Electroceramics
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Lecture No. # 02

Last time we discuss the some fundamentals of structures and bonding. So, we were in the the end of the lecture we were reviewing the packing of atoms in materials.

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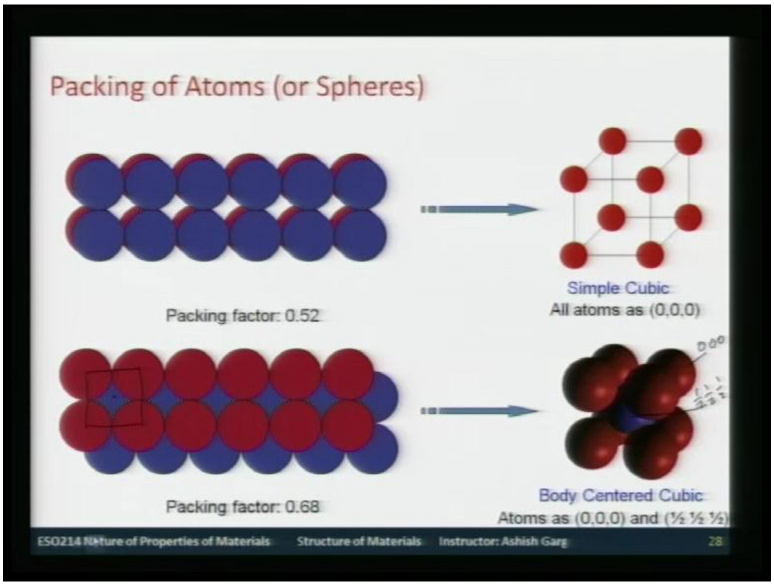

Packing of Atoms (or Spheres)

Packing factor: 0.52

Simple Cubic
All atoms as (0,0,0)

Packing factor: 0.68

Body Centered Cubic
Atoms as (0,0,0) and (½ ½ ½)

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So, for instance a packing of atoms in if you consider atoms is a heard spear, then in the simple cubic structure, so if this is a first layer of atoms, second layer of atoms goes write on top of it I have made it little bit shifted, so that its clear, but goes write on top of it. And the color is also different just for the illustration purposes otherwise both of them a similar. And this makes a simple cubic structure which is like this, and in this is structure the atoms are located at 0 0 0 positions.

In the BCC structure - the first layer is like this, and the second layer goes in the second layer is such that, so that each atom is at the at the center of the square made by the first layer. So, so for instance if I just use the color, so is this is the square, then center of square is this which is occupied by the atoms in second layer and so on and so forth. All the atoms will will be arrange in this manner, and the third layer goes right at the one top of the first layer.

So, the resulting structure in this case is a body centered cubic structure like this, where these are the corner atoms and this is the body centered atom. So, this is at 0 0 0 and this would be at half, half, half the atom the color of the atoms are different only for illustration purposes otherwise for a body centered cubic both the atoms would be same. If it was if the colors of atoms, so the indeed different, then it would be primitive structure as as we will see in some of the ceramic structures.

So, this would be, these would be atomic positions for BCC structure you can work out the packing factor which is nothing but the volume of the atoms in 1 unit cell. So, effectively for a simple cubic structure you will have 1 atom per unit cell and for a body centered cubic structure you will have 2 atoms per unit cell. And for both the structures you have to consider as of the atoms are touching each other.

And then you work out what is the cell volume and divide the number divide the volume of total number of atoms divided by the cell volume which will give give you the packing efficiency or packing factor. So, in case of simple cubic structure the packing factor works out to be 52 percent were is in case of BCC structure works out to be 68 percent.

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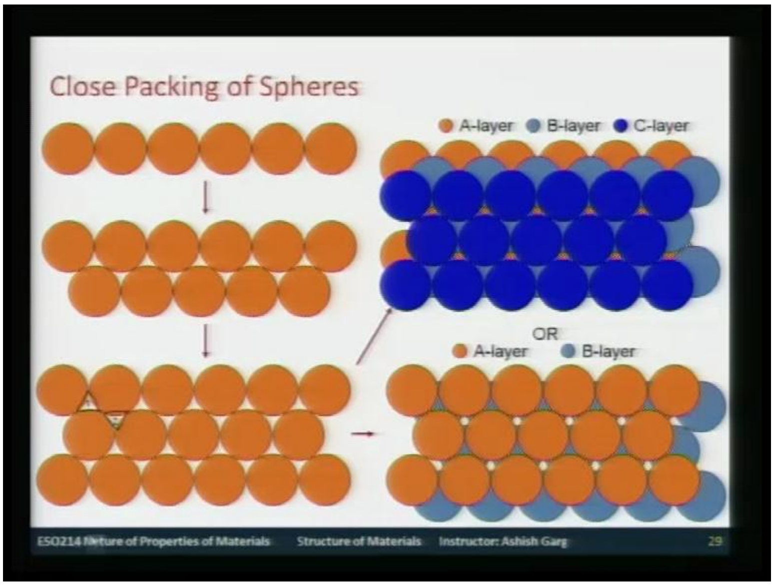

Close Packing of Spheres

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Then we discuss the finally, the closes form of packing where atoms pack themselves in. So, this is for example, of first layer, the second layer in the same plain touches the first layer, so that it has maximum number of needs neighbors. So, this is the arrangement of atoms in 1 layer on the second layer can then go, so you have this two kind of interest is one is these you can say top pointed triangles and another is this bottom pointed triangles.

And the second layer can go on top of either of these two, but it cannot cover simultaneously both of them. So, second layer go like this. So, you can see that the another one number 2 is empty here it is uncovered simply, because size of the atoms such that it cannot cover both of them simultaneously and the colors again a different just for illustration purposes, otherwise it would be same.

And the third layer can either go right on top of the first layer or, so which would be A B A B kind of packing or you can have first layer, second layer and the third layer then covers the number 2 kind of holes. So, this would be your A B C, A B C kind of packing which would be. So, A B A B packing gives rise to a hexagonal close pack structure, and A B C A B C kind of packing gives rise to your face in thread cubic structure.

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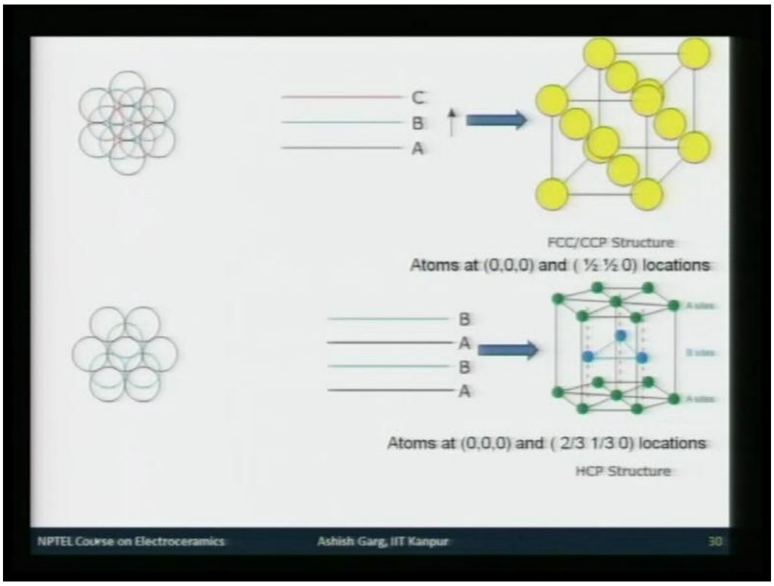

FCC/CCP Structure

Atoms at (0,0,0) and (½ ½ 0) locations

Atoms at (0,0,0) and (2/3 1/3 0) locations

HCP Structure

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This is what it is like, so you have this A B C, A B C kind of packing for HCP structure which would be this. And actually the close pack closes pack plane on which the projection has been shown in previous slide as well as in this slide is actually the 1 1 1 plane and this would be the 1 1 1 plane. So, all you have to do is that you have to stag that comes along along the body diagonal on this particular plain.

So, this would be face 100 cubic or cubic close pack structure the atoms are located at 0 0 0 locations as well as all the half of 0 or face centered locations. In case of FCC in case of hexa hexagonal close pack structure you have a b a b kind of packing. So, a b a b like as shown here and this is the structure which is shown here. So, you have A layer followed by this blue layer again A layer and the colors are different only for illustration and the basic unit cell of this is structure is like this.

So, you draw, so this is the basic unit cell of hexagonal close pack structure. So, you will have atoms at 0 0 0 locations as well as at 2 by 3, 1 by 3, 0 location. 2 by 3, 1 by 3 can also be 1 by 3, 2 by 3, 0 depending upon (( )), so this is your hexagonal close pack structure. Now, as we can see that none of these structures whether it is a C P or be FCC or BCC or simple cubic of them have empty spaces between the atoms. And these empty spaces are called of whites or interstices, these are very important because smaller sized atom can occupy these places.

And they are actually instrumental in determining the properties of these material for instance steel, steel is iron carbon (( )). Now, how does iron does the how does iron increase the strength is by occupying the smaller interstices in the B C C structure of iron. And again the packing factor as you can see, since the A B C or A B kind of packing give rise to much more close pack structure the packing density that can be obtained is about 74 percent. And the proof of this early with you that is a very elementary exercise.

