CERAMICS

Ceramics are inorganic compounds in which atoms are bonded with either ionic or covalent bonds or mixed bond.

- Usually metallic + 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

- Hard and brittle

- Electrical and thermal insulators

- All ceramic compounds are composed of anions and cations.

- Cations lose their valence electrons to anions.

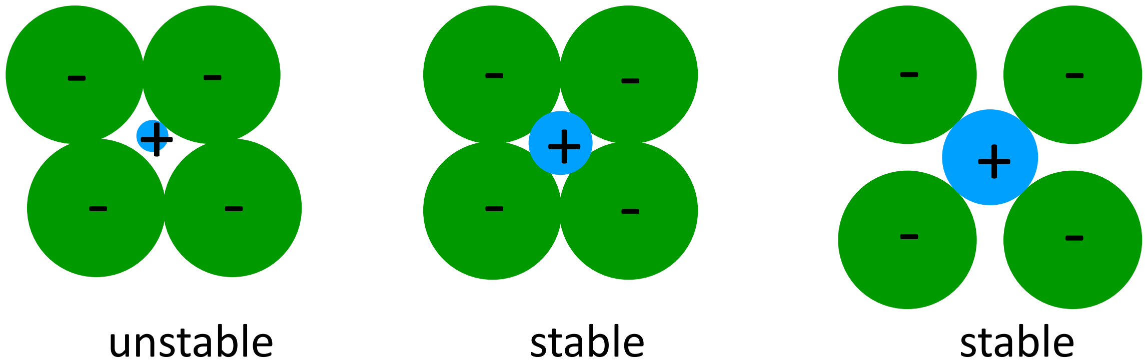
- Cations are smaller in size than anions.

- Ceramic crystals are built of framework of anions in which cations fit in the voids or holes in between.

Factors that Determine Crystal Structure

1. Relative sizes of ions – Formation of stable structures:

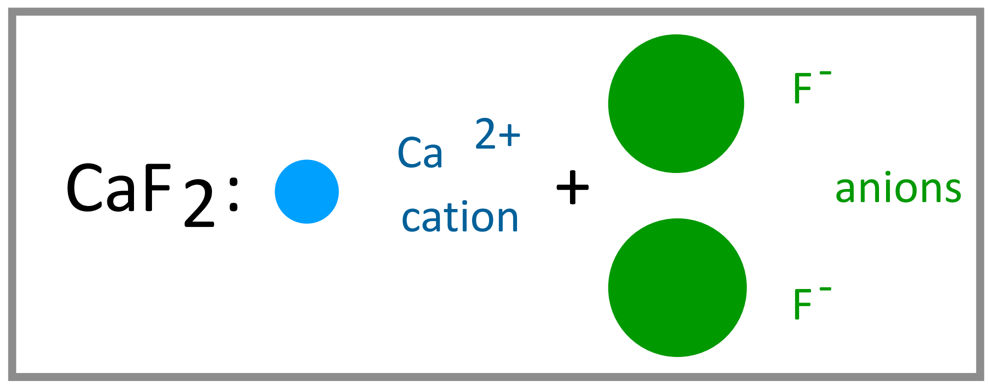
--maximize the # of oppositely charged ion neighbors.



2. Maintenance of Charge Neutrality :

--Net charge in ceramic should be zero.

--Reflected in chemical formula:

