



University of  
South Australia

# ENR116 Engineering Materials

## Module 4 Non-metals and Corrosion

Dr Drew Evans

School of Advanced Manufacturing and Mechanical Engineering

- My name is Drew Evans, and welcome to Module 4 of ENR116 Engineering Materials – Non-Metals and Corrosion



University of  
South Australia

ENR116 – Mod. 4- Slide No. 2

## Copyright Notice

Do not remove this notice.

**COMMONWEALTH OF AUSTRALIA**  
Copyright Regulations 1969

### **WARNING**

This material has been produced and communicated to you by or on behalf of the University of South Australia pursuant to Part VB of the *Copyright Act 1968 (the Act)*.

The material in this communication may be subject to copyright under the Act. Any further reproduction or communication of this material by you may be the subject of copyright protection under the Act.

**Do not remove this notice.**



University of  
South Australia

# Ceramic structures

- This presentation will cover an Introduction to Ceramic Structures



## Intended Learning Outcomes

**At the end of this section, students will be able to:-**

- Identify how **crystal structures** of ceramics are **different** from metals.
- Describe a **range of crystal structure** formulations and arrangements.
- Understand why knowing a materials **crystal structure** is important and useful when designing materials

- By the end of this presentation, you should be able to:
  - Identify how crystal structures of ceramics are different from metals
  - Describe a range of crystal structure formulations and arrangements
  - Understand why knowing a materials **crystal structure** is important and useful when designing materials



# Ceramic bonding

Atomic Bonding: From purely ionic to a mixture of ionic and covalent

% ionic character increases with increasing difference in **electronegativity** of atoms.

IA																	0	
H																	He	
2.1																	-	
Li	Be															Ne		
1.0	1.5															-		
Na	Mg															Ar		
0.9	1.2															-		
		IIIB	IVB	VB	VIB	VII B	VIII					IB	IIB					
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6	1.6	1.8	2.0	2.4	2.8	-	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5	-	
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
0.7	0.9	1.1-1.2	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.8	1.9	2.0	2.2	-	
Fr	Ra	Ac-No																
0.7	0.9	1.1-1.7																

CaF<sub>2</sub>: large 89%

SiC: small 12%

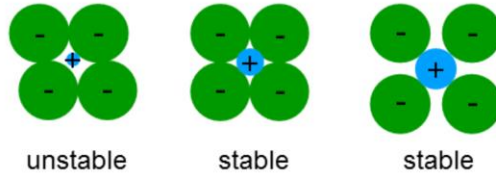
Adapted from Fig. 2.7, Callister & Rethwisch 8e. (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

- Ceramics are inorganic, nonmetallic compounds between metallic and nonmetallic elements
- The nature of the interatomic bond between the elements is either totally ionic, or a bond which appears to be predominantly ionic with some covalent character
- The percentage of ionic character depends on the difference in electronegativity between the elements which are bonded
- For example, calcium fluoride has a large percentage of ionic character, 89%, because the elements reside on the opposite sides of the periodic table
- Silicon carbide has a small percentage of ionic character, 12%, because the elements reside close to each other in the periodic table



# Ionic bonding & structure

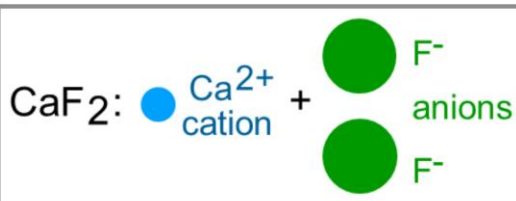
1. **Size** - Stable structures: Maximize the number of nearest, oppositely-charged neighbors.



Adapted from Fig. 12.1,  
Callister & Rethwisch 8e.

2. **Charge Neutrality:**

Net charge in the structure should be **zero**.



General form:  $A_mX_p$   
 $\uparrow \quad \uparrow$   
 $m, p$  determined by charge neutrality






- For ceramic compounds that have high ionic bonding character, the two elements that make up the ceramic can be classified as either a cation or anion
- The cation is the metallic ion, having a positive charge as a result of giving up its valence electrons in the predominantly ionic nature of the atomic bond
- The anion is therefore the nonmetallic ion, having a negative charge as a result of accepting the valence electrons from the cation
- Generally speaking, the cation is the smaller of the two ions because it has given up its valence electrons and the remaining electrons having a stronger attraction to the nucleus of the atom
- Characteristics of the cation and anion that define the resulting crystal structure of the ceramic compound are their relative size and their charge
- With respect to the relative size of the atoms, stable structures are formed when the number of nearest neighbour oppositely-charged atoms is maximised
- The charge of the atoms helps define the structure by specifying the ratio of cation atoms to anion atoms required to balance the total charge, that is, for charge neutrality
- The general form of these ceramic compounds is presented as  $A_mX_p$ , where  $m$  and  $p$  are determined by the charge balance of the cations and anions



# Coordination number and ionic radii

Coordination Number increases with ratio:  $\frac{r_{\text{cation}}}{r_{\text{anion}}}$

**Issue:** How many anions can you arrange around a cation?

$\frac{r_{\text{cation}}}{r_{\text{anion}}}$	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	

Adapted from Table 12.2,  
Callister & Rethwisch 8e.