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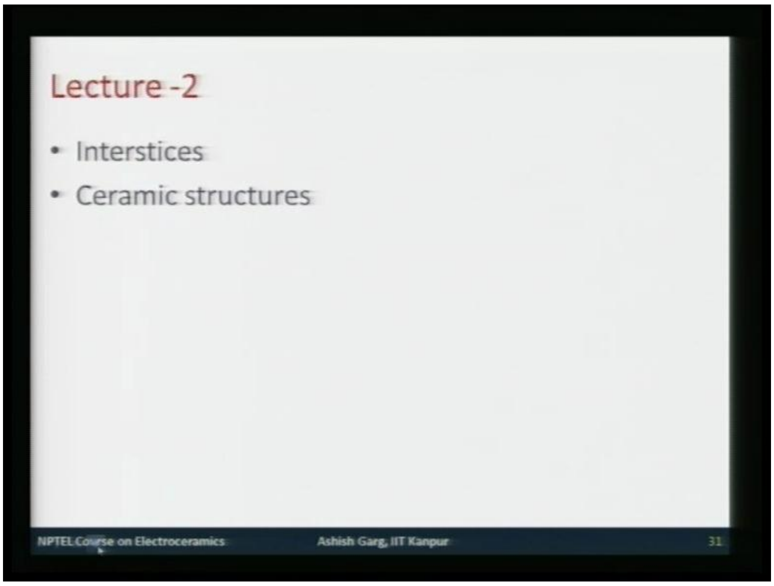

Lecture -2

- Interstices
- Ceramic structures

So, in this lecture we will start with the interstices and the structures which are made in ceramic compounds.

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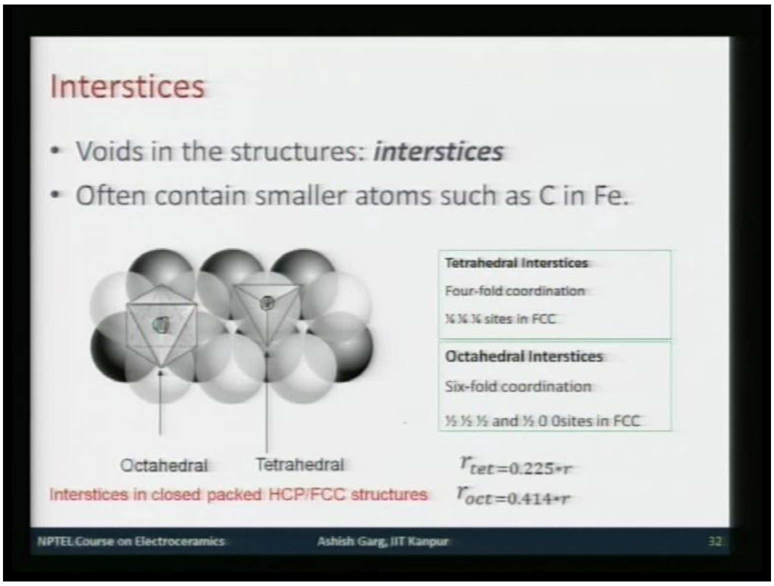

Interstices

- Voids in the structures: ***interstices***
- Often contain smaller atoms such as C in Fe.

Tetrahedral Interstices

Four-fold coordination

¼ ¼ ¼ sites in FCC

Octahedral Interstices

Six-fold coordination

½ ½ ½ and ½ 0 0sites in FCC

Interstices in closed packed HCP/FCC structures

$r_{tet}=0.225*r$

$r_{oct}=0.414*r$

So, these are the two kinds of interstices which are often encountered in these in most of the materials. So, for instance I am showing you the examples in A B C, A B C or A B, A B kind of factor structures, the easiest one is FCC structure. So, if you have this kind of structure then the, so you have a body which can be which can have 8 sides or 6 corners, this body will be called as a octahedral. And this sites will be called as octahedral site where each atom which will sitting here at the center will be occupied by 6 nearest neighbors.

So, this will make a regular octahedral in a A B C, A B C kind of packing, alternatively you can have you can also have a tetrahedral kind of packing were each atom sitting here. So, you have 3 at the bottom, 1 one top this would make a regular of tetra hydra and this would be a tetrahedral of 4 4 coordination. And in case of FCC structures these sits are offend denoted as 1 by 4, 1 by 4 sites in FCC structure whereas in case of octahedral sites their either half, half, half site or any kind of half 0 0 kind of site.

So, half, half, half would be body center and half 0 0 kind of positions would be your edges of the unit cell and 1 by 4, 1 by 4, 1 by 4 would be along the body diagonal at quarter, quarter, quarter location from each corner. So, total half a you will have 4 octahedral sites in a FCC structures, which means 1 per atom and total half 8 tetrahedral sites in FCC structure, which would be 2 per atom. And you can again by taking the touching spear model.

You can work out that the maximum size of atom that can go in a tetrahedral, octahedral interstice would be equal to 0.2 to 5 of radius of atom host atom or 0.414 of radius of host atom. The derivation of these as well as the visualization of interstices of in HCP structure I will leave it to you, it is a simple exercise you refer to any elementary book on material science. And their you can see how these interstices are in most of the structure.

But, these interstices are important, because the concept of interstices important, because the concept of interstices important from the point of view understanding now what we are going to learn is a ceramic structure. So, specially tetrahedral and octahedral interstices in close packed for its which is FCC, HCP structure. I have shown you a layer sequence, where you can visualize octahedral or tetrahedral site. The direction and the location in the real unit cell, that you have to worked out yourself.

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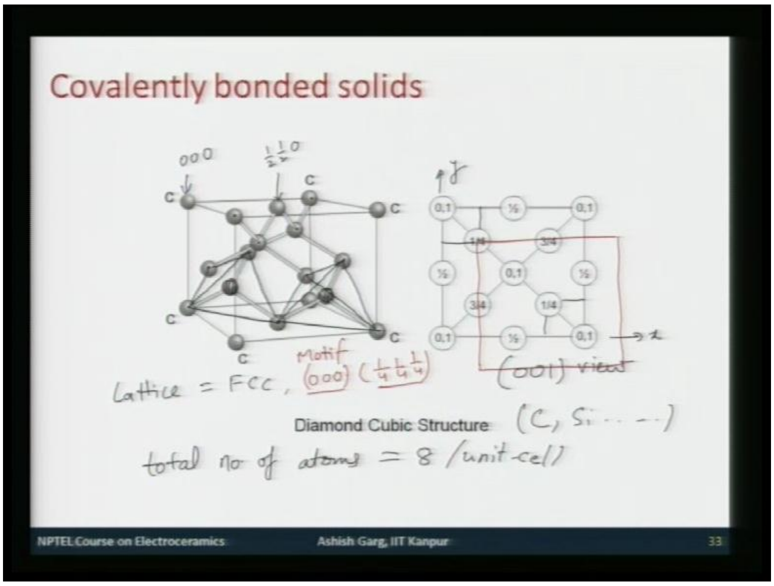

Covalently bonded solids

Lattice = FCC, Motif (000) ($\frac{1}{4}\frac{1}{4}\frac{1}{4}$)

Diamond Cubic Structure (C, Si . . . . .)

total no of atoms = 8 /unit cell

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So, the next thing now is, so these most of these structures are rise shown as their they are followed by metals. Now, covalently sole co covalently bonded solids such as diamond they follow diamond or silicon, they follow as structure which is called diamond cubic structure named after diamond. Here what happens is carbon atoms make a FCC unit cell where you have 6 of 8 of these, 6 phases occupied by 6 carbon atoms as well as 8 corner occupied by 8 carbon atoms.

And these now going for the previous topic you will have since you have FCC unit cell made by these carbon atoms total of 4 carbon atoms per unit cell, this will rise to 8 tetrahedral interstices. And these 8 tetrahedral interstices interstices would be occupied by 4 of these carbon atoms.

So, how do four of these carbon atoms arrange themselves is something like this, what happens is that; suppose this is your these are your corner 0, 0, 0 kind of locations these are your face centers half of zero kind of locations. I am not very particular coordinates here, but all of them all the face interstices are half of 0 kind of locations. So, first tetrahedral which can be formed is by combining 3 face centers, which are edges and faces with the most nearest with the nearest corner.

So, this is one corner for this, this would be one of the nearest one, nearest face center, this would be another nearest face center. And if I correct the all of these together this would make what is called as a your tetrahedral interstice. So, if I connect all these, so this is your tetrahedral at the center of these tetrahedral you have this another carbon atom.

So, this is one carbon atom, second carbon atom occupies the position tetrahedral position which is di diagonal opposite to this which is this locations, this is one carbon atom. Another carbon atom, another carbon atom, which is close to this atom sitting at the corner, another face centre carbon atom. If I again join these together and join with this, this again mix at hydra at the center of this tetra hydro you have this carbon atom. So, you have 2 carbon atoms in the tetrahedral sites along the face diagonal, diagonally to each other along the face diagonal.

And other 2 carbon atoms go in the top half of the lattice coordinated again in the same fashion, but rotated by 180 degree. So, the first two where coordinated by these atoms the tetra apex of tetra hydra was these atoms. And the other two will have tetrahedral which a has coordinated by these atoms in including the face centered atoms. So, this is the location of 2, other 2 carbon atoms and this kind of structure is a structure, which repeat itself in the space and maintenance the periodicity of the lattice.

So, a plan view which is which you can say a 0 0 1 kind of view. So, basically you are looking along the z axis of the unit cell or c axis of the unit cell. So, 0 1, 0 1 are the positions of these corner atoms half, half, half, half are the positions of all the face centered atoms. And 0 1 is again the face centered positions, but for these two top and bottom faces. So, you can see that, they are located half of 0 if this was your x axis, this was your y axis and 0 1 would be never the position which would be along z axis.

