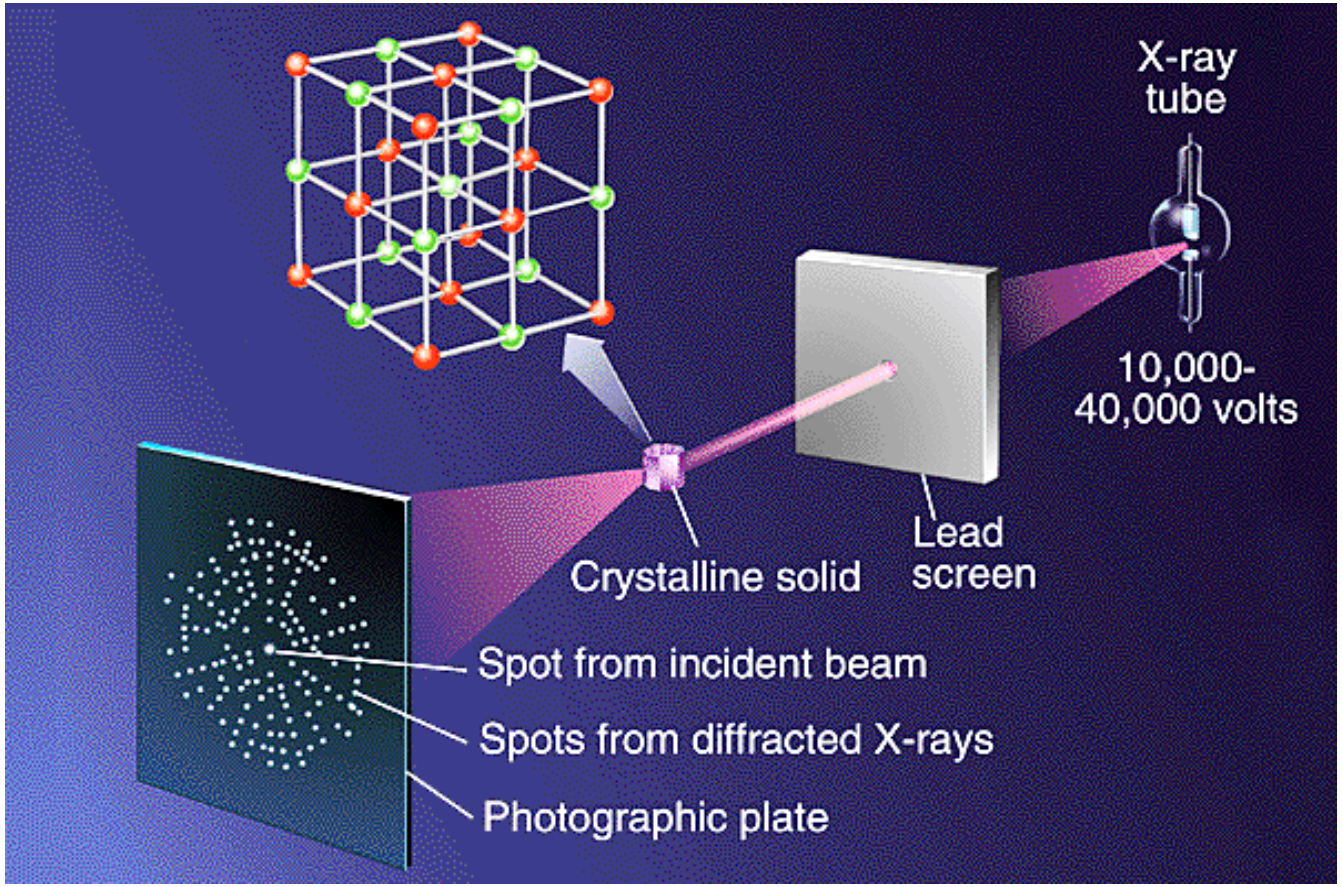
MS31007: Materials Science

Chapter 3 (Part-IV): Crystal Structure

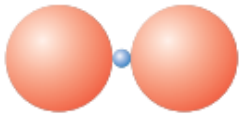
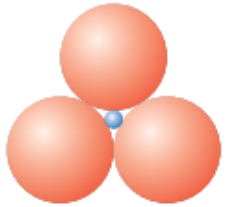
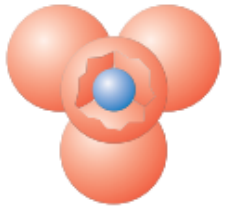
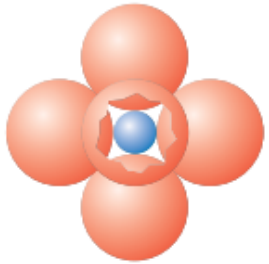
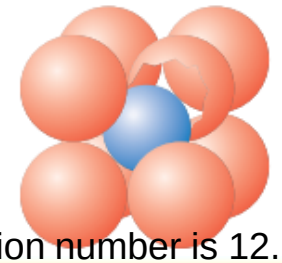
Instructor: Prasana Kumar Sahoo
prasana@matsc.iitkgp.ac.in

Crystal Structure : Solid State Materials

- Lattice structures of common chemical elements.
  Concept of Bravais lattice, definition and examples.
  Primitive vectors of Bravais lattice.
  Primitive/Conventional unit cell.
- Coordination number.
- Examples of common crystal structures.
  - Body-centered cubic lattice.
  - Face-centered cubic lattice.
  - Crystal systems
  - Lattice planes and Miller indices.
- Ceramic Crystal Structures
- Determination of Lattice Spacing : X-ray Diffraction



Ceramic crystal structures

Coordination Number	Cation–Anion Radius Ratio	Coordination Geometry
2	<0.155	
	linear manner	
3	0.155–0.225	
	Equilateral triangle	
4	0.225–0.414	
	Tetrahedron	
6	0.414–0.732	
	Octahedron	
8	0.732–1.0	

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

Coordination number ~ r_C/r_A.

For a specific coordination number, there is a critical or minimum *r*C/*r*A ratio for which this cation–anion contact is established

Ionic radius tends to increase as the number of nearest-neighbor ions of opposite charge increases.

Charge on an ion will influence its radius.

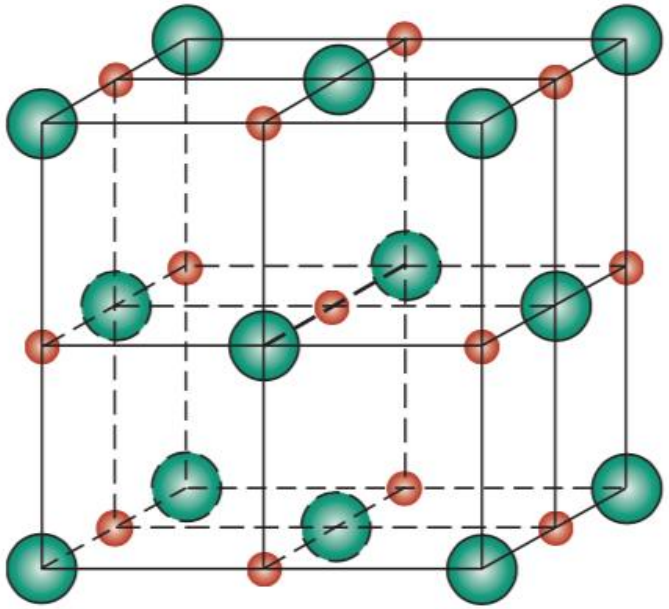
- the radii for Fe^{2+} and Fe^{3+} are 0.077 and 0.069 nm,
- Contrasted to the radius of an iron atom—0.124 nm
- ionic size deceases when electrons are added to the ion

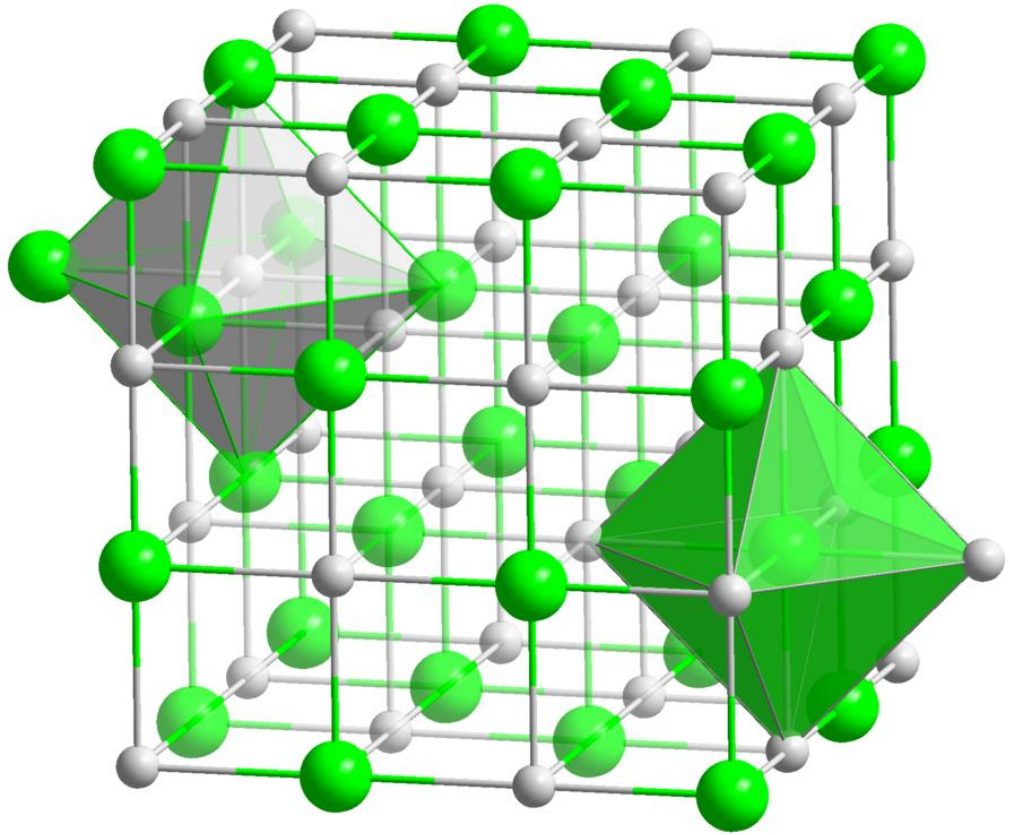
Ceramic AX – Type crystal structures

AX – Type crystal structures

- There are equal numbers of cations and anions (**A** -cation and **X** the anion)
- There are several different crystal structures for AX compounds;

