Chemical Crystallography
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Theoretical Understanding of Crystal Packing and X-Ray Diffraction in Direct and Reciprocal Space
Lecture - 19
Ceramic Structures

Welcome back to the course of Chemical Crystallography. In the previous lecture, we discussed about the atomic packing factors, calculation of cation to anion radius ratios, and we discussed about various interstitials. So, we would like to continue in the same line; and we would like to see some of the well known crystal structures which are the important to understand the packing and the corresponding atomic arrangements.

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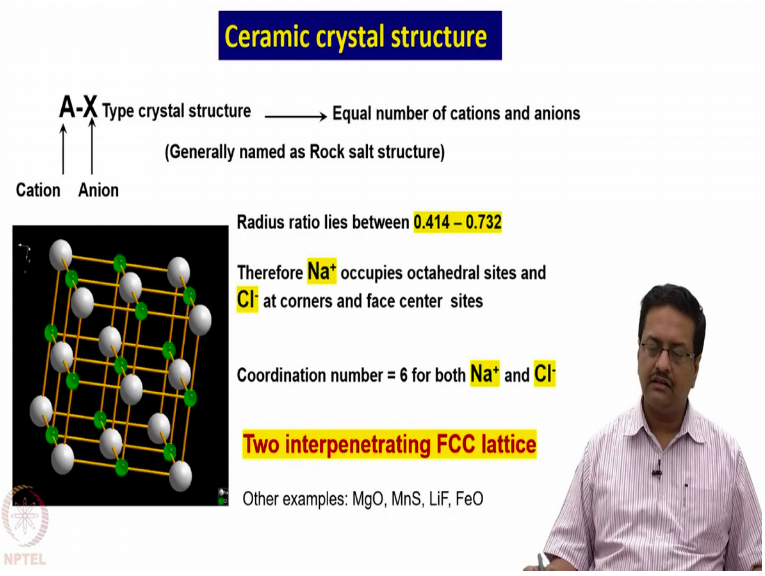

Ceramic crystal structure

A-X Type crystal structure → Equal number of cations and anions

(Generally named as Rock salt structure)

Cation Anion

Radius ratio lies between 0.414 – 0.732

Therefore Na^+ occupies octahedral sites and Cl^- at corners and face center sites

Coordination number = 6 for both Na^+ and Cl^-

Two interpenetrating FCC lattice

Other examples: MgO, MnS, LiF, FeO

Here we are having a ceramic crystal structure of the type A-X crystal structure where you have equal number of cations and anions. The most common example is the Rock salt structure or the NaCl crystal structure of radium chloride. In this case the radius ratio lies between 0.41 to 0.723. So, it means the coordination is 6 is to 6 coordination. So, what we see here is that the sodium cations and the plus cations occupies the octahedral sites; and chloride ions occupies the corners and face centered sides of a face centered cubic lattice. So, it is a 6 is to 6 coordination that means it is 6 coordination with respect to both sodium and chloride, and this ring structure is represented as interpenetrating face centered lattice.

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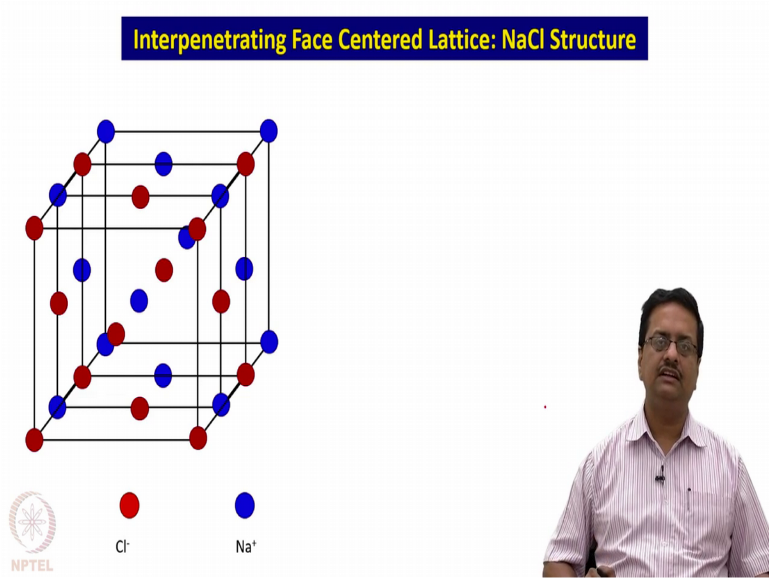