So, that tetrahedral sites one of the, so your bottom a two sites would be this is 1 by 4, this is 1 by 4 you can determine the position along x and y yourself. So, is should be for instance in this case it would be 3 by 4 and 1 by 4, in this case it would be 1 by 4 and 3 by 4. And the the position along z for both of these would be 1 by 4 and for these two which are the other 2 atoms a carbon atoms in tetrahedral sites it would be 3 by 4, 3 by 4 along z axis and x and x and y are self explanatory.

So, this is diamond cubic structure the packing factor of this is structure you can determine yourself the clue is the pa since the, if you remember the previous slide I showed, that the maximum size of tetrahedral atom that can go into tetrahedral site is 0.225 of radius of host atom.

In this case the size of tetrahedral atom is same as the size of the host atom which means structure is much more open. So, packing density of this structure is less as compare to a regular FCC structure again you can use the same touching sphere model and worked out what is the packing density. The total number of atoms now which are contain by 1 unit cell is 8, so total number of atoms would be 8 per unit cell and the structure is shown by materials like carbon, which is diamond carbon, silicon etcetera, etcetera.

And also the structure is shown by, so of this compounds like series in carbide which is a perfectly covalent bonded bonded solid is the the only difference is if this is silicon if you if your face centered lattice is made by silicon atom, the tetrahedral sites will be occupied by carbon atom or visa versa. Now, what would be the lattice type for this is structure, lattice type would be lattice would be FCC because carbon as a still making FCC lattice.

So, all the carbon atoms would make a FCC lattice, whether you put the corner of the unit cell here or here. So, what you can do here, so this is your first square if you keep your lattice corner here, then this is the FCC lattice I am keep the corner of the lattice here I can still make FCC lattice. So, if the corner of the unit cell was here then all these atoms, which were at 0, 1, half, half, 0, 1 they would become your tetrahedral interstices interstitial atoms.

So, no matter were you put the corner of the lattice also source. So, all types of co all all the corbonytal food make FCC lattice. So, your lattice type would still remain FCC with the positions as a positions of atoms could be at 0, 0, 0, if we define FCC lattice the motif would automatically be 0, 0, 0. This will automatically include all the positions at half of 0 the moment you define at has FCC. And the other positions other, so motif would be 0 0 0 as well as quarter, quarter, quarter.

Quarter, quarter, quarter would represent the the tetrahedral atoms and 0, 0, 0 would represent all the face centered cubic lattice atoms. So, this is your diamond cubic structure, the other structure which is followed by other; for example, other form of carbon itself which is graphite that is also covalently bonded solid.

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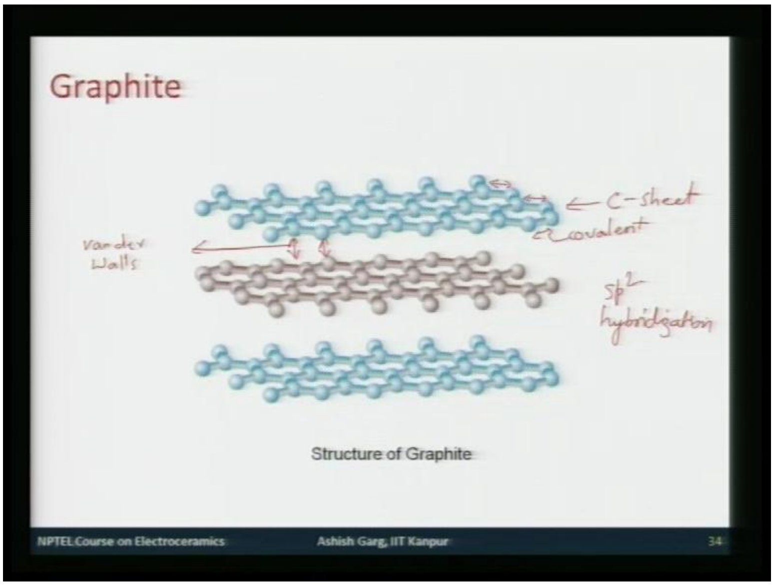

Graphite

Structure of Graphite

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So, in in in that particular structure you have these layers of carbon atoms you can say sheets of carbon atoms. So, this is carbon sheet, so within this sheet all these atoms are covalently bonded. And within the sheets the bonding is winder bolls or secondary bondings. So, as are a result what happens is graphite for example, is the very soft material within the sheet it is very strong, but the, but between the sheets the force are very week.

So, sheets can share against each other that is why graphite is a very good lubricant and this kind of bonding sequence is primarily because of a hybridization which is S p 2 hybridization in, so to fulfill the requirement of this S p 2 hybridization graphite adopts this kind of structure, which is partially covalent structure. Whereas in case of diamond a since diamond in the carbon atoms S p 3 hybridized carbon is forced to adopted tetrahedral coordination and giving rise to a diamond cubic kind of structure which is very hard structure.

So, well there are other covalently bonded solids could be your silicon carbide as I said it is similar to diamond cubic the only difference is you replace the either the face centered cubic atoms or the interstitial atoms with either cilicanor carbon. Now, most of the ceramic materials luckily or or luckily or incidentally are ionic ally bonded materials. So, you take. For example, sodium chloride, magnesium oxide, calcium fluoride (( )) oxide most of this ceramic material, which are useful for engineering applications.

They happen to be either completely ironically bonded or large character of bonding in these materials is ionic bonding. Now, ionic bonding typically, these are two compounds containing anions and cations and because at difference in the electronic activities as we discussed earlier, this primarily ionic bonding character rises. And when the these materials when these to ions support together they form of very strong ionic bond. And since anions happen to be bigger than the cations the anions tend to form the base lattice.

And since if we consider all these anions are as big as big spears they touch each other. And their still as we saw that close packing even if you even if you pack them as closest as possible you will still have empty spaces between them, which are either octahedral, tetrahedral spaces. And between them you have a these cat ion sitting. Now, an ion of course, cannot touch each touch each other because of columbic force of repulsion.

So, the distance between cations and anions such that, so that the electro static forces in the system are electro static energy of the system comes to a minimum. And a as a result the formation of structures in a ionic solids is governed by certain rules. And those rules are to give rise to established structure and this set of rules or guidelines are called as Pauling’s rules, so will go through these rules.

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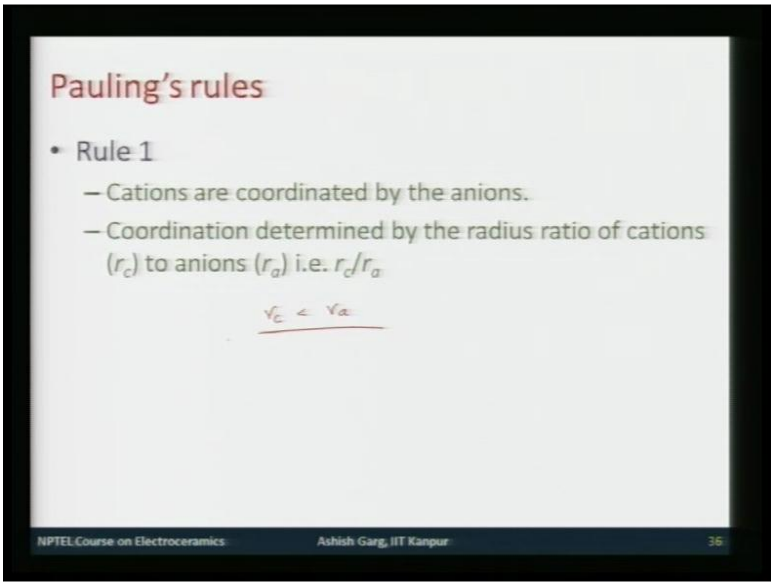

Pauling’s rules

- Rule 1
  - Cations are coordinated by the anions.
  - Coordination determined by the radius ratio of cations (r_c) to anions (r_a) i.e. r_c/r_a

$r_c < r_a$

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So, these these Pauling’s rules and so first rule for example, in case of Pauling rule is that since as I said that anions are bigger than cations a typically an ion. So, cat ions have to be coordinated by anions of I mean you can visualize in whatever way want you can you can say anions are coordinated by cation coordination is nothing but number of mirrors neighbors. So, but from the point from the prospective of formation of a lattice anions make the base lattice and cations go to the interest interstices and as a result cations coordination by anions.

And this coordination number on the number of nearest neighbor is determine by what is the radius radis ratio between 2 ions that is cation to an ion. And so radius ratio typically you would say since r c is smaller than r a you would see that for most of the structure this this this will whole true, but there is a range. So, depending upon what the ranges are various different kind of coordination are preferred, so for instance you can see here.

