

MAT 214: Processing and Properties of Ceramic Materials

Crystal Structures in Ceramics

Prof. Joshua C. Agar

jca318@lehigh.edu

Materials Science and Engineering
Lehigh University

February 12, 2022



Learning Objectives

- An understanding of how the nature of the atomic constituents influence the resulting crystallographic structures



Learning Objectives

- An understanding of how the nature of the atomic constituents influence the resulting crystallographic structures
- A understanding of some of the ways crystal structure can influence properties



Learning Objectives

- An understanding of how the nature of the atomic constituents influence the resulting crystallographic structures
- A understanding of some of the ways crystal structure can influence properties
- An understanding of the relative energetics of different crystallographic configurations



Learning Objectives

- An understanding of how the nature of the atomic constituents influence the resulting crystallographic structures
- A understanding of some of the ways crystal structure can influence properties
- An understanding of the relative energetics of different crystallographic configurations
- A working knowledge of Pauling's Rules



Learning Objectives

- An understanding of how the nature of the atomic constituents influence the resulting crystallographic structures
- A understanding of some of the ways crystal structure can influence properties
- An understanding of the relative energetics of different crystallographic configurations
- A working knowledge of Pauling's Rules
- An understanding of common binary ceramic crystal structures



Learning Objectives

- An understanding of how the nature of the atomic constituents influence the resulting crystallographic structures
- A understanding of some of the ways crystal structure can influence properties
- An understanding of the relative energetics of different crystallographic configurations
- A working knowledge of Pauling's Rules
- An understanding of common binary ceramic crystal structures
- An understanding of common ternary ceramic crystal structures

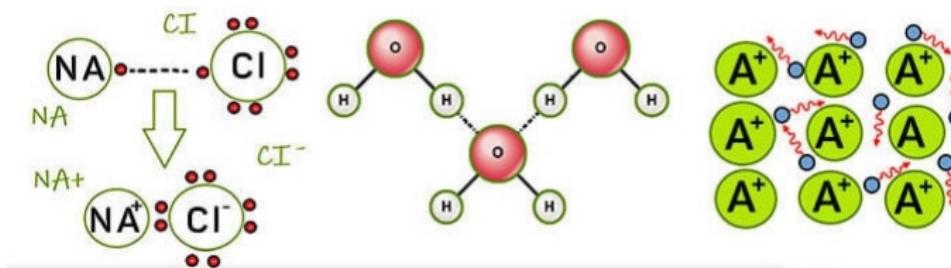


Learning Objectives

- An understanding of how the nature of the atomic constituents influence the resulting crystallographic structures
- A understanding of some of the ways crystal structure can influence properties
- An understanding of the relative energetics of different crystallographic configurations
- A working knowledge of Pauling's Rules
- An understanding of common binary ceramic crystal structures
- An understanding of common ternary ceramic crystal structures
- An appreciation for the complexity of ceramic crystal structures.

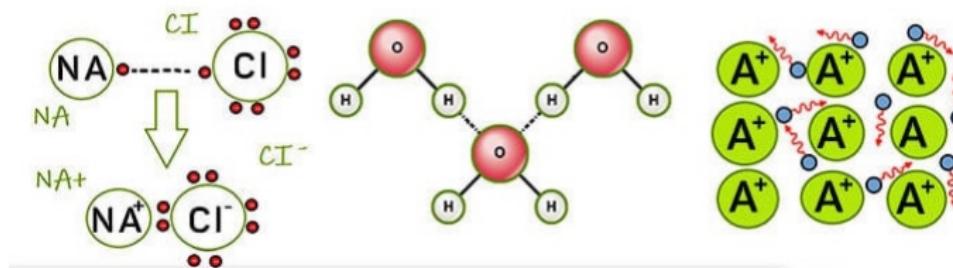


Ceramic Bonding



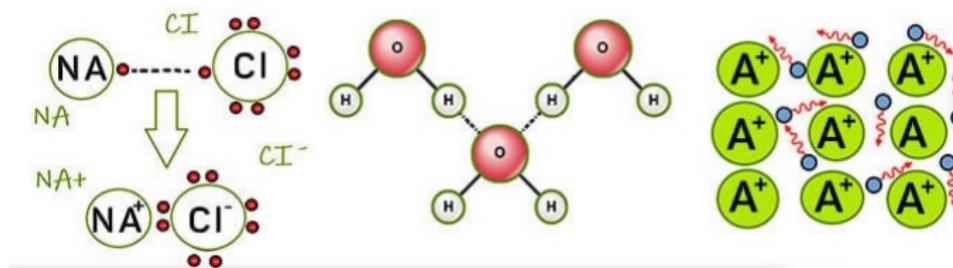
- In the past (MAT 033) we have primarily considered crystal structures formed by metallic or ionic bonds → Ceramics are much more complicated.

Ceramic Bonding



- In the past (MAT 033) we have primarily considered crystal structures formed by metallic or ionic bonds → Ceramics are much more complicated.
- Ceramics tend to have mixed covalent ionic character

Ceramic Bonding

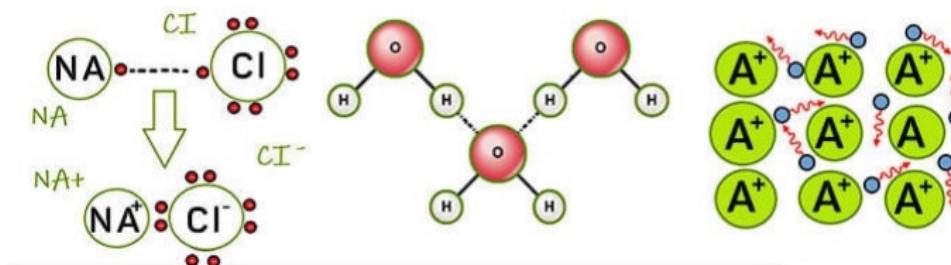


- In the past (MAT 033) we have primarily considered crystal structures formed by metallic or ionic bonds → Ceramics are much more complicated.
- Ceramics tend to have mixed covalent ionic character

Rules:

- Two atoms with similar electronegativity will form metallic or covalent bonds

Ceramic Bonding

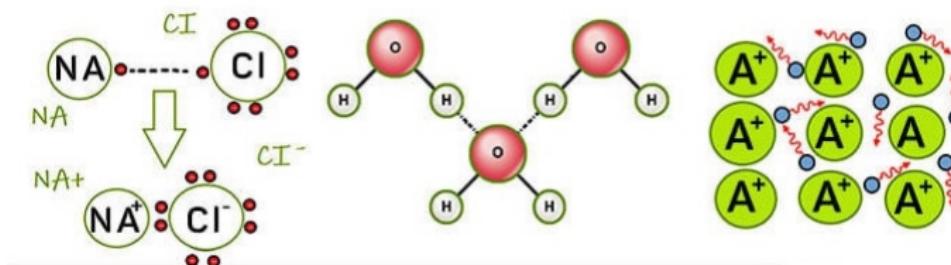


- In the past (MAT 033) we have primarily considered crystal structures formed by metallic or ionic bonds → Ceramics are much more complicated.
 - Ceramics tend to have mixed covalent/ionic character

Rules:

- Two atoms with similar electronegativity will form metallic or covalent bonds
 - Two atoms with different electronegativity will be partially ionic

Ceramic Bonding



- In the past (MAT 033) we have primarily considered crystal structures formed by metallic or ionic bonds → Ceramics are much more complicated.
 - Ceramics tend to have mixed covalent/ionic character

Rules:

- Two atoms with similar electronegativity will form metallic or covalent bonds
 - Two atoms with different electronegativity will be partially ionic

Fraction of Ionic Character

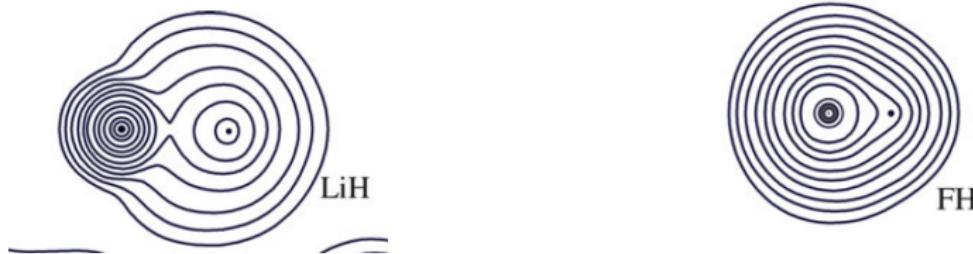
The fraction of ionic character differs with the electronegativity of the two atoms

$$\% \text{ionic} = 1 - \exp[-0.25(X_m - X_x)^2]$$

Fraction of Ionic Character

The fraction of ionic character differs with the electronegativity of the two atoms

$$\% \text{ionic} = 1 - \exp[-0.25(X_m - X_x)^2]$$



Terms and Definitions: Crystal lattice

Crystal lattice: A three-dimensional array of points related by translational symmetry.



Terms and Definitions: Crystal lattice

Crystal lattice: A three-dimensional array of points related by translational symmetry.

- We can fully describe such a lattice by three vectors \mathbf{a} , \mathbf{b} , \mathbf{c} , and three angles, α , β , γ .

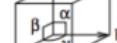


Terms and Definitions: Crystal lattice

Crystal lattice: A three-dimensional array of points related by translational symmetry.

- We can fully describe such a lattice by three vectors \mathbf{a} , \mathbf{b} , \mathbf{c} , and three angles, α , β , γ .

Table 1. Crystal Systems

unit cell	name	geometry	symmetry	unit cell	name	geometry	symmetry
	triclinic (anorthic)	$a \neq b \neq c \neq a$ $\alpha \neq \beta \neq \gamma \neq \alpha$	1		trigonal hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	3 6
	monoclinic	$a \neq b \neq c \neq a$ $\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	2		rhombohedral	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	3 on one body diagonal
	orthorhombic	$a \neq b \neq c \neq a$ $\alpha = \beta = \gamma = 90^\circ$	222		cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	3 on all body diagonals
	tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	4				

Terms and Definitions: Basis

Group of atoms associated with each and every lattice point.