1. Sodium Chloride (NaCl) or Rock Salt type



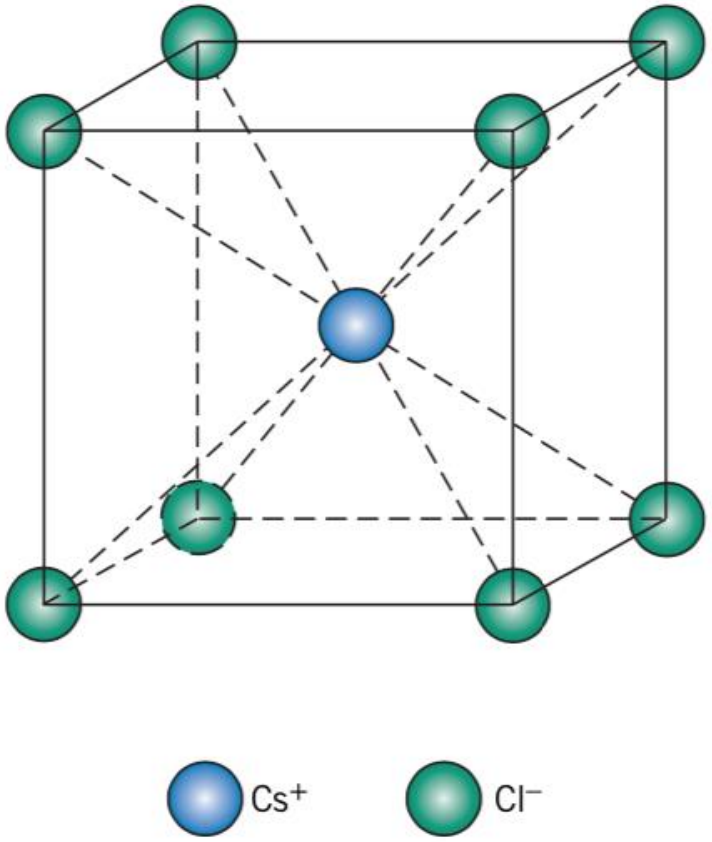


Coordination number is 6 for both cations and anions

- Two interpenetrating FCC lattices
- NaCl, MgO, MnS, LiF, and FeO

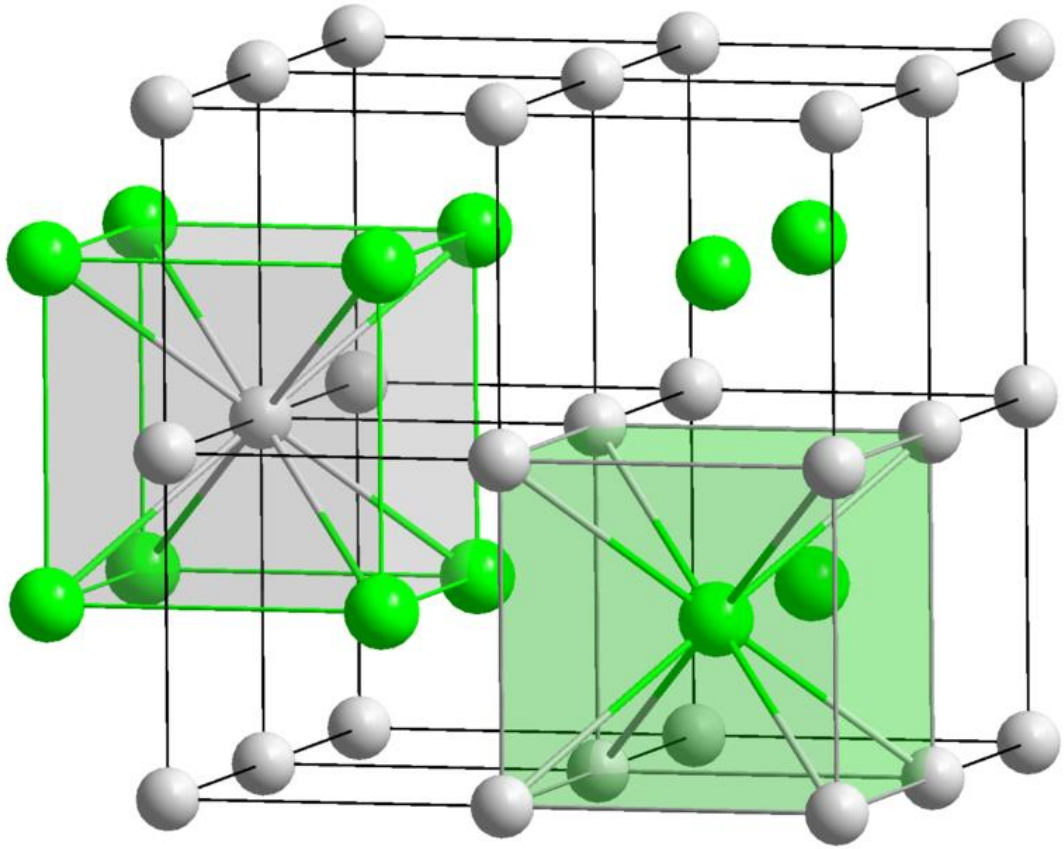
Ceramic **AX – Type** crystal structures

2. Cesium Chloride Structure



Coordination number is 8 for both ion types

- CsCl, CsBr

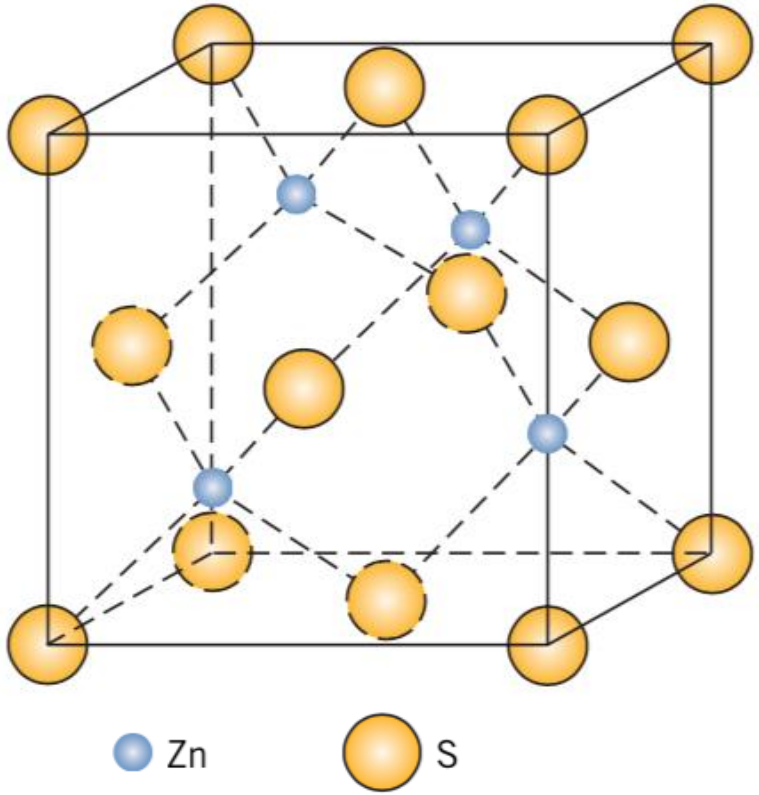


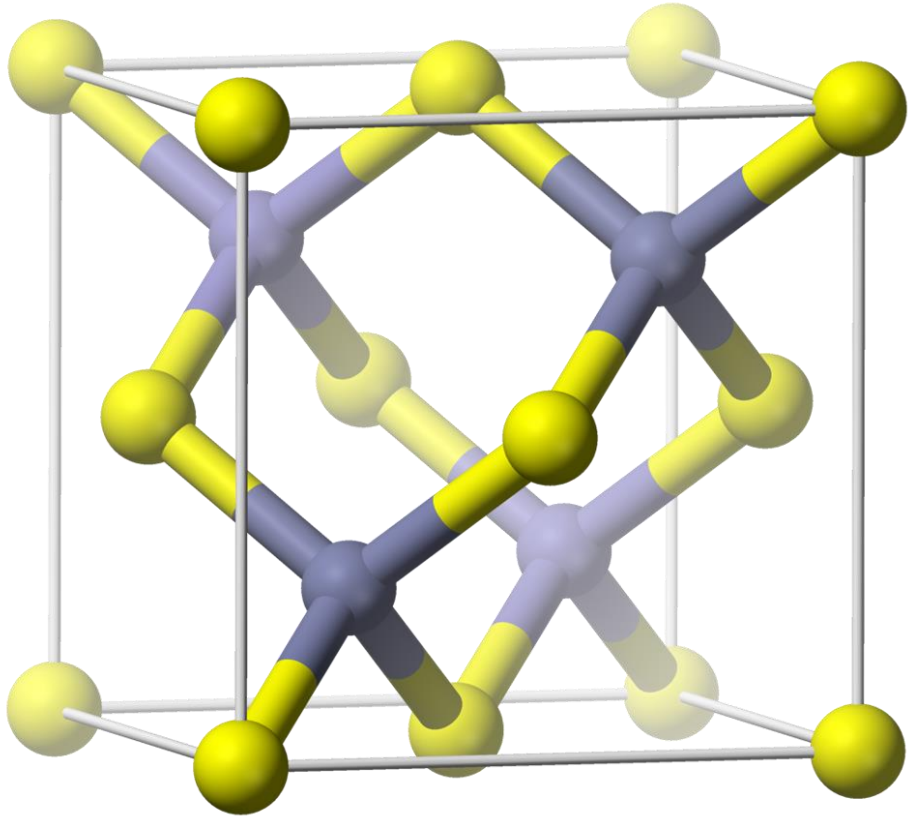
This is *not* a BCC crystal structure because ions of two different kinds are involved.

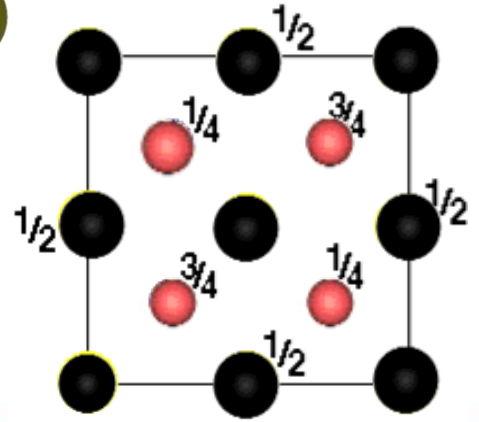
CsCl Application includes **Nuclear medicine and radiography,** preparation of electrically conducting glasses and screens of cathode ray tubes. In conjunction with rare gases CsCl is used in excimer lamps and excimer lasers.

Ceramic AX – Type crystal structures

3. Zinc Blende Structure





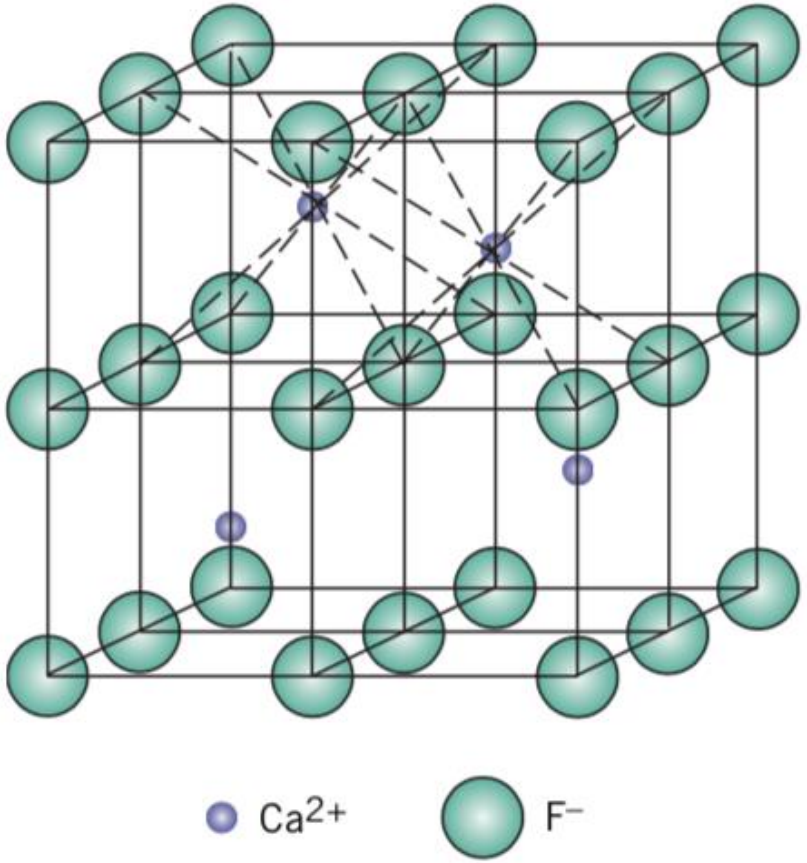


- **Coordination number is 4**
- all ions are tetrahedrally coordinated
- ZnS, ZnTe, SiC, AgI, GaAs, GaSb, InAs
- Atomic bonding is highly covalent

Ceramic A_mX_p – Type Crystal Structures

If the charges on the cations and anions are not the same; a compound can exist with the chemical formula A_mX_p, where *m* and/or $p \neq 1$.

A_mX_p – Type Crystal Structures



A unit cell for the fluorite (CaF_2) crystal structure

Fluorite structure (CaF_2)

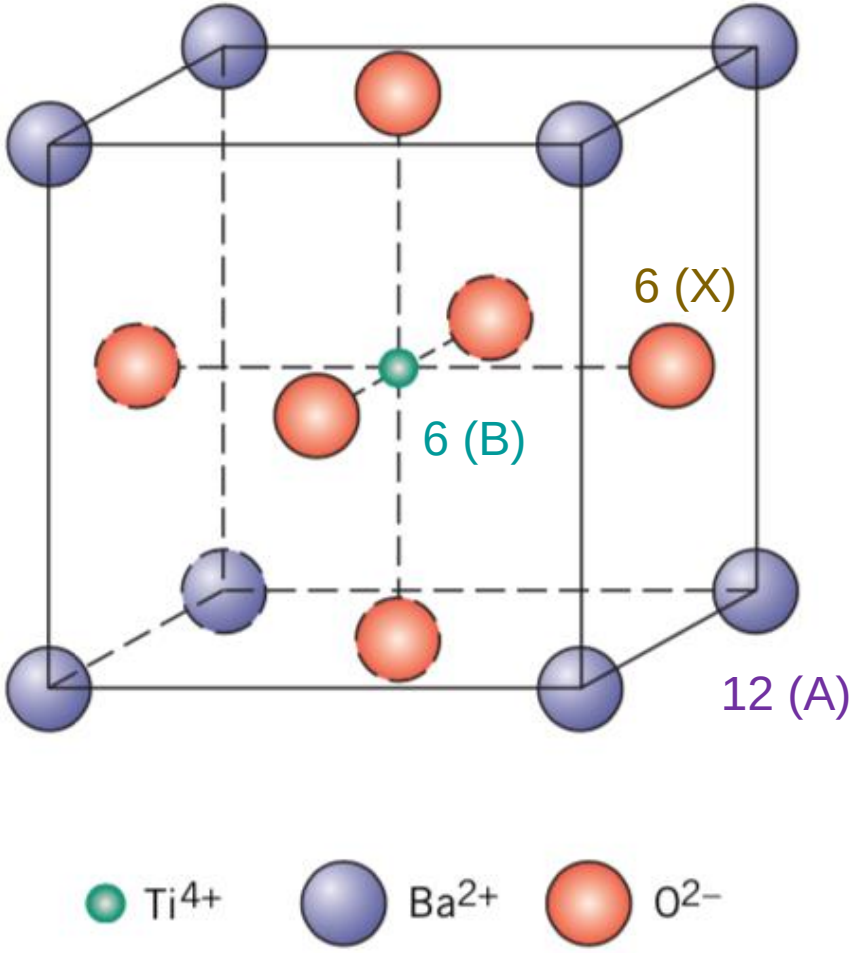
- Calcium ions are positioned at the centers of cubes, with fluorine ions at the corners.
- The chemical formula shows that there are only half as many Ca^{2+} ions as F^- ions
- The ionic radius ratio r_C/r_A for CaF_2 is about 0.8
- coordination number of 8.