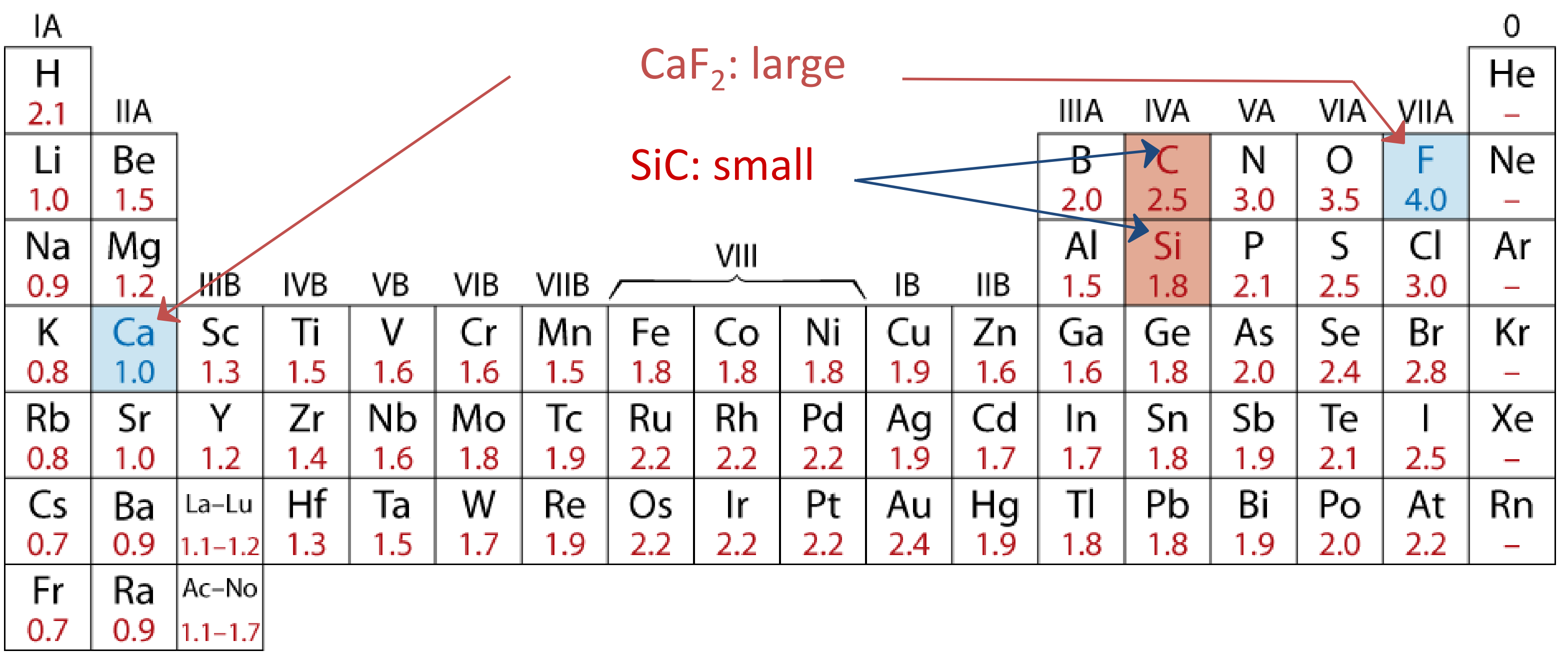


$A_m X_p$

m, p values to achieve charge neutrality

Atomic Bonding in Ceramics

- Bonding:
  - -- Can be ionic and/or covalent in character.
  - -- % ionic character increases with difference in electronegativity of atoms.
    - Degree of ionic character may be large or small:

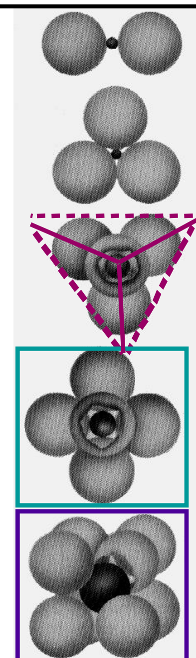


3-Coordination # and Ionic Radii

- Coordination number increases with $\frac{r_{cation}}{r_{anion}}$

To form a stable structure, how many anions can surround a cation?

