An Introduction to Materials: Nature and Properties
(Part 1: Structure of Materials)
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Lecture - 26
HCP Based Structures

So, we have this lecture 26 today.

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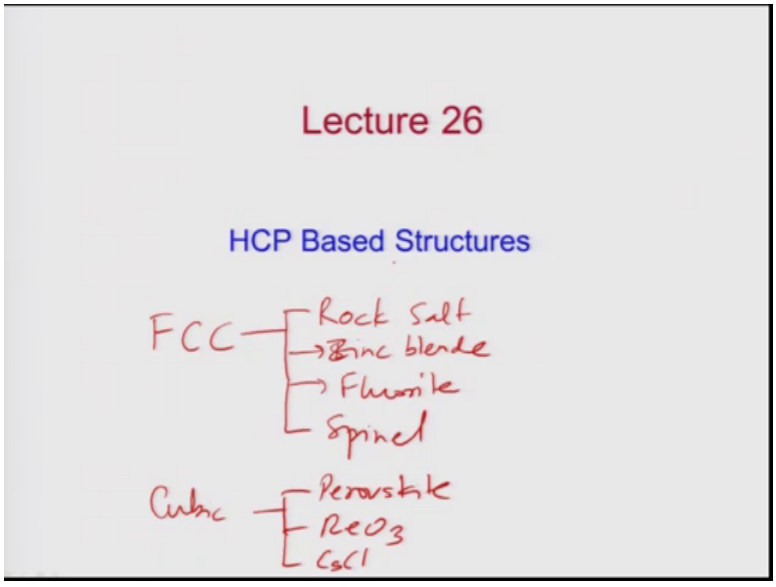

Starting, continuing the same things that we are talking about in the previous lectures about structure of ceramic materials. So, in this case we throw into; so today we are going to talk about materials which are at HCP Based Structures which are based on a HCP packing of anions. So, so far what we have discussed is basically the structures which are based on FCC packing of anions, so we looked at all the structure such as rock salt, zinc blend, and fluorite and finally spinel.

And then we looked at other structures which were cubic in nature. So, we looked at Perovskite, we looked at Reo 3 structure, and we looked at finally CsCl structures. And following this we talked about structures which are non cubic in nature, such as those followed by compounds such as YB Cu and l s c o and the (Refer Time: 01:24) all that, which are basically superconductors,, ferroelectric oxides, which have orthorhombic tetragonal structures, but they are based on Perovskite unit or NaCl unit.

So, in this lecture we will talk about structures which are based on hexagonal close packed packing of anions. So, basically what happens in these structures is that, anions make the hexagonal lattice, close packed lattices and cations occupy the interstices in them. So, depending upon the ratio of radiuses between the two they occupy either tetrahedral or octahedral interstices, as we have seen earlier also in case of Fcc.

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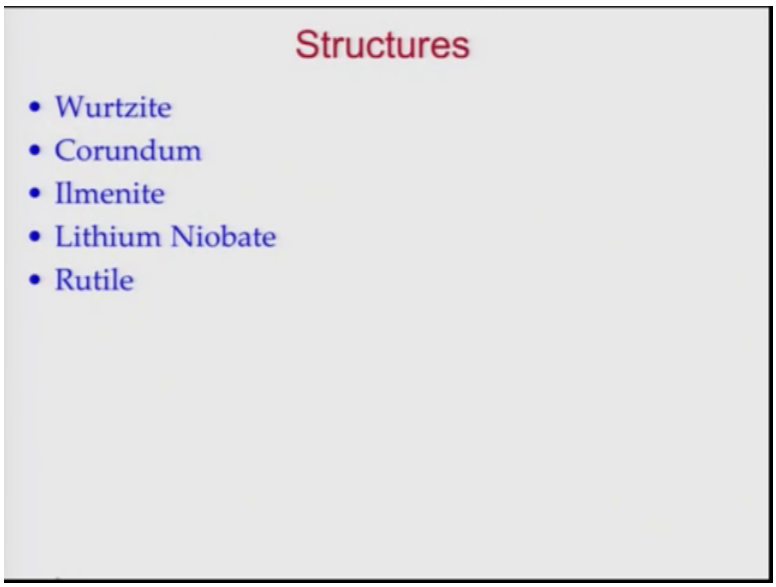

So, moving to the next slide, the common structures that we are going to discuss in this category are Wurtzite structure, Corundum structure, Ilmenite, Lithium Niobate and Rutile based structures.