ZrO_2 (cubic), UO_2, PuO_2, and ThO_2

Ceramic $A_mB_nX_p$ – Type Crystal Structures

Compounds having more than one type of cation; represented by A and B

A_mB_nXp – Type Crystal Structures



Perovskite structure

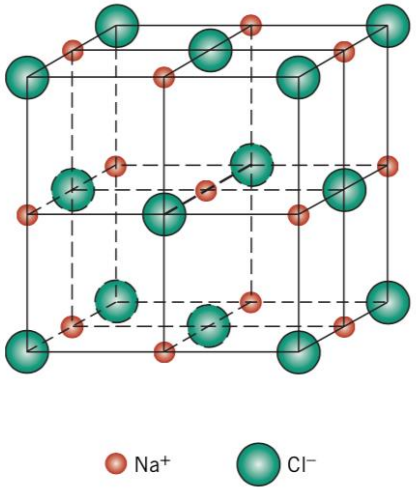
- Barium titanate ($BaTiO_3$), having both Ba^{2+} and Ti^{4+} cations, falls into this classification. This material has a ***perovskite crystal structure***

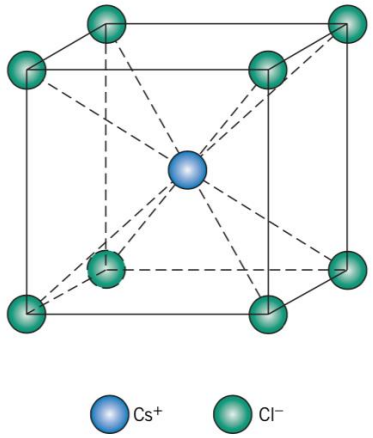
- Ba^{2+} ions are situated at all eight corners of the cube, and a single Ti^{4+} is at the cube center, with O^{2-} ions located at the center of each of the six faces.

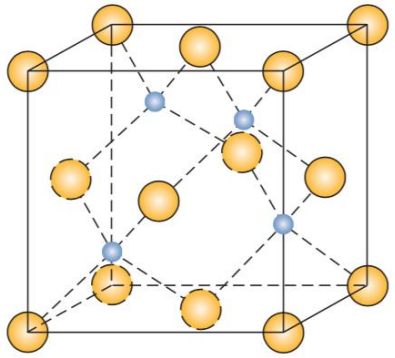
Example: $BaTiO_3$, $SrZrO_3$, $SrSnO_3$

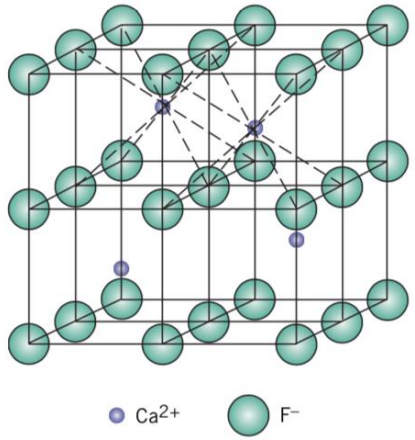
Summary of Some Common Ceramic Crystal Structures

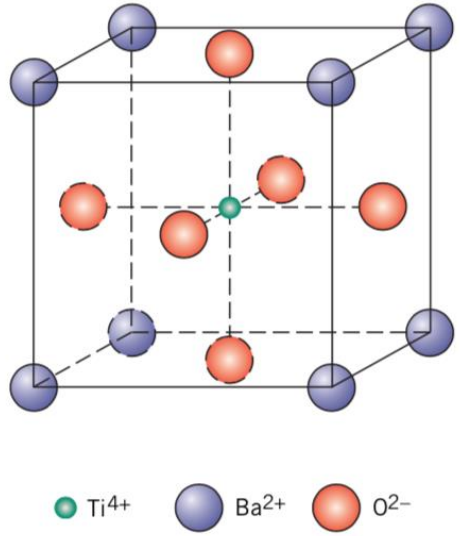
Structure Name	Structure Type	Anion Packing	Coordination Number		Examples
			Cation	Anion	
Rock salt (sodium chloride)	AX	FCC	6	6	NaCl, MgO, FeO
Cesium chloride	AX	Simple cubic	8	8	CsCl
Zinc blende (sphalerite)	AX	FCC	4	4	ZnS, SiC
Fluorite	AX_2	Simple cubic	8	4	CaF_2, UO_2, ThO_2
Perovskite	ABX_3	FCC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







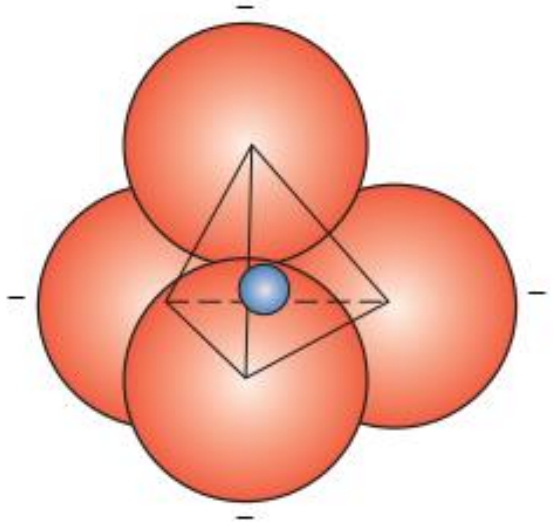




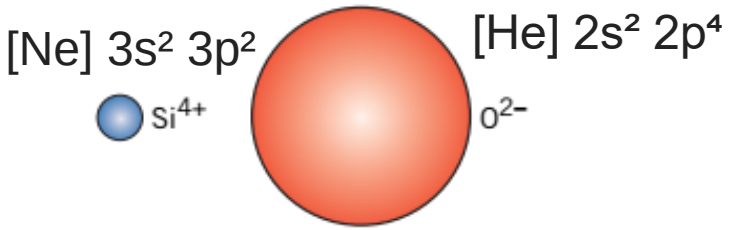
Silicate Ceramics

Silicates are materials composed primarily of silicon and oxygen; the two most abundant elements in Earth's crust; consequently, the bulk of soils, rocks, clays, and sand come under the silicate classification

A silicon–oxygen (SiO_4^{4-}) Tetrahedron



Various silicate structures arise from the different ways in which the SiO_4^{4-} units can be combined into one-, two-, and three dimensional arrangements.



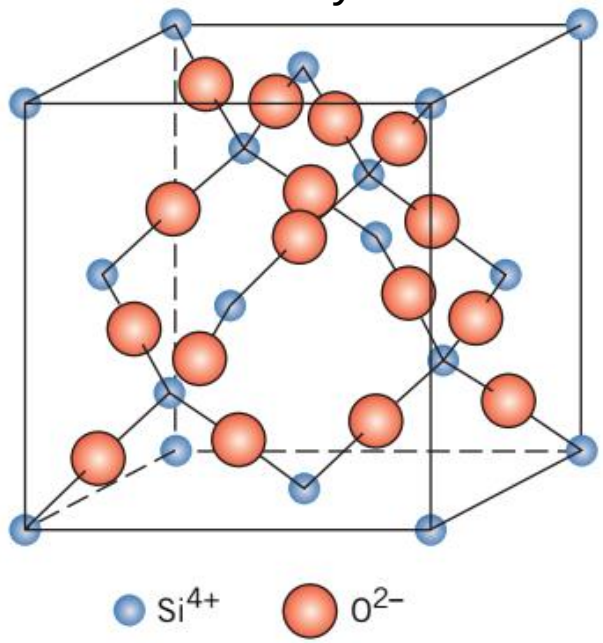
-4 charge is associated with every SiO_4^{4-} tetrahedron because each of the four O atoms requires an extra electron to achieve a stable electronic structure.

Silica, silicon dioxide (SiO_2)

There are three primary polymorphic crystalline forms of silica:

Cristobalite, Quartz, tridymite

Material is electrically neutral



Unit cell of cristobalite

Silicates Ceramics

For the various silicate minerals, one, two, or three of the corner oxygen atoms of the SiO_4^{4-} tetrahedra are shared by other tetrahedra to form some rather complex structures.

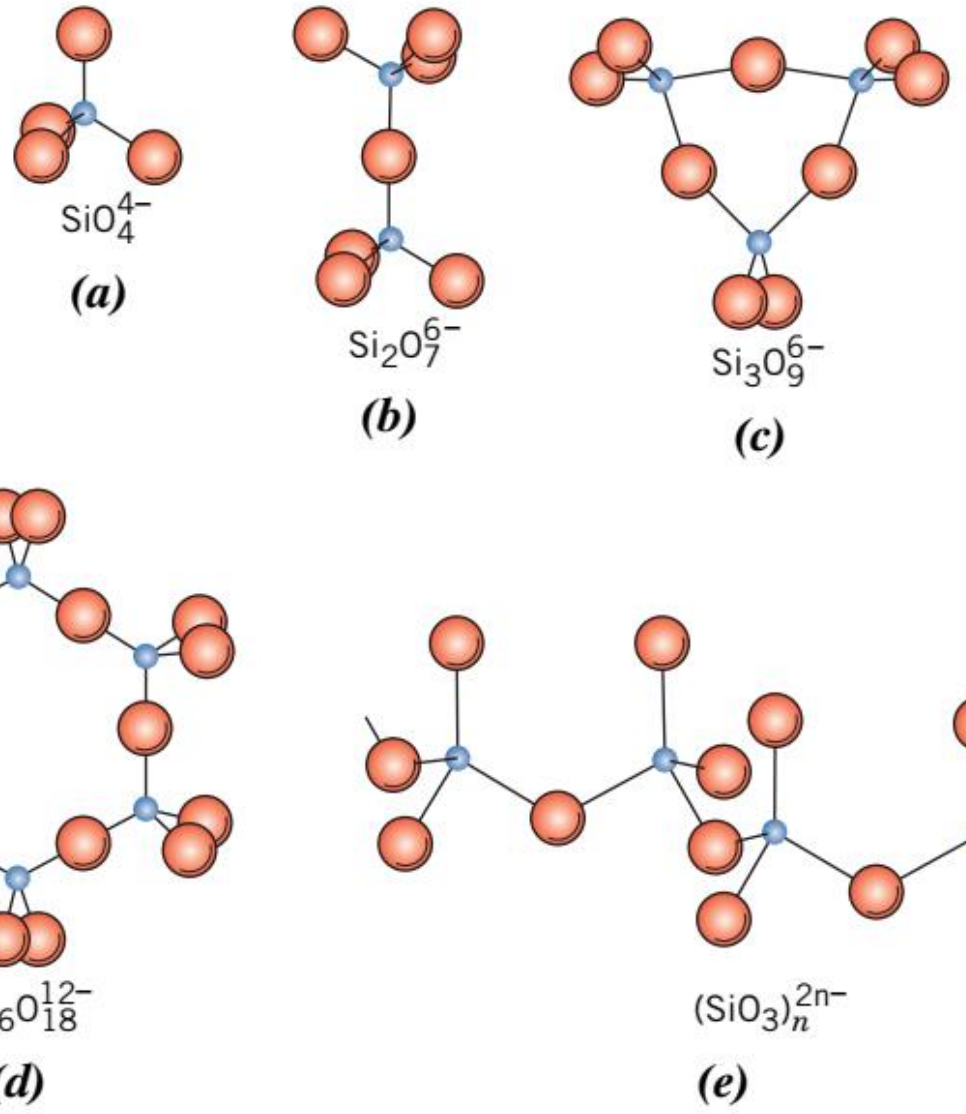
Simple Silicates forsterite (Mg_2SiO_4), Akermanite ($Ca_2MgSi_2O_7$)

Positively charged cations such as Ca^{2+}, Mg^{2+}, and Al^{3+} serve two roles:

First, they compensate the negative charges from the SiO_4^{4-} units so that charge neutrality is achieved;

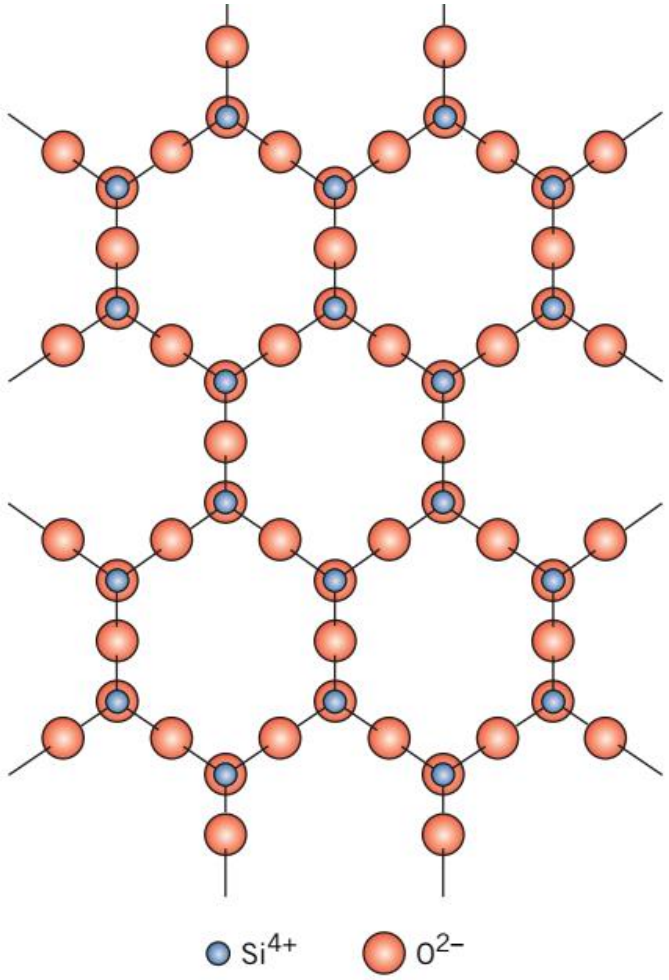
second, these cations ionically bond the SiO_4^{4-} tetrahedra together.

