Ceramics - I

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Contents

Introduction

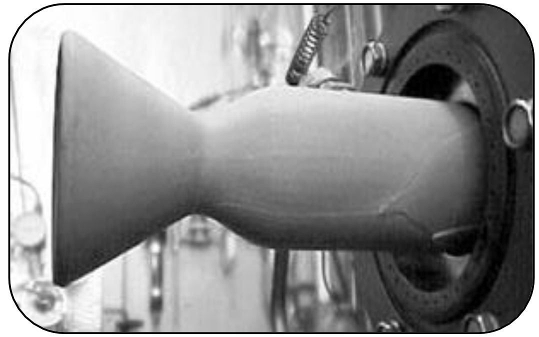
- **Ceramics** word is derived from **Greek** term *keramikos* means "**burnt stuff**".
- **Clay** is the one **earliest** known **ceramics** used for making **pottery**.
- **Ceramic materials** are the **inorganic crystalline** materials made from compounds of a **metal and a non metal** primarily held by **ionic** and **covalent** bonds.
- **Glass** by **definition** is exactly **not** a **ceramic** because it is an **amorphous** solid (non-crystalline) but its **mechanical properties** behave **similar** to ceramic materials.
- Common characteristics are:
  - ✓ **Hard** and **brittle** (carbon in the form of **diamond** - hardest known material).
  - ✓ **Strong** in **compression** (typically 10 times), **weak** in **tension**.
  - ✓ Chemically **inert**.
  - ✓ **Insulators** of heat and electricity (exception – carbon in the form of **diamond** & **graphite**).
  - ✓ **High** and well defined **melting point**.

Clay (Alumina & silica) Pottery

Few examples

SiC – as abrasive (grinding wheel) & disc brake

Image: www.waleapparatus.com & Wikipedia

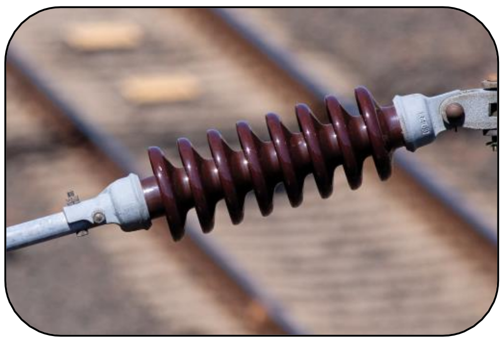


Silicon nitride - rocket thruster

Image : Wikipedia

Uranium oxide – nuclear fuel

Image: http://hyperphysics.phy-astr.gsu.edu/



Porcelain – High voltage electric insulators

Titanium carbide – Space shuttle heat shield

Image: NASA

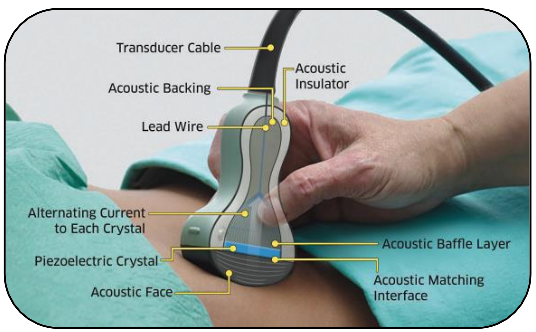
ZnO - semi-conductor, sunscreen, cigarette filters

Image: Wikipedia

Bearing - Silicon nitride

Boron nitride – crucible

Image: Wikipedia



PZT – Ultrasonic transducer

Image: sensorsmag.com

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Ceramics:
Classification and Application

Natural Ceramics

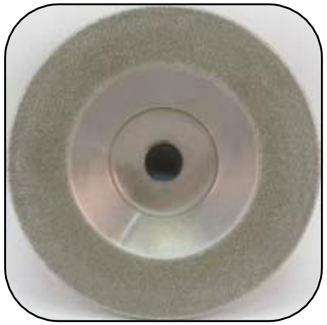
Limestone (largely $CaCO_3$)

Sandstone (largely SiO_2)

Granite (Aluminium silicate)

Abrasives

- Typical examples – Silicon carbide, Tungsten carbide, Al_2O_3 (or corundum), silica sand.
- Used to grind, or cut away other relatively softer material.
- Posses high hardness and wear resistance.
- Used in form as -
  - ✓ Bonded to grinding wheel by glassy ceramic or an organic resin.
  - ✓ Abrasive powder coated on paper or cloth, E.g., Sandpaper.



Tungsten carbide wheel

Diamond abrasive

Refractories

- ✓ Usually used in furnaces operating around 1500°C.
- ✓ Withstand high temperatures without melting.
- ✓ Remain unreactive and inert under severe environments.
- ✓ Example : Alumina, silica, bricks, Fireclay, Zirconia, Magnesia or Periclase (MgO), BeO, etc.

Fireclay (Al_2O_3+SiO_2)

ZrO_2

Refractory Type	*Composition (wt%)* Al_2O_3	SiO_2	MgO	Cr_2O_3	Fe_2O_3	CaO	TiO_2	*Apparent Porosity (%)*
Fireclay	25–45	70–50	0–1		0–1	0–1	1–2	10–25
High-alumina fireclay	90–50	10–45	0–1		0–1	0–1	1–4	18–25
Silica	0.2	96.3	0.6			2.2		25
Periclase	1.0	3.0	90.0	0.3	3.0	2.5		22
Periclase–chrome ore	9.0	5.0	73.0	8.2	2.0	2.2		21

Reference: W.D Callister, 7 Ed.

Ceramic Composites

- Ceramics combined with metals or polymers to make composites.
- Done to take advantages of individual component properties.

Ceramic Composites

Ceramic Composite	Components	Typical Uses
Fiber glass CFRP	Glass – polymer Carbon – polymer	High-performance structures.
Cermet	Tungsten carbide–cobalt	Cutting tools, dies.
Bone	Hydroxyapatite–collagen	Main structural material of animals.
New ceramic composites	Alumina–silicon carbide	High temperature and high toughness applications.

Reference: Engineering Materials 2: Ashby & Jones, 4th Ed.

Cement & Concrete

- Used as construction material.
- Cement is a mixture of a combination of lime (CaO), silica (SiO_2), and alumina (Al_2O_3), which sets when mixed with water.
- Concrete is sand and stones (aggregate) held together by cement.