- The number of nearest neighbours an atom has is referred to as the Coordination Number
- The Coordination Number increases with an increase in the relative size of the cation to anion
- Here, the size of the cation and anion are defined by their ionic radii
- The Coordination Number of the cation can be determined based on a geometric argument of packing anion spheres around a central cation
- The ratio of the ionic radii then gives a prediction of the Coordination Number and hence the unit cell structure of the ceramic compound
- Examples of the more common unit cell structures are,
  - ZnS is made up of tetrahedral unit cells
  - NaCl is made up of octahedral unit cells
  - CsCl is made up of cubic unit cells



## Example: Predicting structure of FeO

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

Cation      Ionic radius (nm)

Al<sup>3+</sup>      0.053

Fe<sup>2+</sup>      0.077

Fe<sup>3+</sup>      0.069

Ca<sup>2+</sup>      0.100

Anion

O<sup>2-</sup>      0.140

Cl<sup>-</sup>      0.181

F<sup>-</sup>      0.133

Answer:

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{0.100}{0.140}$$

$$= 0.714$$

Based on this ratio:

Coordination # = 6

Structure is that of NaCl

Data from Table 12.3,  
Callister & Rethwisch 8e.

- A quick demonstration of how the ratio of the ionic radii of the cation to anion can be used to predict the Coordination Number can be taken from the example of CaO
- Taking the ionic radius of Ca<sup>2+</sup> is 0.100 nm and O<sup>2-</sup> is 0.140 nm
- Their ratio gives the value of 0.714
- Based on this ratio the Coordination Number is predicted to be 6, and hence it's classified as having a rock salt type structure



## Types of crystal structure

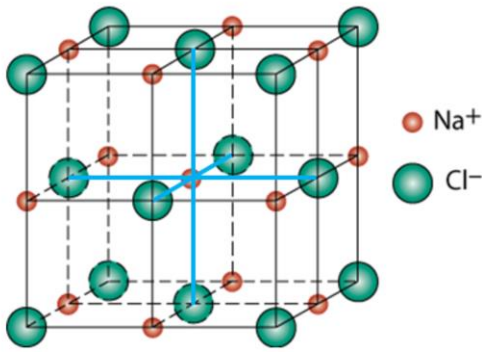
The different ceramic compounds are defined by the  $A_mX_p$  labeling convention, where  $m$  and  $p$  are defined by the cation and anion charge balance.

- The ceramic compounds are labelled using the  $A_mX_p$  convention, where  $m$  and  $p$  capture the relative charge of the atoms that make up the ceramic
- Within these categories the structures observed still depend on the relative size of the cation and anion
- The first category of ceramics is where  $m$  equals  $p$ , that is, the cation and anion have the same charge magnitude but obviously they are opposite in sign
- Examples within this category are sodium chloride, cesium chloride and zinc sulfide
- The second category of ceramics is where  $m$  does not equal  $p$ , implying that the cation and anion have different charge magnitudes
- Examples here are calcium fluoride and zirconium oxide (also known as zirconia)
- The third category that will be discussed in this presentation has the form  $A_mB_nX_p$ , indicating that the ceramic compound is made from mixing three different elements, typically two cations and one anion
- An interesting example from this category is barium titanate

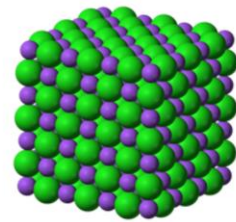


## AX structures

Example: NaCl (rock salt) structure.



Adapted from Fig. 12.2,  
Callister & Rethwisch 8e.



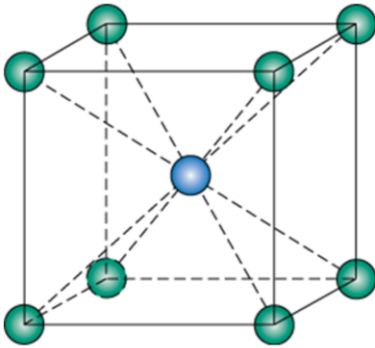
MgO and FeO also have the NaCl structure.