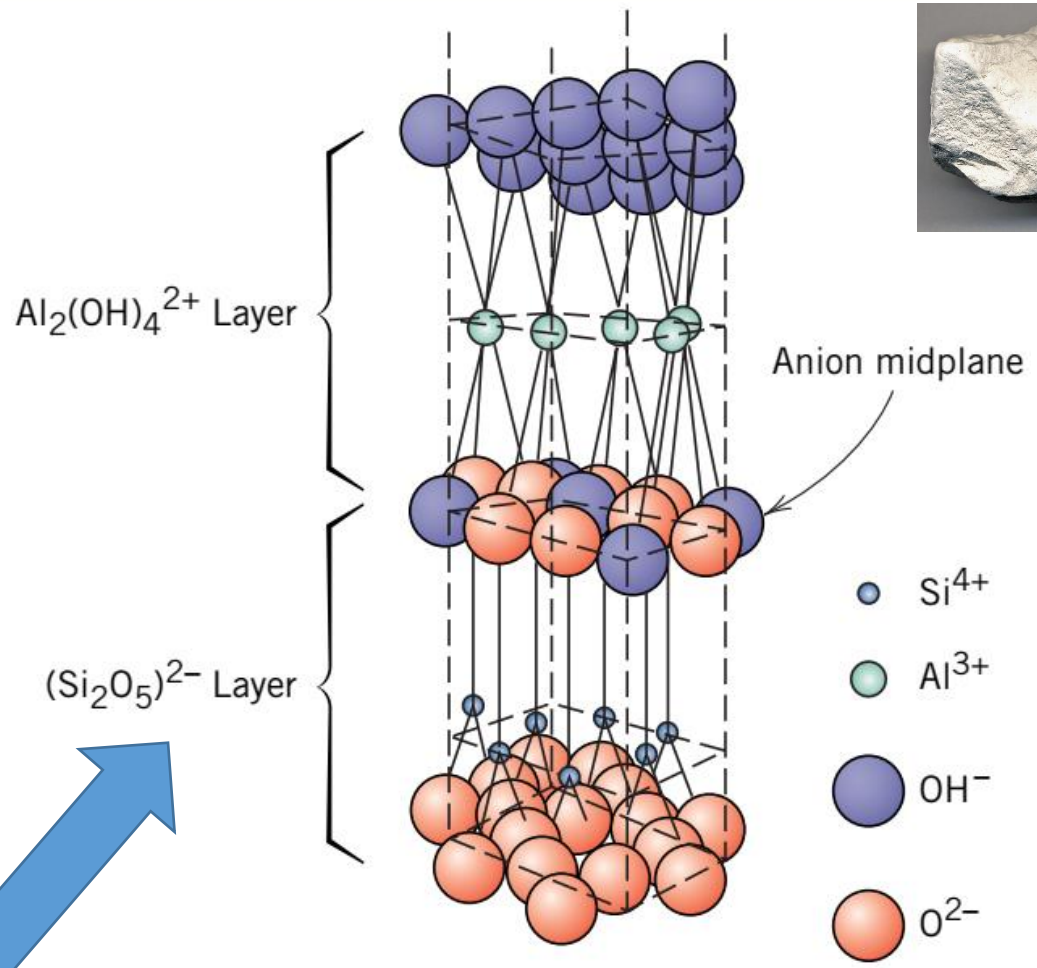
Five silicate ion structures formed from SiO_4^{4-} tetrahedra



Layered Silicates

Two-dimensional silicate sheet structure $(Si_2O_5)^{2-}$.





The structure of kaolinite clay

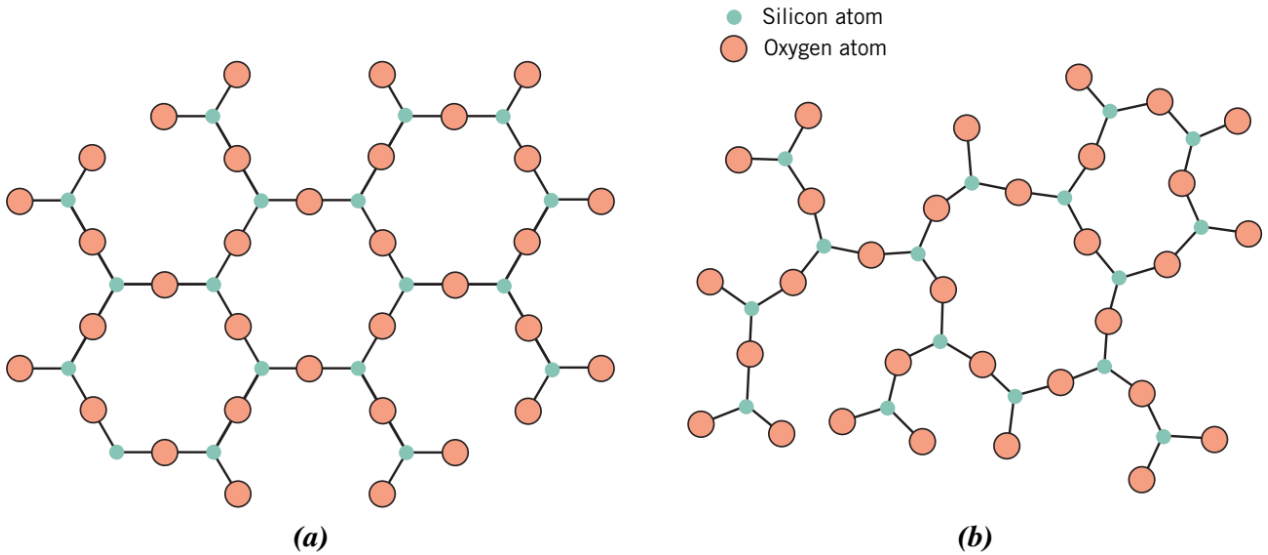
$Al_2Si_2O_5(OH)_4$ **china clay**

Micas $[KAl_3Si_3O_{10}(OH)_2]$

Electroneutrality is ordinarily established by a second planar sheet structure having an excess of cations, which bond to these unbonded oxygen atoms from the Si_2O_5 sheet

NONCRYSTALLINE SOLIDS

Non-crystalline solids lack a systematic and regular arrangement of atoms over relatively large atomic distances. Sometimes such materials are also called **amorphous** (meaning literally “without form”) or supercooled liquids, inasmuch as their atomic structure resembles that of a liquid.

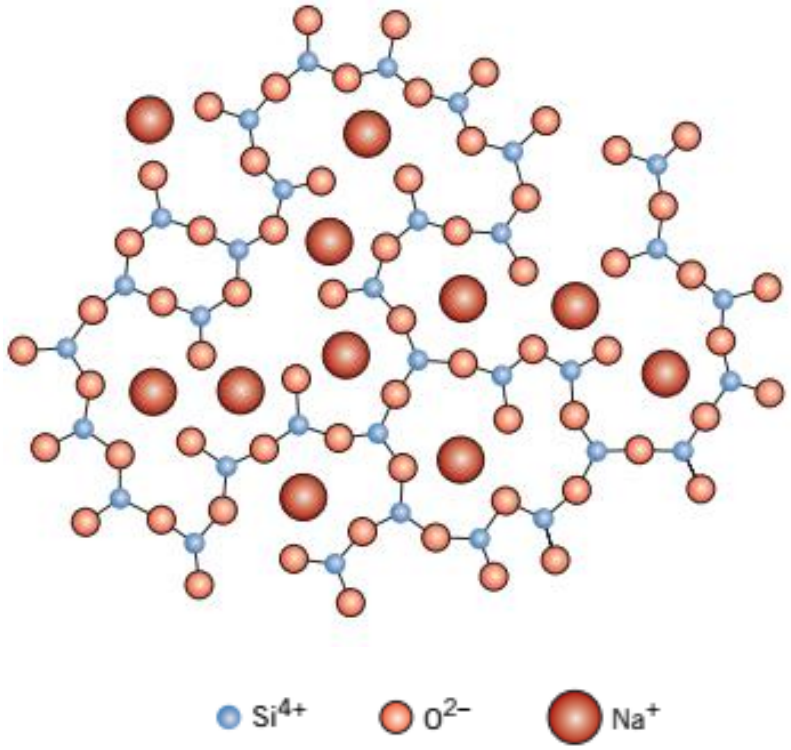


Two-dimensional schemes of the structure of (a) crystalline silicon dioxide and (b) noncrystalline silicon dioxide.

- Silica/SiO_2 in the noncrystalline state is called *fused silica,* or *vitreous silica*
- Other oxides (e.g., B2O3 and GeO2) may also form glassy structures

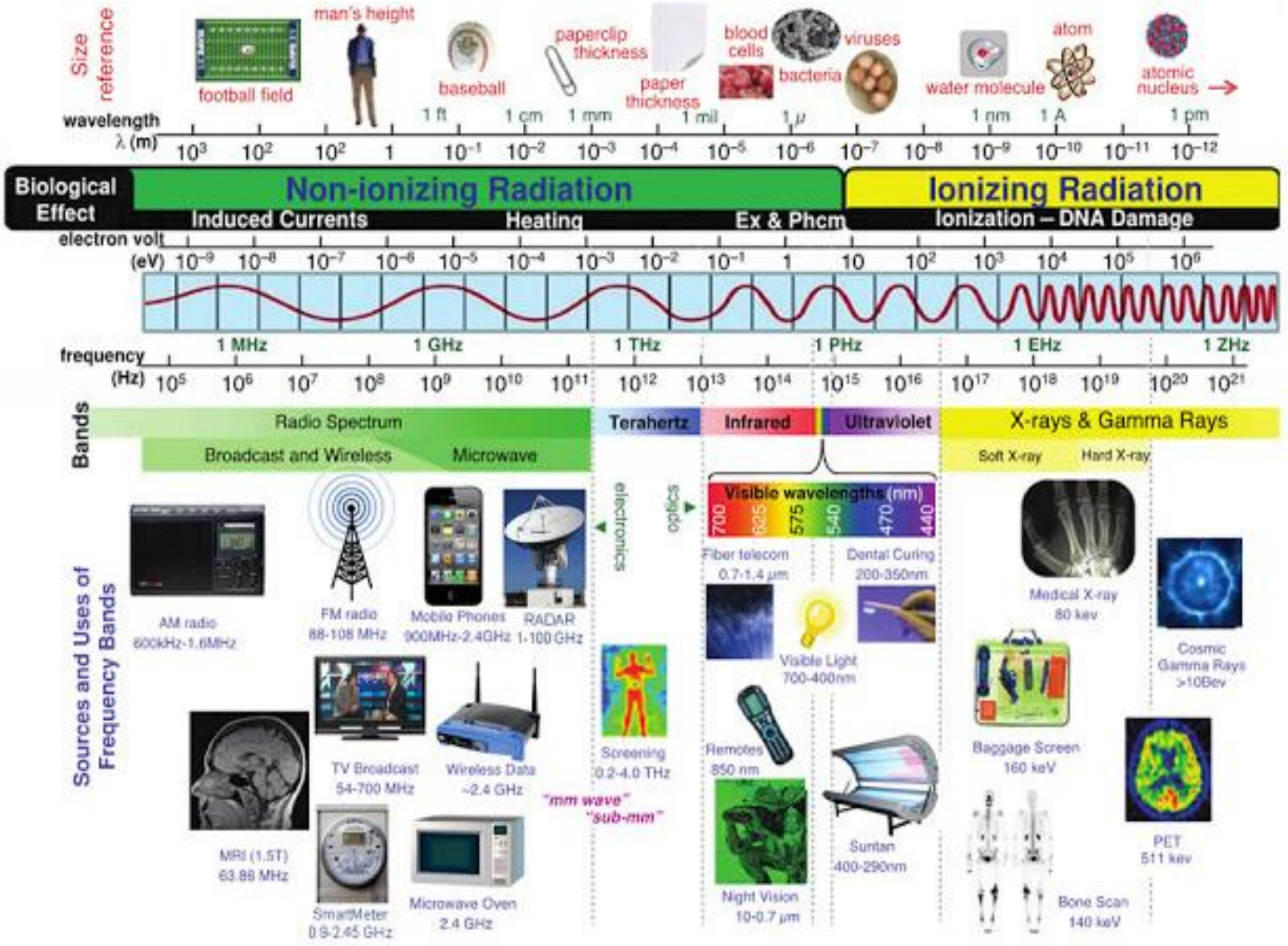
The common inorganic glasses that are used for containers, windows, and so on are silica glasses to which have been added other oxides such as CaO and Na_2O.