Cement

+ Sand, stones & water =

Concrete

High Performance Ceramics

They posses

- ✓ High resistance to fracture.
- ✓ High temperature stability.
- ✓ High load carrying & wear resistant properties.

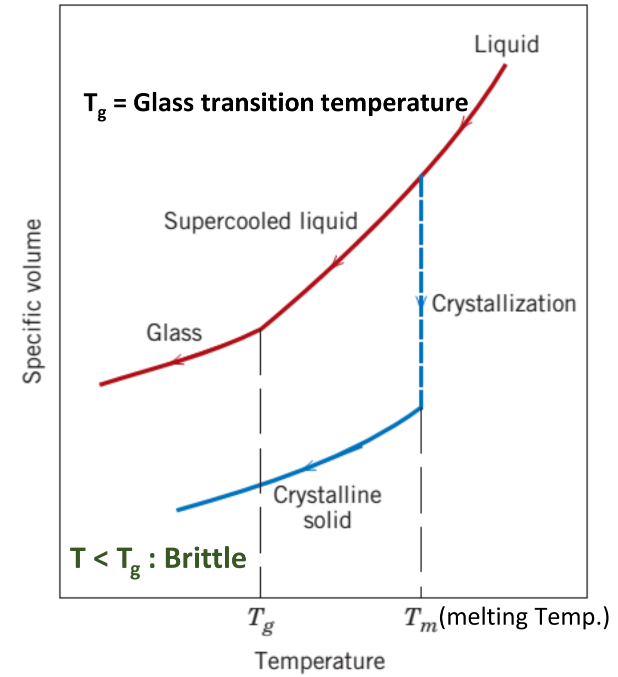
High-Performance Ceramics

Ceramic	Typical Composition	Typical Uses
Dense alumina Silicon carbide, nitride Sialons	Al_2O_3 SiC, Si_3N_4 Si_2AlON_3	Cutting tools, dies; wear-resistant surfaces, bearings; medical implants; engine and turbine parts; armor.
Cubic zirconia	$ZrO_2 + 5$ wt% MgO	

Reference: Engineering Materials 2: Ashby & Jones, 4th Ed.

Glasses

- Non-crystalline silicates containing other oxides, notably CaO, Na_2O, K_2O, and Al_2O_3, etc., which influence the glass properties.
- Glasses behave like a liquid at high temperature.
- Can be made **crystalline** by the proper high-temperature heat treatment, then called as ***Glass-ceramic.***



Reference: W.D Callister, 7 Ed.

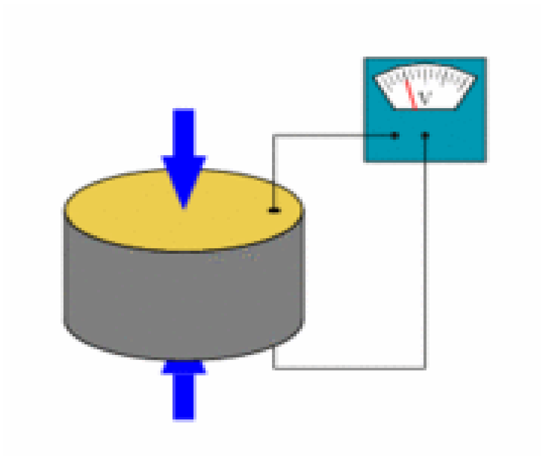
Glasses

Glass	Typical Composition (wt%)	Typical Uses
Soda-lime glass	70 SiO_2, 10 CaO, 15 Na_2O	Windows, bottles, etc.; easily formed and shaped.
Borosilicate glass	80 SiO_2, 15 B_2O_3, 5 Na_2O	Pyrex; cooking and chemical glassware; high-temperature strength, low coefficient of expansion, good thermal shock resistance.

Reference: Engineering Materials 2: Ashby & Jones, 4th Ed.

Piezoelectric Ceramics

- Exhibit reversible piezoelectric phenomenon.
- **Example**: Barium Titanate ($BaTiO_3$), Lead Titanate ($PbTiO_3$), Lead Zirconate Titanate (PZT), Potassium Niobate ($KNbO_3$).
- **Applications**: Ink-jet printing head, ultrasonic testing, strain gauges, etc.



Piezo ceramics

Image: Wikipedia

Stress → **Direct Effect** (Sensor) → Electric potential

Electric stimulus → **Reverse Effect** (Actuator) → Strain

Bonding
&
Crystal Structure

Bonding between Atoms

Bonding between Atoms

ISSUES TO ADDRESS...

- What promotes bonding?
- What types of bonds are there?
- What properties are inferred from bonding?

Periodic Table

Columns : Similar valence structure

$1e^-$ Donate	$2e^-$ Donate	$3\ e^-$ Donate													Accept $2e^-$	Accept $1e^-$	Inert Gases
IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 H 1.0080																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.87	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.69	29 Cu 63.54	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	Rare earth series	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.2	76 Os 190.23	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.19	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	Acti- nide series	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (281)								

Key: 29 – Atomic number; Cu – Symbol; 63.54 – Atomic weight

Metal

Nonmetal

Intermediate

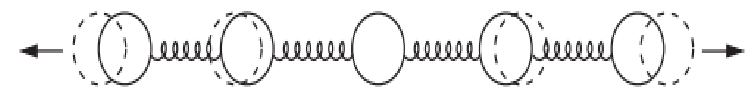
Electropositivity increases
Readily give up electrons to become +ve ions.
(Cesium most electropositive)

Electronegativity increases
Readily acquire electrons to become -ve ions.
(Fluorine most electronegative)

Reference: W.D Callister, 7Ed.

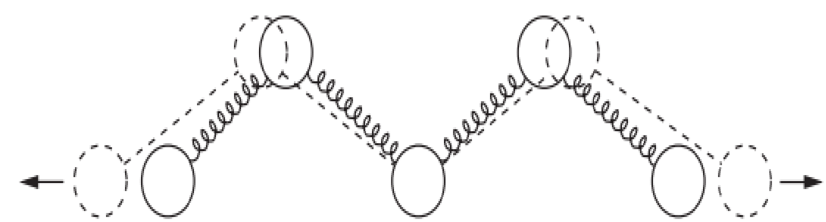
Understanding the origin of material properties requires study at the atomic level.

Interatomic bonds : Hold atoms together and act like spring by linking one to atom to other in solid state.



Bonds (like a spring)

Atomic packing : Signifies the way in which atoms are packed together.
No. of little springs per unit area and angle at which they are pulled.