- Lets now look at the first category where  $m=p$ , the AX ceramic compounds
- There are several different structures that have been observed for different combinations of cations and anions of the same charge magnitude
- The most common AX structure is the sodium chloride type, otherwise known as rock salt
- Both the cation and anion have a coordination number of 6
- The resulting structure is an interpenetrating network of face centered cubic lattices of the cations and anions
- The ionic radius ratio of the cation to anion for this structure lies between 0.414 and 0.732, in the example of NaCl it is 0.564
- Other ceramics to display the sodium chloride or rock salt type structure are magnesium oxide and iron oxide



## AX structures

### Cesium Chloride structure:



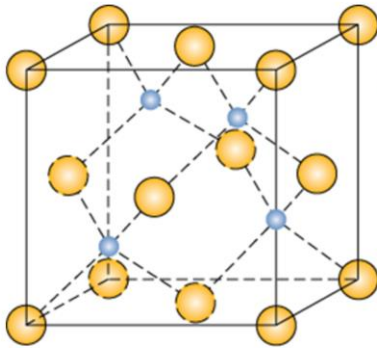
Adapted from Fig. 12.3,  
*Callister & Rethwisch 8e.*

- Another structure that can be observed with AX ceramic compounds is that observed for cesium chloride
- Now, this structure may appear to be a body centered cubic structure, but closer inspection shows the central atom is the cesium atom
- The ionic radius ratio of the cation to anion for cesium chloride is 0.939, therefore the predicted structure is cubic
- Each cesium atom has coordination number of 8
- An interesting point about this structure is that if the positions of the cations and anions are swapped within the crystal structure, the cubic structure is still maintained



## AX structures

### Zinc Blende (ZnS) structure:



Adapted from Fig. 12.4,  
Callister & Rethwisch 8e.

$$\begin{array}{ll} \bullet \text{ Zn}^{2+} & \frac{r_{\text{Zn}^{2+}}}{r_{\text{S}^{2-}}} = \frac{0.074}{0.184} = 0.402 \\ \bullet \text{ S}^{2-} & \end{array}$$

Size arguments predict  $\text{Zn}^{2+}$  in octahedral sites.

- The final structure for the AX ceramic compounds to be discussed in this presentation is observed for the zinc sulfide
- This structure is known as zinc blende type or sphalerite
- The predicted structure from the ratio of the ionic radius of the cation to anion is octahedral
- However, when observing the structure the zinc ions are found in a tetrahedral structure
- To rationalise this observation we need to look at the bonding in this ceramic
- The interatomic bonds in this ceramic are low in ionic character, that is, they are highly covalent
- To satisfy the electronic structure of the zinc, four lone pairs of electrons are donated by the anions
- This leads to each zinc atom having four neighbouring sulfur atoms, hence the tetrahedral structure
- This is similarly observed for other ceramics where the charge is +2 on the cation and -2 on the anion
- Examples are zinc oxide and silicon carbide

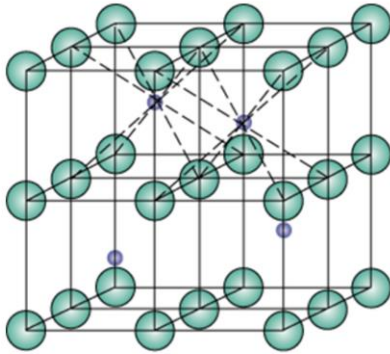


## $A_mX_p$ (i.e. $AX_2$ ) structures

**Fluorite** structure: Charges on cations and anions are different.



Calcium Fluorite ( $CaF_2$ )



Radii ratio = 0.8, coordination  
number = 8

Cubic structure

Examples:  $UO_2$ ,  $ThO_2$ ,  $ZrO_2$ ,  $CeO_2$

Antifluorite structure – cations and  
anions reversed.

Adapted from Fig. 12.5,  
Callister & Rethwisch 8e.

- The next category of ceramic compounds to be discussed are those where the cation and anion do not have the same charge magnitude
- That is, in the general formula of  $A_mX_p$ ,  $m$  does not equal  $p$
- An example of this category is calcium fluorite, where charge on the calcium is  $2+$  and the charge on each fluorine atom is  $-1$
- In this case,  $m = 1$  and  $p = 2$  to obtain charge neutrality
- For these atoms, the ratio of the ionic radius of the cation to anion is 0.8
- This leads to a coordination number for the cation of 8, resulting in a cubic structure
- The cubic crystal structure is the same geometry as observed for the cesium chloride ceramic in the  $AX$  ceramic category
- This demonstrates that while the number of anions and cations required to balance their charges might be different, the observed crystal structure may indeed be the same
- Within this category of ceramic compounds, a well known example is zirconium oxide (better known as cubic zirconia)



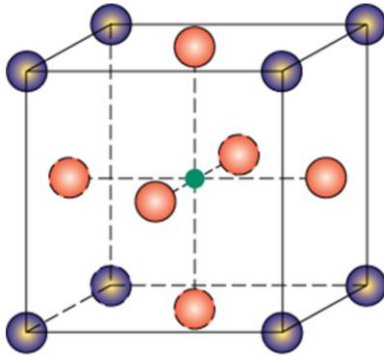
## $A_mB_nX_p$ (i.e. $ABX_3$ ) structures

**Perovskite:** Ceramic compounds with more than one type of cation.



Example:

Barium titanate ( $BaTiO_3$ )



Adapted from Fig. 12.6,  
Callister & Rethwisch 8e.