Sodium Silicate Glasses



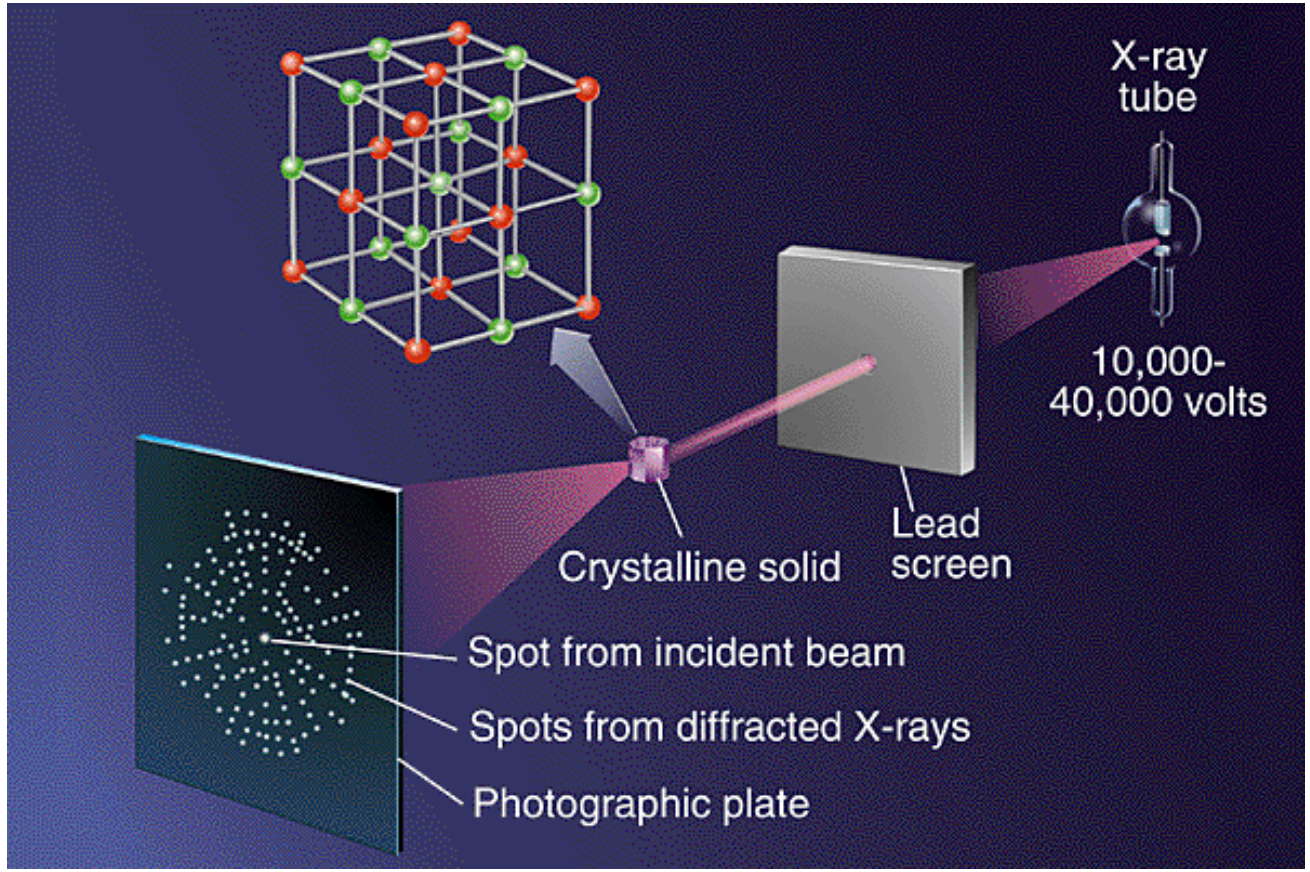
Schematic representation of ion positions in a sodium–silicate glass.

Electromagnetic Radiation Spectrum



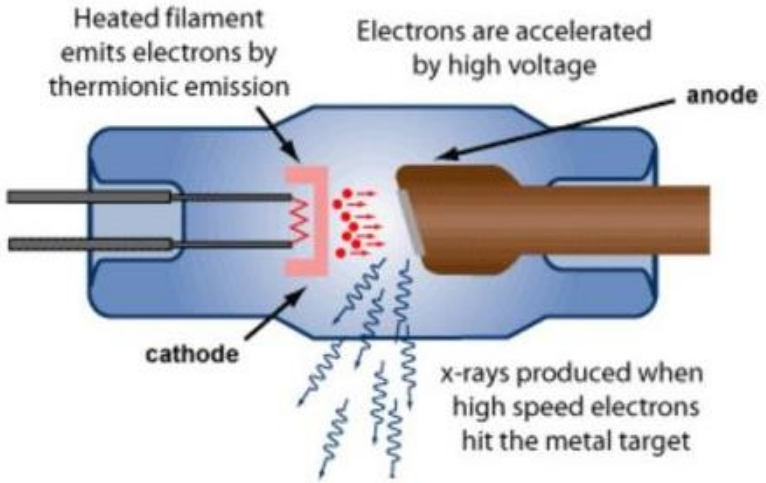
X-ray Diffraction

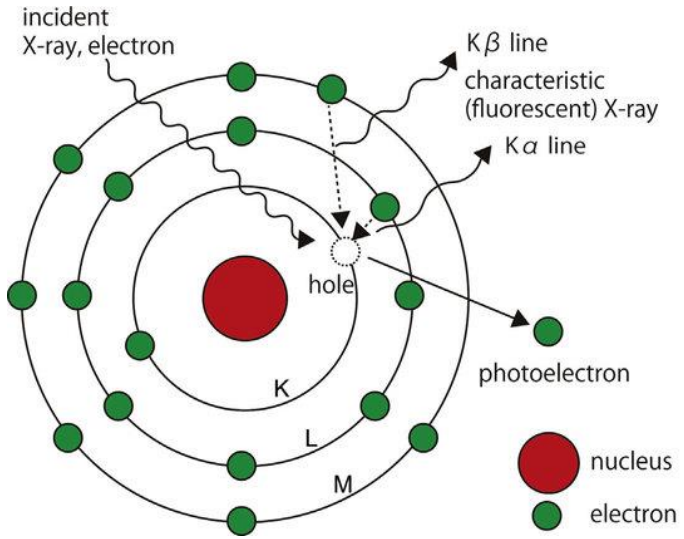
X-ray diffraction is a method of determining the structure of a crystal from its diffraction pattern. X-ray diffraction techniques are based on the elastic scattering of x-rays from structures that have long range order

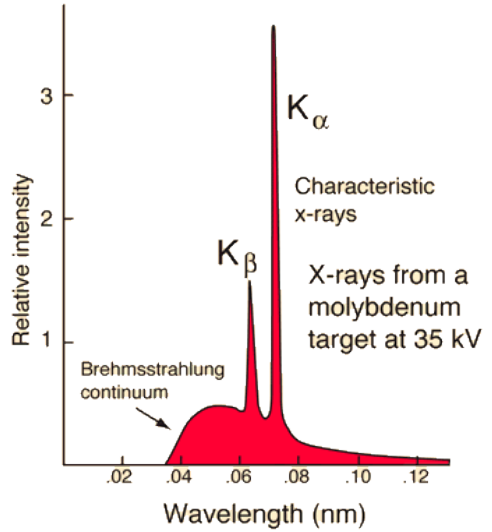


- Max von Laue was awarded the 1914 Nobel Prize in Physics for his discovery of the diffraction of X-rays by crystals.
- He theorized that if X-rays were waves, the wavelengths must be extremely small (on the order of 10^{-10} meters)

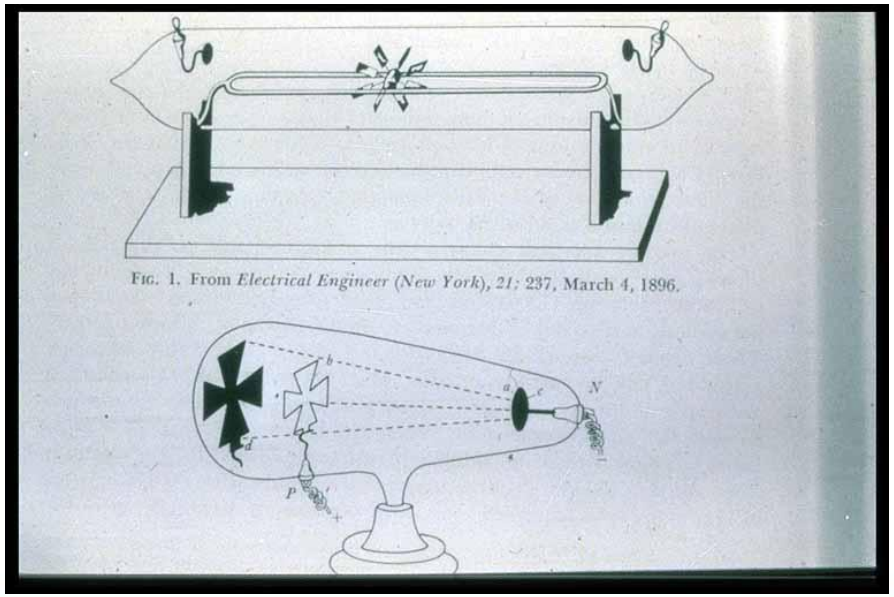
X-Rays



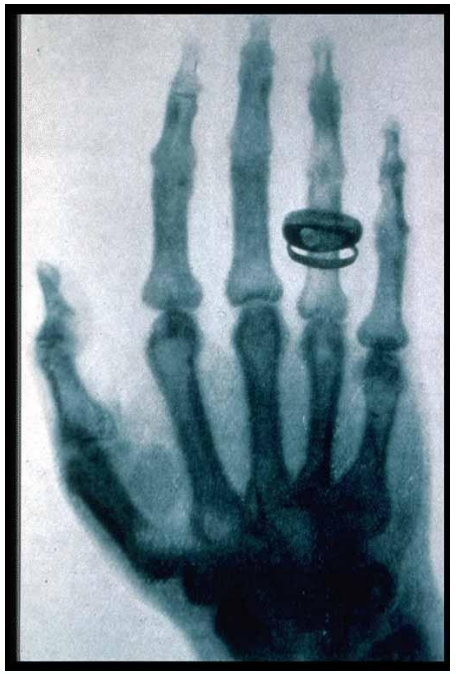




Early experimental tubes like those used by Roentgen and others to investigate the nature of light.

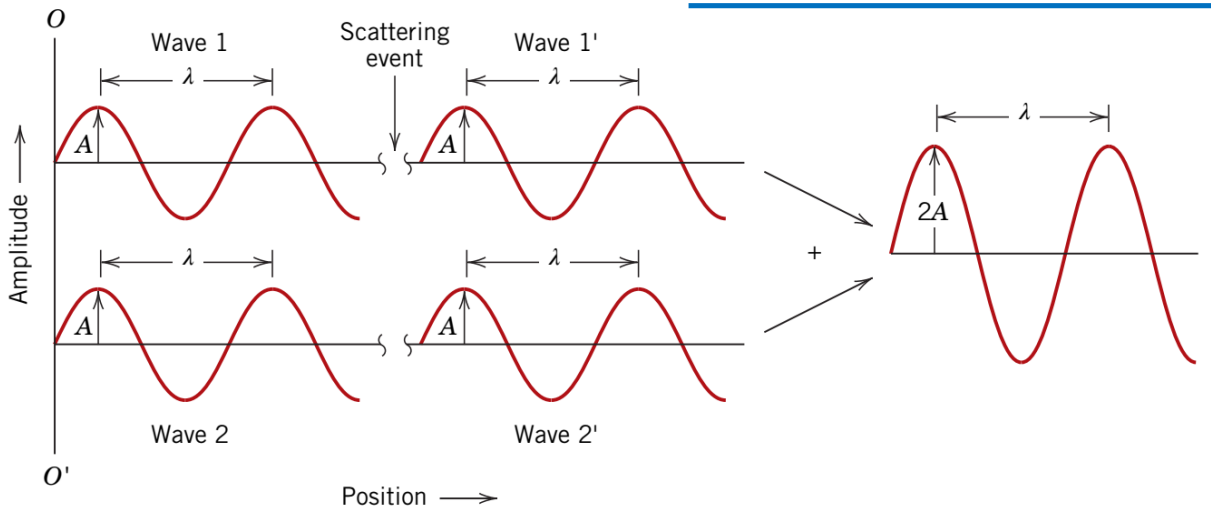


- The famous radiograph made by Roentgen on 22 December 1895, and sent to physicist Franz Exner in Vienna.
- This is traditionally known as "the first X-ray picture" and "the radiograph of Mrs. Roentgen's hand."