Atomic Packing

Reference: Engineering Materials 1: Ashby & Jones, 4th Ed.

The ways in which atoms can be bound together are :

- **<u>Primary Bonds</u>** – Ionic, Covalent and Metallic bonds.
  - They are relatively strong.
  - Generally melt between 1000 – 4000 K.

- **<u>Secondary Bonds</u>** – Van der Waals and Hydrogen bonds.
  - Both are relatively weak.
  - They melt between 100-500 K.

Primary Interatomic Bonding

1. *Ionic Bonds*

- ✓ Found in compounds that are composed of both **metallic** and **nonmetallic** element.
- ✓ **Large difference in electronegativity** required, means bonding occurs between elements that are situated at the horizontal extremities of the periodic table.
- ✓ Requires **electron transfer** to achieve stabilized outermost electronic configuration.
- ✓ The bonding forces are **coulombic,** i.e., attraction between opposite charges.
- ✓ Example : $NaCl$, $AgCl$, $CsCl$, ZnS, CaF_2, LiF, MgO, Al_2O_3

Ionic Bonding in NaCl

Anion = negatively charged ion
Cation = positively charged ion

- Sodium atom transfers its valence electron (expending 5.14 eV of work) to a vacant position in a chlorine atom giving back 4.02 eV of energy.

Net work done to make isolated ions,

$$U_i = 5.14 - 4.02 = 1.12\text{eV}$$

- The force between opposite charges is

$$\mathbf{F} = \frac{(Z_1 e)(Z_2 e)}{4\pi\ \varepsilon_o r^2},$$

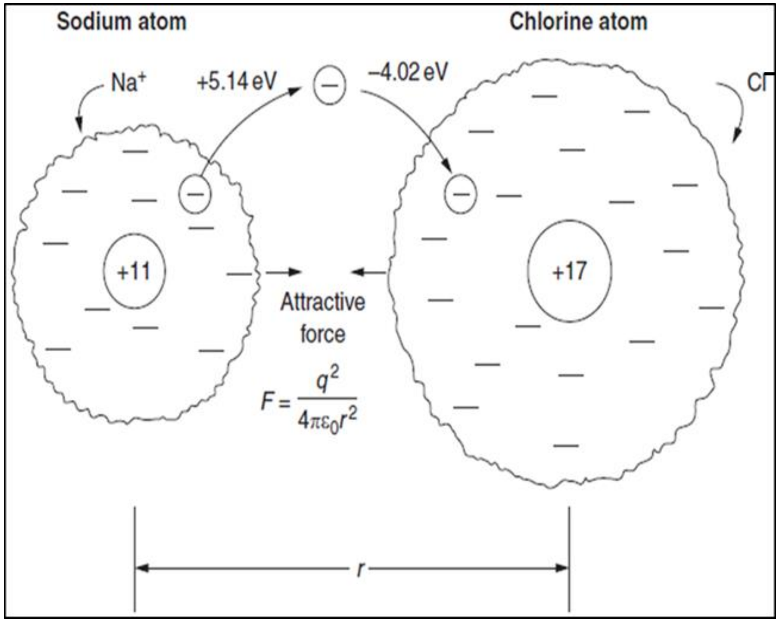
Z_1, Z_2 : Valences of the two ion types

e : Electronic charge = 1.6×10^{-19} C

ε_o: Permittivity of vacuum (8.85×10^{-12} F/m)

r : Separation between the ions

- The work done as the ions are brought to a separation r is $U = \int_r^\infty F dr = \frac{q^2}{4\pi\ \varepsilon_o r}$
- For r < 1 nm , ionic bond becomes more stable.
- For stable NaCl, r = 0.28 nm (1nm = 10^{-9}m).
- Below a certain 'r' repulsion starts.



NaCl – ionic bond formation

$$\boxed{1\text{ eV} = 1.6 \times 10^{-19}\text{ J}}$$

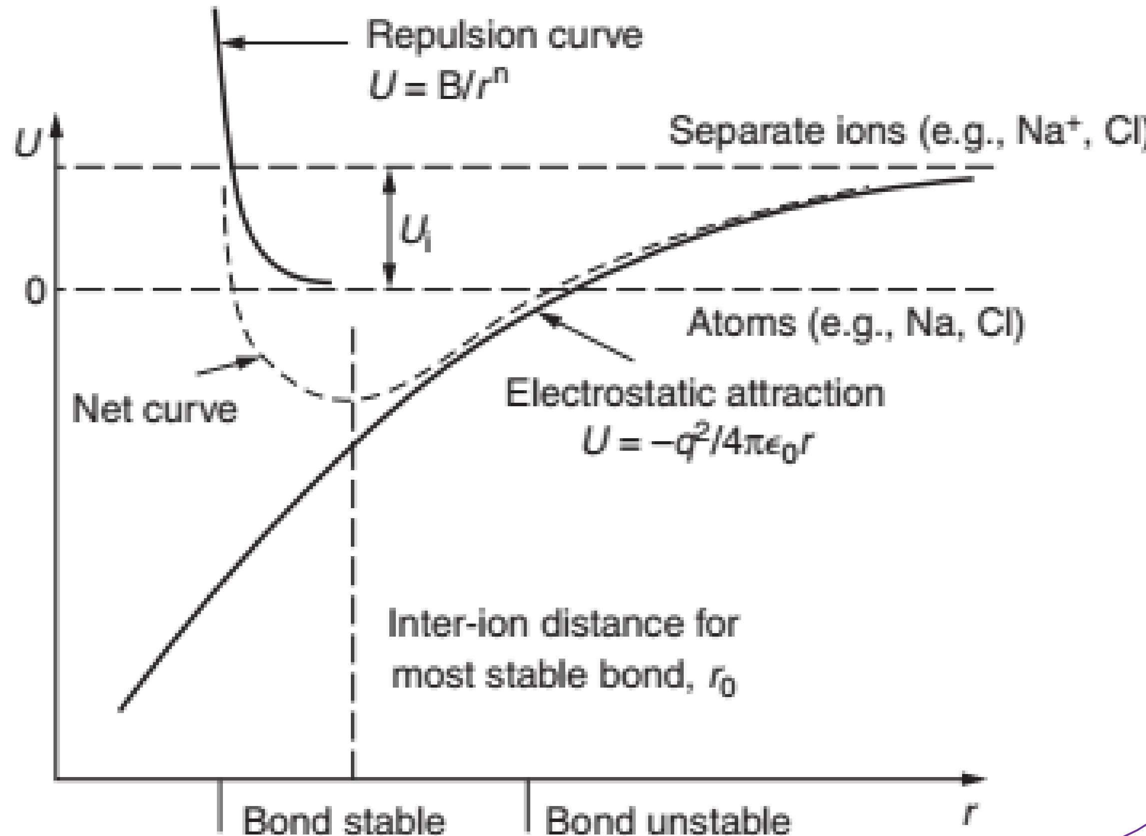
POTENTIAL ENERGY

$$\boxed{U(r) = U_i - \underbrace{\frac{q^2}{4\pi\varepsilon_0 r}}_{\text{attractive part}} + \underbrace{\frac{B}{r^n}}_{\text{repulsive part}}}$$