$\frac{r_{cation}}{r_{anion}}$	Coord #	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	tetrahedral
0.414 - 0.732	6	octahedral
0.732 - 1.0	8	cubic



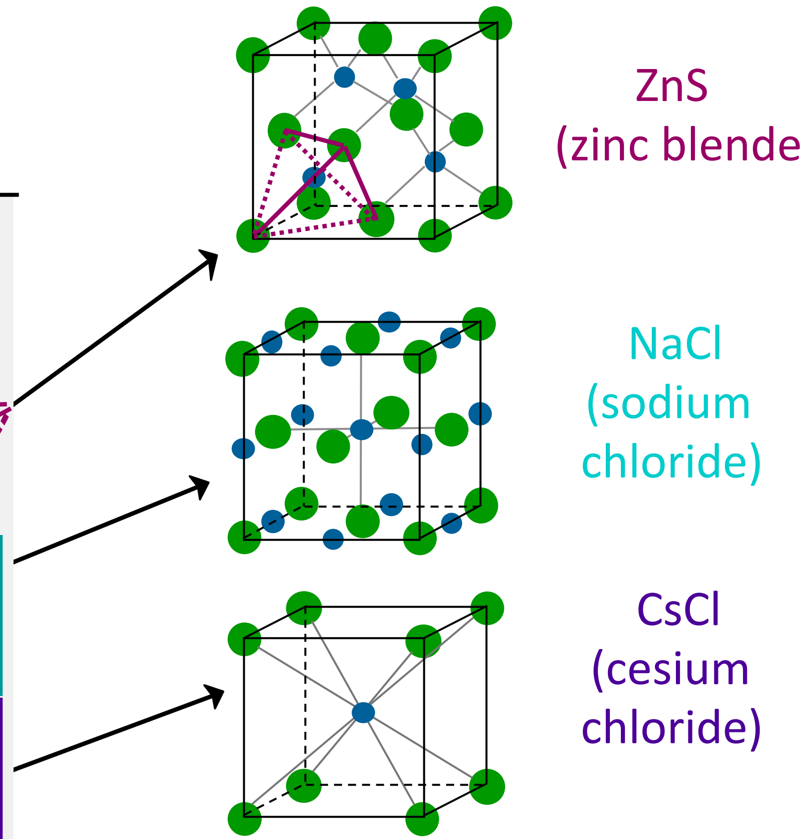
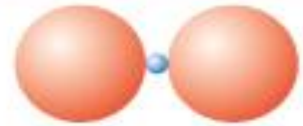
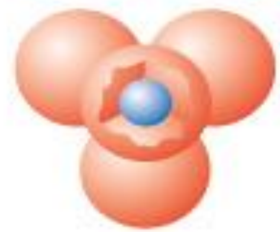
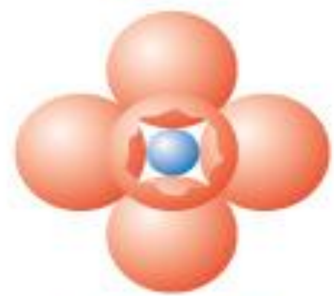
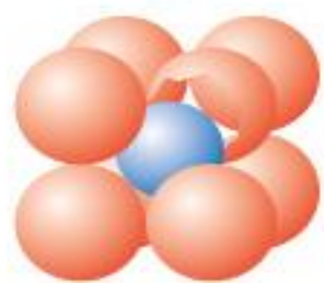
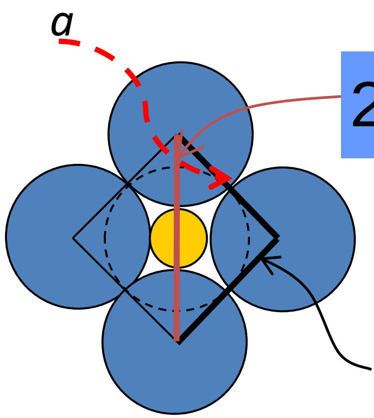


Table 3.3 Coordination Numbers and Geometries for Various Cation–Anion Radius Ratios (r_C/r_A)

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	

Computation of Minimum Cation-Anion Radius Ratio

- Determine minimum r_{cation}/r_{anion} for an octahedral site (C.N. = 6)



$$2r_{anion} + 2r_{cation} = \sqrt{2}a$$

Measure the radii (blue and yellow spheres)

$$a = 2r_{anion}$$

Substitute for **"a"** in the above equation

$$2r_{anion} + 2r_{cation} = 2\sqrt{2}r_{anion}$$

$$r_{anion} + r_{cation} = \sqrt{2}r_{anion}$$

$$r_{cation} = (\sqrt{2} - 1)r_{anion}$$

$$\frac{r_{cation}}{r_{anion}} = \sqrt{2} - 1 = 0.414$$

Example Problem: Predicting the Crystal Structure of FeO

- On the basis of ionic radii, what crystal structure would you predict for FeO?