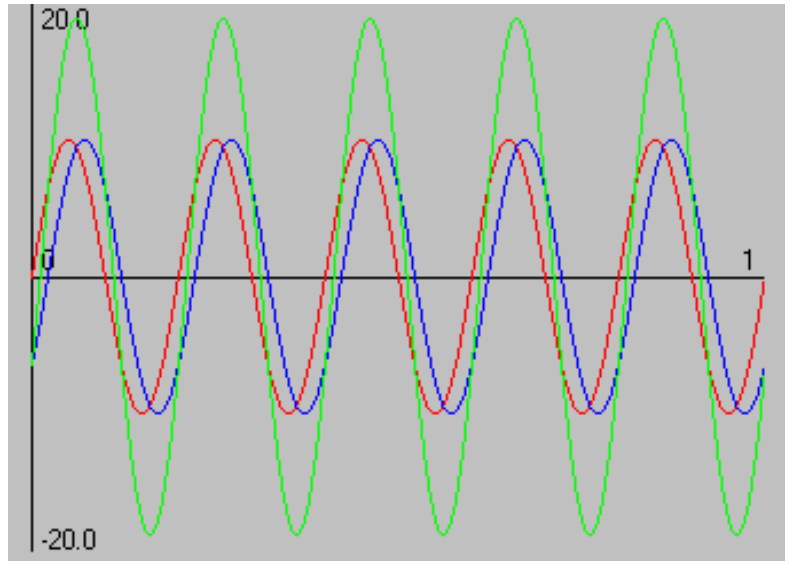


Superposition of Waves

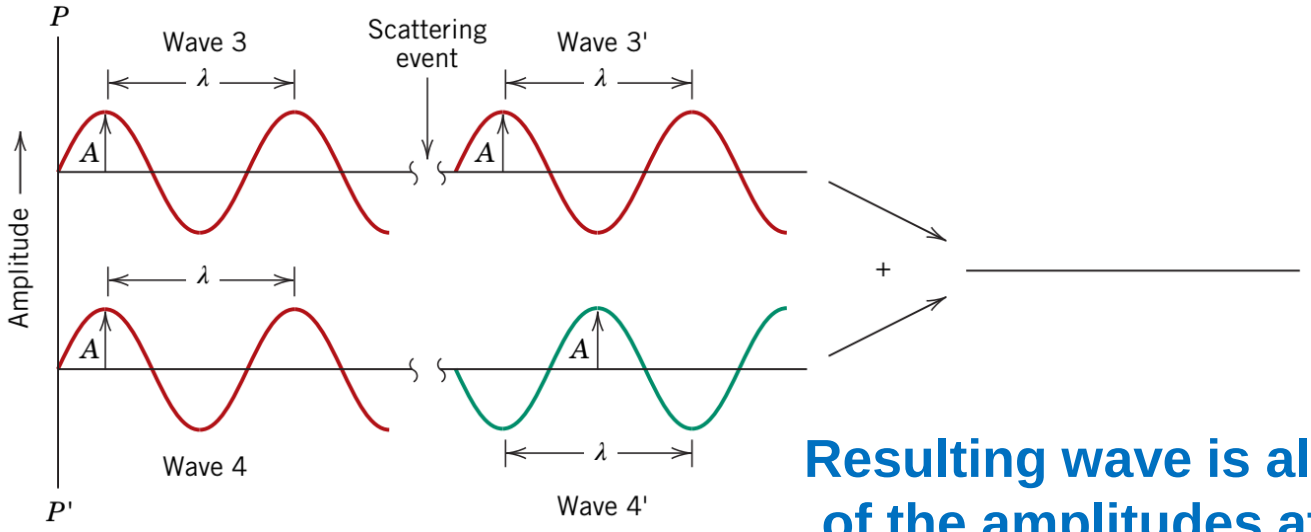
Constructive interference



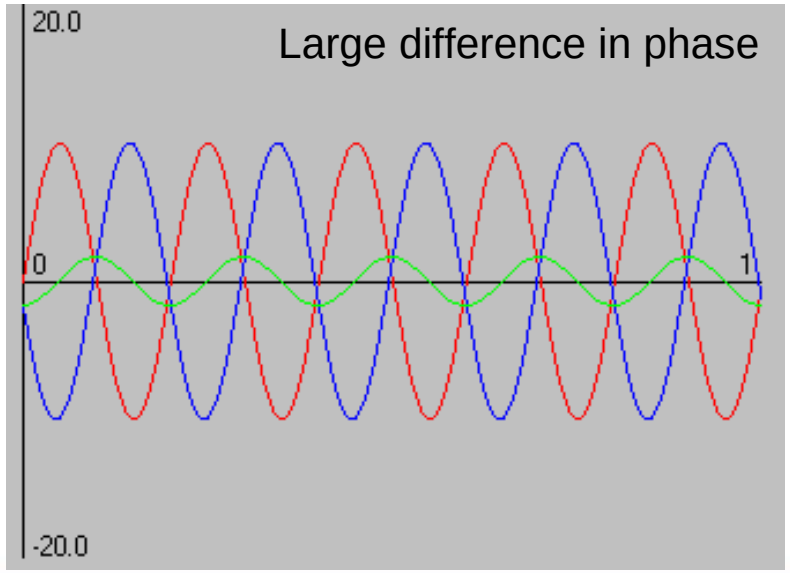
Small difference in phase



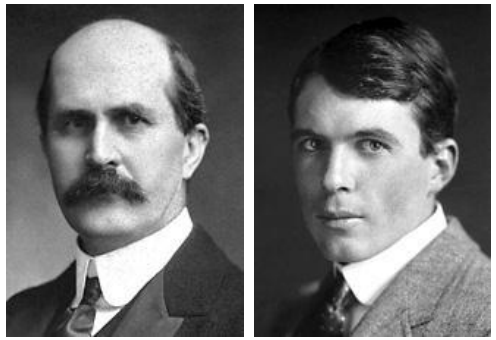
Destructive interference



Resulting wave is algebraic sum of the amplitudes at each point

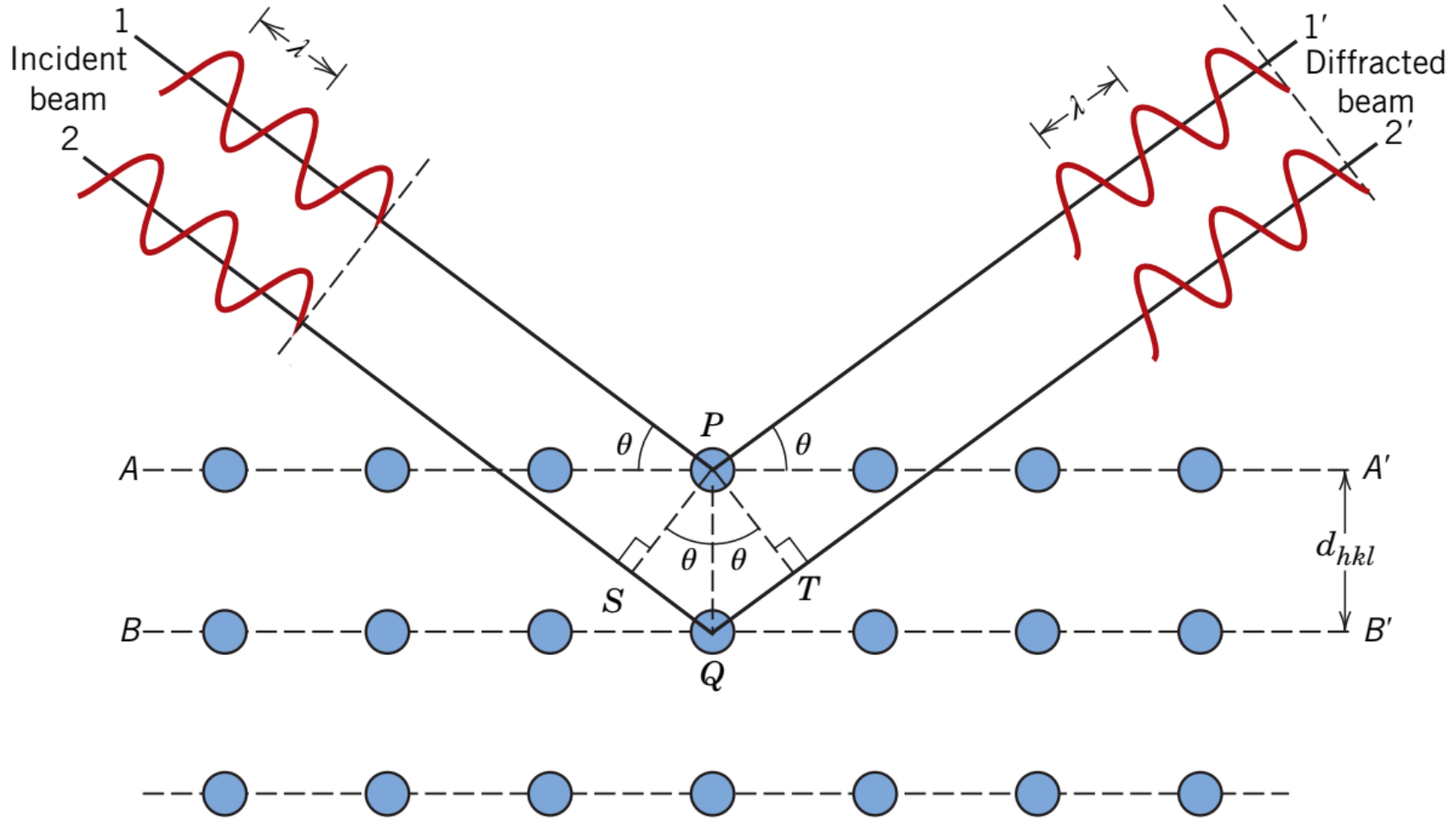


Bragg's Law

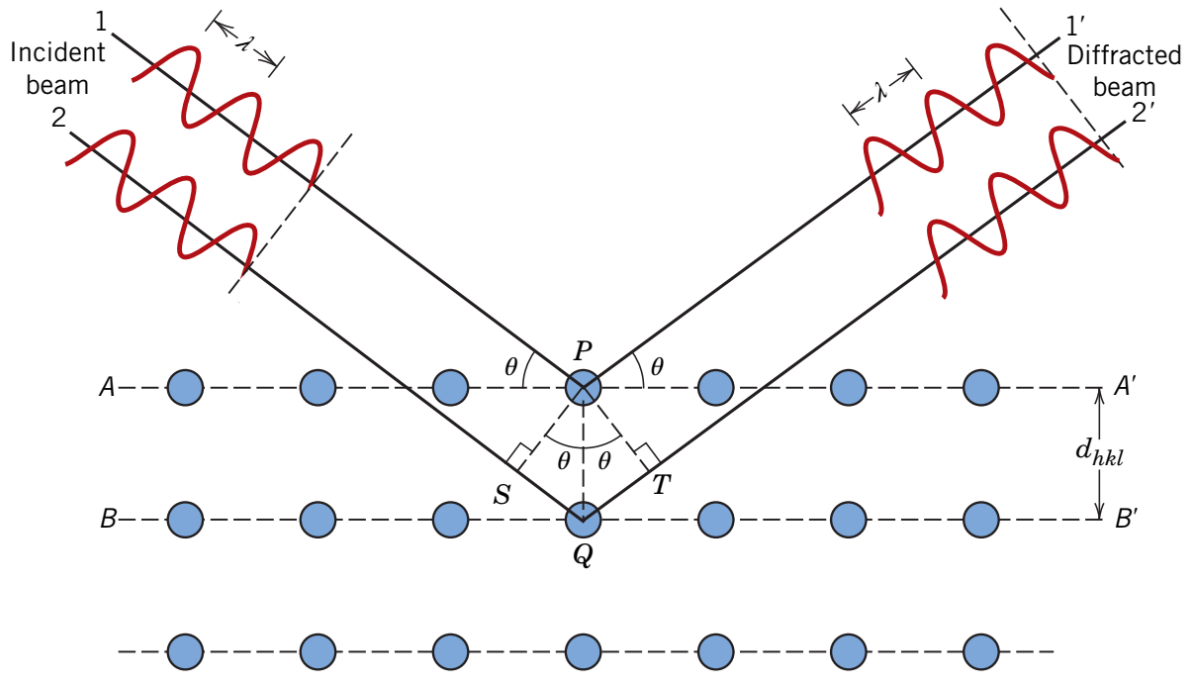


In 1915, William Henry Bragg and William Lawrence Bragg were awarded the Nobel Prize.

They discovered that diffraction of X-rays by solids could be treated as reflection from evenly spaced planes if monochromatic x-rays were used.



Bragg's law : Structural Analysis



Constructive interference of the scattered rays 1′ and 2′ occurs also at an angle θ to the planes if the path length difference between 1–*P*–1′ and 2–*Q*–2′ (i.e., *SQ* + *QT*) is equal to a whole number, *n*, of wavelengths.