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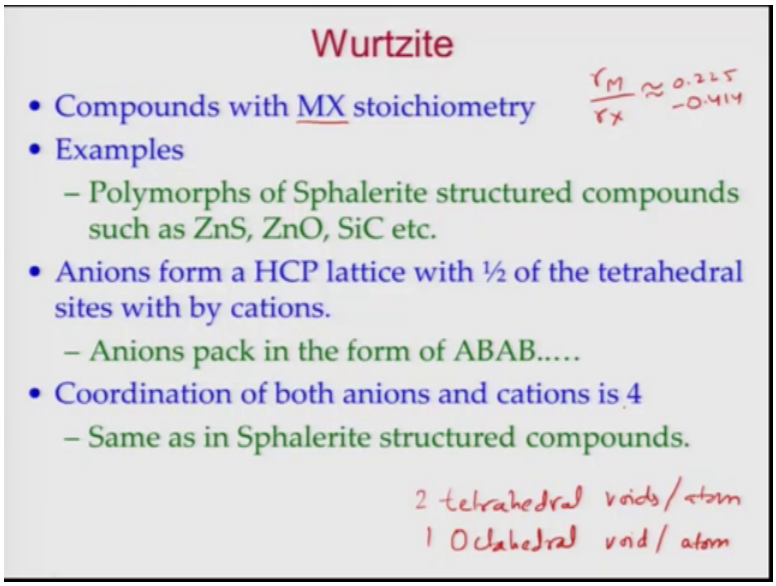

So, let us first discuss Wurtzite based structure. Wurtzite is the mineral name. It is basically the compounds with stoichiometry in which cation and anion are present in 1 is to 1 ratio, basically MX type of compounds. And there are various examples which follow the structures and they happen to be many of them happen to be Polymorphs of Sphalerite or zinc sulfide based zinc blend structures. So, zinc sulfide itself exist in both zinc blend and cubic zinc blend and hexagonal Wurtzite form.

Similarly, zinc oxide, zinc silicon carbide in many other compounds; I will show you table at the end, showing the examples of various materials in each of the category.

So, in this case anions form a hexagonal close packed lattice. So, if you have a hexagonal closed pack structure. So, you are going to have 2 tetrahedral voids per atom and you are going to have 1 octahedral void per atom; void in the unit cell. So, the radius ratio allows so r m by r x is between 0.225 to 0.414 in by and large in every case. This ensures that cations occupy the tetrahedral sites. Now tetrahedral sites are twice of the number of atoms. As a result only half of the tetrahedral sites are filled.

So, anions make a ABAB structure and cations occupy the tetrahedral interstices in them, only 50 percent of them not all of them. And the stoichiometry determines the radial coordination of both anions and cations to be equal to 4. Since cations are occupied surrounded by 4 anions, anions also happen to be surrounded by 4 cations to maintain the

stoichiometry and electrical neutrality. It is same as what we saw in zinc sulfide, sphalerite or zinc blend based compounds.

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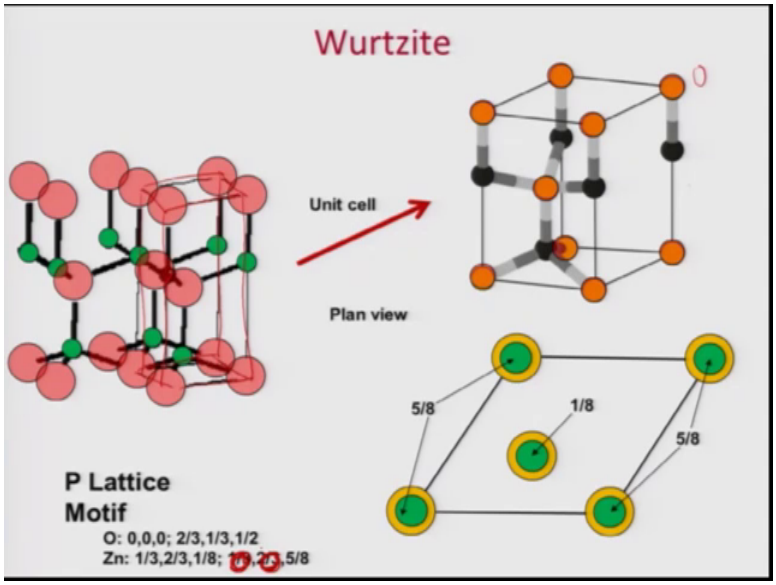