Cation	Ionic radius (nm)
Al^{3+}	0.053
Fe^{2+}	0.077
Fe^{3+}	0.069
Ca^{2+}	0.100

Anion	
O^{2-}	0.140
Cl^{-}	0.181
F^{-}	0.133

- Answer:

$$\frac{r_{cation}}{r_{anion}} = \frac{0.077}{0.140}$$

$$= 0.550$$

based on this ratio,
-- coord # = 6 because

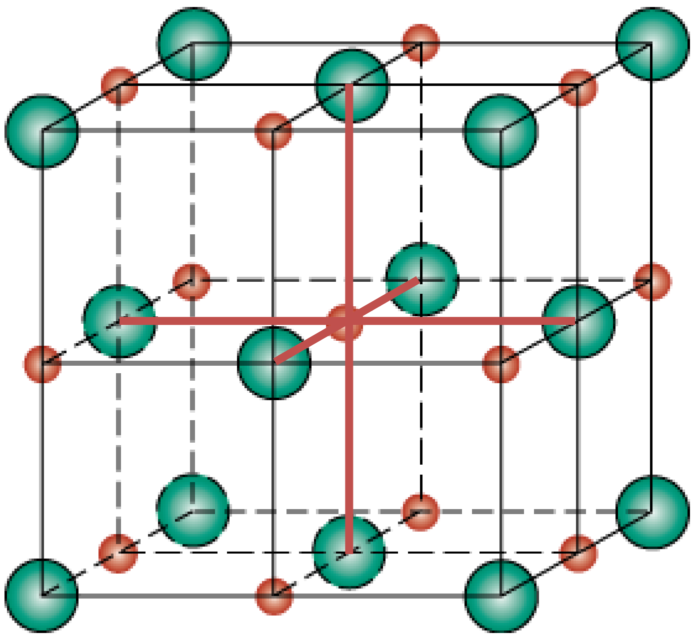
$0.414 < 0.550 < 0.732$

-- crystal structure is similar to NaCl

Rock Salt Structure

Same concepts can be applied to ionic solids in general.