n ≈ 8

Reference: Engineering Materials 1: Ashby & Jones, 4th Ed.

Ionic bond formation – Energy consideration



$$U(r) = U_i - \underbrace{\frac{q^2}{4\pi\varepsilon_0 r}}_{\text{attractive part}} + \underbrace{\frac{B}{r^n}}_{\text{repulsive part}}$$

$n \approx 8$

Reference: Engineering Materials 1: Ashby & Jones, 4th Ed.

Properties of Ionic Bond

- ✓ Ionic bonds are **non-directional** because magnitude of the bond is equal in all the directions around an ion.
- ✓ **Higher melting point** because of large bond energy typically 600-1500 kJ/mol or (3-8 eV/atom).
- ✓ **Often hard**, brittle materials.
- ✓ Ionic solids are **good insulators** of electricity in their **solid state** and **good conductors** of electricity in their **molten state.**

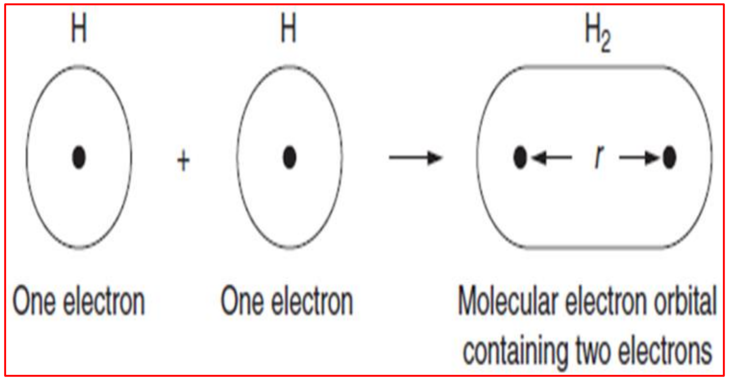
Primary Interatomic Bonding

2. ***Covalent Bonds***

- ✓ **Stable** electron configurations are obtained by the **sharing of electrons** between adjacent atoms.
- ✓ The covalent bond is generally **directional in nature [**occurs between specific atoms and only in the direction between one atom and another that participates in the electron sharing].
- ✓ No. of covalent bond for a particular atom = 8 – N, where N is the no. of valence electrons.
- ✓ Example :
  - Non-metallic molecules – H_2, F_2, Cl_2 , etc.
  - Molecules containing dissimilar atoms – CH_4, H_2O, HNO_3, HF, etc.
  - Elemental solids – Diamond (carbon), Si, Ge
  - Solid Compounds - Gallium arsenide (GaAs), Indium Antimonide (InSb), and Silicon Carbide (SiC).
  - Polymers – also contains secondary bonds

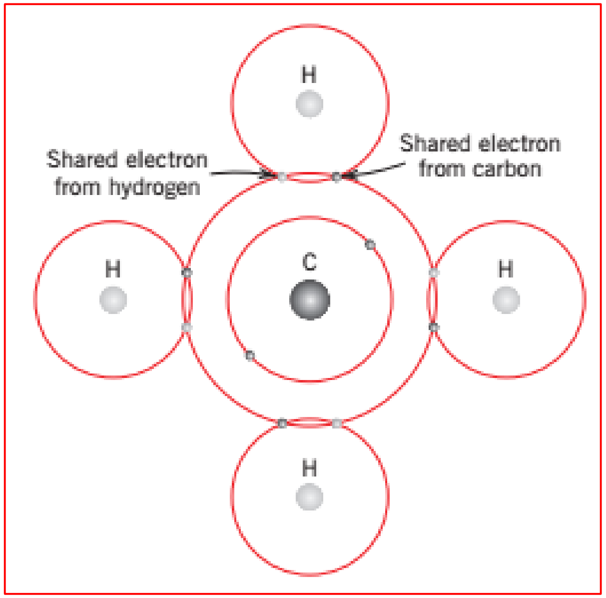
Examples

Covalent bond formation between two hydrogen atoms – making hydrogen molecule



Reference: Engineering Materials 1: Ashby & Jones, 4th Ed.

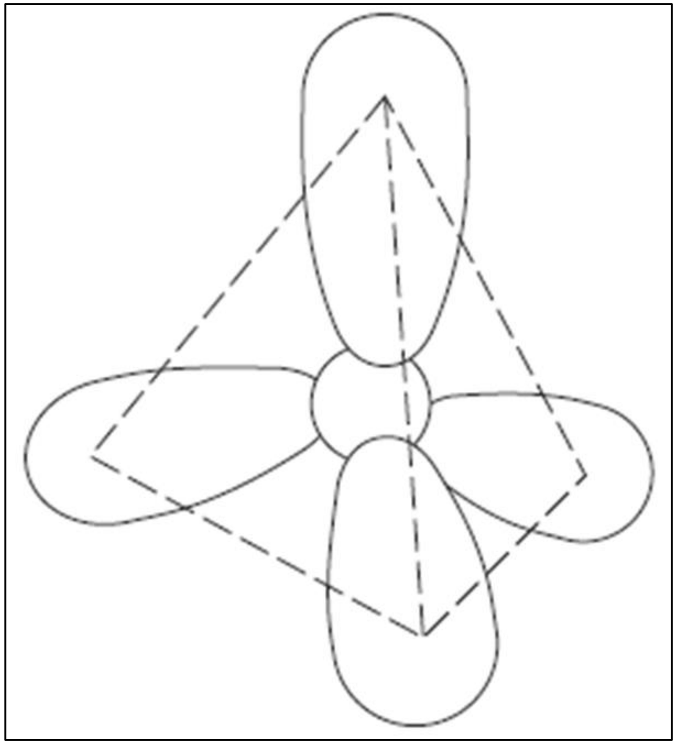
Covalent bonding in Methane molecule : Carbon atom shares it 4 valence electron with four hydrogen atoms



Reference: W.D Callister, 7Ed.