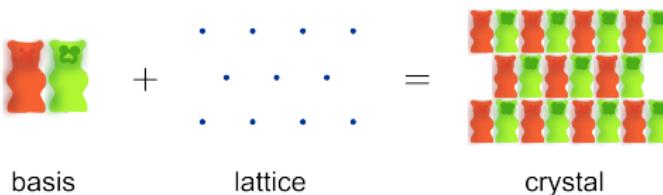
Bravais Lattice = Basis + Crystal Structure



Terms and Definitions: Basis

Group of atoms associated with each and every lattice point.

$$\text{Bravais Lattice} = \text{Basis} + \text{Crystal Structure}$$



Terms and Definitions: Bravais lattice

Within each crystal lattice there are 14 different ways to arrange lattice points.



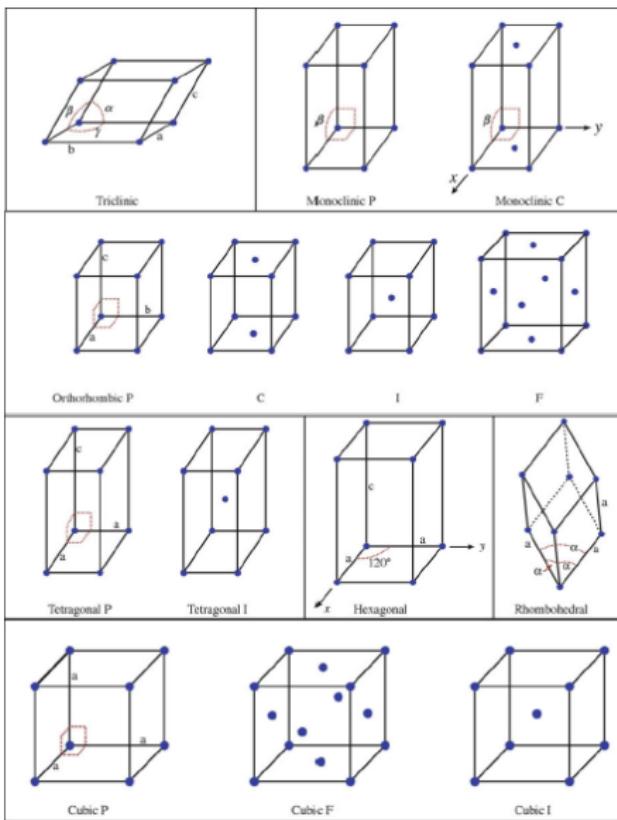
Terms and Definitions: Bravais lattice

Within each crystal lattice there are 14 different ways to arrange lattice points.

- Primitive (P) lattices—one lattice point per unit cell
- Body-centered (I) lattices—a lattice point at the corners and one in the center of the cell
- A-, B-, C- or F-centered lattices—a lattice point at the corners and others at one (A, B, C) or all three (F) of the faces



Terms and Definitions: Bravais lattice





Coordination Number

Coordination number (CN): Number of nearest neighbors.

coordination	bonds	polyhedron
linear (2-fold)		
triangular (3-fold)		
tetrahedral (4-fold)		
octahedral (6-fold)		
cubic (8-fold)		
dodecahedral (12-fold)		

Why do we care so much about crystallography?

All properties are based on the underlying crystallography



Why do we care so much about crystallography?

All properties are based on the underlying crystallography

- **Diffusion:** Depends on size and number of interstitial sites



Why do we care so much about crystallography?

All properties are based on the underlying crystallography

- **Diffusion:** Depends on size and number of interstitial sites
- **Deformation by slip or twinning:** The slip direction is usually along a close-packed direction. The slip plane is usually a closely packed plane or one that does not put like charges in juxtaposition.



Why do we care so much about crystallography?

All properties are based on the underlying crystallography

- **Diffusion:** Depends on size and number of interstitial sites
- **Deformation by slip or twinning:** The slip direction is usually along a close-packed direction. The slip plane is usually a closely packed plane or one that does not put like charges in juxtaposition.
- **Piezoelectricity:** Crystals must be noncentrosymmetric



Why do we care so much about crystallography?

All properties are based on the underlying crystallography

- **Diffusion:** Depends on size and number of interstitial sites
- **Deformation by slip or twinning:** The slip direction is usually along a close-packed direction. The slip plane is usually a closely packed plane or one that does not put like charges in juxtaposition.
- **Piezoelectricity:** Crystals must be noncentrosymmetric
- **Thermal conductivity:** Electrical and phonon conductivity is directly determined by the underlying crystal structure



Why do we care so much about crystallography?

All properties are based on the underlying crystallography

- **Diffusion:** Depends on size and number of interstitial sites
- **Deformation by slip or twinning:** The slip direction is usually along a close-packed direction. The slip plane is usually a closely packed plane or one that does not put like charges in juxtaposition.
- **Piezoelectricity:** Crystals must be noncentrosymmetric
- **Thermal conductivity:** Electrical and phonon conductivity is directly determined by the underlying crystal structure
- **Fracture:** Often crystallographic but not always (e.g., glass and cubic zirconia)



Why do we care so much about crystallography?

All properties are based on the underlying crystallography

- **Diffusion:** Depends on size and number of interstitial sites
- **Deformation by slip or twinning:** The slip direction is usually along a close-packed direction. The slip plane is usually a closely packed plane or one that does not put like charges in juxtaposition.
- **Piezoelectricity:** Crystals must be noncentrosymmetric
- **Thermal conductivity:** Electrical and phonon conductivity is directly determined by the underlying crystal structure
- **Fracture:** Often crystallographic but not always (e.g., glass and cubic zirconia)
- **Cleavage:** Always crystallographic. Cleavage planes have high atomic density, but we also need to consider charge.



Why do we care so much about crystallography?

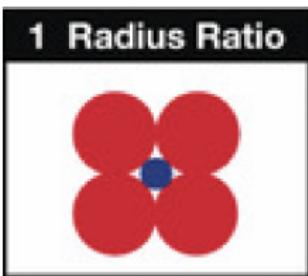
All properties are based on the underlying crystallography

- **Diffusion:** Depends on size and number of interstitial sites
- **Deformation by slip or twinning:** The slip direction is usually along a close-packed direction. The slip plane is usually a closely packed plane or one that does not put like charges in juxtaposition.
- **Piezoelectricity:** Crystals must be noncentrosymmetric
- **Thermal conductivity:** Electrical and phonon conductivity is directly determined by the underlying crystal structure
- **Fracture:** Often crystallographic but not always (e.g., glass and cubic zirconia)
- **Cleavage:** Always crystallographic. Cleavage planes have high atomic density, but we also need to consider charge.
- **Ferrimagnetism:** In ferrimagnets the coordination number of the magnetic cation (usually a Fe ion) determines its behavior in an applied magnetic field.



Pauling's Rule 1

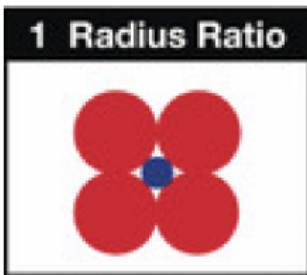
Rule 1: A coordinated polyhedron of anions is formed about each cation. The cation–anion distance is determined by the sum of the two radii, and the CN is determined by the radius ratio:



$$\text{Radius Ratio} = \frac{r_c}{r_a}$$

Pauling's Rule 1

Rule 1: A coordinated polyhedron of anions is formed about each cation. The cation–anion distance is determined by the sum of the two radii, and the CN is determined by the radius ratio:

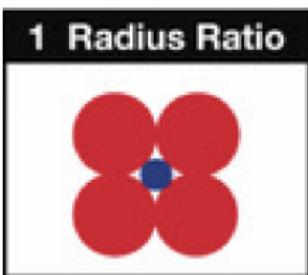


$$\text{Radius Ratio} = \frac{r_c}{r_a}$$

- Cation (+ charged) are always smaller than anions (- charged)

Pauling's Rule 1

Rule 1: A coordinated polyhedron of anions is formed about each cation. The cation–anion distance is determined by the sum of the two radii, and the CN is determined by the radius ratio:



$$\text{Radius Ratio} = \frac{r_c}{r_a}$$

- Cation (+ charged) are always smaller than anions (- charged)

TABLE 5.4 Pauling's Critical Radius Ratios

Polyhedron	CN	Minimum ($= r_M/r_X$)
Cube	8	0.732
Octahedron	6	0.414
Tetrahedron	4	0.225
Triangle	3	0.155

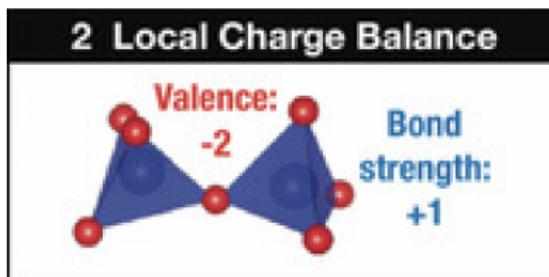
Pauling's Rule 2

Rule 2: In a stable structure, the total electrostatic strength of the bonds, S , reaching an anion in a coordination polyhedron from all neighboring cations should be equal to the charge of the anion.



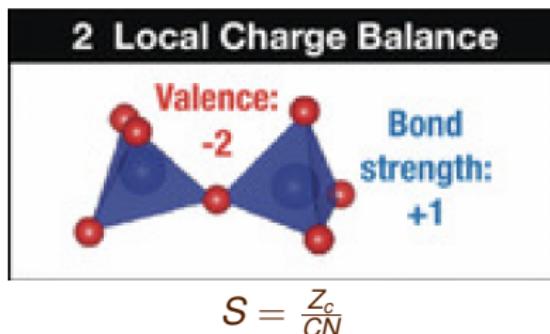
Pauling's Rule 2

Rule 2: In a stable structure, the total electrostatic strength of the bonds, S , reaching an anion in a coordination polyhedron from all neighboring cations should be equal to the charge of the anion.