Path difference should satisfy $n\lambda$ for constructive interference :

$$n\lambda = \overline{SQ} + \overline{QT}$$

$$n\lambda = d_{hkl}\sin\theta + d_{hkl}\sin\theta$$
$$= 2d_{hkl}\sin\theta$$

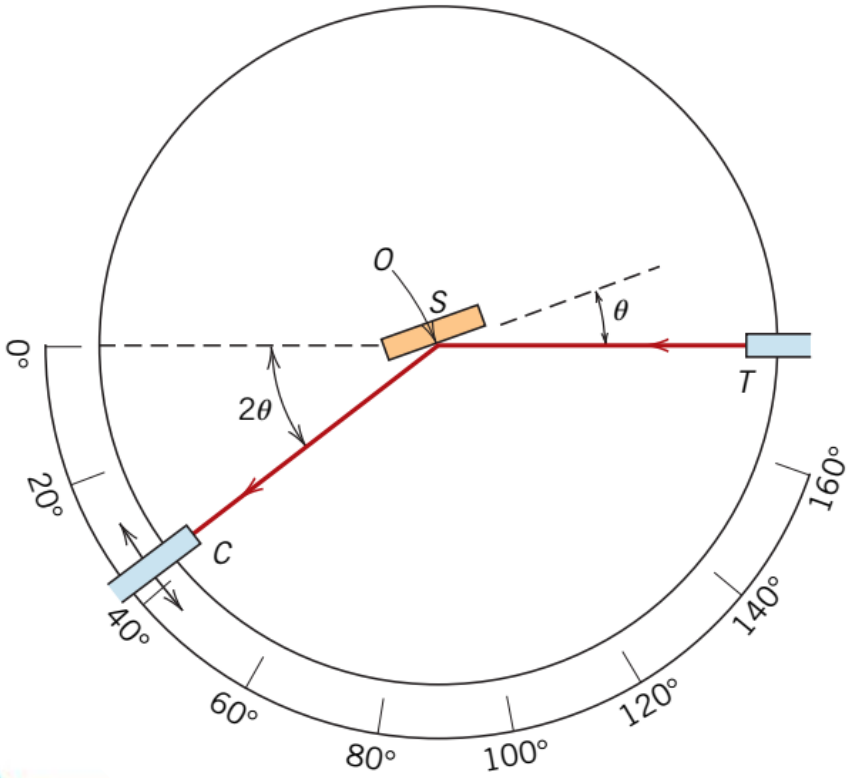
$$n\lambda = 2d\sin\theta$$

where *n* is an integer, the order of reflection
 is the wavelength of the X-radiation *d* is the interplanar spacing
 θ is the diffraction angle

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Bragg's law, is a necessary but not sufficient condition for diffraction by real crystals

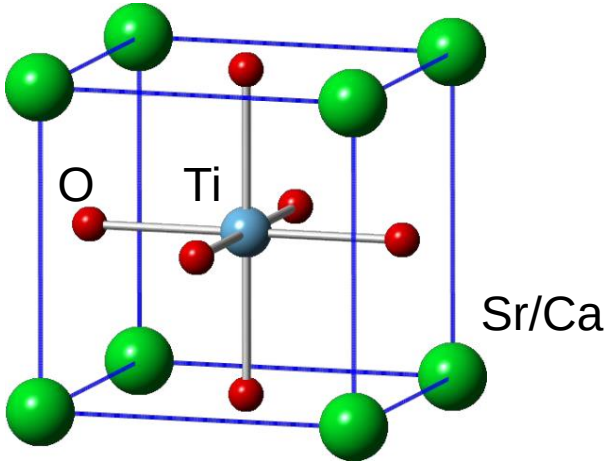
Diffraction Techniques



Two perovskites: $SrTiO_3$ and $CaTiO_3$

20	$^1S_0$
Ca	
Calcium	
40.078	
$[Ar]4s^2$	
6.1132	

38	$^1S_0$
Sr	
Strontium	
87.62	
$[Kr]5s^2$	
5.6949	

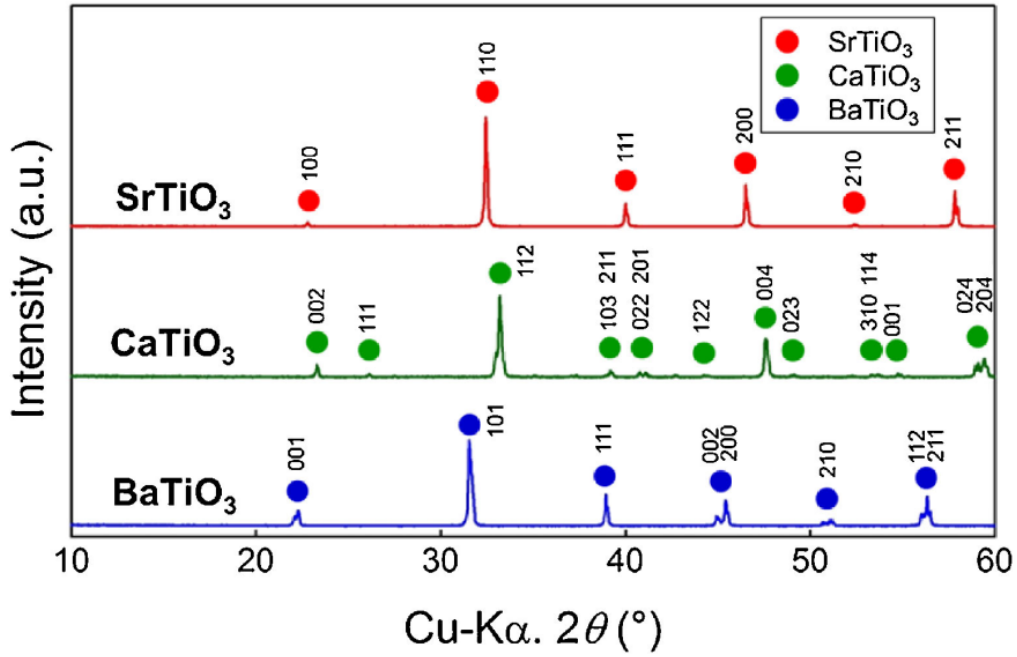


a_{STO} = 3.905 Å

a_{CTO} = 3.795 Å

Differences:

- Peak position – d-spacing.
- Peak intensity – atom type



Reflection rules

Specific sets of crystallographic planes that do not give rise to diffracted beams depend on crystal structure.

- **For SC**, all sets of crystallographic planes are present
- **For the BCC** crystal structure, $h + k + l$ must be even if diffraction is to occur,
- **For FCC**, h, k, and l must all be either odd or even

Crystal Structure	*Reflections Present*	*Reflection Indices for First Six Planes*
BCC	$(h + k + l)$ even	110, 200, 211, 220, 310, 222
FCC	h, k, and l either all odd or all even	111, 200, 220, 311, 222, 400
Simple cubic	All	100, 110, 111, 200, 210, 211

Interpretation of X-Ray Data from unknown sample

$$n\lambda = 2d_{hkl}\sin\theta$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$\sin^2\theta = \frac{\lambda^2 (h^2 + k^2 + l^2)}{4a^2}$$

- ***For BCC structure, the first two sets of principal diffracting planes are {110} and {200}. XRD data can be used to determine crystal structure of metal with cubic crystal structures.***

$$\frac{\sin^2\theta_A}{\sin^2\theta_B} = \frac{h_A^2 + k_A^2 + l_A^2}{h_B^2 + k_B^2 + l_B^2}$$

$$\frac{\sin^2\theta_A}{\sin^2\theta_B} = \frac{1^2 + 1^2 + 0^2}{2^2 + 0^2 + 0^2} = 0.5$$

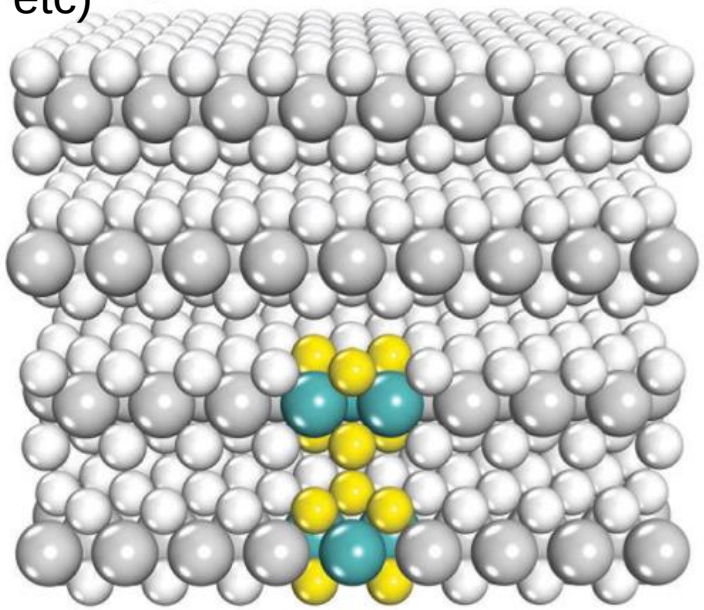
If the crystal structure of the unknown metal is BCC, the ratio of the $\sin^2\theta$ that correspond to the first two principal diffracting planes will be 0.5

For FCC

$$\frac{\sin^2\theta_A}{\sin^2\theta_B} = 0.75$$

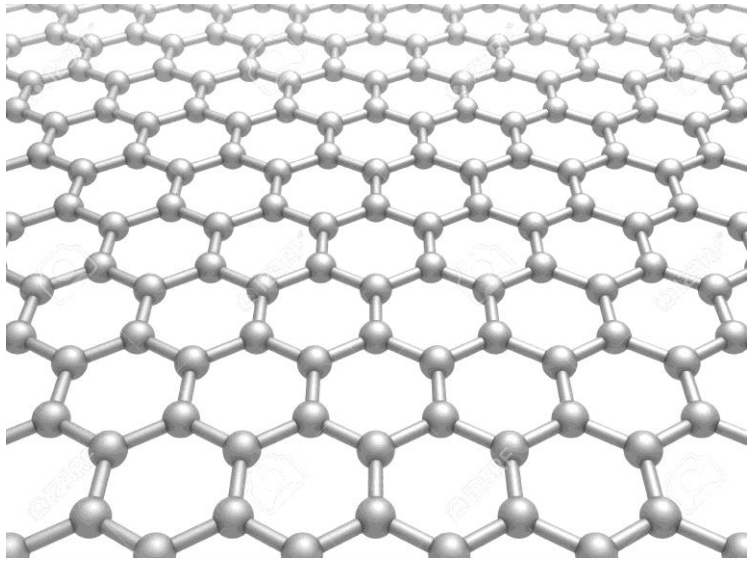
How to get Crystallographic information from single atomic layer?

Bulk layered Materials (Transition Metal Dichalcogenides (TMD), MoS2, WS2 etc)

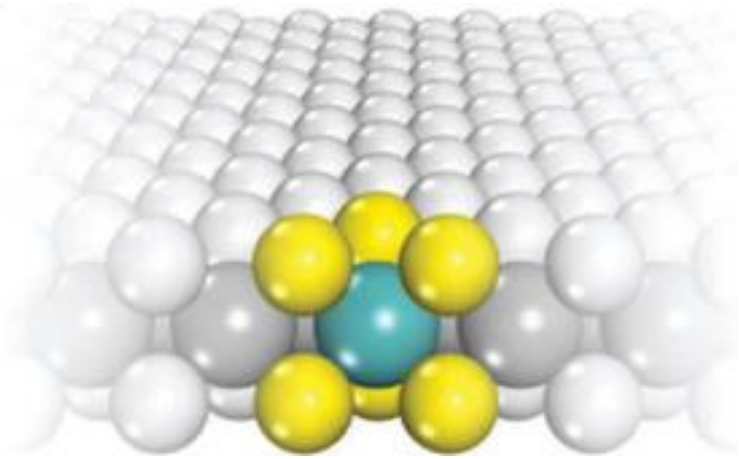


?

Graphene



1L- Transition Metal Dichalcogenides

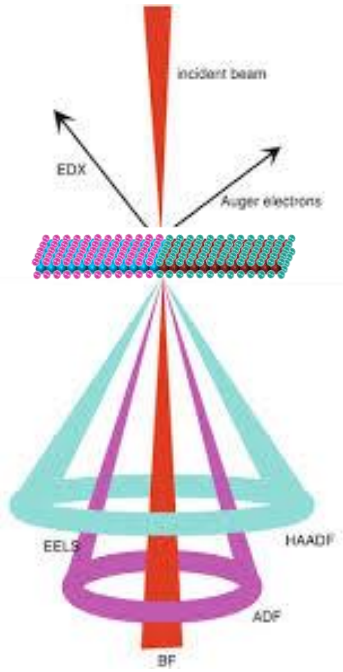


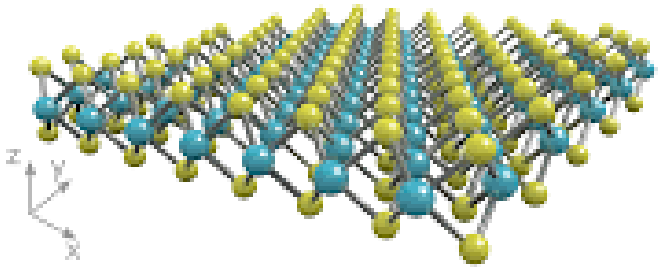
Difficult to obtain information
Related to crystal structure!