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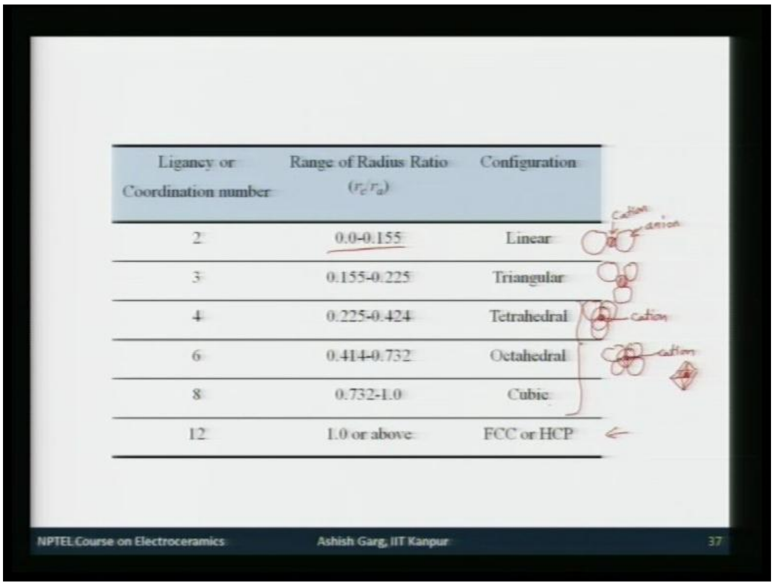

Ligancy or Coordination number	Range of Radius Ratio (r_c/r_a)	Configuration
2	0.0-0.155	Linear
3	0.155-0.225	Triangular
4	0.225-0.424	Tetrahedral
6	0.414-0.732	Octahedral
8	0.732-1.0	Cubic
12	1.0 or above	FCC or HCP

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That when the radius ratio is between smaller than 0.155, which is the an ion is very small as compare sorry cation is very small as compare to an ion. The configuration happens to be linear which means you will have coordination like this, this is your cation and this is your an ion. To fold coordination or coordination number of 2, when your radius ratio is between 0.155 and 0.225, then the coordination happens to be triangular.

So, in this case if you have, so this is your, so this will be your coordination for example, in this case and when you have radius ratio between 0.225 and 0.24 to 4 then the coordination happens to be of tetrahedral in nature. Tetrahedral coordination you are aware of, so you have this cations anions like this and in between you will have cation here I am making touching is fears thing. But in most case in in ceramic structures these anions own be touching each other, because otherwise the electro static reposition will be huge.

So, job of cations you can say in some sense is also to keep this anions a part from each other. And if the radius ratio is between 0.414 to 0.732, then the coordination tense to be octahedral or 6 fold coordination. So, octahedral coordination would be something like this, so this is top as well as bottom cation and in between an ion and in between you will have cation. So, this will make a body like this, this would be in the middle you have a cat ion and then if if radius ratio is really large as large as 0.7321, then the coordination happens to be cubic or 8 fold.

And the and when the cat ion is almost as big as the an ion it happens to be FCC or HCP type of coordination or 12 fold of coordination. So, in in reality you you this is not very common, but and what you see that most of the radius ratios sit these 3 kind of coordination's. These are actually guidelines they are not very strict rules in some cases rules these radius ratios are the boundary line cases can fall any where.

And some times these rules are not followed exactly and that could be because of a certain pre preference for certain kind of coordination due to nature of bonding. So, especially in case of covalently solids the bonding tense to determine the coordination than the radius ratio. So, so these are more or less guidelines than strict rules.

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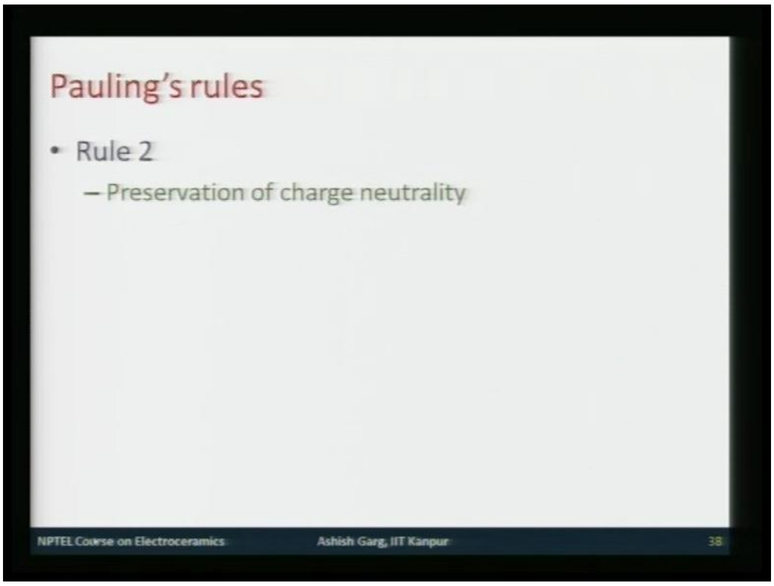

Pauling's rules

- Rule 2
  - Preservation of charge neutrality

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Second rule of Pauling is no matter what you do when I ceramic structure is formed from a come it has to maintained the stoichiometry and it has to maintain the charge neutrality. Stoichiometry as you will see may know may or may not be followed some cations or anions can go missing or whatever. But a the charge neutrality has to maintained in all cases, which means number of charges carried out by this is called as electrostatic Williams rules number of charges due to anions must be equal to number of charges due to cations.

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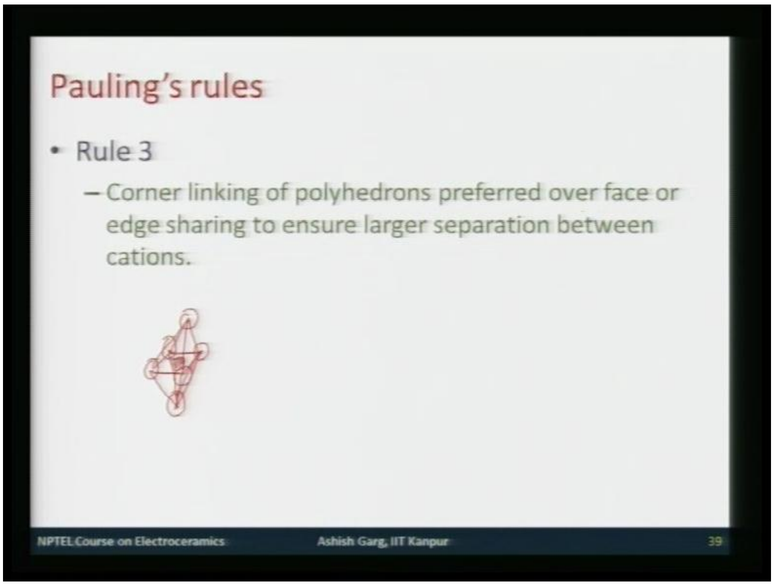

Pauling's rules

- Rule 3
  - Corner linking of polyhedrons preferred over face or edge sharing to ensure larger separation between cations.

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The third rule is in this case is the polyhedral that are formed as a result of coordination corner linking of these polyhedral is preferred over face or edge sharing. Now, this as you can understand if they are connected at the corners. So, for example, if you have octahedral, so this is for example, octahedral. So, these octahedral are sharing each other at the corners, the separation between the like ions would be, so if suppose these are your this your cation and these are your anions if these are linked at the corners.

Then cornel linking with will give rise to largest separation between the like ions, which means the minimum electro static repulsion. So, corner linking is preferred over either face or edge sharing, because the lantern these two kind of face or edge sharing tense to bring these ions close at to each other, which may not be very favor favor scenario. So, corner linking is a more preferable scenario.

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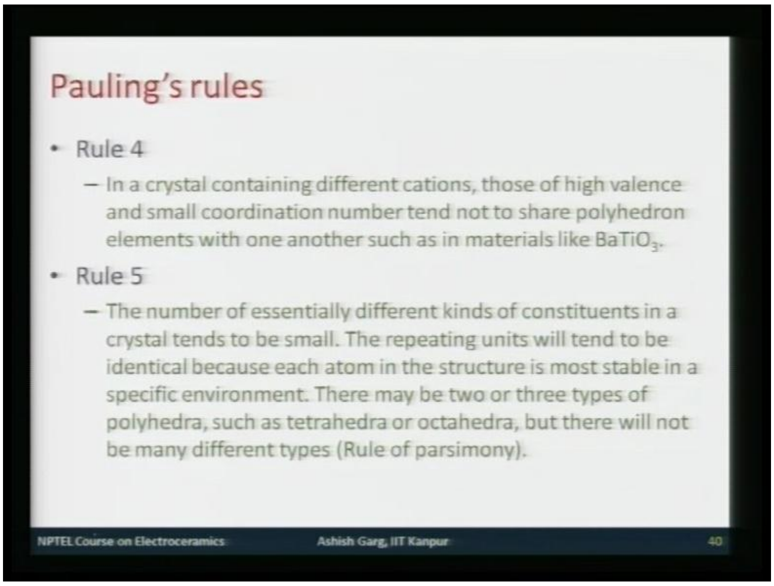

Pauling's rules

- Rule 4
  - In a crystal containing different cations, those of high valence and small coordination number tend not to share polyhedron elements with one another such as in materials like $BaTiO_3$.
- Rule 5
  - The number of essentially different kinds of constituents in a crystal tends to be small. The repeating units will tend to be identical because each atom in the structure is most stable in a specific environment. There may be two or three types of polyhedra, such as tetrahedra or octahedra, but there will not be many different types (Rule of parsimony).

And the the forth guideline of forth rule is that crystals, which contain various different cations, cations of different wiliness the the polyhedral which are made by for instance elements like titanium in barium titanide, which happen to high wiliness cations high wiliness. And small coordination number cations as a result of their small sizes, they do not tend to share these polyhedrons with one another such as in for polyhedral, which are made by titanium are not shared by polyhedral which are made by barium.

And the rule five is rule of parsimony. So, as you can understand from the word parsimony itself the number of basically different kinds of constituents in any crystal, this number tense to be very small, which means, which also means that the repeating units in the structure will will be more or less similar of will be identical, because each atom in this is structure will prefer a particular environment.

So, they may be as a result of this this particular condition there are not too many different kinds of polyhedra which has formed for instants you may have formation of tetrahedral. And octahedral such as in as you will see in spinal structure, but they not too many different kind of polyhedral which are formed in these structures.