Pauling's Rule 2

Rule 2: In a stable structure, the total electrostatic strength of the bonds, S , reaching an anion in a coordination polyhedron from all neighboring cations should be equal to the charge of the anion.

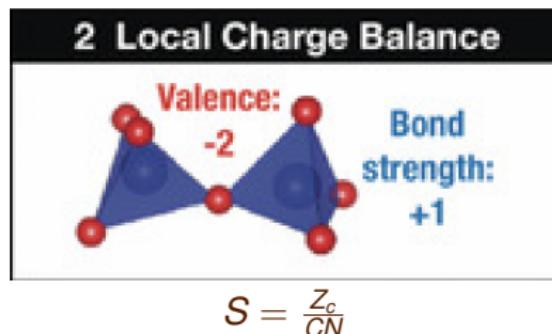


Z_c - is the charge of the cation

CN - is the coordination number

Pauling's Rule 2

Rule 2: In a stable structure, the total electrostatic strength of the bonds, S , reaching an anion in a coordination polyhedron from all neighboring cations should be equal to the charge of the anion.



Z_c - is the charge of the cation

CN - is the coordination number

A stable ionic structure is arranged to preserve local *electroneutrality*, so that the sum of the strengths of the electrostatic bonds to an anion equals the charge on that anion.

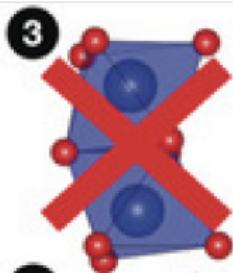
Pauling's Rule 3

Rule 3: Polyhedra in a structure prefer not to share edges or faces. Clearly, if the faces are shared, at least three edges are also shared.



Pauling's Rule 3

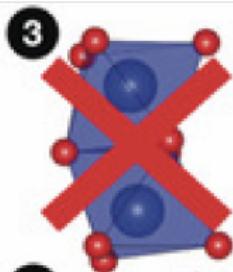
Rule 3: Polyhedra in a structure prefer not to share edges or faces. Clearly, if the faces are shared, at least three edges are also shared.



- The decrease in stability is the result that sharing edges and faces places cations in closer proximity to each other, so that cation-cation electrostatic repulsion is increased.

Pauling's Rule 3

Rule 3: Polyhedra in a structure prefer not to share edges or faces. Clearly, if the faces are shared, at least three edges are also shared.



- The decrease in stability is the result that sharing edges and faces places cations in closer proximity to each other, so that cation-cation electrostatic repulsion is increased.
- The effect is largest for cations with high charge and low C.N. (especially when $\frac{r_c}{r_a}$ approaches the lower limit of the polyhedral stability).

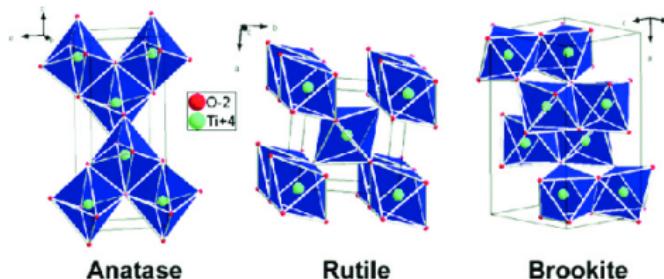
Pauling's Rule 3: Example TiO_2

Ti in an octahedron CN=6

Rutile - most stable - Shares 2 edges with no faces

Brookite - slightly lower stability - Shares 3 edges with no faces

Anatase - lowest stability - Shares 4 edges with no faces.



Pauling's Rule 4

Rule 4: Crystals containing different cations of high valence and a small CN tend not to share polyhedron elements with each other.

Pauling's Rule 4

Rule 4: Crystals containing different cations of high valence and a small CN tend not to share polyhedron elements with each other.

Example CaTiO_3 :

CaO_{12} polyhedra share edges

TiO_6 polyhedra share corners

Pauling's Rule 4

Rule 4: Crystals containing different cations of high valence and a small CN tend not to share polyhedron elements with each other.

Example CaTiO_3 :

CaO_{12} polyhedra share edges

TiO_6 polyhedra share corners

The Ti^{4+} cation is more highly charged than the Ca^{2+} cation, so the CN is smaller; the Coulombic repulsion between cations is proportional to the product of the charges.

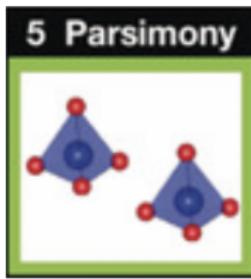


Pauling's Rule 5

Rule 5: The number of essentially different kinds of constituents in a crystal tends to be small

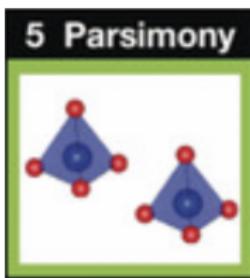
Pauling's Rule 5

Rule 5: The number of essentially different kinds of constituents in a crystal tends to be small



Pauling's Rule 5

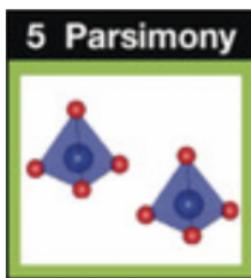
Rule 5: The number of essentially different kinds of constituents in a crystal tends to be small



- As much as possible the environment of chemically similar atoms should be similar

Pauling's Rule 5

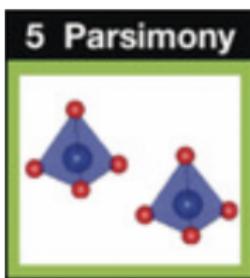
Rule 5: The number of essentially different kinds of constituents in a crystal tends to be small



- As much as possible the environment of chemically similar atoms should be similar
- This applies mostly to the coordination number (CN)

Pauling's Rule 5

Rule 5: The number of essentially different kinds of constituents in a crystal tends to be small



- As much as possible the environment of chemically similar atoms should be similar
- This applies mostly to the coordination number (CN)
- There is not a requirement that the structures are geometrically identical or indistinguishable.

Summary of Rules

1 Rule 1: A coordinated polyhedron of anions is formed about each cation. The cation–anion distance is determined by the sum of the two radii, and the CN is determined by the radius ratio





Summary of Rules

- 1 Rule 1:** A coordinated polyhedron of anions is formed about each cation. The cation–anion distance is determined by the sum of the two radii, and the CN is determined by the radius ratio
- 2 Rule 2:** In a stable structure, the total electrostatic strength of the bonds, S, reaching an anion in a coordination polyhedron from all neighboring cations should be equal to the charge of the anion

Summary of Rules

- 1 Rule 1:** A coordinated polyhedron of anions is formed about each cation. The cation–anion distance is determined by the sum of the two radii, and the CN is determined by the radius ratio
- 2 Rule 2:** In a stable structure, the total electrostatic strength of the bonds, S , reaching an anion in a coordination polyhedron from all neighboring cations should be equal to the charge of the anion
- 3 Rule 3:** Polyhedra in a structure prefer not to share edges or faces. Clearly, if the faces are shared, at least three edges are also shared

Summary of Rules

- 1 Rule 1:** A coordinated polyhedron of anions is formed about each cation. The cation–anion distance is determined by the sum of the two radii, and the CN is determined by the radius ratio
- 2 Rule 2:** In a stable structure, the total electrostatic strength of the bonds, S , reaching an anion in a coordination polyhedron from all neighboring cations should be equal to the charge of the anion
- 3 Rule 3:** Polyhedra in a structure prefer not to share edges or faces. Clearly, if the faces are shared, at least three edges are also shared
- 4 Rule 4:** Crystals containing different cations of high valence and a small CN tend not to share polyhedron elements with each other



Summary of Rules

- 1 Rule 1:** A coordinated polyhedron of anions is formed about each cation. The cation–anion distance is determined by the sum of the two radii, and the CN is determined by the radius ratio
- 2 Rule 2:** In a stable structure, the total electrostatic strength of the bonds, S , reaching an anion in a coordination polyhedron from all neighboring cations should be equal to the charge of the anion
- 3 Rule 3:** Polyhedra in a structure prefer not to share edges or faces. Clearly, if the faces are shared, at least three edges are also shared
- 4 Rule 4:** Crystals containing different cations of high valence and a small CN tend not to share polyhedron elements with each other
- 5 Rule 5:** The number of essentially different kinds of constituents in a crystal tends to be small



Binary Ceramic Crystal Structures: Preface

- Crystal structures in ceramics are incredibly complex



Binary Ceramic Crystal Structures: Preface

- Crystal structures in ceramics are incredibly complex
- We are going to introduce some of the most important ceramic crystal structure (some of which you might have seen before)





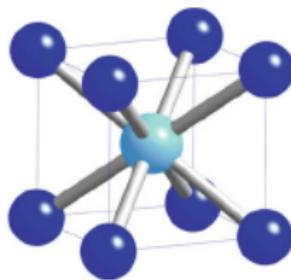
Binary Ceramic Crystal Structures: Preface

- Crystal structures in ceramics are incredibly complex
- We are going to introduce some of the most important ceramic crystal structure (some of which you might have seen before)
- There are entire textbooks written on a single crystallographic structure or polymorphs of a single compound → We are going to cover this in part of a lecture



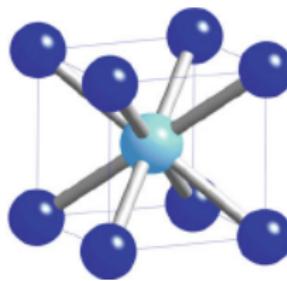
Cesium Chloride - CsCl

- This is the simplest structure



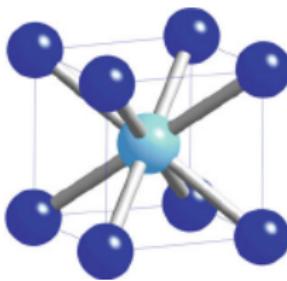
Cesium Chloride - CsCl

- This is the simplest structure
- Bravais lattice is simple cubic



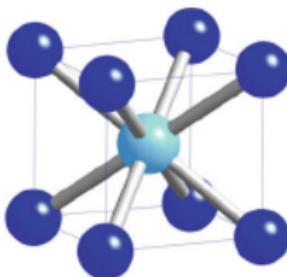
Cesium Chloride - CsCl

- This is the simplest structure
- Bravais lattice is simple cubic
- Two interpenetrating sc lattices, one of Cs^+ and one of Cl^- . The two sublattices are displaced by $1/2\langle 111 \rangle$.