Interpenetrating Face Centered Lattice: NaCl Structure

● Cl^-

● Na^+

So, what does it mean? See, here what I have drawn is a chloride lattice which is corresponding to these red circles at 8 corners and 6 phases of this unit cell. And then I have one slightly offset which is actually offset by half unit along one direction. A lattice of Na plus ions represented in blue; again it is a face centered lattice with 8 corner atoms and 6 face centered atoms. So, now if we try to merge these two in this way what you see is that the two face centered lattices are penetrated in with each other. So, two face centered lattices when they inter penetrate, we call it as interpenetrating face centered lattice.

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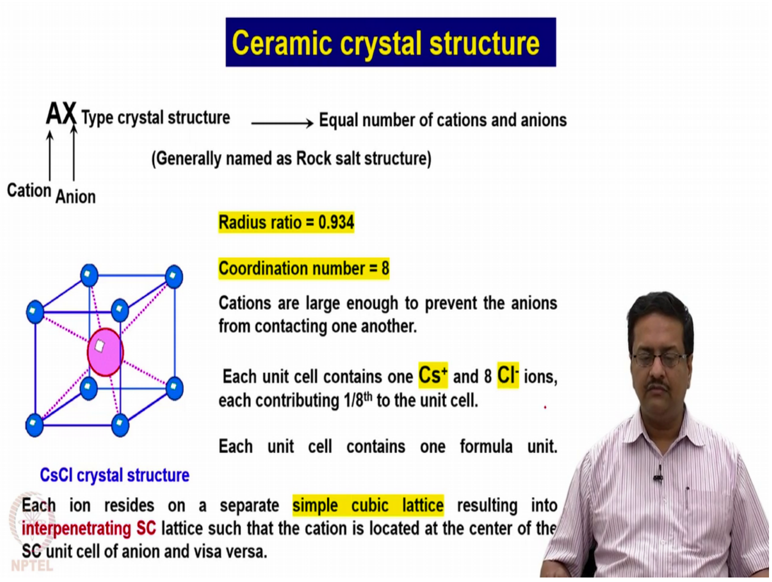

Ceramic crystal structure

AX Type crystal structure → Equal number of cations and anions

(Generally named as Rock salt structure)

Cation Anion

Radius ratio = 0.934

Coordination number = 8

Cations are large enough to prevent the anions from contacting one another.

Each unit cell contains one Cs^+ and 8 Cl^- ions, each contributing 1/8th to the unit cell.

Each unit cell contains one formula unit.

CsCl crystal structure

Each ion resides on a separate simple cubic lattice resulting into **interpenetrating SC** lattice such that the cation is located at the center of the SC unit cell of anion and visa versa.

So, the next type that we would like to discuss is the A-X type of crystal structure, where again we have equal number of cations and anions, generally named as a rock salt structure when we have the radius ratio very close to 1. As we have seen in the previous lecture that when the radius ratio approaches 1, we get coordination number 8 that means, cations are large enough to prevent the anions from contacting each other or they are not in touch.

So, the unit cell contain cesium plus, and 8 Cl minus anions each contributing one-eight through the unit cell. So, what we have is cesium atoms at 8 corners, sorry chloride atoms at the 8 corners and cesium atom at the center of the unit cell. So, this is remember this is not a body centered lattice, because the body centered atom here is not same as the corner atoms. So, it is actually a simple cubic lattice of chloride ions, and a simple cubic lattice of cesium ions, and they are then interpenetrated just like the sodium chloride interpenetrating face centered lattice.