For a summary of all  
these crystal structures  
see Table 12.4, p460 of  
*Callister & Rethwisch 8e*.

- The final category of ceramic compounds that will be discussed in this presentation involves the mixing of three different elements
- This category is labelled as  $A_mB_nX_p$ , where A and B are typically cations
- This type of ceramic has a slightly different crystal structure compared to the previous categories, owing to the presence of three different elements
- Perovskite is the general name given to the observed crystal structure within this category of ceramic compounds
- An example of a ceramic compound having the Perovskite crystal structure is barium titanate
- From the illustration of the crystal structure presented here, the observed Perovskite structure is cubic in nature
- Ceramic compounds having the Perovskite crystal structure have interesting and useful electromechanical properties that can be exploited in certain applications
- The crystal structures for the different ceramic compounds presented here are summarised in Table 12.4 of the course text
- This table is helpful for relating the general name for a given structure (i.e. rock salt) with the structure type (i.e. AX) and the coordination number of the cation and anion (i.e. 6), with some real world examples of the structure (i.e. magnesium oxide)

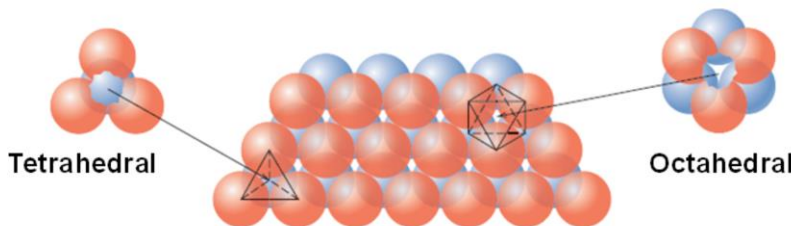
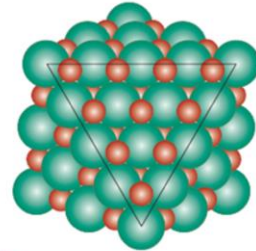


## Crystal Structures from the close packing of anions

Define the crystal structure from the close packing of the anions

1. The close-packing of **anion layers** can be both FCC or HCP arrangements, which correspond to ABCABC... and ABABAB... sequences, respectively
2. The **interstitial sites** are filled with **cations**.

**NaCl**



Figs. 12.07, 12.08, Callister  
& Rethwisch 8e.

- Another way to describe the crystal structure of ceramics is by the close packing structure of the anions, rather than the unit cell concept described in the previous slides
- In this analysis, the anions are close packed within a layer, and then subsequent layers are arranged to build up a three dimensional structure
- The layers can be close-packed in both the face centered cubic or hexagonally close packed arrangements, resulting in either the ABCABC or ABABAB layer sequences
- To complete the ceramic compound, the cations in this case will reside in the interstitial positions between the layers of anions
- Two different positions exist where the cations can reside, as shown in the schematic
- In one case, four anion atoms, three in one plane and one in the adjacent plane, surround one position for the cation
- The interstitial position within these four anion atoms is termed as the tetrahedral position because the centre of each anion atom form the corners of a four sided tetrahedron
- In the other case, six anion atoms, three in one plane and three in the adjacent plane, surround one position for the cation
- This interstitial position is termed the octahedral position because the centre of each anion atom forms the corners of an octahedron
- Lets now look at an example of how to describe a ceramic compounds crystal structure using this method by examining the rock salt crystal structure, i.e. sodium chloride
- The unit cell for this is cubic, with each sodium atom having six nearest neighbour chlorine atoms which reside at the centre of each face of the cube
- This means that the chlorine anions pack in a face centred cubic structure
- To achieve a coordination number of six for the sodium cation, it therefore must reside in the octahedral position
- Because the ceramic compound category for sodium chloride is AX (that is,  $m=p$ ), every octahedral position must be filled to achieve one sodium atom per chlorine atom
- This is illustrated in the schematic on the right, showing the layer by layer close packing of chlorine anions in a face centered cubic structure and sodium cations filling every octahedral position
- An important note here is that while other ceramic compounds can be described by close packing the anions and positioning cations at particular interstitial sites, not all ceramic compound crystal structures can be described by this method