Example: NaCl (rock salt) structure



Na^+ $r_{Na} = 0.102$ nm

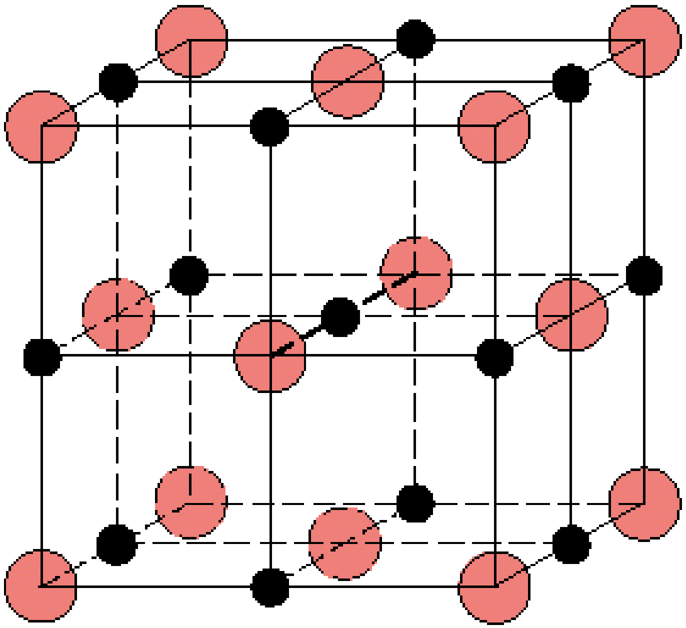
Cl^- $r_{Cl} = 0.181$ nm

$r_{Na}/r_{Cl} = 0.564$

$\therefore$ cations (Na^+) prefer octahedral sites

MgO and FeO

MgO and FeO also have the NaCl structure



O^{2-} $r_O = 0.140$ nm

Mg^{2+} $r_{Mg} = 0.072$ nm

$r_{Mg}/r_O = 0.514$

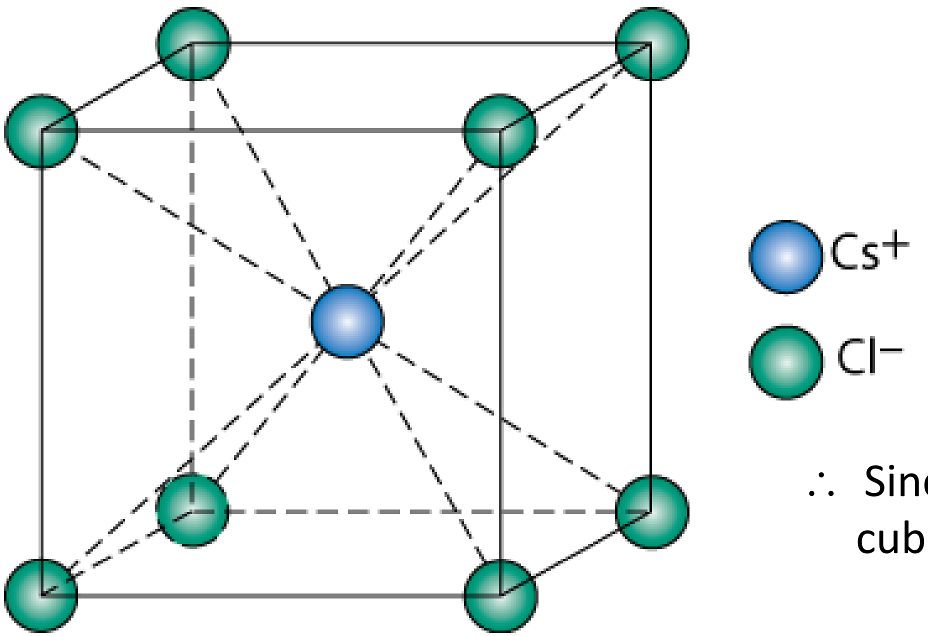
∴ cations prefer octahedral sites

So each Mg^{2+} (or Fe^{2+}) has 6 neighbor oxygen atoms

AX Crystal Structures

AX–Type Crystal Structures include NaCl, CsCl, and zinc blende

Cesium Chloride structure:



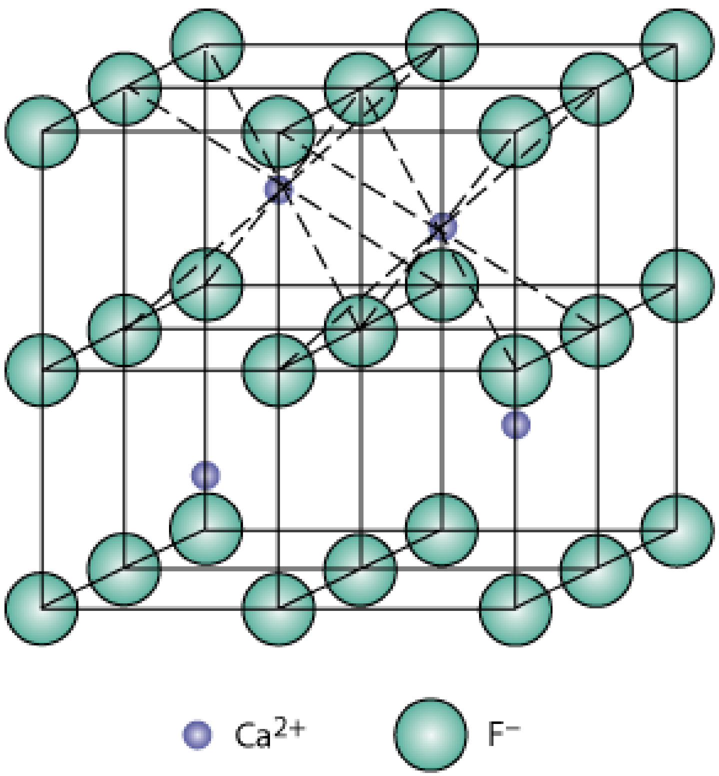
$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{0.170}{0.181} = 0.939$$