Diamond

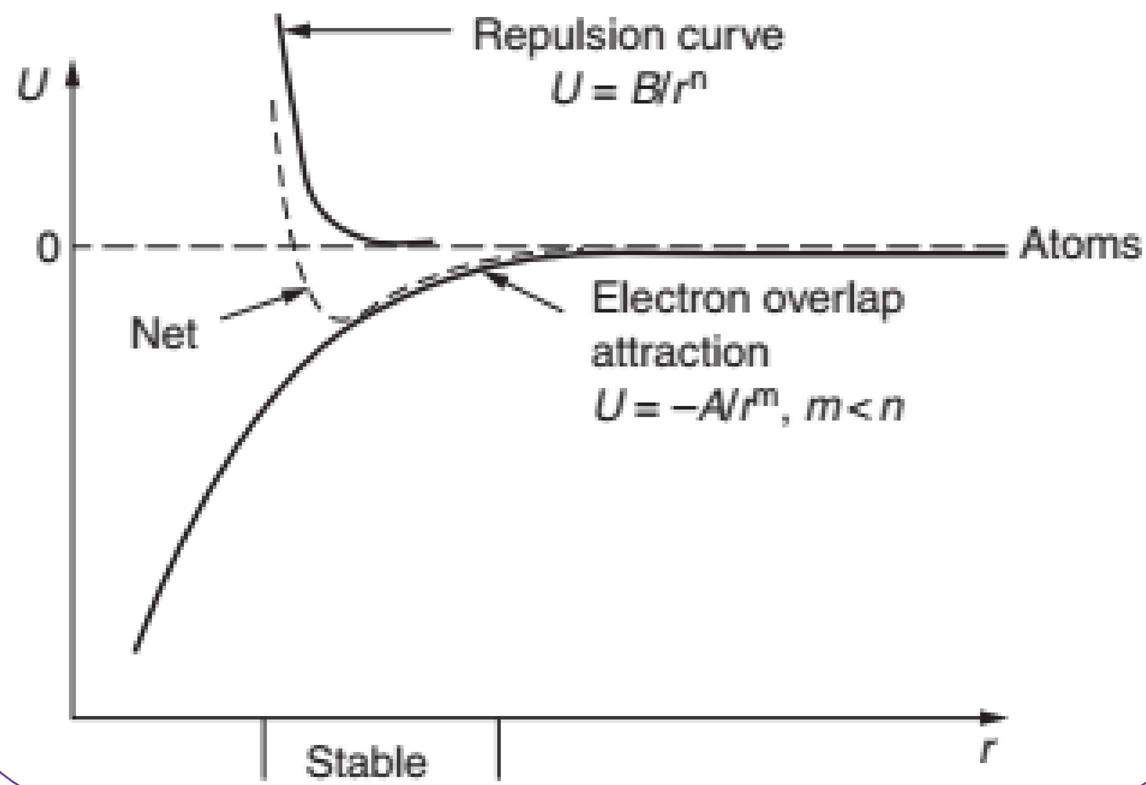
- Diamond has **high thermal conductivity** (2000 W/m-K, 5 times of Cu) and **high melting temperature** (3600 ^oC) due to the presence of **tetrahedral geometry** and **highly directional covalent bonding**.
- **No free electrons**, heat conduction only by **lattice vibration**
- Used in applications such as cutting tools, polishing wheels, precision bearings, etc.



Directional covalent bonding in Diamond

Reference: Engineering Materials 1: Ashby & Jones, 4th Ed.

Covalent bond formation – Energy consideration



$$U = -\underbrace{\frac{A}{r^m}}_{\text{attractive part}} + \underbrace{\frac{B}{r^n}}_{\text{repulsive part}}$$

where m, n = 5 to 12
If m < n, then attraction else repulsion

Reference: Engineering Materials 1: Ashby & Jones, 4th Ed.

Important Points : Covalent Bond

- ✓ Very few compounds exhibit pure ionic or covalent bonding.
- ✓ Usually partially ionic and partially covalent.

More difference in electronegativity : **Ionic bond predominates**

- ✓ The percentage ionic character of a bond between elements A (most electronegative) and B is given by:

$$\% \text{ Ionic character} = \{ 1 - \exp [-(0.25)(X_A - X_B)^2]\} \times 100$$

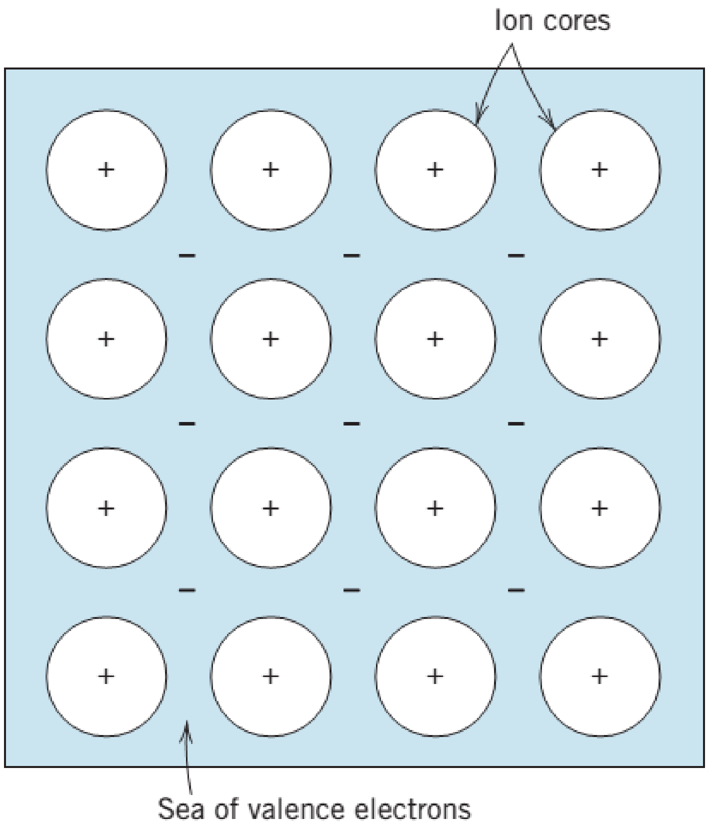
where X_A and X_B are the electronegativity's for element A & B.