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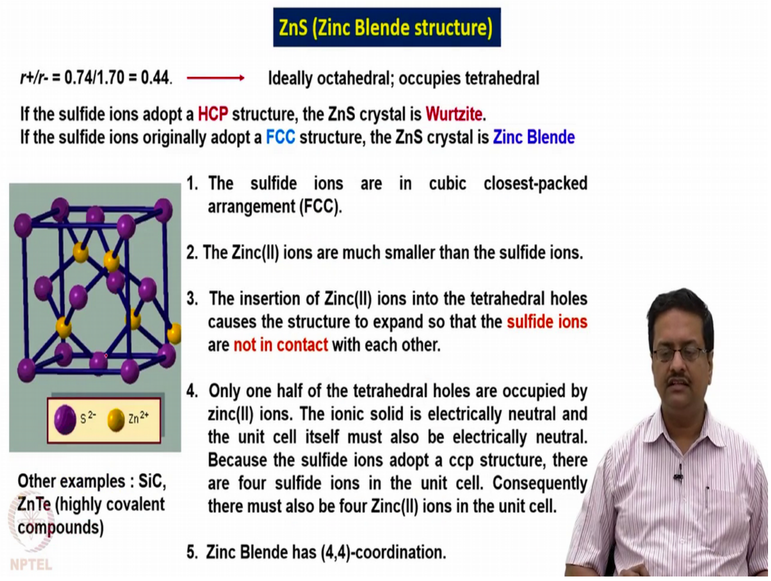

ZnS (Zinc Blende structure)

$r_+/r_- = 0.74/1.70 = 0.44$. ⟶ Ideally octahedral; occupies tetrahedral

If the sulfide ions adopt a **HCP** structure, the ZnS crystal is **Wurtzite**.
If the sulfide ions originally adopt a **FCC** structure, the ZnS crystal is **Zinc Blende**

1. The sulfide ions are in cubic closest-packed arrangement (FCC).
2. The Zinc(II) ions are much smaller than the sulfide ions.
3. The insertion of Zinc(II) ions into the tetrahedral holes causes the structure to expand so that the **sulfide ions** are **not in contact** with each other.
4. Only one half of the tetrahedral holes are occupied by zinc(II) ions. The ionic solid is electrically neutral and the unit cell itself must also be electrically neutral. Because the sulfide ions adopt a ccp structure, there are four sulfide ions in the unit cell. Consequently there must also be four Zinc(II) ions in the unit cell.
5. Zinc Blende has (4,4)-coordination.

Other examples : SiC, ZnTe (highly covalent compounds)

Now, let us see what is zinc blende structure or ZnS structure. It gives of zinc blende structure; the radius ratio is 0.44. So, ideally it should have been that the octahedral sites are occupied by the cations, but in reality the tetrahedral sites are occupied by the cations. So, now, if the sulfides add up the hexagonal close packed structure, then the structure of zinc sulfide is called as Wurtzite structure. If the sulfide ions originally adopt a face centered lattice, then there is this particular zinc sulfide structure crystal structure is called the zinc blende structure.

So, in this case, the sulfide ions are in the cubic closed-pack arrangement that is FCC. So, if you look at the figure on my on the left, you have sulfide atoms occupying the four 8 corners and 6 phases; and then the zinc ions are occupying the alternate tetrahedral sites inside the unit cell. So, this indicates that for one unit cell, you have 1, 2, 3, 4 zinc ions which are fully occupied; and then you have 8 sulfide ions and 6 sulfide ions had phases which means there are total number of sulfide ions is 4. So, again it is one is to one coordinates one is to one formula unit zinc sulfide, but in case here the alternate tetrahedral sites are occupied.

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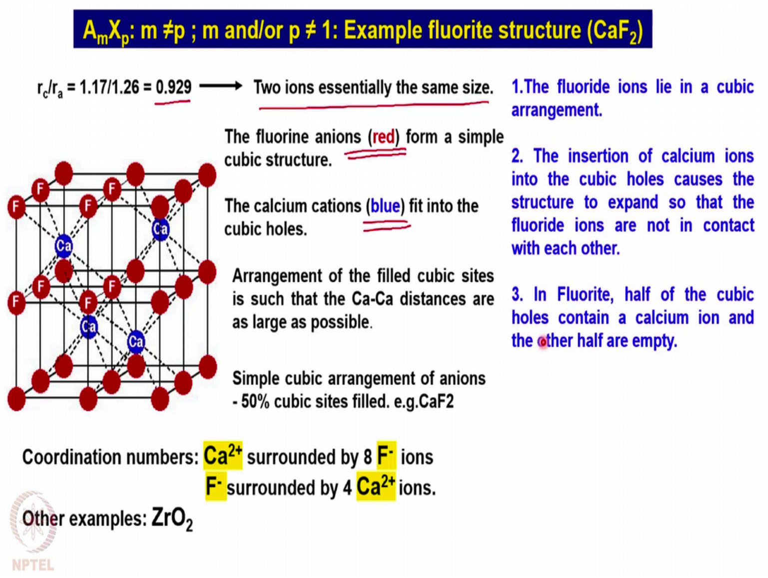

A_mX_p: m ≠ p ; m and/or p ≠ 1: Example fluorite structure (CaF_2)

$r_c/r_a = 1.17/1.26 = 0.929$ ⟶ Two ions essentially the same size.