Cesium Chloride - CsCl

- This is the simplest structure
 - Bravais lattice is simple cubic
 - Two interpenetrating sc lattices, one of Cs^+ and one of Cl^- . The two sublattices are displaced by $1/2\langle 111 \rangle$.



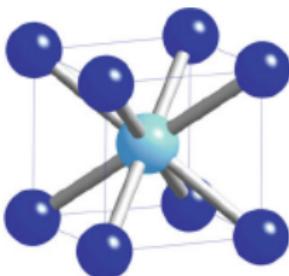
Using Pauling's Rules:

$$r_{Cs^+}/r_{Cl^-} = 170/181 = 0.94$$

This is > 0.732 thus the CN = 8

Cesium Chloride - CsCl

- This is the simplest structure
- Bravais lattice is simple cubic
- Two interpenetrating sc lattices, one of Cs^+ and one of Cl^- . The two sublattices are displaced by $1/2\langle 111 \rangle$.



Using Pauling's Rules:

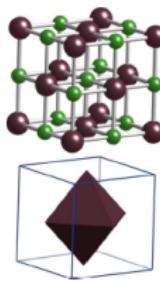
$$r_{\text{Cs}^+}/r_{\text{Cl}^-} = 170/181 = 0.94$$

This is > 0.732 thus the CN = 8

- This structure does not appear to occur for oxides because the (divalent) cation radius would need to be > 102.5 pm (O^{2-} is 140 pm)

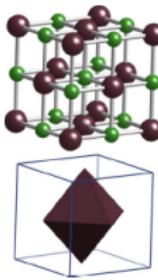
Rock Salt - NaCl

- The NaCl (rock salt or halite) structure is quite simple.



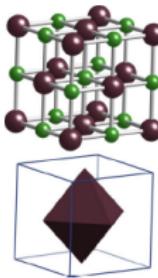
Rock Salt - NaCl

- The NaCl (rock salt or halite) structure is quite simple.
- Found for sulfides and carbides and some oxides, including MgO, CaO, SrO, BaO, CdO, FeO, and NiO



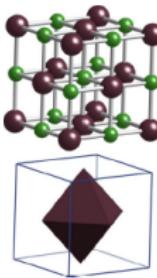
Rock Salt - NaCl

- The NaCl (rock salt or halite) structure is quite simple.
- Found for sulfides and carbides and some oxides, including MgO, CaO, SrO, BaO, CdO, FeO, and NiO
- Two interpenetrating FCC lattices: one of anions and the other of cations displaced by $1/2<001>$ or by $1/2<111>$.



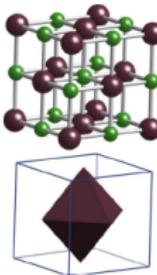
Rock Salt - NaCl

- The NaCl (rock salt or halite) structure is quite simple.
- Found for sulfides and carbides and some oxides, including MgO, CaO, SrO, BaO, CdO, FeO, and NiO
- Two interpenetrating FCC lattices: one of anions and the other of cations displaced by $1/2<001>$ or by $1/2<111>$.
- NaCl is not closed-packed \rightarrow six nearest neighbors (CN is 6) so the packing of the anions must be less dense than fcc



Rock Salt - NaCl

- The NaCl (rock salt or halite) structure is quite simple.
- Found for sulfides and carbides and some oxides, including MgO, CaO, SrO, BaO, CdO, FeO, and NiO
- Two interpenetrating FCC lattices: one of anions and the other of cations displaced by $1/2<001>$ or by $1/2<111>$.
- NaCl is not closed-packed \rightarrow six nearest neighbors (CN is 6) so the packing of the anions must be less dense than fcc



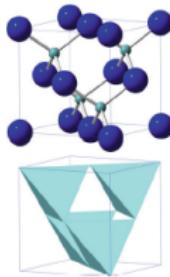
Using Pauling's Rules:

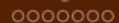
$$r_{Mg^+}/r_{O^-} = 0.6$$

This is > 0.414 but < 0.732 thus the CN = 6

Zinc Blend - GaAs (β -SiC)

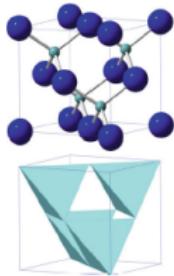
- This is the Zinc blend structure





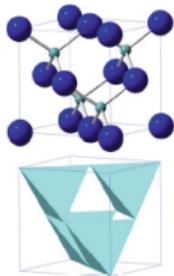
Zinc Blend - GaAs (β -SiC)

- This is the Zinc blend structure
- A very open crystallographic structure APF = 0.41



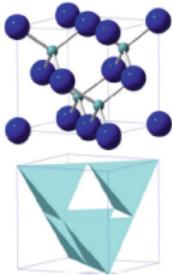
Zinc Blend - GaAs (β -SiC)

- This is the Zinc blend structure
- A very open crystallographic structure APF = 0.41
- Two interpenetrating FCC lattices: one of anions and the other of cations displaced by $1/4<111>$



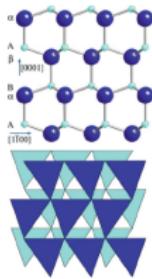
Zinc Blend - GaAs (β -SiC)

- This is the Zinc blend structure
- A very open crystallographic structure APF = 0.41
- Two interpenetrating FCC lattices: one of anions and the other of cations displaced by $1/4<111>$
- Alternatively, you could consider this as an FCC lattice with 1/2 the tetrahedral sites occupied



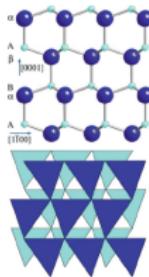
Würzite AlN, BeO, ZnO

- HCP crystal structure with half of the tetragonal indexes with cations



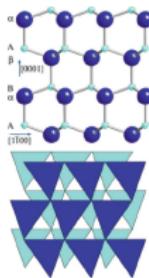
Würzite AlN, BeO, ZnO

- HCP crystal structure with half of the tetragonal indexes with cations
- The CN is 4 for both the cations and the anions



Würzite AlN, BeO, ZnO

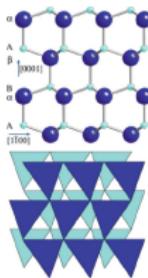
- HCP crystal structure with half of the tetragonal indexes with cations
- The CN is 4 for both the cations and the anions



- BeO and AlN have both been used for electronic packaging because of their high thermal conductivity

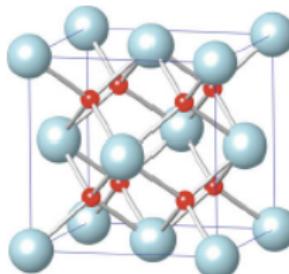
Würzite AlN, BeO, ZnO

- HCP crystal structure with half of the tetragonal indexes with cations
- The CN is 4 for both the cations and the anions



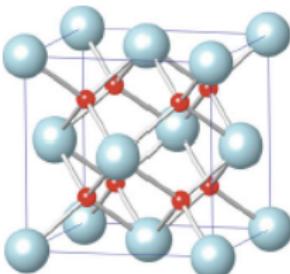
- BeO and AlN have both been used for electronic packaging because of their high thermal conductivity
- GaN is of great interest for manufacturing blue-green laser diodes and blue and green light-emitting diodes (LEDs)

CaF₂



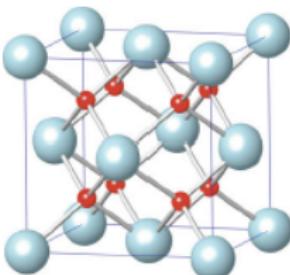
- arranging the Ca²⁺ ions on an fcc lattice and then placing the F⁻ anions on the 1/4,1/4,1/4 sites

CaF₂



- arranging the Ca²⁺ ions on an fcc lattice and then placing the F⁻ anions on the 1/4,1/4,1/4 sites
- CaF₂ is then the material of choice for semiconductor lithography. It is one of only a few materials that are transparent at the shorter wavelengths of deep-UV light

CaF₂

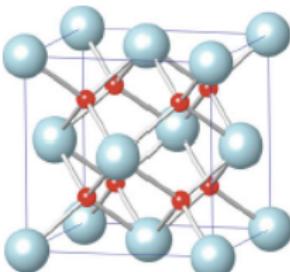


- arranging the Ca²⁺ ions on an fcc lattice and then placing the F⁻ anions on the 1/4,1/4,1/4 sites
- CaF₂ is then the material of choice for semiconductor lithography. It is one of only a few materials that are transparent at the shorter wavelengths of deep-UV light

Using Pauling's Rules:

$$r_{Ca^{2+}} = 100 \text{ pm} \text{ and } r_{F^-} = 130 \text{ pm} \quad r_{Ca^{2+}}/r_{F^-} = 0.8$$

CaF₂



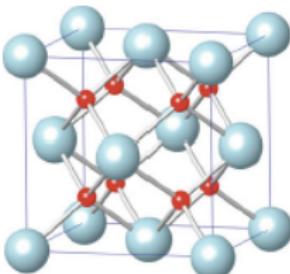
- arranging the Ca²⁺ ions on an fcc lattice and then placing the F⁻ anions on the 1/4,1/4,1/4 sites
- CaF₂ is then the material of choice for semiconductor lithography. It is one of only a few materials that are transparent at the shorter wavelengths of deep-UV light

Using Pauling's Rules:

$$r_{Ca^{2+}} = 100 \text{ pm} \text{ and } r_{F^-} = 130 \text{ pm} \quad r_{Ca^{2+}}/r_{F^-} = 0.8$$

Thus the coordination number of Ca²⁺ is 8, where F⁻ is 4.