## Ceramic density computation

Number of formula units /unit cell

Atomic  
weights of all  
the cations  
and anions

$$\text{density} = \rho = \frac{n'(\sum A_C + \sum A_A)}{V_C N_A}$$

Volume of unit  
cell

Avogadro's  
Number

**Formula units:** All the ions that are included in the chemical formula; *i.e.* one sodium and one chlorine in NaCl

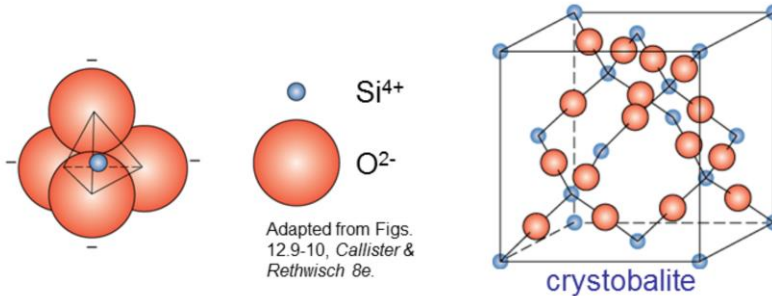
An example of calculating the theoretical density for NaCl can be found in Example Problem 12.3 on p463 of *Callister & Rethwisch 8e*.

- An important property of any material is its density, as this is one factor that will define a materials performance when used in the real world
- The density of a ceramic can be theoretically determined from information about its unit cell, similar to the calculation made for metals
- The density can be determined by knowing,
  - $n'$ , the number of formula units within the unit cell, where the formula unit is the total number of atoms (not type of atoms) that make up the chemical formula
  - For example, in the typical unit cell of rock salt there are four sodium atoms and four chlorine atoms
  - Because the chemical formula has one sodium and one chlorine, then there are four formula units per unit cell
  - $\sum A_C$  is the sum of the atomic weights of all the cations in the formula unit
  - $\sum A_A$  is the sum of the atomic weights of all the anions in the formula unit
  - $V_C$  is the unit cell volume
  - and  $N_A$  is Avogadro's number, 6.022 times 10 to the power 23 formula units per mole of material



# Silicate ceramics

Most common elements in the earth's crust are Si & O



- So far the discussion has been about categorising ceramic structures with respect to their chemical formula and crystal structure
- Armed with this new knowledge of how to classify a ceramic, let's now look at some examples of compounds which can be found in various structures within nature
- The first compound to explore is referred to as a "silicate"
- Silicates are made up of the two most abundant elements in the Earth's crust
- Given this, it is obvious to see why silicates are an interesting class of materials, and why the majority of soils, rocks, clays and sand fall under this classification
- Despite the emphasis of defining a ceramic compounds structure by the geometry of the unit cell, silicates are more conveniently described by the various arrangements of an  $\text{SiO}_4$  tetrahedron
- The ratio of the ionic radius of the cation to anion is approximately 0.286, indicating why a tetrahedral structure is observed
- This tetrahedron has a formal charge of -4, despite the interatomic bond between Si and O being highly covalent
- The most simple of the silicates is silicon dioxide, or silica
- Overall this ceramic compound is charge neutral, as indicated by its chemical formula
- Examples of silica are quartz, cristobalite and tridymite
- As shown in the schematic of the cristobalite structure, the silica

based structures are rather complex

- In the silica structure the atoms are not closely packed together, which in practice means they have a relatively low density (for example quartz at room temperature has a density of 2.65 grams per cubic centimeter)
- Despite the atoms not being closely packed together, the Si-O bond is quite strong, which is reflected in a relatively high melting temperature of 1710°C

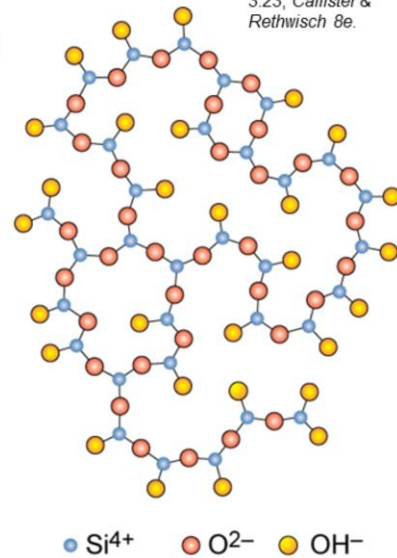


# Silica Glasses

Silica glasses are amorphous

$\text{Si}^{4+}$  and  $\text{O}^{2-}$  are not in a well-ordered lattice.

Adapted from Fig.  
3.23, Callister &  
Rethwisch 8e.



