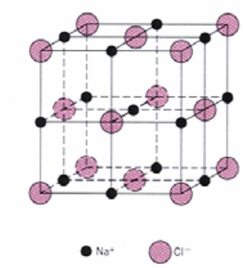
Table 13.2 Coordination Numbers and Geometries for Various Cation–Anion Radius Ratios (r_C/r_A)

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	

AX-type crystal structure

Rock salt structure

- Sodium chloride (NaCl) is the most common
- Rc/Ra =0.414-0.732
- CN=6 for both cations and anions
- Unit cell: FCC arrangement of anions with one cation at center of each of 12 cube edges
- Two interpenetrating FCC lattices



A unit cell of rock salt

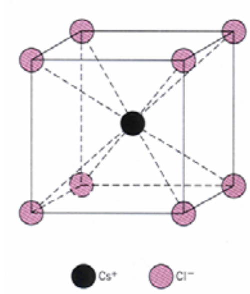
AX-type crystal structure (*continue*)

Cesium chloride structure

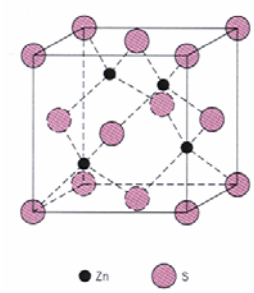
- **CN=8, 8 anions at cube corners and 1 cation at center of cube, simple cubic (not BCC)**

Zinc Blende structure

- **CN=4, FCC structure of S with Zn at interior tetrahedral**



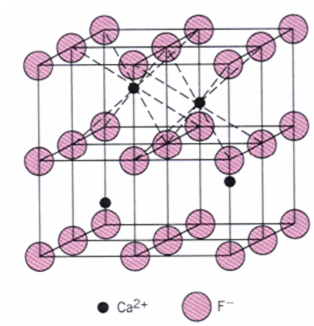
A unit cell of cesium chloride



A unit cell of zinc blende

The AmXp type crystal structures

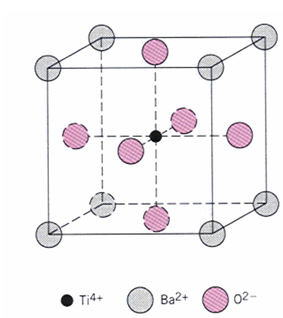
- Rc/Ra=0.8, CN_{Ca}=8, CN_F=4
- Ca atoms at center of cubes with F atoms at cube corners, similar to CsCl, but only 1/2 of sites are filled with Ca atoms
- Unit cell consists of 8 cubes



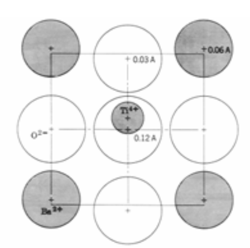
A unit cell of CaF_2

The AmBnXp type crystal structures

- Ba at cubic corner, O at center of 6 faces, Ti at body center
- CN_O=12, CN_{Ba}=6, and CN_{Ti}=6
- Large A cation and oxygen form an FCC lattice
- Cubic--tetragonal at 130^{0}C (Curie points)
- Cubic -- orthrhombic and rhombohedral at low T



A unit cell of perovskite crystal structure



A unit cell of tetragonal perovskite

Summary of crystal structures of some common ceramics

Structure Name	Structure Type	Anion Packing	Coordination Numbers		Examples
			Cation	Anion	
Rock salt (sodium chloride)	AX	FCC	6	6	NaCl, MgO, FeO
Cesium chloride	AX	Simple cubic	8	8	CsCl
Zinc blende (sphalerite)	AX	FCC	4	4	ZnS, SiC
Fluorite	AX_2	Simple cubic	8	4	CaF_2, UO_2, ThO_2
Perovskite	ABX_3	FCC	12(A) 6(B)	6	$BaTiO_3$, $SrZrO_3$, $SrSnO_3$
Spinel	AB_2X_4	FCC	4(A) 6(B)	4	$MgAl_2O_4$, $FeAl_2O_4$

Source: W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, 2nd edition. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

Ceramic density computations

$$\rho = \frac{n'(\Sigma A_C + \Sigma A_A)}{V_C N_A} \qquad (13.1)$$

where

n' = the number of formula units[1] within the unit cell

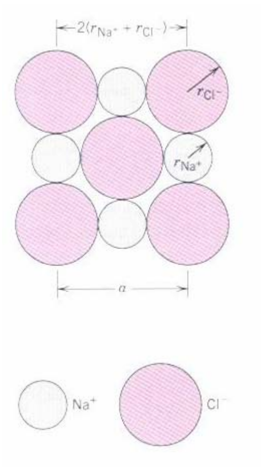
ΣA_C = the sum of the atomic weights of all cations in the formula unit

ΣA_A = the sum of the atomic weights of all anions in the formula unit

V_C = the unit cell volume

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

Ceramic density computations (example)



n’=4

$$\sum Ac = A_{Na} = 22.99 g/mol$$

$$\sum A_A = A_{Cl} = 35.45 g/mol$$

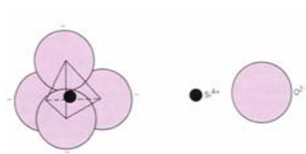
$$a = 2r_{Na^+} + 2r_{cl^-}$$

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

$$\rho = 2.14 g/cm^3$$ (page 392)

Silicate ceramics

- Silicates are materials composed primarily of silicon and oxygen (soils, rocks, clays, sand, and glass)

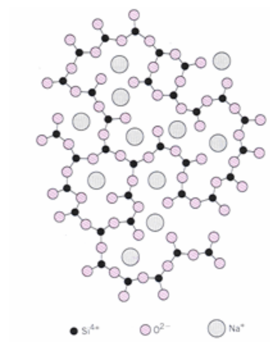


- Silica, silicon oxide (SiO_2),
  - Three crystal structures: quartz, cristobalite, and tridymite
  - Open structure, not close-packed, low density

Cristobalite

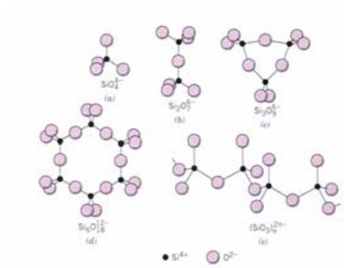
Silicate ceramics (*continue*)

- Silica glasses
  - **amorphous, a high degree of atomic randomness**
  - **additives, CaO and NaO, network modifier, modify the silicon and oxide network and low melting T**



Sodium-silicate glass

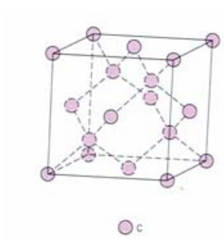
- The silicates



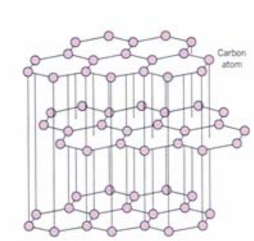
Various silicate ion structures

Carbon

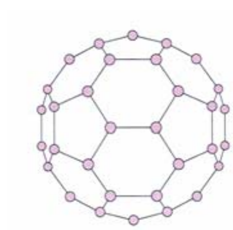
Polymorphic crystal structures of carbon



Diamond structure



Structure of graphite



Structure of buckyball C60 (buckminsterfullerence)