The fluorine anions (red) form a simple cubic structure.

The calcium cations (blue) fit into the cubic holes.

Arrangement of the filled cubic sites is such that the Ca-Ca distances are as large as possible.

Simple cubic arrangement of anions - 50% cubic sites filled. e.g.CaF2

1. The fluoride ions lie in a cubic arrangement.
2. The insertion of calcium ions into the cubic holes causes the structure to expand so that the fluoride ions are not in contact with each other.
3. In Fluorite, half of the cubic holes contain a calcium ion and the other half are empty.

Coordination numbers: Ca^{2+} surrounded by 8 F^- ions
F^- surrounded by 4 Ca^{2+} ions.

Other examples: ZrO_2

So, now let us see the crystal structure of the fluorite structure calcium fluoride, where the radius ratio is about 1, very close to 1, 0.929 that means two ions are essentially of same size. So, here what we have on the left hand side is that the fluoride anions are represented as red circles and the calcium cations are represented as blue circles. And what we see is that we have a simple cubic lattice of fluorine fluoride ions; and at the centre of that same simple cubic lattice, we have a calcium ion present. But if you look at the corresponding adjacent unit cell, the fluoride ions are forming a simple cubic lattice, but the center is vacant.

The same is true for the lower part also; that means, the simple cubic arrangement which is filled with 50 percent cubic sites are filled in this case of calcium fluoride. So, coordination number for calcium is 8, and coordination number for fluoride is 4. Let us see the same in a different arrangement. What does here the fluoride ions lie in the cubic arrangement. The insertion of calcium ions into the cubic holes causes the structure to expand so that the fluoride ions are not in contact with each other. In fluoride, half of the cubic holes contain a calcium ion and the other half is empty.

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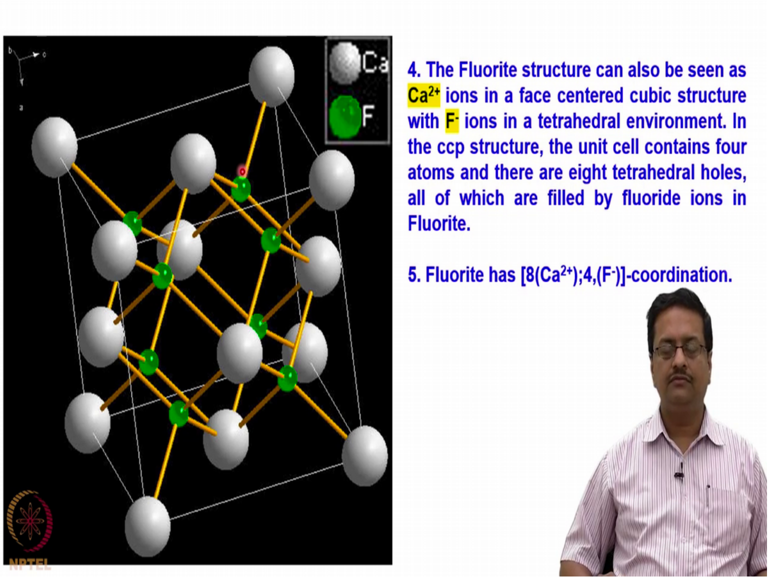

4. The Fluorite structure can also be seen as Ca^{2+} ions in a face centered cubic structure with F^- ions in a tetrahedral environment. In the ccp structure, the unit cell contains four atoms and there are eight tetrahedral holes, all of which are filled by fluoride ions in Fluorite.