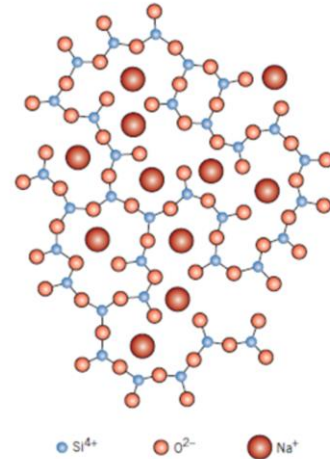
- Another form observed in the silicates are silica glasses
- These are noncrystalline compounds derived from the same elements of silicon and oxygen, sometimes referred to as amorphous silica
- As the name suggests, amorphous implies a lack of morphology or structure
- In fact, the high degree of randomness in the atomic arrangement is more characteristic of a liquid than a solid
- In order to achieve charge neutrality for the structure hydrogen atoms are found at the “dangling” bonds to form hydroxide and counter the -4 charge on the  $\text{SiO}_4$  tetrahedron
- Other oxides can form this glassy structure as well, such as boron oxide
- Materials that form such glassy structures are termed network formers



## Silica glass

The density of the amorphous silica can be increased with additives, and melting temperature lowered

Adapted from Fig.  
12.1, Callister &  
Rethwisch 8e.

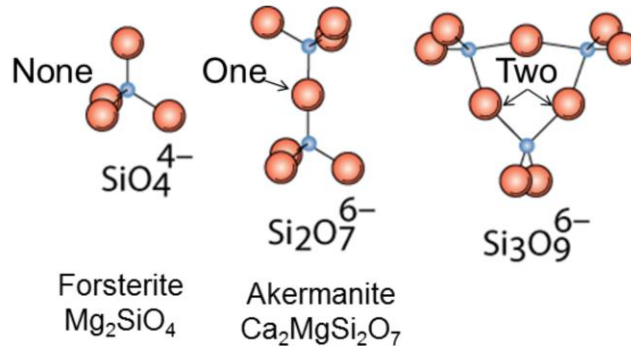


- Because of the lower density of silica, and its relatively high melting temperature, additives to the silica have been explored to improve its practical “workability”
- It is possible to incorporate other oxides into the silica structure
- These are added so that the cations of the oxide being incorporated into the silica balance the -4 charge of the  $\text{SiO}_4$  tetrahedron
- These oxide additives are termed network modifiers
- From the perspective of their practical use, the additives to the silica glass lower the melting point and viscosity of the glass, making it easier to work with
- A practical example of such glasses is Borosilicate glass, commercially known as Pyrex, where boron is used as a cation to balance the  $\text{SiO}_4$  charge



# Silicates

Combine  $\text{SiO}_4^{4-}$  tetrahedra by having them share corners, edges, or faces.



Adapted from Fig.  
12.12, Callister &  
Rethwisch 8e.

Presence of cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , &  $\text{Al}^{3+}$

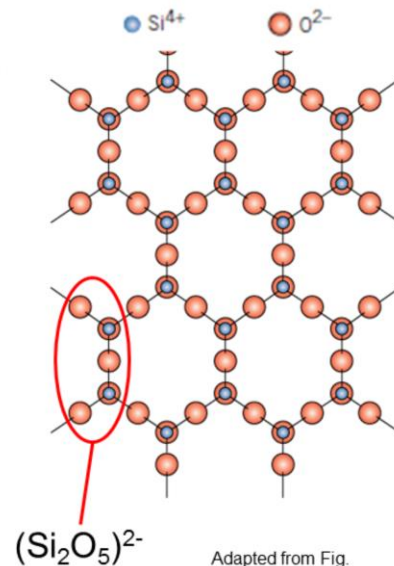
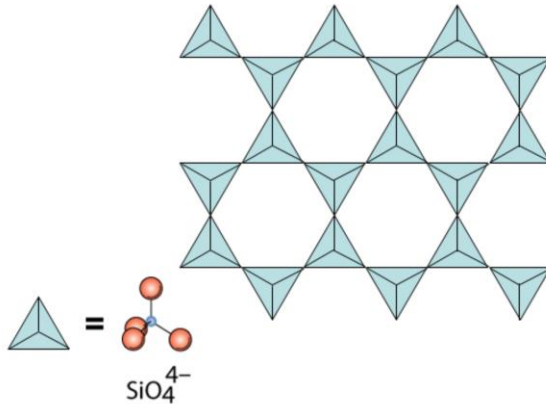
1. Act to neutralize charge
2. Provide ionic bonding