CaF₂



- arranging the Ca²⁺ ions on an fcc lattice and then placing the F⁻ anions on the 1/4,1/4,1/4 sites
- CaF₂ is then the material of choice for semiconductor lithography. It is one of only a few materials that are transparent at the shorter wavelengths of deep-UV light

Using Pauling's Rules:

$$r_{Ca^{2+}} = 100 \text{ pm} \text{ and } r_{F^-} = 130 \text{ pm} \quad r_{Ca^{2+}}/r_{F^-} = 0.8$$

Thus the coordination number of Ca²⁺ is 8, where F⁻ is 4.

This is because of the charge

TiO₂

- TiO₂ exists as rutile, anatase, and brookite



TiO₂

- TiO₂ exists as rutile, anatase, and brookite
- Each of these structures is different and it is more than just the packing



TiO₂

- TiO₂ exists as rutile, anatase, and brookite
- Each of these structures is different and it is more than just the packing
- Ti₄⁺ cations in the center of oxygen octahedra

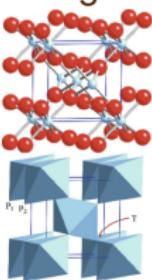


Rutile

- Has a tetragonal symmetry

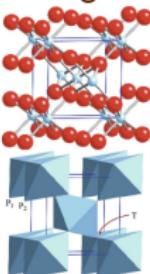
Rutile

- Has a tetragonal symmetry
- Structure is constructed by linking octahedra



Rutile

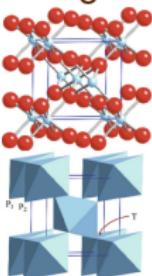
- Has a tetragonal symmetry
- Structure is constructed by linking octahedra



- An octahedron is placed at each of the eight corners such that two are actually sharing an apex (e.g., at T)

Rutile

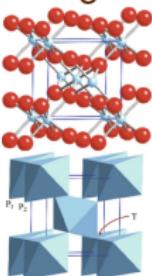
- Has a tetragonal symmetry
- Structure is constructed by linking octahedra



- An octahedron is placed at each of the eight corners such that two are actually sharing an apex (e.g., at T)
- The six points on these octahedra are then connected by one rotated octahedron sitting in the center of the unit cell

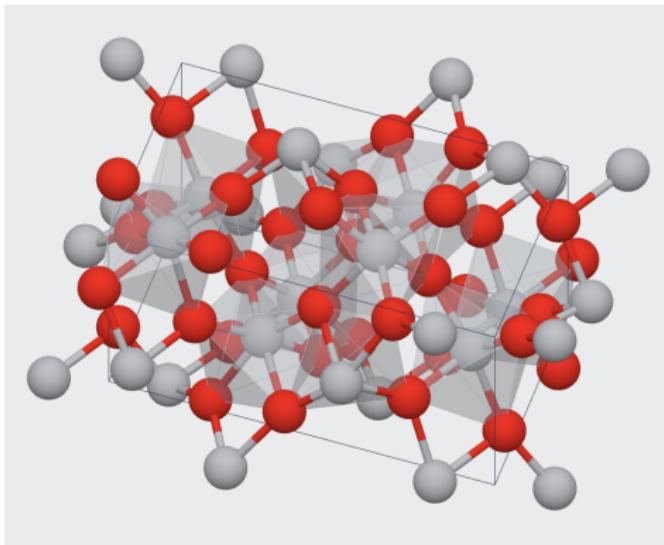
Rutile

- Has a tetragonal symmetry
- Structure is constructed by linking octahedra



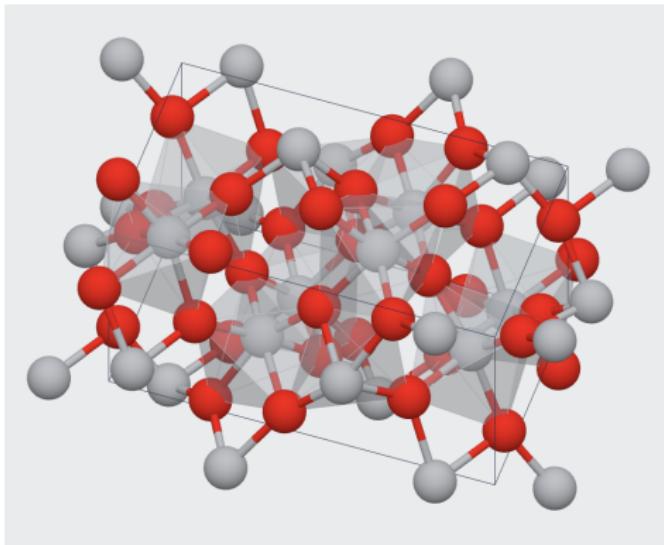
- An octahedron is placed at each of the eight corners such that two are actually sharing an apex (e.g., at T)
- The six points on these octahedra are then connected by one rotated octahedron sitting in the center of the unit cell
- Rutile is the most stable → recall from Pauling rules shares 2 edges

Brookite



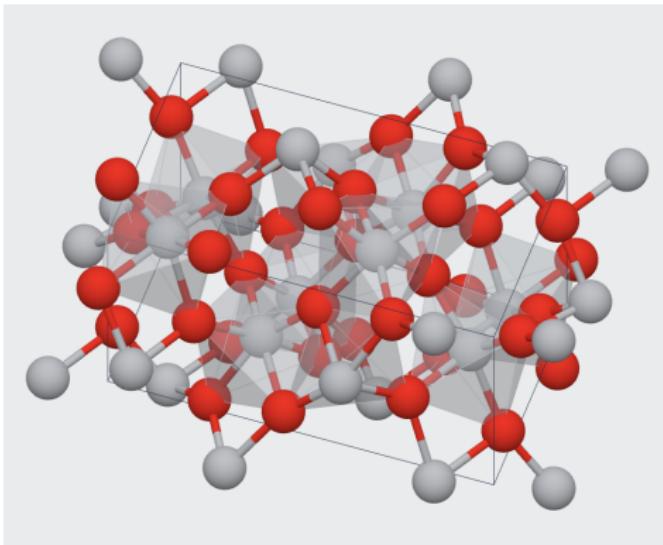
- Becomes orthorhombic in structure

Brookite



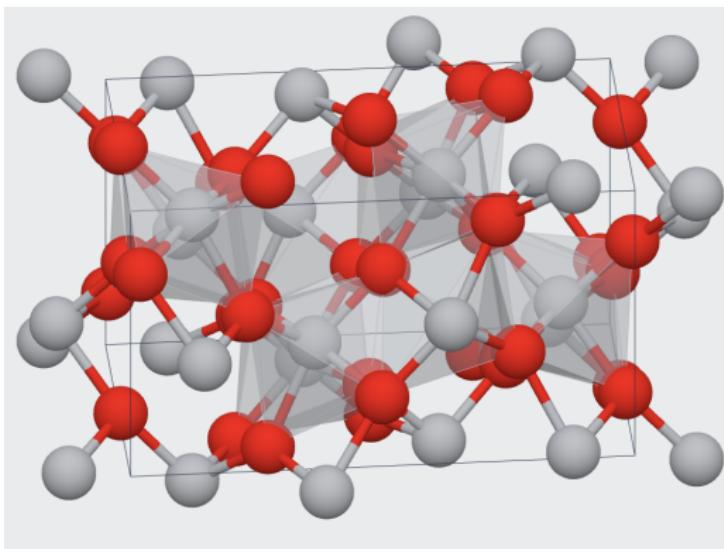
- Becomes orthorhombic in structure
- Each octahedron shares 3 of its edges

Brookite



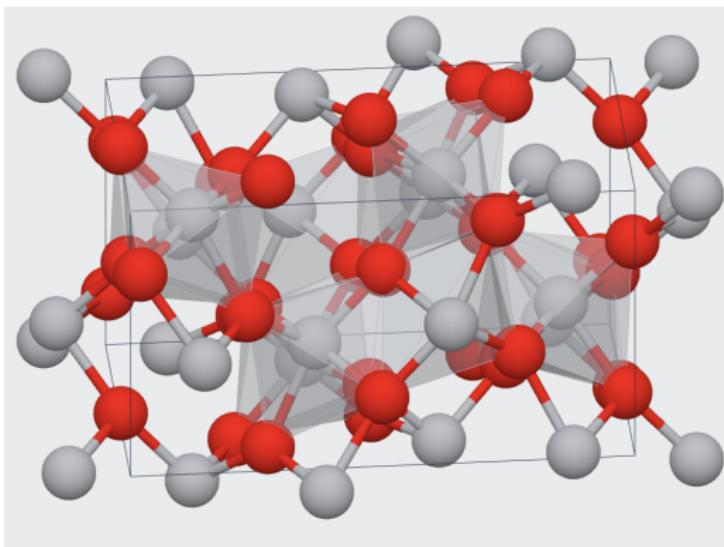
- Becomes orthorhombic in structure
- Each octahedron shares 3 of its edges
- Brookite is less stable than Rutile → shares 3 edges instead of 2