5. Fluorite has $[8(Ca^{2+});4,(F^-)]$-coordination.

So, this is the structure that we are discussing where we have calcium represented as grace spheres. The calciums are now represented to form a phase centered lattice because you have 8 corner atoms sites occupied by calcium; 6 face centers occupied by calcium. So, it is a face centered lattice of calcium and then every tetrahedral interstitial is occupied by fluoride ions. If you remember the zinc blende structure, where we had sulfide ions at all the face centered positions; that means, 8 corners and 8 face centered positions, and we had zinc ion at every alternate tetrahedral holes; here the fluoride ion occupies all the possible tetrahedral holes and forms this calcium fluoride structure. So, the fluoride structure can also be seen as calcium ions in the face centered arrangement; and fluoride ions occupying the tetrahedral sites. So, fluorite has a 4 is, 8 is to 4 coordination geometry.

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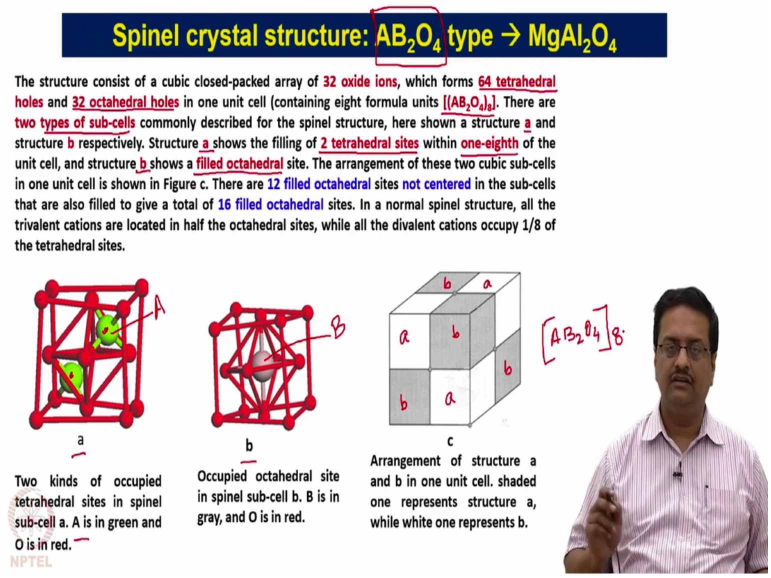

Spinel crystal structure: AB_2O_4 type → $MgAl_2O_4$

The structure consist of a cubic closed-packed array of 32 oxide ions, which forms 64 tetrahedral holes and 32 octahedral holes in one unit cell (containing eight formula units $[(AB_2O_4)_8]$. There are two types of sub-cells commonly described for the spinel structure, here shown a structure a and structure b respectively. Structure a shows the filling of 2 tetrahedral sites within one-eighth of the unit cell, and structure b shows a filled octahedral site. The arrangement of these two cubic sub-cells in one unit cell is shown in Figure c. There are 12 filled octahedral sites not centered in the sub-cells that are also filled to give a total of 16 filled octahedral sites. In a normal spinel structure, all the trivalent cations are located in half the octahedral sites, while all the divalent cations occupy 1/8 of the tetrahedral sites.

a

Two kinds of occupied tetrahedral sites in spinel sub-cell a. A is in green and O is in red.

b

Occupied octahedral site in spinel sub-cell b. B is in gray, and O is in red.

c

Arrangement of structure a and b in one unit cell. shaded one represents structure a, while white one represents b.

So, now the last type of structure that we wanted to discuss is a spinel structure. Spinel structures have a general formula of AB 2 O 4; and example of spinel is Mg Al 2 O 4. So, here we see that the cation A is divalent, and cation B is a trivalent cation. So, in this case, what we have is slightly complicated. You see the structure consists of a cubic closed-packed array of 32 oxide ions, which forms 64 tetrahedral holes and 32 octahedral holes in one unit cell containing eight formula units that is this is the formula unit which we are talking about eight such formula unit is present in one unit cell. So, in this large unit cell, there are two types of sub-cells you have two structures a and b. In case of structure a, we have two tetrahedral sites within one-eighth of the unit cell is occupied, so the oxygens are occupying the face centered lattice positions in this one-eighth of structure; and then inside you have two cations present in that.

So, here two kinds of occupied tetrahedral sites in spinel sub-cell a. So, the atom a or the cation a is represented as green. So, this is the cation a. In the structure b, it shows a filled octahedral site which is this one. So, this is the cation of type b; that means, a trivalent cation is sitting at that particular sub-cell of this face centered cubic structure. So, here the second sub-cell also has face centered cubic lattice of oxide ions and the center of who is occupied by a trivalent cation. So, this particular arrangement is then stacked in a three-dimensional lattice. So, in on the right hand side, if we identify the different sub-cells as a, b, a, b, b, a, b, so this corresponds to the unit cell of a spinel structure corresponding to 8 formula units part unit cell.