$MoSe_2$–WSe_2 lateral Heterostructure: Interface Study

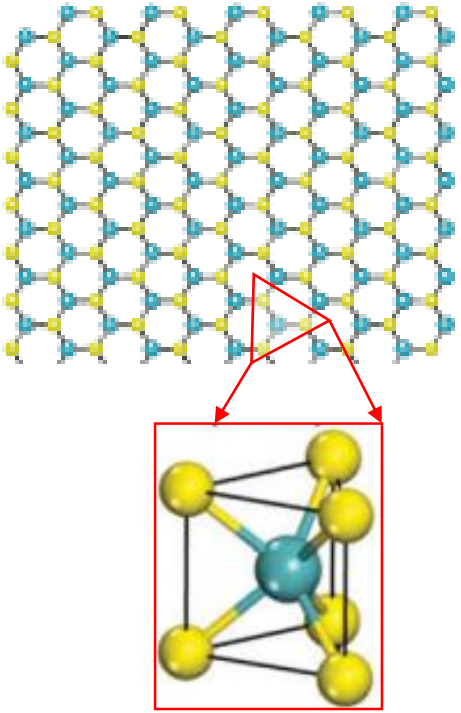
P. K. Sahoo et al. Nature 2018

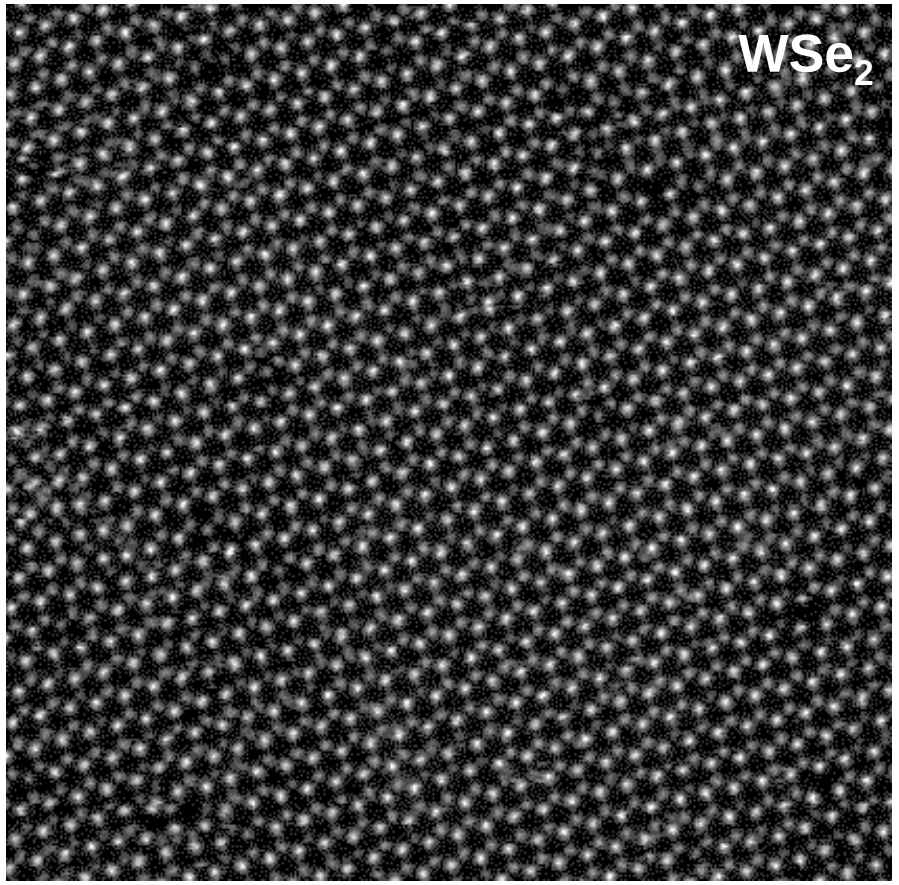
Electron Microscope
(Wavelength ~ pm)





Honeycomb-like atomic arrangement: Monolayer film





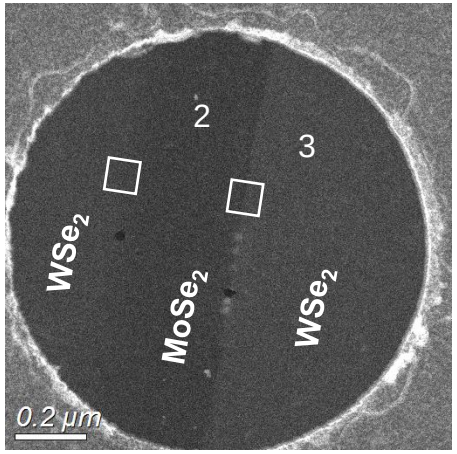
2D sheets of MX_2 display the **1H-phase** with the **hexagonal D_{3h} point group symmetry**.

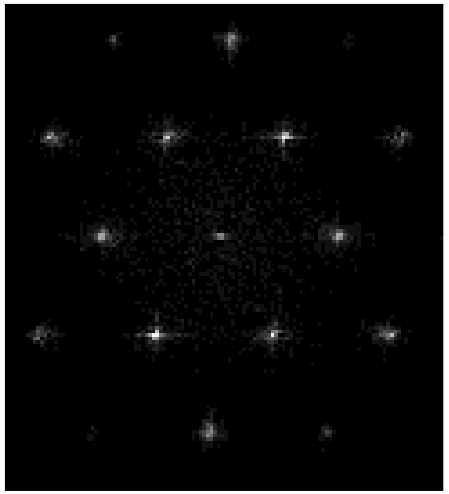
The atomic-resolution Z-contrast images consist of a **honeycomb-like atomic arrangement**

$MoSe_2$–WSe_2 lateral Heterostructure: Coherent Interface

P. Sahoo *et al.* Nature 2018
P. Sahoo *et al.* ACS Nano 2019

$MoSe_2$–WSe_2 on holy carbon Grid

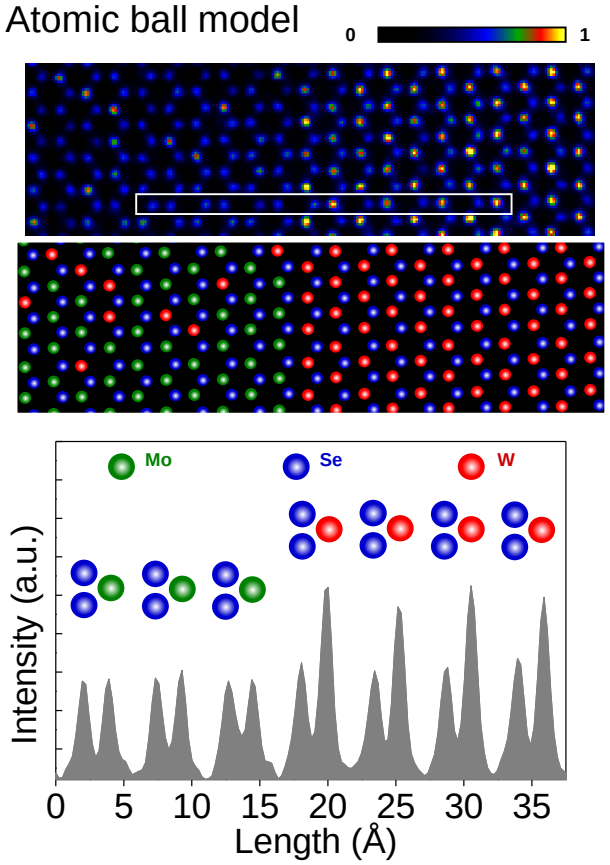


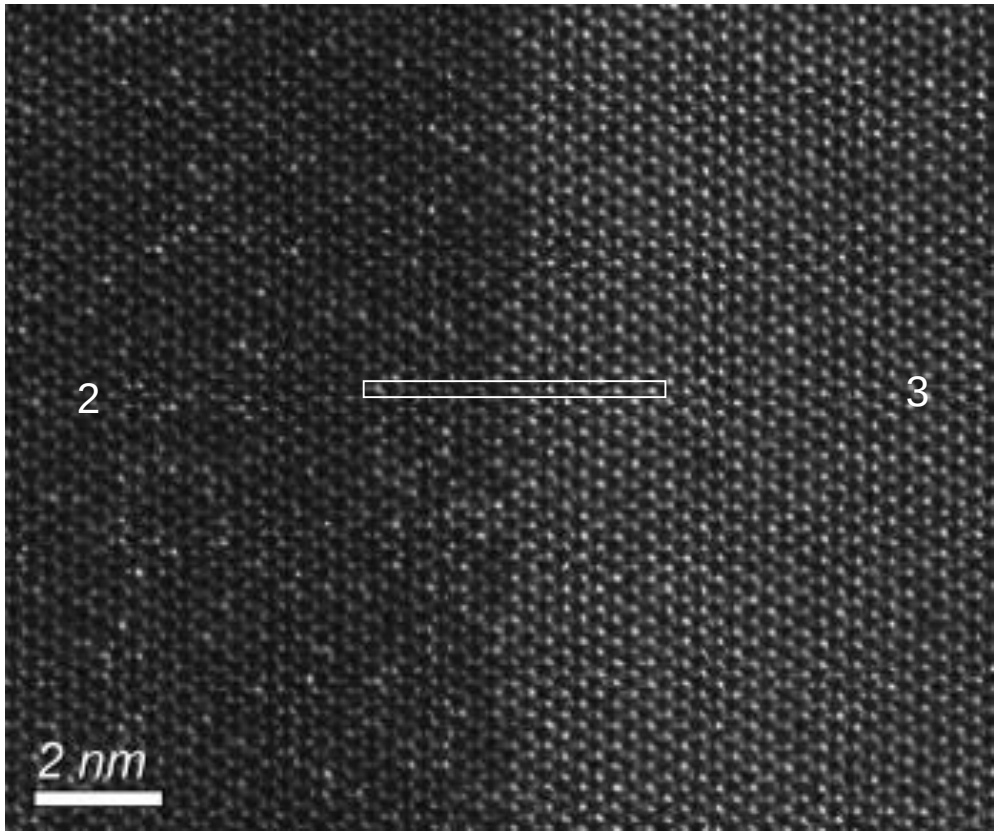


Fourier transform (FT): single-crystalline structure, suggesting both interfaces result from an epitaxial lateral growth

In plane heterostructure: monolayers of $MoSe_2$–WSe_2

Atomic ball model





Summary

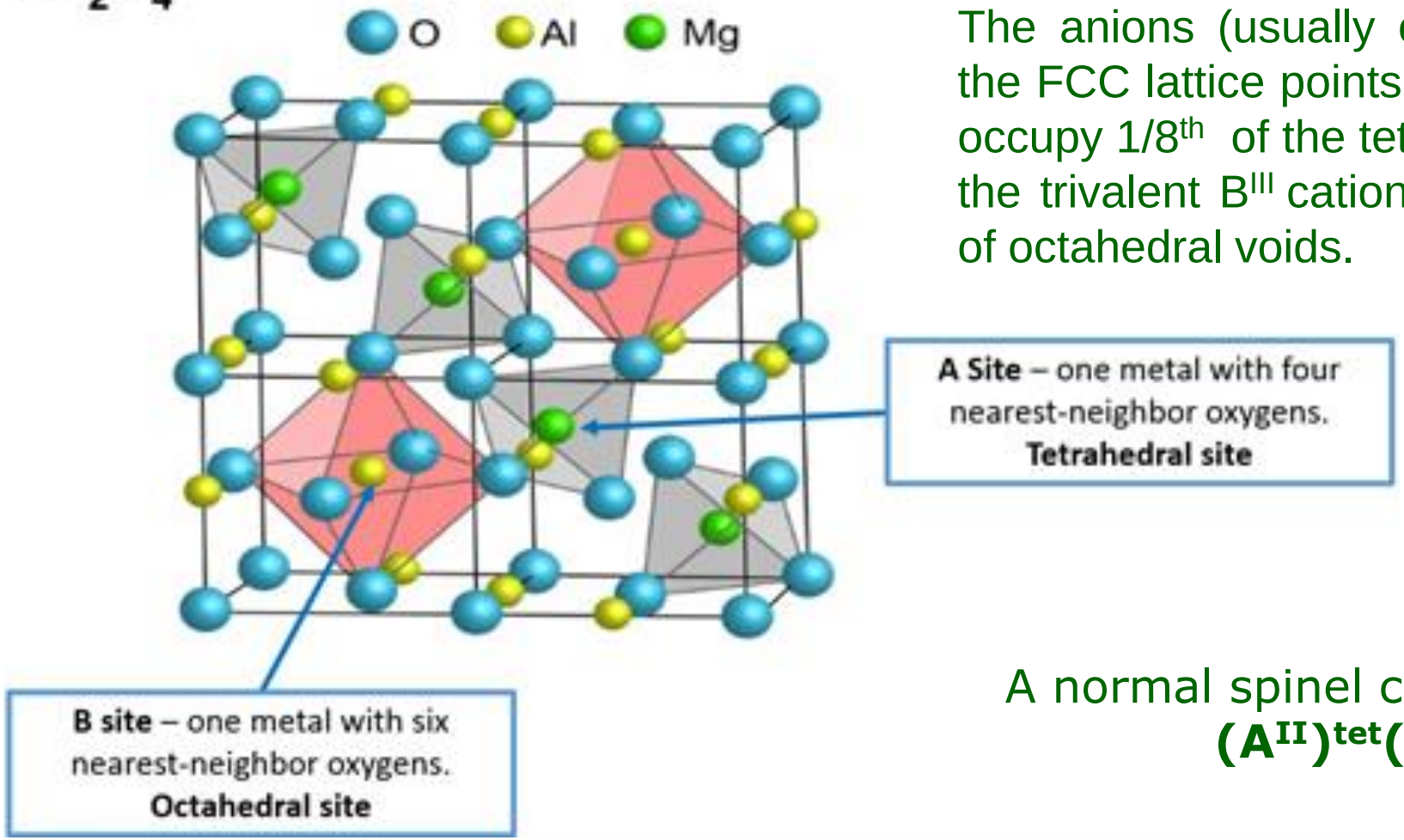
1. Understand how crystal have particular shape and size
2. Identify crystal structures
3. Assign crystallographic planes and directions
4. Crystal structures of metals and Ceramic
5. Using X-ray to identify crystal structure of unknown samples

Spinels

The **spinels** have the general chemical formula $\mathbf{AB_2X_4}$.

$MgAl_2O_4$

Spinel AB_2O_4



A spinel unit cell is made up of 8 FCC cells. The anions (usually oxide ions: O^{2-}) occupy the FCC lattice points. The divalent A^{II} cations occupy 1/8th of the tetrahedral voids, whereas the trivalent B^{III} cations occupy one half (1/2) of octahedral voids.

A normal spinel can be represented;

$\mathbf{(A^{II})^{tet}(B^{III})_2{}^{oct}O_4}$