So, these are basically five guidelines which are suggested by Pauling towards a formation of ceramic crystal structures in general radius rule is is more or less a most followed rue that that you can see much more easily as compare other rules. Of course, electrical neutrality has to be maintain and as you will see that corner linking and sharing of polyhedral and number of polyhedra that is not, so explicit, but you will have to see from structure to structure to structure.

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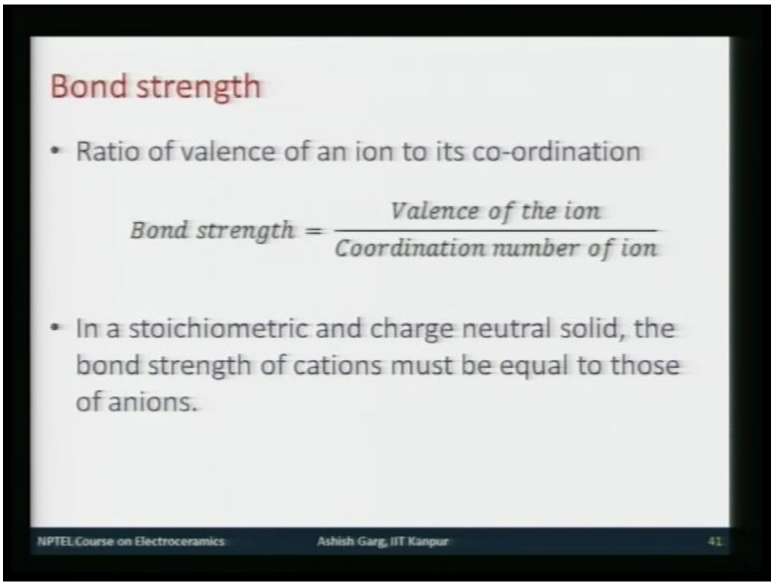

Bond strength

- Ratio of valence of an ion to its co-ordination

$$\text{Bond strength} = \frac{\text{Valence of the ion}}{\text{Coordination number of ion}}$$

- In a stoichiometric and charge neutral solid, the bond strength of cations must be equal to those of anions.

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And other thing that sometimes helps you to work out the stoichiometry correctory to know whether stoichiometry that you have used this correct or not is bond strength. Now, bond strength is basically ratio of valence of that a particular ion divided by the coordination number ions, if you have cat ion valence of cations divided by coordination number of cation, which means how many anions around the cation.

And in stoichiometric as well as a charge neutral solid the bond strength of cations must be equal to that of anions, this is if the if you get it if you get this write which means your stoichiometry is correct. So, when you when have various coordination numbers you can cross check, whether you got the correct structure not by using this particular concept. So, now, we will what we will do is that, we will move on to various different kind of ceramic structures.

Fortunately, for us there are not too many a different kind of ceramic structures happen to be simpler than we expect, as we know that there are many 7 different kind of crystal systems 14 by by lattices and specially structures like triclinic or monoclinic can make our life much more difficult. But what happens is that most of the useful material tends to show structures which are simpler.

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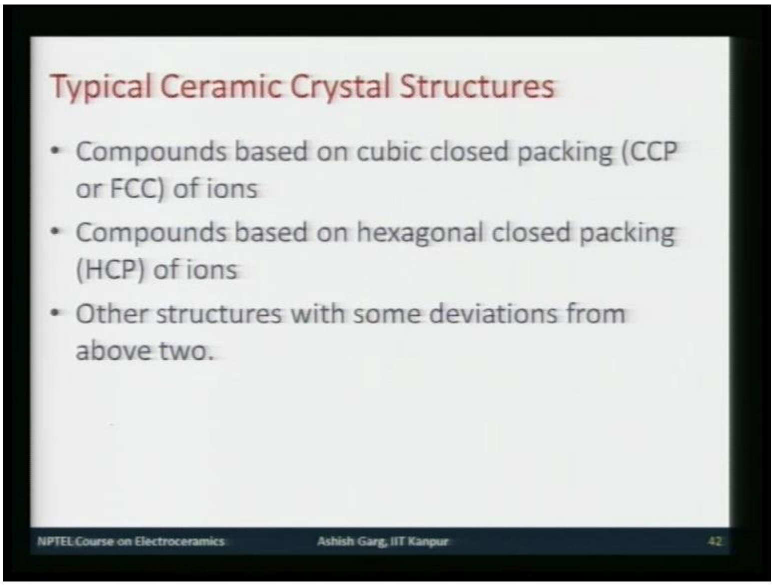

Typical Ceramic Crystal Structures

- Compounds based on cubic closed packing (CCP or FCC) of ions
- Compounds based on hexagonal closed packing (HCP) of ions
- Other structures with some deviations from above two.

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By end large we can divide the ceramic structures into 3 categories the structures can be there are compounds, which have a structures based on cubic close packing of anions or CCP or FCC packing of anions. There are compounds, which have their structures based on hexagonal close packing or HCP packing of anions and there are some deviations from these two such as a cubic packing of anions etcetera; as we will see in subsequent slides. So, first we will look at the structures which are based on cubic close packing of anions.

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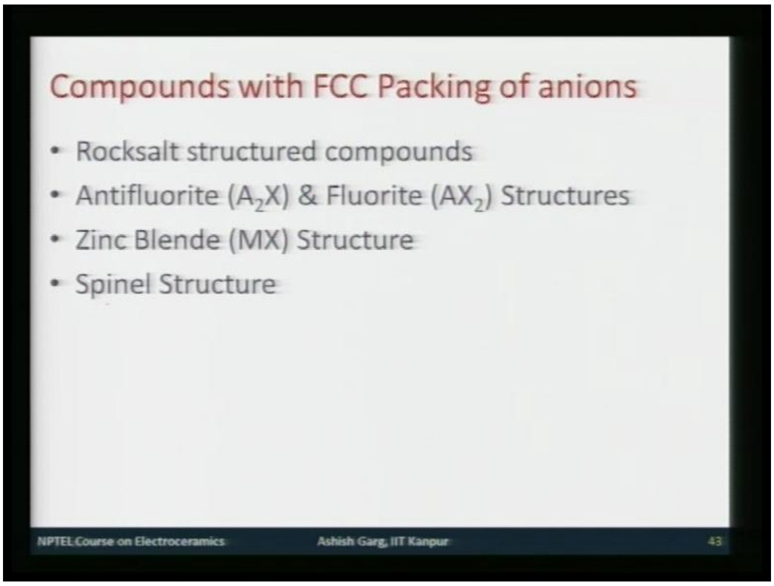

Compounds with FCC Packing of anions

- Rocksalt structured compounds
- Antifluorite (A_2X) & Fluorite (AX_2) Structures
- Zinc Blende (MX) Structure
- Spinel Structure

In this category there are I will discuss these commune structures, I will discuss the structures, which are based on rock salt or sodium chloride. So, rock salt is structure compounds and then I will discuss the anti fluorite or fluorite structured compounds for example, calcium fluorite or zirconium oxide or lithium oxide. The zinc blend structures such as zinc oxide or zinc sulphide based structures.

And then a spinally structures, which are basically spinals are your ferrites kind of structures which are basically many of your magnetic materials follow this structure. So, first we will have a look at the sodium chloride or rock salt structured compounds.

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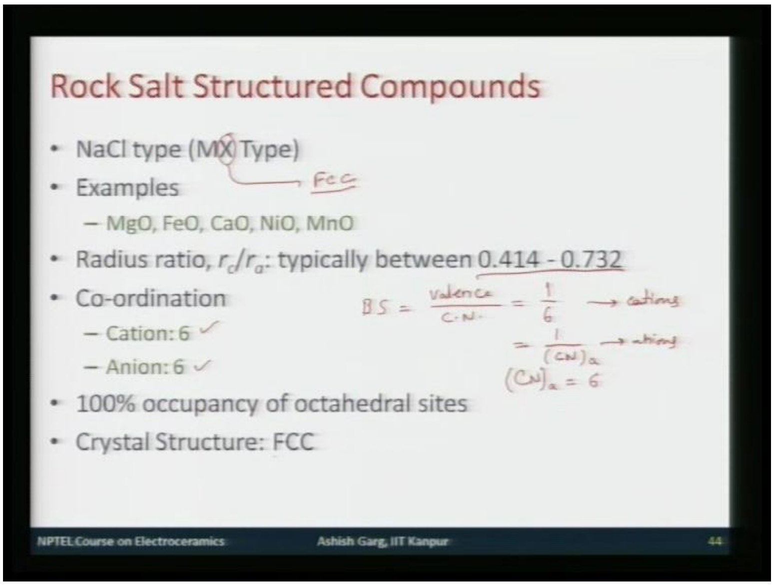

Rock Salt Structured Compounds

- NaCl type (MX Type)
- Examples
  - MgO, FeO, CaO, NiO, MnO
- Radius ratio, r_c/r_a: typically between 0.414 - 0.732
- Co-ordination
  - Cation: 6 ✓
  - Anion: 6 ✓
- 100% occupancy of octahedral sites
- Crystal Structure: FCC

FCC

$$B.S = \frac{\text{valence}}{C.N.} = \frac{1}{6} \rightarrow \text{cations}$$

$$= \frac{1}{(CN)_a} \rightarrow \text{anions}$$

$$(CN)_a = 6$$

Tees structures have stoichiometry which is M X type which means for each cation you have 1 ion or each an ion. So, the, so ratio of cat ion number of ions cations to anions is same and and the parents structure is sodium chloride, that is why most of these compounds are also called as rock salt structure or sodium chloride type compounds. The examples can be your magnesium oxide, iron oxide, calcium oxide, nickel oxide, manganese oxide, many transition metal oxides follow this particular structure.