Material	% Ionic Character
CaF_2	89
MgO	73
$NaCl$	67
Al_2O_3	63
SiO_2	51
Si_3N_4	30
ZnS	18
SiC	12

Primary Interatomic Bonding

3. ***Metallic Bonds***

- **Found in metals and their alloys**.
- Metallic materials have at most three valence electrons which are not bound to any particular atom in the solid forming "**electron cloud**".
- Rest non-valence and atomic nuclei form ion cores having net positive charge.
- There is a force of attraction between valence electrons and the metal ions.
- **Free electrons** act as a "**glue**" to hold the ion cores together.
- The metallic bond imparts properties such as strength, malleability, ductility, luster, conduction of heat and electricity.

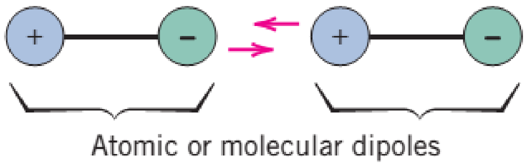


Reference: W.D Callister, 7Ed.

Secondary Interatomic Bonding

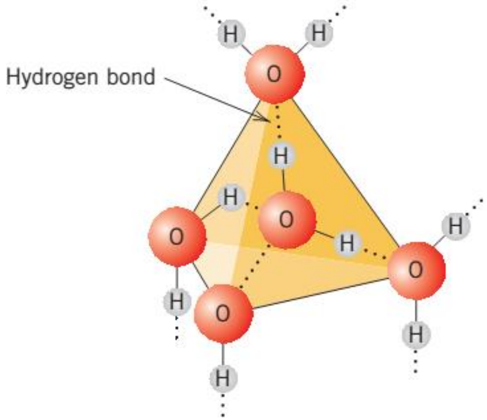
1. Van der Waals Bonding

- **Weak** in comparison to primary bonding (bond energy of order 10kJ/mol or 0.1 eV/atom).
- Occur to some extent in all materials but are particularly important in plastics and polymers.
- Result from attractive forces between electric dipoles.



2. Hydrogen Bonding

- Strong dipole-dipole attractions that involve molecules with -OH, -NH, or FH groups.
- Example: **Water expands upon freezing**.
- In solid ice, each water molecule participates in 4 hydrogen bonds.
- Hydrogen bond keeps molecule apart, thus relatively open structure. Hence ice has lower density than liquid water and it floats.



Solid Ice

Reference: W.D Callister, 7Ed.

Summary

Ceramics

(Ionic & covalent bonding):

Large bond energy
High melting temperature T_m
Large elastic modulus E
Small coefficient of expansion α

Metals

(Metallic bonding):

Variable bond energy
moderate T_m
moderate E
moderate α

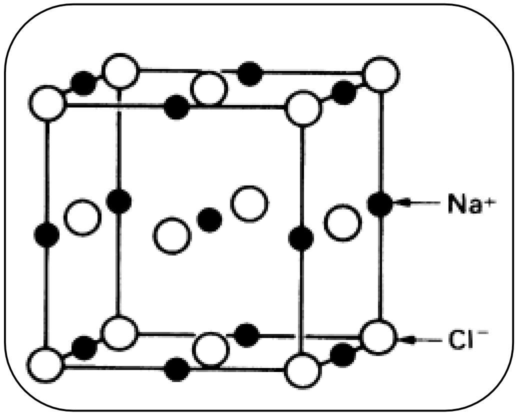
Polymers

(Covalent & Secondary):

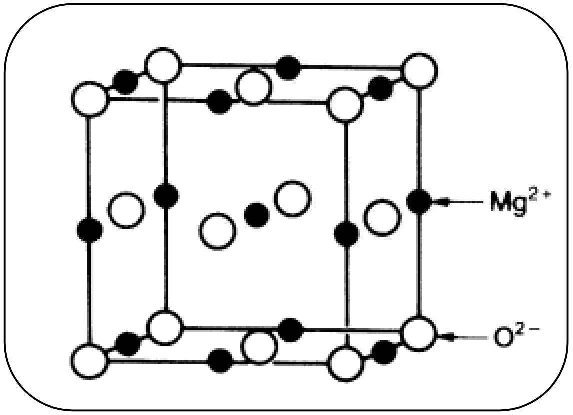
Directional Properties
Secondary bonding dominates
small T_m
small E
large α

Ionic Ceramics

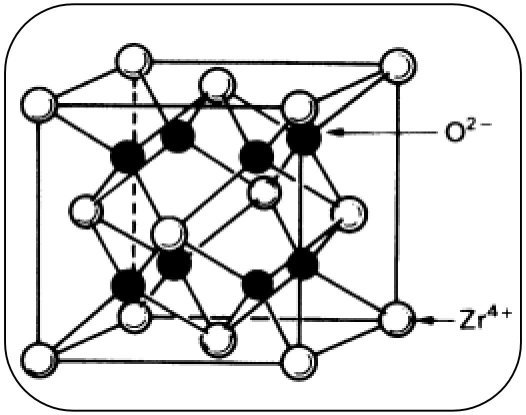
- ✓ Ionic bonding is predominant.
- ✓ They are compounds of a **metal** with a **nonmetal**.
- ✓ The **electrostatic attraction** between the unlike charges is responsible for **dense packing**.
- ✓ Example: NaCl, MgO, ZrO_2, Al_2O_3, etc.