Anatase



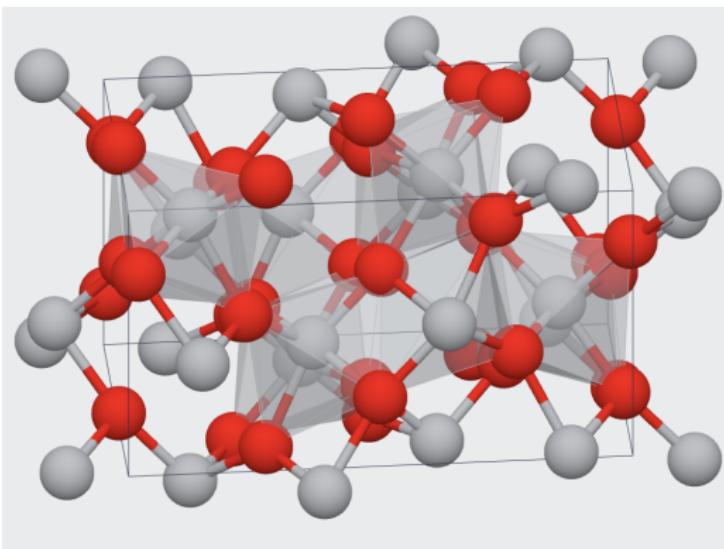
- Still tetragonal but has a distorted octahedron

Anatase



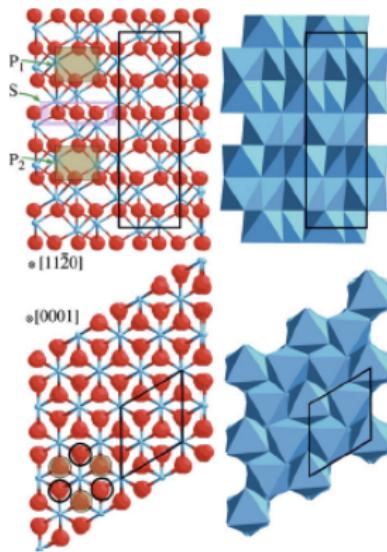
- Still tetragonal but has a distorted octahedron
- Each octahedron shares 4 of its edges

Anatase



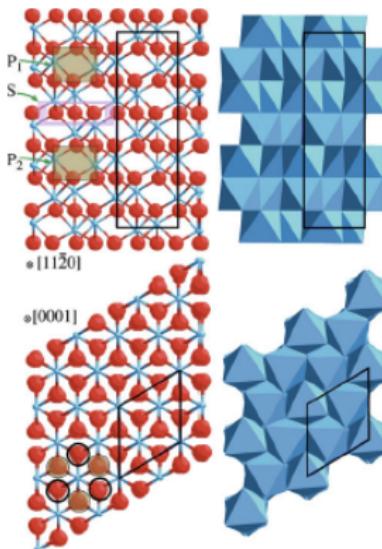
- Still tetragonal but has a distorted octahedron
 - Each octahedron shares 4 of its edges
 - Anatase is less stable than Rutile or Brookite → shares 4 edges instead of 3 or 2

Al₂O₃



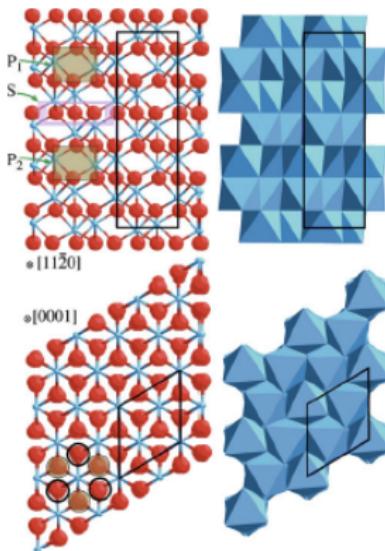
- Alumina refers to α -Al₂O₃

Al₂O₃

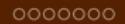
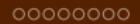


- Alumina refers to α -Al₂O₃
- Ruby \rightarrow doped with Cr³⁺

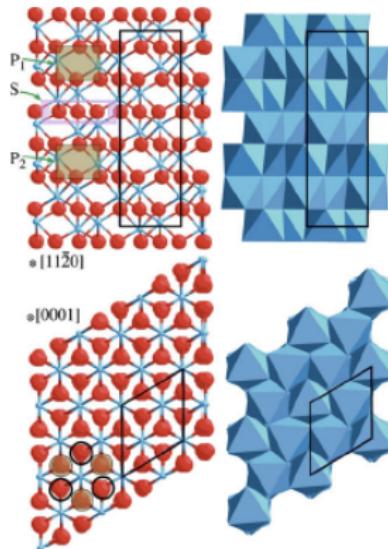
Al₂O₃



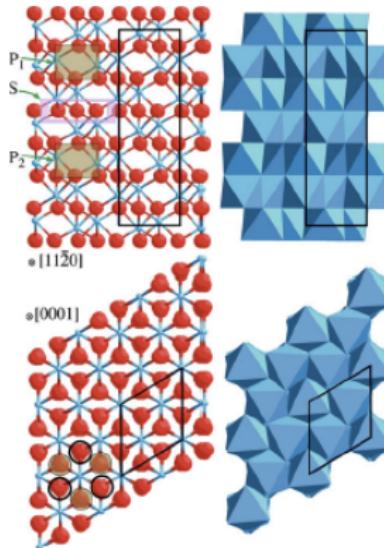
- Alumina refers to α -Al₂O₃
- Ruby \rightarrow doped with Cr³⁺
- Sapphire \rightarrow doped with Ti^{3+/4+} and Fe²⁺



Al₂O₃

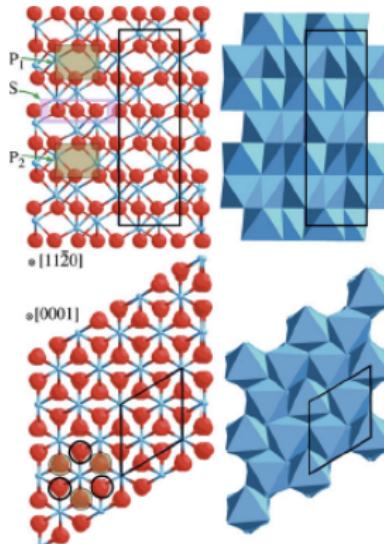


Al₂O₃



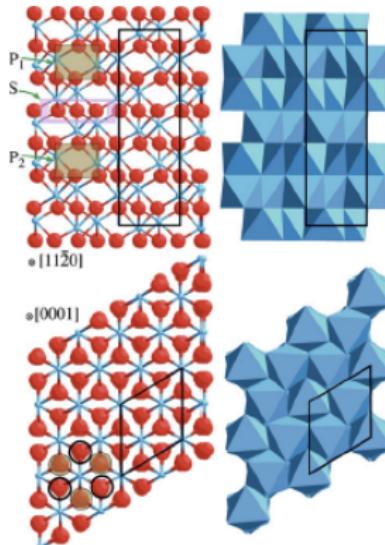
- Actually has a $\bar{3}m$ symmetry but close to 6-fold so common to use hcp conventions

Al₂O₃



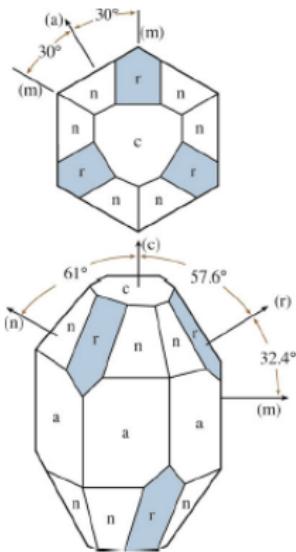
- Actually has a $\bar{3}m$ symmetry but close to 6-fold so common to use hcp conventions
- Can be thought of as HCP for the oxygen with Al³⁺ occupying 2/3 of the octahedral interstices (P_1 and P_2) are the missing octahedral

Al₂O₃



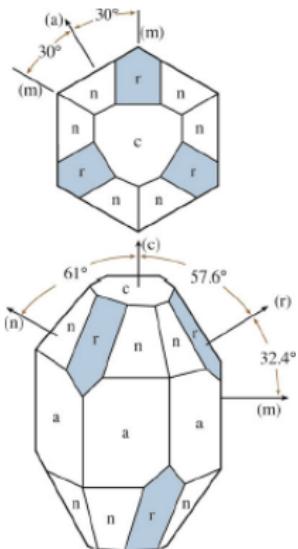
- Actually has a $\bar{3}m$ symmetry but close to 6-fold so common to use hcp conventions
- Can be thought of as HCP for the oxygen with Al³⁺ occupying 2/3 of the octahedral interstices (P₁ and P₂) are the missing octahedral
- To avoid sharing a face the bond lengths distort

Al₂O₃



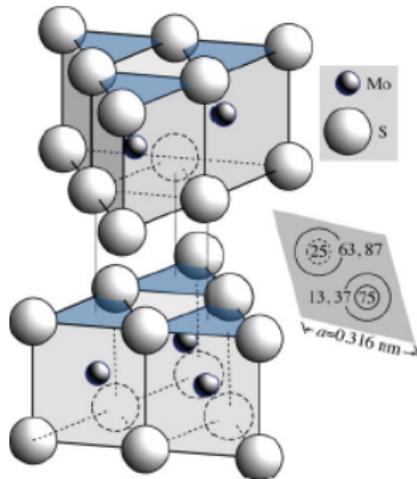
- There are common names for the different crystallographic faces in Al₂O₃

Al₂O₃



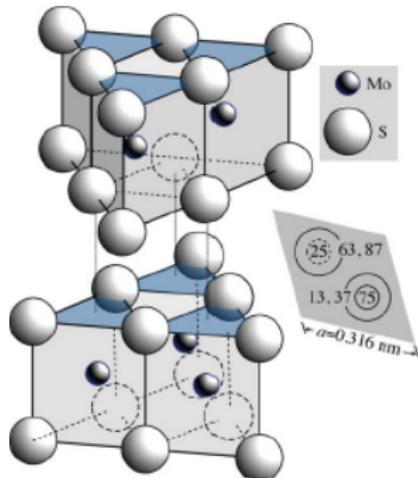
- There are common names for the different crystallographic faces in Al₂O₃
- The properties are highly directional dependent