So, as a result this happens to be very important, but simple structure., typically in these structures the radius ratio were is between 0.4142, 0.732, if you go back to Pauling's rule this gifts price to 6 fold coordination of cations, which means each cation is coordinated by 6 anions. Now, from the bond is strength rule, bond strength, so you have bond strength was equal to valence divided by coordination number right.

So, in this let us say take example of sodium chloride, so was I said was for a stoichiometric compound and charge neutral compound bond strength of both an ion and cation has to be same. So, for since I know based on various ratio that the coordination of cat ion is 6 which means for sodium chloride this would be 1 by 6. What does means is that the coordination number of anions should also be 6 to maintain this equality, because for anions.

So, this would be for cat ions, for anions again the valence I know, because of formula. So, valence of an ion is also 1, coordination number of an ion I do not know let us say. So, this is for anions C N of a. Now, if these two are equal which means C N of a must be equal to 6, which means anions and cations both must have 6 fold coordination, in order to maintain the stoichiometry and charge neutrality.

And so based on this radius ratio 0.4142, 0.732, 6 fold coordination is nothing but octahedral coordination, which means which simply means that, if now I am saying that these structures are FCC based on FCC packing of anions which means all these anions. So, x x atom makes FCC kind of lattice and in these FCC lattice, we know that this structure will contain 4 octahedral sides which or 1 octahedral side per atom.

So, based on the stoichiometry 100 percent occupancy of octahedral sites is obtained, which means all the octahedral sides is obtained, which means all the octahedral sites are filled and crystal structure is nothing but FCC type. So, we will see how this structure formed.

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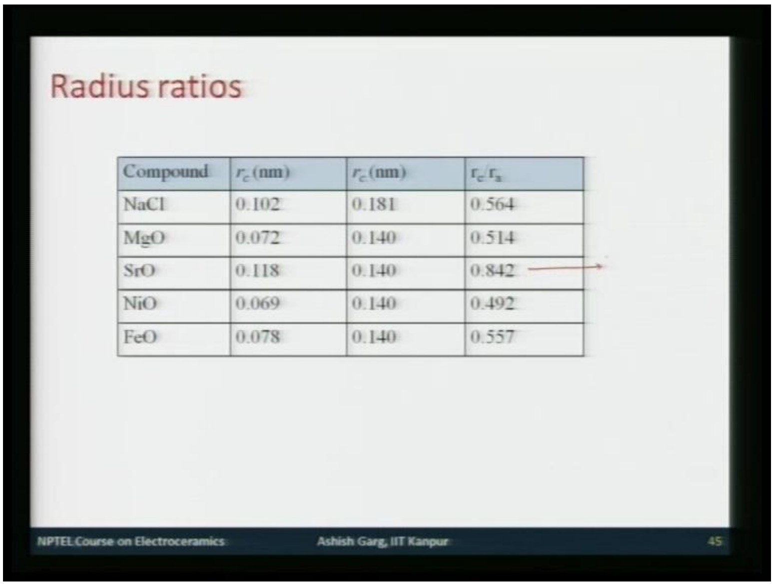

Radius ratios

Compound	r_c (nm)	r_c (nm)	r_c/r_a
NaCl	0.102	0.181	0.564
MgO	0.072	0.140	0.514
SrO	0.118	0.140	0.842
NiO	0.069	0.140	0.492
FeO	0.078	0.140	0.557

So, these are some of the radius ratios for various compounds and as we can see that the examples which are shown here are more or less between the predicted once accept with the acceptation of (( )) oxide. But as I said these are mainly guidelines they are not strict rules that these have to be followed there are some deviations sometimes.

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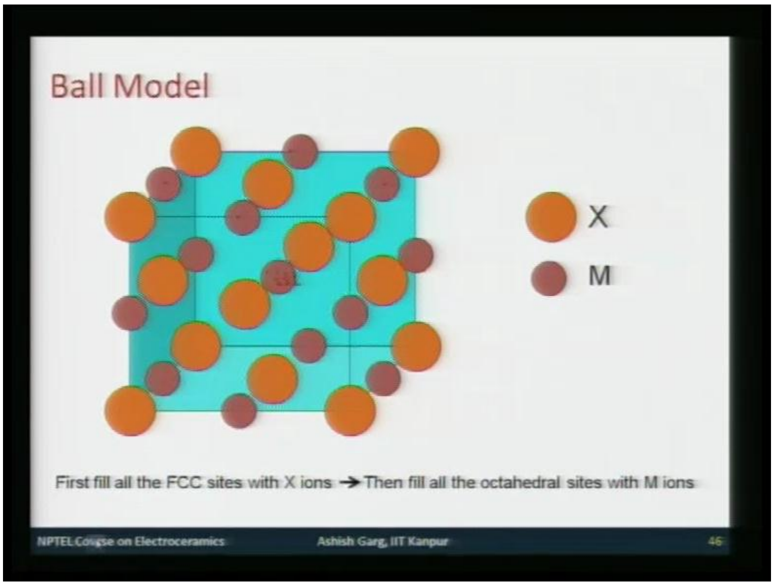

Ball Model

First fill all the FCC sites with X ions → Then fill all the octahedral sites with M ions

And, so that way this is structure is formed, so this is for example, taking a ball model concerting each atom as a hard ball. So, you make a cubic lattice, so this is the cubic unit cell. So, first I fill all the FCC sides with x or x ion or anions. So, what are the FCC sides, FCC sides are all the corners as well as the face centered of the unit cell. So, these are all FCC sides filled with all x type of ions.

Then what I do is that I fill all the octahedral sites with m ion were are the octahedral sites octahedral sites for this structure one would be at the body center, which would be at half, half, half; and others would be at the edges. Now, there are total of twelve edges twelve edges means they are shared by each edges shared by 4 unit cells which means total effectively 3 edges. So, 3 plus 1 total of 4 sites all these sides are, now occupied by cat ions these are the cations which fill all the octahedral site. So, this makes a sodium chloride type of structure.

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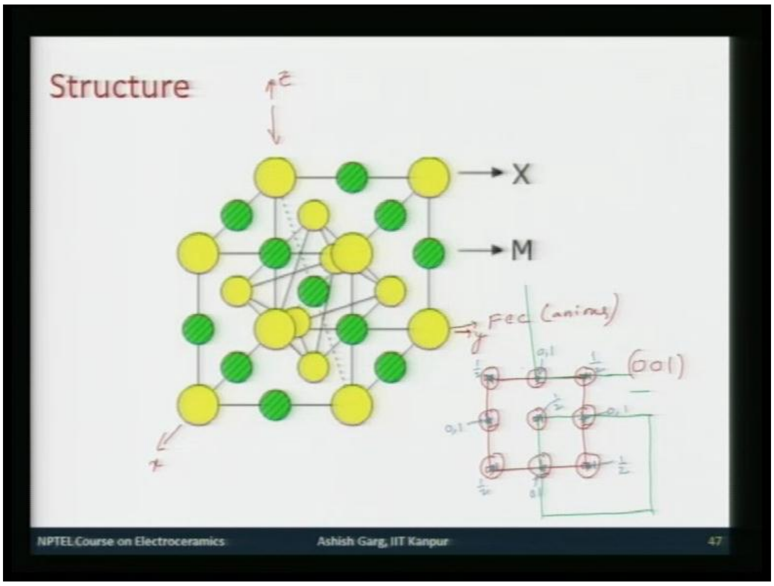
Structure

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So, you can see now that this is the center polyhedral or octahedral form by the cat ions and from from there is anions and cations occupy the octahedral sides Now, question is now the question to ask is, what is the lattice type this is structure must have? I am saying that anions are making FCC lattice and all the cations are occupying octahedral site.

So, what should be the lattice type, lattice type is always FCC, what it means is that crystal graphic crystal graphically whether you make FCC, lattice considering anions or considering cations lattice in both cases will remain FCC lattice. So, what it means is that basically if you make a plan view of this. So, what what I am what may want to now see is that let us say if anions make FCC lattice and cations go to octahedral side then what is the lattice type. Lattice type will always be your FCC lattice.

Because, let us say if you draw this plan view and in this plan view or 0 0 1 plain view, which means we look along the, we look along this direction if this was your x, this was your y and this was your z axis. So, we look along 0 0 1 direction on the 0 0 1 plain. So, these would be your anions. Now, here I can see the x y positions very clearly, so all I need to do is that I need to note down the z z position. So, this would be 0 1, this would be half, this would be 0 1, this would be half, this would be 0 1, this would be half, 0 1, 0 1 and half, this are all anions.

Now, where do cations go, cations go at the center of edges and the center of the unit cell 1 cation goes here, but what we will the location at z it would be half and another cations go here and all the centers of all these vertical edges. So, again the position would be half z is equal to half x y to you can see, x y is not very difficult to find out and all the other cations will go at these locations again x y positions, you can see and z positions of these are 0 and 1 0, 1, 0 1, 0 1 and all these are half, half and half.

So, you can see very easily that when cut when the an ion is at 0 1 cation is at half and when the cation is at 0 1 and ion is at half it is very simple to see. Now, what you can do is that, now you can change this, change the position of this unit cell. So, instead of taking the corner here, I can take the corner here right or I can take the corner here, here I can just shift it. So, what I am doing basically is I am just shifting the corner of the unit cell.

So, you will find your self that earlier 0 1 was an ion at the corner, now at the corner 0 1 is cat ion. So, matter what you do is that lattice will always remain FCC and you can say that this is a structure in which 2 FCC lattices 1 made by cat ion and 1 made by an ion inter penetrate into each other with 6 fold coordination both cation and an ion preserved.