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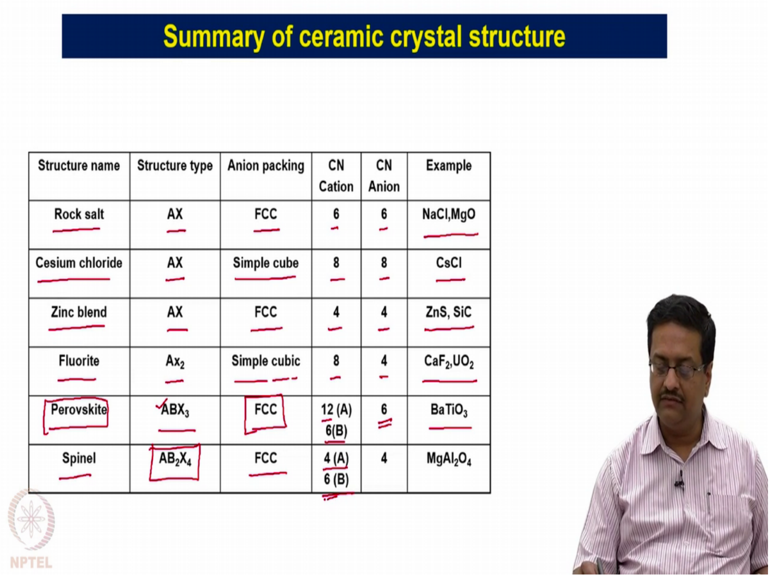

Summary of ceramic crystal structure

Structure name	Structure type	Anion packing	CN Cation	CN Anion	Example
Rock salt	AX	FCC	6	6	NaCl,MgO
Cesium chloride	AX	Simple cube	8	8	CsCl
Zinc blend	AX	FCC	4	4	ZnS, SiC
Fluorite	Ax_2	Simple cubic	8	4	CaF_2,UO_2
Perovskite	ABX_3	FCC	12 (A) 6(B)	6	$BaTiO_3$
Spinel	AB_2X_4	FCC	4 (A) 6 (B)	4	$MgAl_2O_4$

So, to summarize this we have a set of ceramic crystal structures with different coordination numbers. We have seen when it is named as rock salt structure the structure has a type AX that is the common formula AX. And ions are packed in face centered lattice the cation and anion both have coordination 6 is to 6. And there are examples like sodium chloride magnesium chloride, they occupied these rocks all structures.

A cesium chloride structure is also of type AX, but you see this is simple cubic as I already indicated that it is interpenetrating simple cubic lattice having 8 is to 8 coordination for both cation and anion. So, a cesium chloride structure is interpenetrating body interpenetrating simple cubic lattice with eight is to eight coordination.

The next type that we discussed is a zinc blende structure where the formula is again AX that is the stoichiometric formula, but this is a face centered cubic lattice where the coordination number is 4 is to 4 that means, anions are occupied in face centered lattice; cations are located at the interstitials the tetrahedral interstitials. So, these are the examples are zinc sulphide silicon carbide etcetera.

The next type that we have seen is a fluorite structure it is having a general formula AX 2. This is again a simple cubic structure with 8 is to 4 coordination. And calcium fluoride and uranium oxide are two examples of such structure. We have not discussed about perovskites which I would like you to read yourself. The formula is about like A B X 3. We have two types of atoms just like spinels. It occupies a face centered cubic system where the coordination number of cation is 12 for the cation a; and coordination number 6 is for cation b; and the anion is always a 6 coordinated, example is barium titanate.

And we discussed about the spinel structures where you have A B 2 X 4 kind of molecular formula or the stoichiometric formula. It again occupies FCC where the cation a which is A divalent cation which occupies which has coordination number four a trivalent cation B occupies octahedral sites with coordination number 6; the anion has coordination 4 coordination number 4, and the example is Mg Al 2 O 3. So, with this we would like to conclude this lecture on ceramics and ceramic structures and their coordination numbers radius ratios etcetera. I would like to request all of you to go through a standard textbook to understand this.