MoS₂



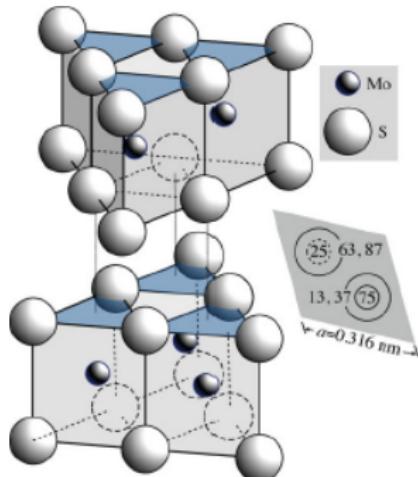
- Mo atoms are located in hcp structure

MoS₂



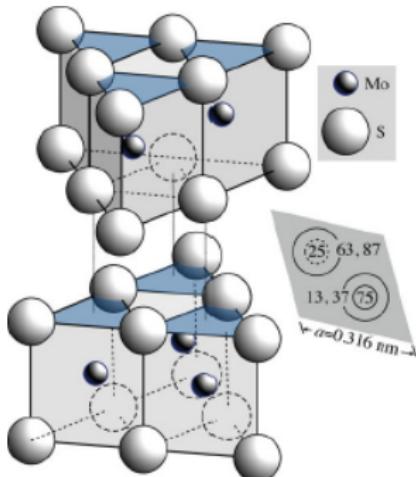
- Mo atoms are located in hcp structure
- An S–S pair is centered along the c-direction directly opposite the Mo atoms

MoS₂



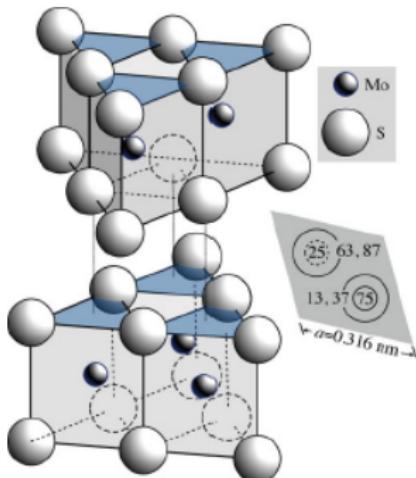
- Mo atoms are located in hcp structure
- An S–S pair is centered along the c-direction directly opposite the Mo atoms
- Similar structure to graphite w/ weak van der Waals bonds between the planes

MoS₂



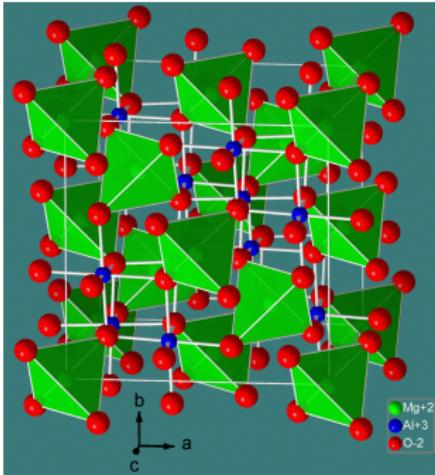
- Mo atoms are located in hcp structure
- An S–S pair is centered along the c-direction directly opposite the Mo atoms
- Similar structure to graphite w/ weak van der Waals bonds between the planes
- Various stacking configurations because of the weak bonds

MoS₂



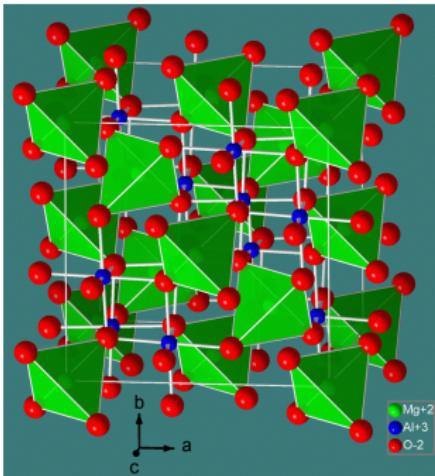
- Mo atoms are located in hcp structure
- An S–S pair is centered along the c-direction directly opposite the Mo atoms
- Similar structure to graphite w/ weak van der Waals bonds between the planes
- Various stacking configurations because of the weak bonds
- Makes an excellent dry lubricant

Spinel



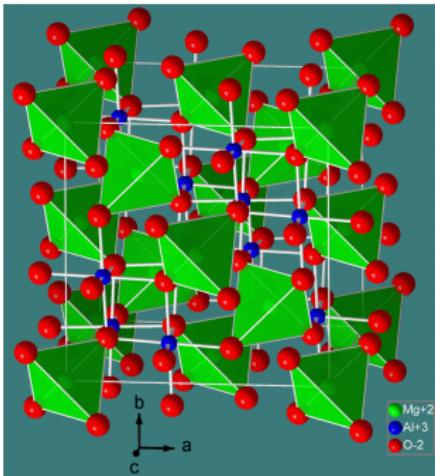
- General formula AB_2O_4

Spinel



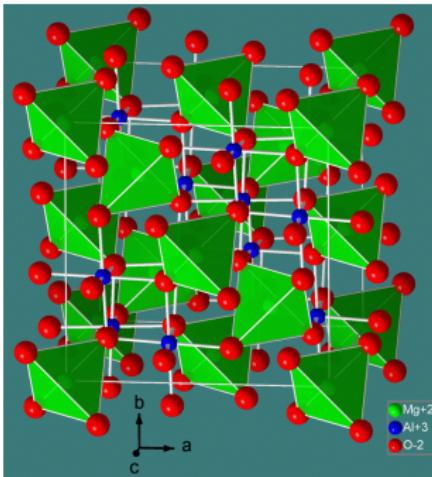
- General formula AB_2O_4
- Important because the magnetic ferrites are spinels

Spinel



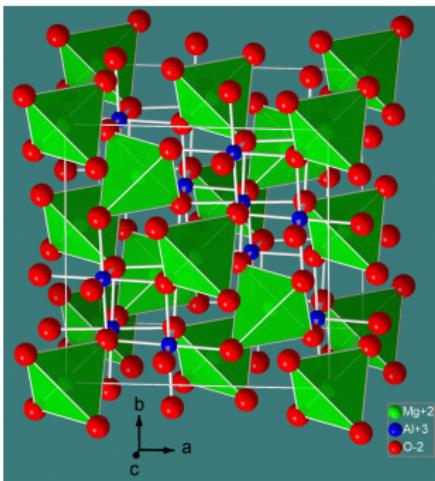
- General formula AB_2O_4
- Important because the magnetic ferrites are spinels
- The Bravais lattice is fcc, and the unit cell contains a total of 56 ions (32 oxygen ions).

Spinel



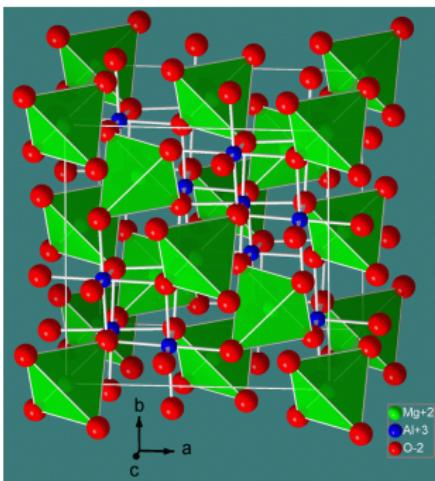
- General formula AB_2O_4
 - Important because the magnetic ferrites are spinels
 - The Bravais lattice is fcc, and the unit cell contains a total of 56 ions (32 oxygen ions).
 - O^{2-} ions as sitting on FCC lattice sites, A-site cation in some tetragonal sites, and B-site cation on some of the octahedral sites

Spinel



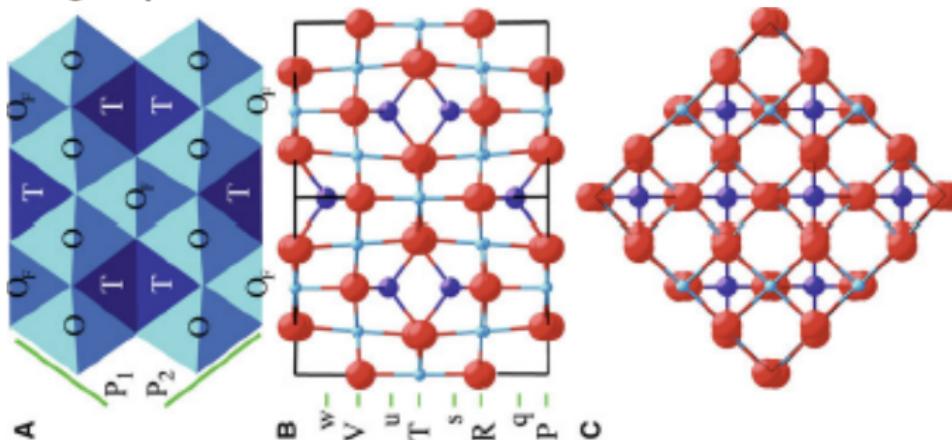
- **Normal Spinel:** The A²⁺ ions occupy only tetrahedral sites, and the B³⁺ ions occupy only octahedral sites

Spinel



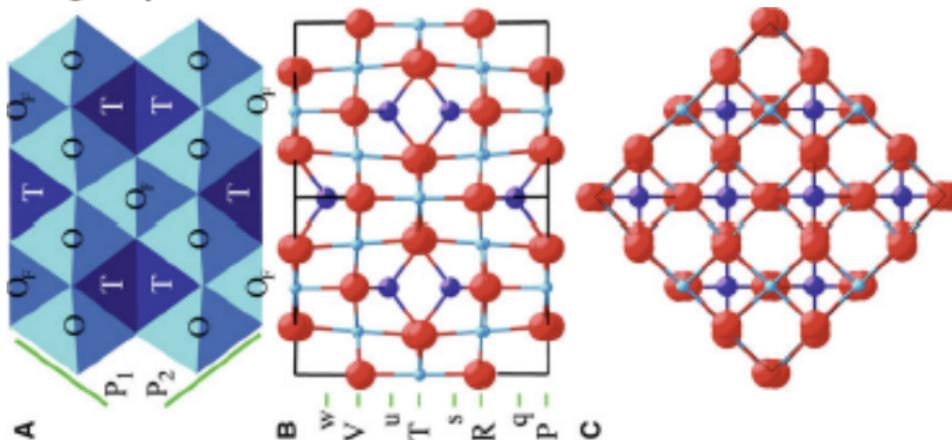
- **Normal Spinel:** The A^{2+} ions occupy only tetrahedral sites, and the B^{3+} ions occupy only octahedral sites
 - **Inverse spinel:** All the A^{2+} ions and half the B^{3+} ions sit on the octahedral sites; the tetrahedral sites are occupied now by the other half of the B^{3+} ions.