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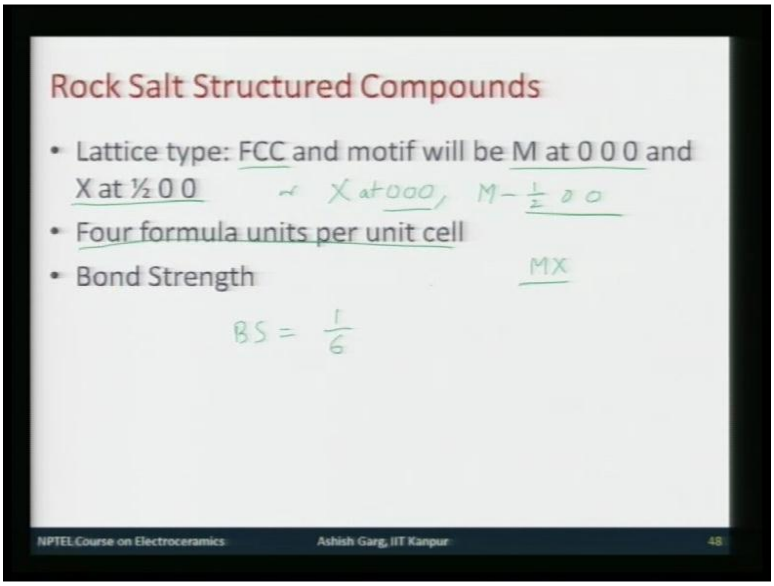

Rock Salt Structured Compounds

- Lattice type: FCC and motif will be M at 0 0 0 and X at ½ 0 0 ~ X at 000, M – $\frac{1}{2}$ 0 0
- Four formula units per unit cell
- Bond Strength MX

$BS = \frac{1}{6}$

So, lattice type for this particular kind lattice would be always FCC and motif will be at if you if you consider metal at 0 0 0 which means metal at all the face centered positions.

Then cat ion will be at half 0 0 or if you say x at 0 0 0 then metal will be at all the half 0 0 positions. Now, all the half 0 0 positions and all the 0 0 positions for FCC lattice would automatically mean all the FCC write of positions. And if you cough the number of formula units since each FCC lattice contains 1 4 type of atom 4, 4 atoms.

So, in this case motif is since motif is M X it will contain 4 M X formula unit per unit cell and you can verify this again using bond strength as I said bond strength would be 1 by 6 for both cations and anions and this can prove whether you maintain the stoichiometry.

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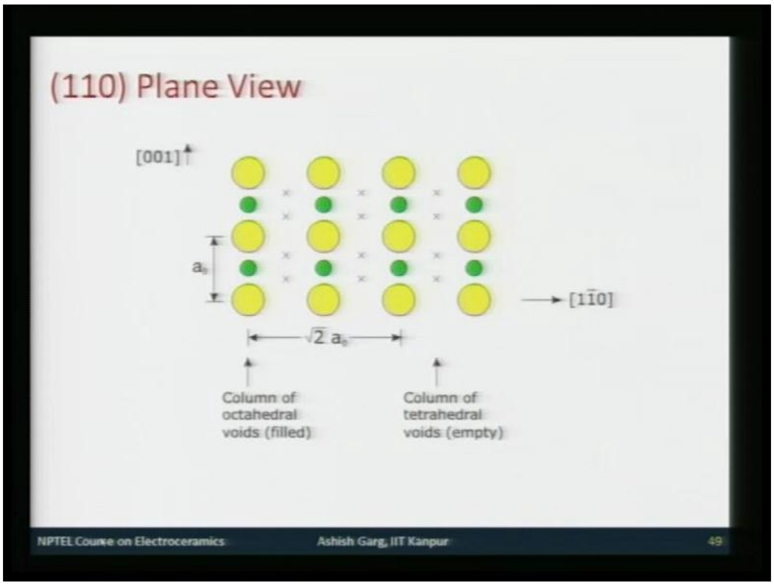

(110) Plane View

Column of octahedral voids (filled)

Column of tetrahedral voids (empty)

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Now, you can do you can play round with this is structure for instance you can draw apply and view of 0 0 1 plain view. Now, I am looking down the 0 0, 1 1 0 plain of the structure. So, if you do that then this direction would be 0 0 1. So, if you go to previous slide 1 1 0 would be this particular plain, this would be your 1 1 0 plain. So, these are corners and one thing you must remember that both these yellow or atoms are of same size just for the sack of illustration they are made of different size, otherwise they at same type of atoms.

So, here you can see that these if if you draw this 1 1 0 kind of structure and based on the lattice parameter, this distance let us say a naught. So, this would be your 1 plane, plane within 1 unit cell. So, if this distance is a naught this would naturally we route of a naught and you can see since all the octahedral sites of field all the columns, which are empty columns here they are nothing but columns of empty tetra hydro cites and these are columns of octahedral voice which are filled. So, this is another way of looking at the structure, another way of playing around with the structure to enhance the understanding.

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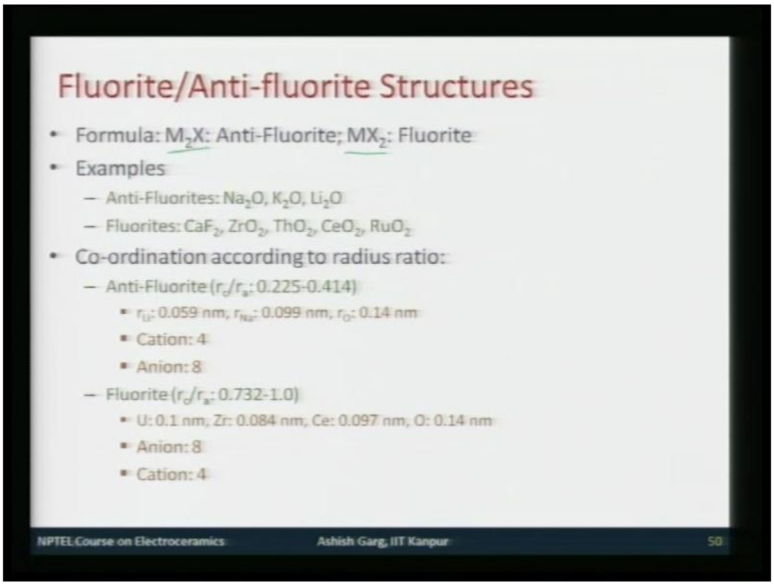

Fluorite/Anti-fluorite Structures

- Formula: M_2X: Anti-Fluorite; MX_2: Fluorite
- Examples
  - Anti-Fluorites: Na_2O, K_2O, Li_2O
  - Fluorites: CaF_2, ZrO_2, ThO_2, CeO_2, RuO_2
- Co-ordination according to radius ratio:
  - Anti-Fluorite (r_c/r_a: 0.225-0.414)
    - r_{Li}: 0.059 nm, r_{Na}: 0.099 nm, r_O: 0.14 nm
    - Cation: 4
    - Anion: 8
  - Fluorite (r_c/r_a: 0.732-1.0)
    - U: 0.1 nm, Zr: 0.084 nm, Ce: 0.097 nm, O: 0.14 nm
    - Anion: 8
    - Cation: 4

Now, the next structure in this series is fluorite and anti fluorite structure both are similar structures with with the the change in position of cations and anions that is why they are called as fluorite or anti fluorite inverses structures, fluorite is inverse of anti fluorite. The formula unit for this anti fluorite is M 2 X and for anti fluorite it is M 2 X and for fluorite M X 2. And the examples that you see in practice, anti fluorite are sodium oxide, potassium oxide, lithium oxide typically you have assembly charges cation two simply charge cations with 1 an ion which is oxygen.

And fluorite structures are they are called as fluoride, because they are based on calcium fluoride, which is a parent structure, but other compounds could be zirconium oxide or cerium oxide or ithenium oxide, etcetera all these are fluoride structure. Now, if you worked out the coordination according to radius ratio what you will see that in the anti fluoride structure. The radius ration of cat ions to anions worked out between 0.225 to 0.414, what is this translate to this translates to 4 four coordination of cation as predicted by Pauling's rules.

Now, if coordination of cation is 4 based on the bond strength rule and based on the stoichiometry coordination of an ion has to be 8 right. Because each ion is surrounded by for each ion you have to cation. So, if cat ion is surrounded by 4 anions anions has to be surrounded by 8 cations. So, this is again based on the bond balance rule. And for fluoride structure these are some of the examples sorry for anti fluorite structure this is lithium radius, sodium radius iron radius oxygen radius you can worked out the radius ratios.

For fluoride structure red the radius reduce predict about 0.7321 and this gifts rise to 8 fold or cubic coordination of anions. And again to maintain the stoichiometry as per bond valence rule the the coordination of cat ions has to be 4. So, this is felly simple to work at out you can do on the bases of 1 valence rule.