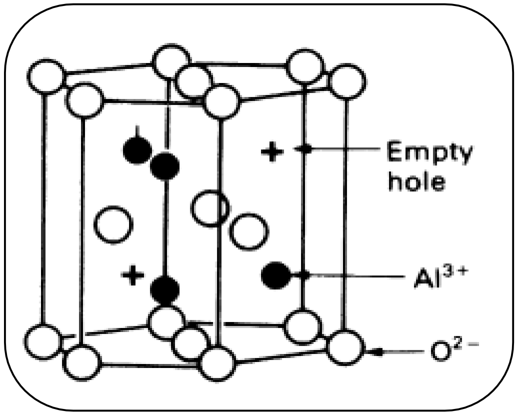
Rocksalt or NaCl



Magnesia, MgO



Cubic Zirconia, ZrO_2

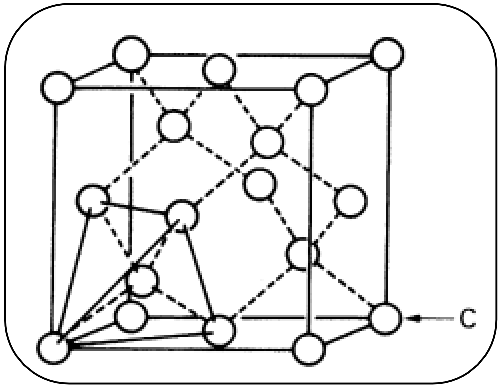


Alumina, Al_2O_3

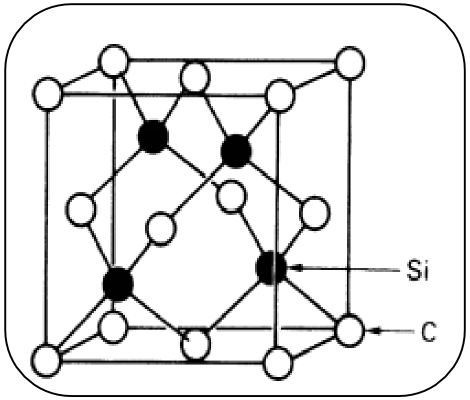
Reference: Engineering Materials 2: Ashby & Jones, 4th Ed.

Covalent Ceramics

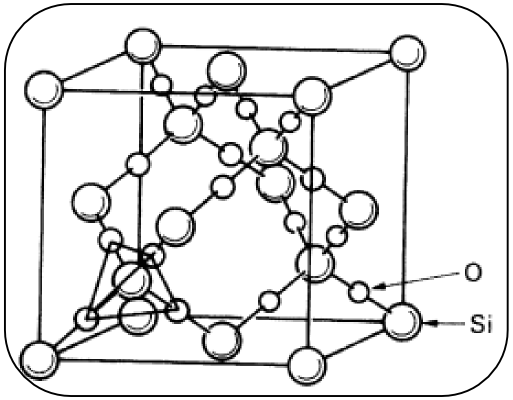
- ✓ Covalent bonding is predominant.
- ✓ They are compounds of **two nonmetals** or occasionally pure element (diamond, C).
- ✓ Bonds are formed by **sharing electrons** with its neighbors to give a fixed number of **directional bonds.**



Diamond cubic structure



Silicon carbide

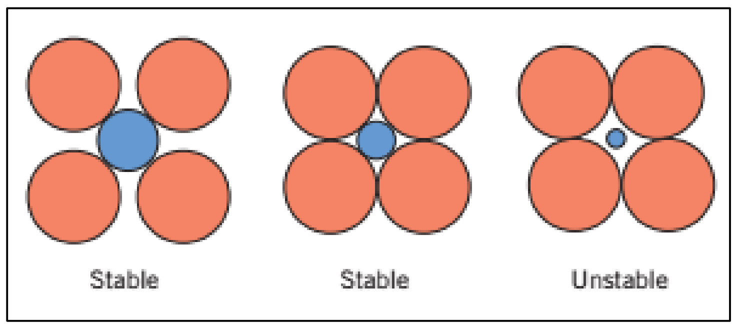


Silica cubic structure

Reference: Engineering Materials 2: Ashby & Jones, 4th Ed.

Ceramic crystal structure

- Stable ceramic crystal structures form when anions surrounding a cation are all in contact with that cation.
- **Cations** (+ve charge, gives up e^-) are **smaller than anions** (-ve charge, accepts e^-) in size.
- The coordination number (i.e., number of anion nearest neighbors for a cation) is related to the cation–anion radius ratio.



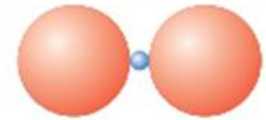
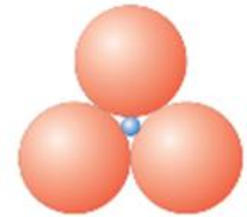
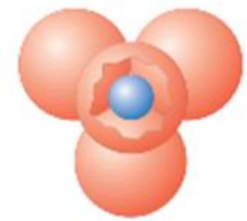
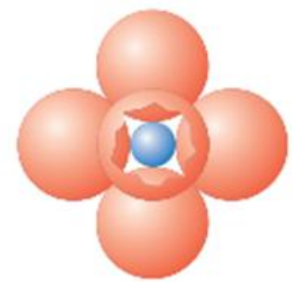
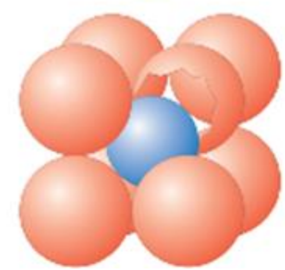
Orange circle - Anion, Blue circle - Cation

Reference: W.D Callister, 7 Ed.

Coordination Numbers and Geometries

Orange circle - Anion
Blue circle - Cation

For a **radius ratio greater** than **unity**, the coordination number is **12**

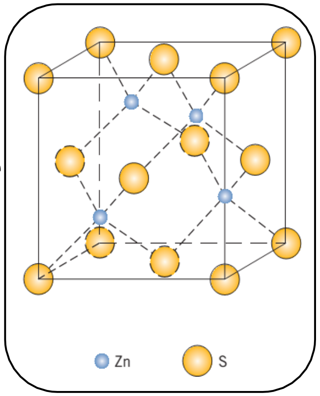
Coordination Number	*Cation–Anion Radius Ratio*	*Coordination Geometry*	
2	<0.155		**Linear Manner**
3	0.155–0.225		**Planar Equilateral Triangle**
4	0.225–0.414		**Tetrahedron**
6	0.414–0.732		**Octahedron**
8	0.732–1.0		**Cubic**

Reference: W.D Callister, 7 Ed.