Visualizing Spinels



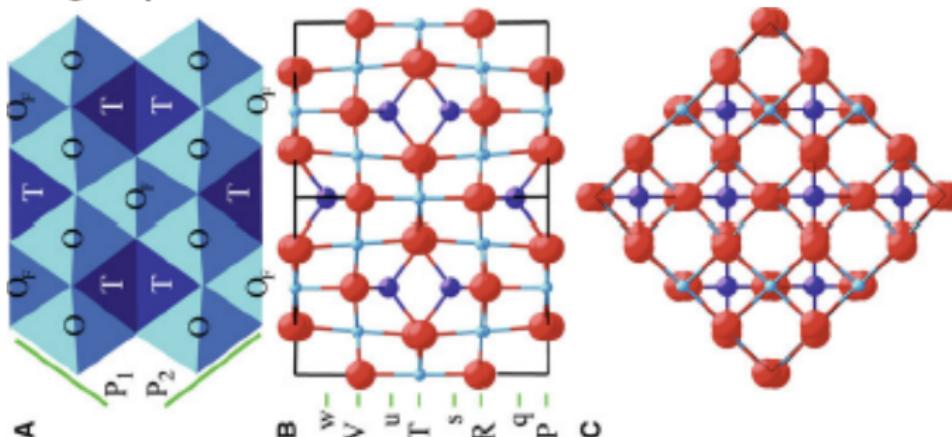
- We can start by looking along the [110] → this is the closed-packed Oxygen plane.

Visualizing Spinel



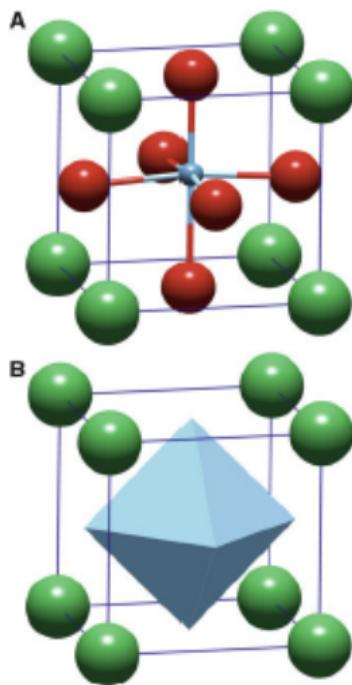
- We can start by looking along the [110] → this is the closed-packed Oxygen plane.
- This sequence is PqRsTuVw, where the upper case refers to mixed O²⁻ plus octahedral cation layers, and the lower case refers to the tetrahedral cations.

Visualizing Spinel



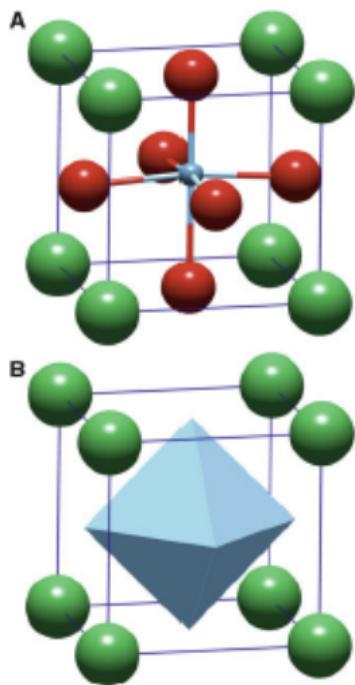
- We can start by looking along the [110] → this is the closed-packed Oxygen plane.
- This sequence is PqRsTuVw, where the upper case refers to mixed O^{2-} plus octahedral cation layers, and the lower case refers to the tetrahedral cations.
- You might ask how did they ever figure out this crystal structure
→ They used structure factor and X-ray diffraction!

Perovskite



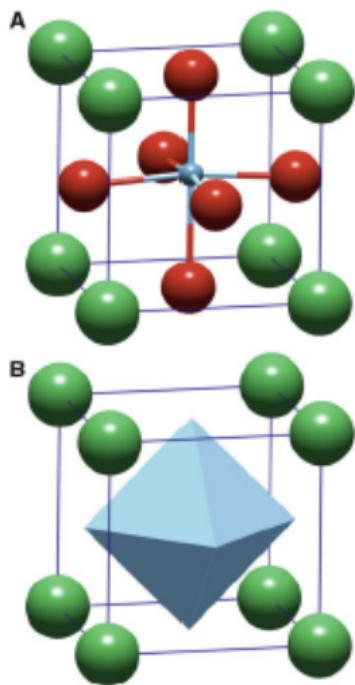
- ABO_3 , the A cation and the anions effectively form an FCC array with a large octahedron in the center

Perovskite



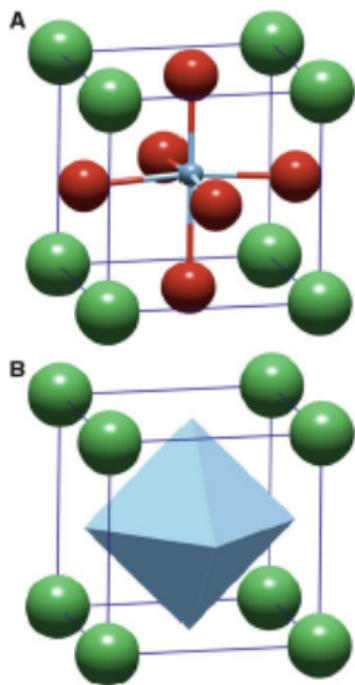
- ABO_3 , the A cation and the anions effectively form an FCC array with a large octahedron in the center
- Ideal, high-temperature structure is simple cubic \rightarrow can undergo tetrahedral, monoclinic, and rhombohedral distortions

Perovskite



- ABO_3 , the A cation and the anions effectively form an FCC array with a large octahedron in the center
- Ideal, high-temperature structure is simple cubic → can undergo tetrahedral, monoclinic, and rhombohedral distortions
- Larger 2+ cations at the corners, smaller 4+ cation in the octahedral sites

Perovskite



- ABO_3 , the A cation and the anions effectively form an FCC array with a large octahedron in the center
- Ideal, high-temperature structure is simple cubic → can undergo tetrahedral, monoclinic, and rhombohedral distortions
- Larger 2+ cations at the corners, smaller 4+ cation in the octahedral sites
- We will talk about Perovskites w/ ferroelectrics most good ferroelectrics are Perovskites

Important Concepts to Master

- How to calculate ionic character of a bond



Important Concepts to Master

- How to calculate ionic character of a bond
- Definition of a Bravais Lattice



Important Concepts to Master

- How to calculate ionic character of a bond
- Definition of a Bravais Lattice
- How to determine simple bonding configuration from constituent atoms with support of equations and tables

Important Concepts to Master

- How to calculate ionic character of a bond
- Definition of a Bravais Lattice
- How to determine simple bonding configuration from constituent atoms with support of equations and tables
- How to determine relative stability of different crystallographic structure in common materials (e.g., TiO_2)



Important Concepts to Master

- How to calculate ionic character of a bond
- Definition of a Bravais Lattice
- How to determine simple bonding configuration from constituent atoms with support of equations and tables
- How to determine relative stability of different crystallographic structure in common materials (e.g., TiO_2)
- Given a crystallographic structure be able to predict some of the properties determined by the crystallographic structure

Important Concepts to Master

- How to calculate ionic character of a bond
- Definition of a Bravais Lattice
- How to determine simple bonding configuration from constituent atoms with support of equations and tables
- How to determine relative stability of different crystallographic structure in common materials (e.g., TiO_2)
- Given a crystallographic structure be able to predict some of the properties determined by the crystallographic structure
- How coordination number relates to bonding and structural configuration (e.g. CN = 6, octahedral)



Important Concepts to Master

- How to calculate ionic character of a bond
- Definition of a Bravais Lattice
- How to determine simple bonding configuration from constituent atoms with support of equations and tables
- How to determine relative stability of different crystallographic structure in common materials (e.g., TiO_2)
- Given a crystallographic structure be able to predict some of the properties determined by the crystallographic structure
- How coordination number relates to bonding and structural configuration (e.g. CN = 6, octahedral)
- Be able to relate atomic radius and formal charge to bonding configuration



Important Concepts to Master

- How to calculate ionic character of a bond
- Definition of a Bravais Lattice
- How to determine simple bonding configuration from constituent atoms with support of equations and tables
- How to determine relative stability of different crystallographic structure in common materials (e.g., TiO_2)
- Given a crystallographic structure be able to predict some of the properties determined by the crystallographic structure
- How coordination number relates to bonding and structural configuration (e.g. CN = 6, octahedral)
- Be able to relate atomic radius and formal charge to bonding configuration

Things you should not attend to:

- Names of specific crystallographic structures
- Chemical composition of specific crystallographic structures
- The structure and drawings of specific crystallographic structures