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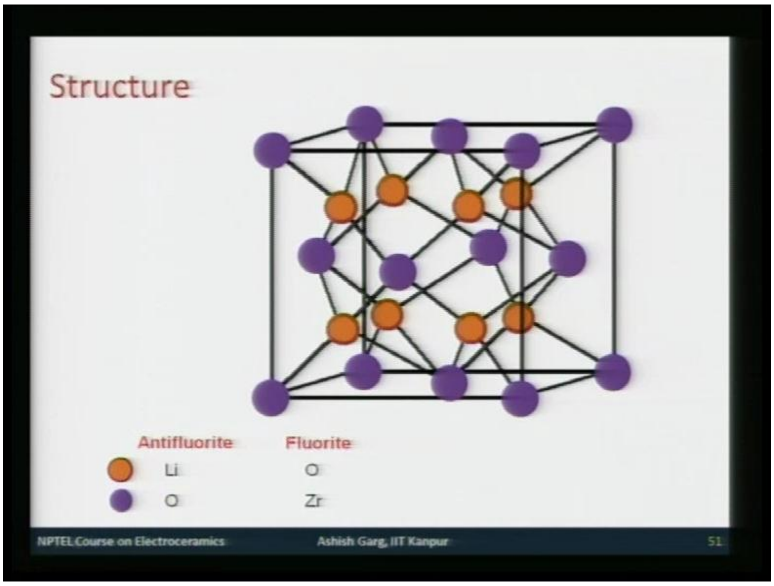

Structure

	Antifluorite	Fluorite
🟠	Li	O
🟣	O	Zr

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And the structure is like this, for anti fluorite material a structure material oxygen or let us say the anions make FCC lattice fine. And the cat ions as we know the coordination number must be 4, 4 coordination in FCC lattice is only tetrahedral coordination. And since you have 2 cat ions for each an ion and you know that FCC structures contain 8 tetrahedral side 2 per atom, which means you have 8 tetrahedral sides to be filled by 8 tetra 8 cations.

So, all the cations in this is structure occupy all the available tetrahedral interstices this will make your thru anti fluorite structure. The fluorite structure is opposite to it, in fluorite structure what happens is, in fluorite structure now this universal color now. So, all the face centered positions are occupied by cations and all the interstitial tetrahedral positions are occupied by anions. So, this is why it is called as fluorite anti fluorite structure, because of this inverse nature of position occupied by cations and anions.

However, since we know that anions are typically bigger that cat ions the base lattice has to be made by the the an ion. So, you can very well see that in case of anti fluorite structure, if this is your cation, cation is surrounded by 4 anions and since each unit cell has 8 corners each cation will be surrounded by each anion will be surrounded by 8 cations. So, this maintenance stoichiometry, in case of fluorite structure again you can use the same logic, each an ion is occupied by 4 cations and each cat ion is occupied by 8 anions, which is cubic coordination.

Now, the question is how to represent this lattice for fluoride structure such that it is made. So, such that we make the base lattice by anions and then fill the voids within this base lattice by cations that works out to be slightly different.

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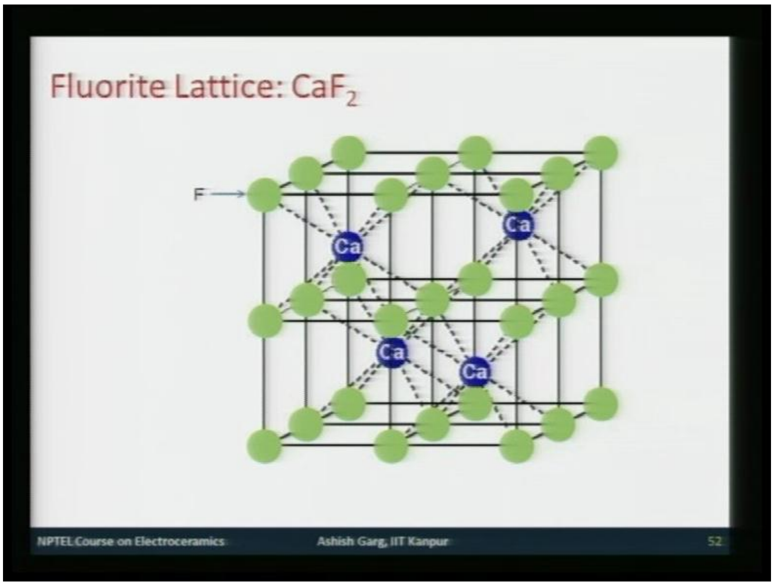
Fluorite Lattice: CaF_2

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Now, in this case what we do is that we know that coordination of cation is cubic coordination, which means each cation surrounded by 8 anions. So, what we do is that now we know that in 1 cube you can fill only 1 such whole so which means what we do is that to make a proper repeatable lattice, we make 8 we put 8 of these cubic lattices made by anions together. So, you put you make a big cube made by 8 cubes of anions 4 on top, 4 on the bottom and then you fill in the in the top layer two diagonally opposite centers of 2 small cubes.

And the bottom layer again 2 diagonally opposite center of 2 small cubes, but in the opposite orientation as in the first layer. So, if in in the top layer the front left and the front left and the right back connect with each other, in the bottom layer front right and left back they connected with each other. So, this makes a lattice, which is repeatable in a space. So, now, you can see that what is the, so this is correct representation of the lattice because the base lattice is now made by anion and the interstitial sites are filled by cations.

And again the stoichiometry, now again the what is the lattice type, lattice type will again remain FCC. So, whether you make the corner of unit cell on anions, whether you make on cat ions a lattice will always remain FCC. The only difference here is here since you have 2 2 anions or 2 act ions for each an ion or cat ion depending upon what structure you consider fluorite, anti fluorite. So, basically you have 3 FCC lattices 2 of 1 ion and 1 of 1 ion another ion inter penetrating in to each other.

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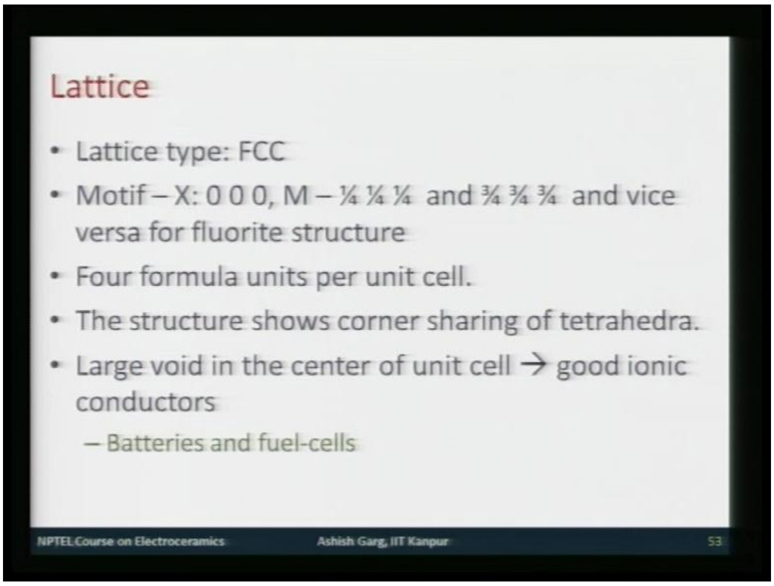

Lattice

- Lattice type: FCC
- Motif – X: 0 0 0, M – ¼ ¼ ¼ and ¾ ¾ ¾ and vice versa for fluorite structure
- Four formula units per unit cell.
- The structure shows corner sharing of tetrahedra.
- Large void in the center of unit cell → good ionic conductors
  - Batteries and fuel-cells

To let us type will be FCC the motif would be again, if you consider for the structure were anion makes the FCC that is an cat ions occupy the tetrahedral sides. Then it would be the motif for that structure, which is the anti fluorite structure and if and the visa versa would be true for you just replace X M each other it would be true for fluoride structure. And if you count the number of formula units, it would be 4 formula units per unit cell.

And you can see in this is structure you can prove to yourself that you have corner sharing of tetrahedral in the N a C l structure you can also prove that this is corner sharing of octahedral. So, again in this corner sharing rule of Pauling is favored here. And this these structure you can see the there is a big void in the center of unit cell, if you if you look at that structure there is big void in the center of this unit cell nothing is occupied their. And this big void can be useful for good ionic conduction.

So, for example, material like zirconium oxide they show good conduct ionic conductivity and that is why there are used in applications like batteries and fuel cells.

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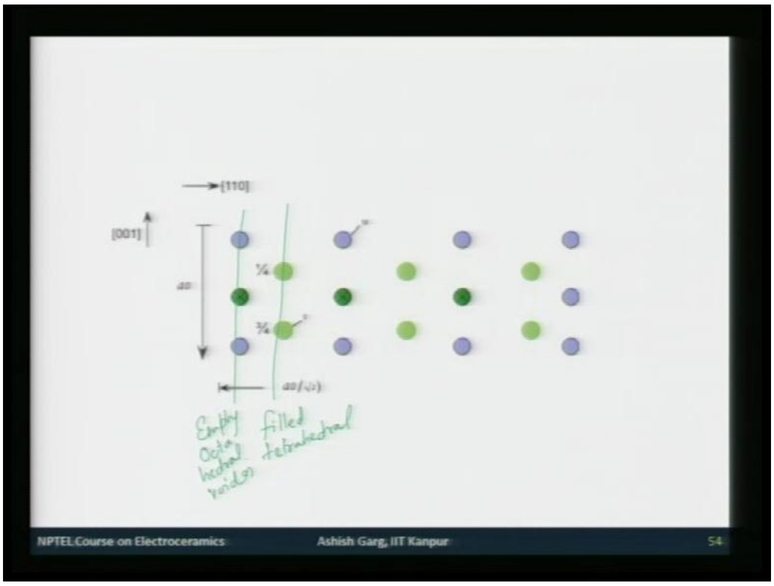

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You can again play round with structure, so again unlike sodium chloride structure in this is structure you have columns of filled tetrahedral voids and alternative and columns of empty octahedral. So, this is filled tetrahedral voids and this would be empty octahedral voids, these are the games that you can play with these structures. So, this is were I will end lecture today in the next lecture we will look at that remaining FCC packed structures of ceramic various ceramics and other structures like those which follow non FCC and HCP kind of packing.

Thank you.