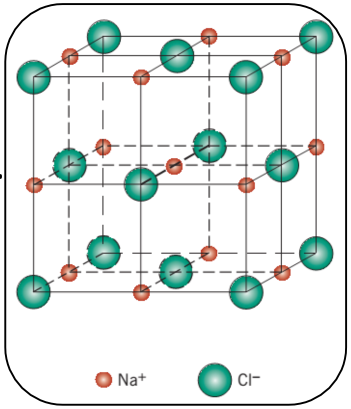
AX - Type Crystal Structures

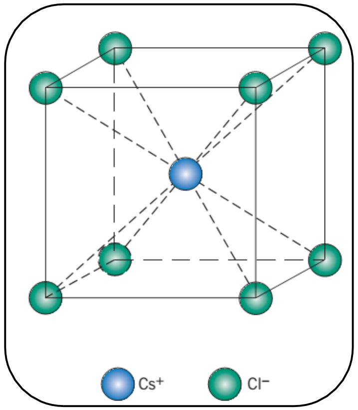
- Those in which there are **equal** numbers of **cations** and **anions**.
- Often referred to as **AX compounds**, where **A** denotes the **cation** and **X** the **anion**.

1) **Zinc Sulphide** (ZnS)
   - ✓ **Coordination number** is **4**, i.e, all ions are tetrahedrally coordinated.
   - ✓ Other examples – SiC, ZnTe



2) Rock salt or **Sodium Chloride** (NaCl)
   - ✓ **Coordination number** for both cations and anions is **6**.
   - ✓ Other examples - MgO, MnS, LiF, and FeO.



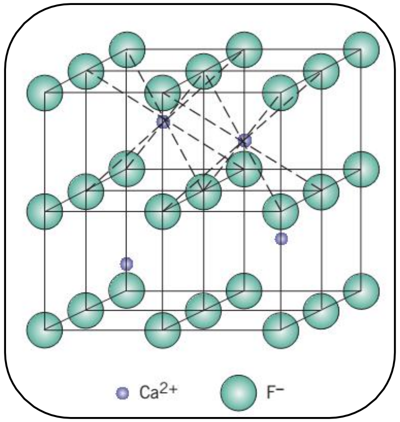


3) **Cesium Chloride** (CsCl)
   - ✓ Coordination number is 8 for both ion types.

Reference: W.D Callister, 7 Ed.

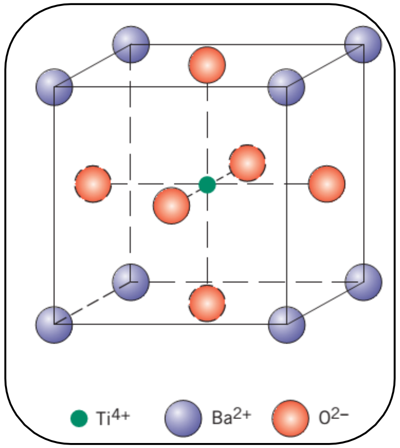
A_mX_p - Type Crystal Structures

- Charges on the cations and anions are not the same.
- Example: CaF_2, ZrO_2, UO_2, PuO_2, ThO_2



$A_mB_nX_p$ - Type Crystal Structures

- Have more than one type of cation
  Example: Barium Titanate ($BaTiO_3$) having both $Ba^{2+}$and Ti^{4+} cations.
  It has a *perovskite crystal structure – an inorganic Chameleon*



Piezoceramic

Summary

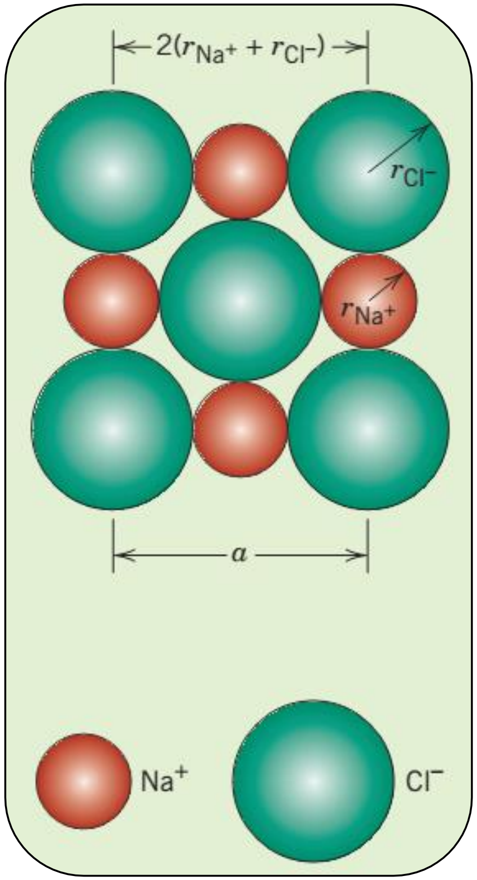
Structure Name	Structure Type	Anion Packing	Coordination Numbers: Cation	Coordination Numbers: Anion	Examples
Rock salt (sodium chloride)	AX	FCC	6	6	NaCl, MgO, FeO
Cesium chloride	AX	Simple cubic	8	8	CsCl
Zinc blende (sphalerite)	AX	FCC	4	4	ZnS, SiC
Fluorite	AX_2	Simple cubic	8	4	CaF_2, UO_2, ThO_2
Perovskite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

Reference: W.D Callister, 7 Ed.

Theoretical density Computation

$$\rho = \frac{n(\sum A_c + \sum A_A)}{V_C N_A}$$

Where,
n = no. of ions in the chemical formula
ΣA_C = sum of atomic weights of all cations in the formula unit
ΣA_A = sum of atomic weights of all anions in the formula unit
V_C = unit cell volume
N_A = Avogadro's number, 6.023×10^{23} formula units/mol



Theoretical density of NaCl ?

Given: Atomic weight of Sodium = 22.99 g/mol
Atomic radius of Sodium = 0.102 nm = 0.102×10^{-7} cm
Atomic weight of Chlorine= 35.45 g/mol
Atomic radius of Chlorine = 0.181 nm = 0.181×10^{-7} cm
n = no. of ions in NaCl = 2

If 'a' is unit cell edge length, then its volume,

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

Thus, $\rho = \frac{n\,(\sum A_{Na} + \sum A_{Cl})}{(2r_{Na^+} + 2r_{Cl^-})^3 N_A} = \frac{2\,(22.99 + 35.45)}{[2(0.102 \times 10^{-7}) + 2(0.181 \times 10^{-7})]^3\,(6.023 \times 10^{23})}$

Theoretical value of NaCl density = 2.14 g/cm^3

While, Experimental value = 2.16 g/cm^3

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Reference: W.D Callister, 7 Ed.

In the **next lecture**, we will learn about :-

- ✓ Ceramics : Mechanical behaviour
- ✓ Failure
- ✓ Processing

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