∴ Since $0.732 < 0.939 < 1.0$,
cubic sites preferred

So each Cs^+ has 8 neighbor Cl^-

AX_2 Crystal Structures

Fluorite structure



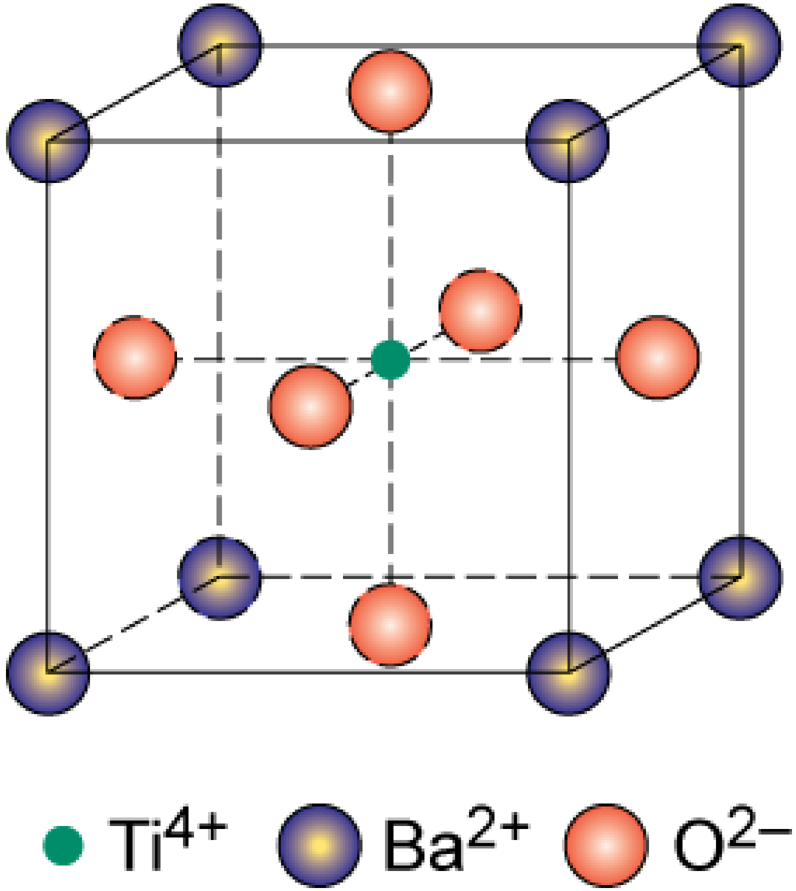
- Calcium Fluorite (CaF_2)
- Cations in cubic sites
- UO_2, ThO_2, ZrO_2, CeO_2
- Antifluorite structure – positions of cations and anions reversed

ABX_3 Crystal Structures

- Perovskite structure

Ex: complex oxide

$BaTiO_3$



SUMMARY

- Atoms may assemble into crystalline or amorphous structures.
- Common metallic crystal structures are FCC, BCC and HCP. Coordination number and atomic packing factor are the same for both FCC and HCP crystal structures.
- We can predict the density of a material, provided we know the atomic weight, atomic radius, and crystal geometry (e.g., FCC, BCC, HCP).
- Interatomic bonding in ceramics is ionic and/or covalent.
- Ceramic crystal structures are based on:
  -- maintaining charge neutrality
  -- cation-anion radii ratios.