- Other silicates arise from the combination of one or more  $\text{SiO}_4$  tetrahedra, which share one, two or three of the oxygen atoms
- In the schematic here, there are examples of  $\text{SiO}_4$  tetrahedra sharing no oxygens, one oxygen and two oxygens
- Cations such as calcium, magnesium and aluminium are employed to achieve charge neutrality and to provide ionic bonding between the different  $\text{SiO}_4$  tetrahedra
- Of the simple silicates, forsterite has two magnesium cations per  $\text{SiO}_4$  tetrahedron, and akermanite has two calcium and one magnesium per  $\text{Si}_2\text{O}_7$  unit
- Remembering that the  $\text{Si}_2\text{O}_7$  unit comprises two  $\text{SiO}_4$  tetrahedra which share one oxygen atom



## Layered silicates

Layered silicates (clay silicates)  $\text{SiO}_4$  tetrahedra connected together to form 2-D plane.



Need cations balance charge

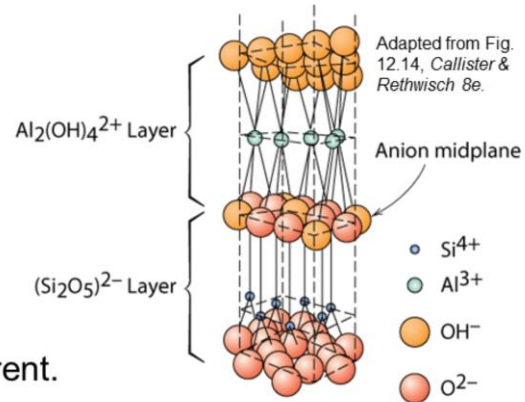
Adapted from Fig.  
12.13, Callister &  
Rethwisch 8e.

- Through the sharing of oxygens by neighbouring  $\text{SiO}_4$  tetrahedra, a two dimensional sheet or layer can be produced
- Rather than referring to the  $\text{SiO}_4$  tetrahedron as the unit,  $\text{Si}_2\text{O}_5^{2-}$  is used as the repeat unit within one layer
- The two silicon atoms and three of the oxygen atoms lie in the same plane, with the remaining two oxygen atoms projecting out of the plane
- The net negative charge is associated with the two oxygen atoms projecting out of the plane
- To balance the net negative charge, cations are required which exist in excess within a layer parallel to the  $\text{Si}_2\text{O}_5$  layer
- Typically these layers would build up in an alternating layer structure, hence the name sheet or layered silicates
- Clays and other minerals are characterised by this basic layered structure



## Layered silicates

Kaolinite clay alternates  $(\text{Si}_2\text{O}_5)^{2-}$  layer with  $\text{Al}_2(\text{OH})_4^{2+}$  layer.



Cation-rich layers can be different.

Micas  $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ ;

Talc  $[\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2]$

Sheets are strongly bound within, but loosely bound between adjacent sheets

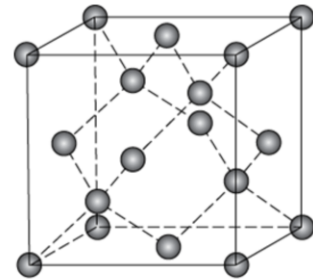
- An example of a common clay mineral is kaolinite
- In this layer structure, aluminium hydroxide is observed as the layer with excess cations to balance the negative charge of the  $\text{Si}_2\text{O}_5$  layer
- In the schematic the distance between sheets has been expanded to highlight how the sheets interact with each other
- At the “interface” between the two layer structures, known as the anion midplane, there is a mixture of  $\text{O}^{2-}$  atoms from the  $\text{Si}_2\text{O}_5$  layer and the  $\text{OH}^-$  ions from the  $\text{Al}_2\text{OH}_4$  layer
- Within any given sheet the interatomic bonding is strong and has reasonable ionic character, while the bonding between adjacent sheets is not as strong, predominately being defined by the interaction of hydrogen and oxygen
- With the layered silicates there are many other cation-rich layers can be employed to balance the negative charge of the  $\text{Si}_2\text{O}_5$  layer
- Depending on what cation-rich layer is employed, the physical and chemical properties of the material can change
- For example, changes may occur in the inter-layer spacing or the absorption rate of water
- Other examples of layered silicates are micas, employing potassium and aluminium cations, and talcs, which employ magnesium cations



## Carbon forms

### Carbon black:

Amorphous – lack of an ordered structure



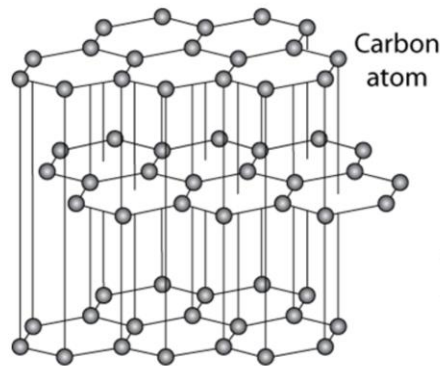
Adapted from Fig.  
12.15, Callister &  
Rethwisch 8e.

- Similar to silicon and oxygen being responsible for a variety of different structures depending on how they are combined, carbon by itself also represents a variety of forms
- For example, carbon black is the amorphous form of carbon, and is readily used in inks and toners as black for printing
- On the other hand, well ordered structures of carbon exist in a zinc blende-type structure, known as diamond
- Note that all positions in the crystal structure are occupied by the same type of atom as shown in the schematic here, rather than the mixture of zinc and sulfide in the zinc blende structure
- There are many commercial uses for diamond owing to its optical and mechanical properties
- Interestingly, the change in material properties between the amorphous form and the well ordered form results in a significant difference in the cost of the two forms (carbon black is relatively cheap compared to diamond)



## Carbon forms: Graphite

Layer structure – aromatic layers.



Adapted from Fig.  
12.17, Callister &  
Rethwisch 8e.

Weak van der Waal's forces between layers.

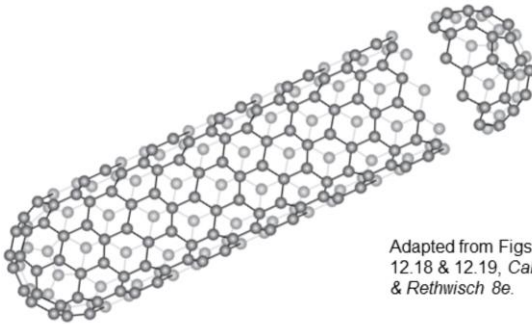
Layers (planes) **slide easily** hence a good lubricant.

- Another form of carbon that is readily used is graphite
- Graphite is the layered structure of carbon, where the atoms within a layer are arranged in a hexagonal pattern
- In this structure, strong covalent bonding occurs between one carbon atom and its three nearest neighbours
- This then leaves one electron free for interaction with the carbons of the adjacent layer
- The properties of graphite are different again from the carbon black and diamond, leading to a long list of different applications
- One example is its use as a lubricant, where the weak bonding between adjacent layers allows them to easily slide past each other, therefore reducing friction between surfaces
- For further examples of the use of graphite, please consult Chapter 12 of the course text



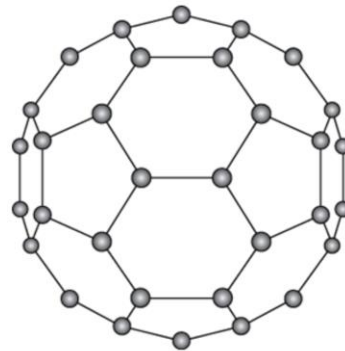
## Carbon Forms: Fullerenes and nanotubes

Wrap the graphite sheet by curving into ball or tube.



Carbon NanoTube (CNT)

Adapted from Figs.  
12.18 & 12.19, Callister  
& Rethwisch 8e.



Buckminsterfullerenes - like a  
soccer ball  $C_{60}$  - also  $C_{70}$  and  
others.

- The hexagonal pattern of carbons that make up a layer in graphite do not necessarily need to exist as a two dimensional sheet
- Other forms of carbon exist where a sheet of the graphite is wrapped upon itself to form a ball or tube
- The ball form of the carbon structure is known as a buckminsterfullerene, while the tube is known as a carbon nanotube or CNT
- As with the other forms of carbon, the buckminsterfullerenes and carbon nanotubes have characteristic physical and chemical properties that make them materials of choice for a range of different applications
- In light of this, the carbon nanotubes are featured in the course text on p471 as a material of importance



## Summary

Ceramic crystal structures are based on:

- Maintaining charge neutrality of the ceramic compound
- The ratio of the cation to anion ionic radii
- The ionic character of the bonding

Silicates and Carbon are materials that:

- Display a range of different structures
- Demonstrate why/how structure is important

- In summary,
  - The crystal structure of a ceramic compound is based upon achieving charge neutrality within the compound, and the ratio of the ionic radius of the cation to anion
  - The ratio of the ionic radius of the cation to anion describes the type of sphere close packing that will be observed
  - Importantly, the ionic character of the interatomic bond also plays a role in defining the packing structure
  - The silicates and carbon are materials that display a range of different structures depending on how they are formed and what additives are present
  - Comparing these different structures within either the silicates or carbon demonstrates why knowing a materials structure is very useful and important when selecting or designing materials for a given application



**Thank you**

- This concludes the presentation on the introduction to ceramic structures
- If you have any questions or desire further clarification please post a question or comment on the ENR116 Discussion Forum
- For further reading please consult the course text, specifically Chapter 12