So moving on to the next one, this is where we see their structures. So, we have a hexagonal arrangement of cations. So, you can see that if I just change it to so here what you have is, so these are all; this is the first layer of anions. This is the second layer of anions and this is the third layer of anions. So, this is a b a; between these tetrahedral interstices are filled in such a manner, so that only 50 percent of them are filled.

So, these tetrahedral interstices are filled. And these tetrahedral interstices are filled. Not all of them are filled ok. So, if I draw for example, yeah so this is the structure that you see for example, of if you just take a small unit cell, this is the small unit cell, the one drawn here. So, if I just draw this by it is a small unit cell the one here will be the unit cell ok.

So, this is the smaller unit cell. If I blow it up this looks something like that. So, you have these oxygen atoms sitting at the corner of the unit cell and then you have these zinc atoms sitting at the tetrahedral interstices. So, this is zinc atom, this is zinc atom, this is zinc atom, this is zinc atom and these are all surrounded by side unit cell. So, each of these tetrahedral in void is going to be surrounded by 4 neighbors. So, as a result this is 1 by 4 and the one you have it sitting in the middle. So, as a result you have to roll off

2 tetra hedra in this interstices fill, but their structure will have 4 as we have seen it typically structures.

So, this is filled, these 4 constituting 1 tetrahedral void are filled. So, these are tetrahedral voids. So, you can see the top view. This is the unit cell made by orange or yellow sort of atoms and tetrahedral voids are located at 5 by 8 on the edges and 1 by 8 and the within the body.

So, the it is a primitive lattice with motive being at 0, 0, 0, 2 by 3, 1 by 3, half this is the position of oxygen atom and zinc present at 1 by 3, 2 by 3, 1 by 8 and 1 by 3 2 by sorry 0, 0 its not 1 by 3, 2 by 3 its 0, 0, 0, 0, 5 by 8 this is the typo here.

It is along the edges ok. So, so this is Wurtzite structure compound very all the materials which make this structure will follow this structure ok.

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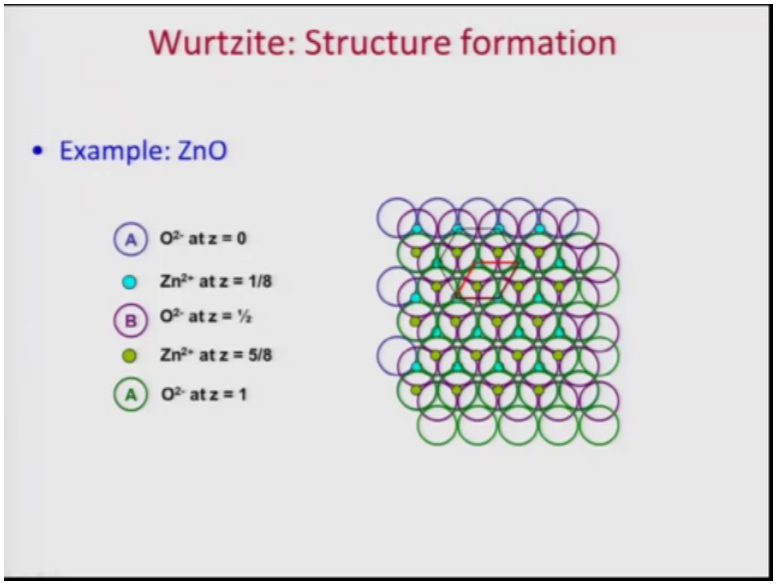

So, let us see how does it work in case of ZnO. So, first layer of oxygen goes at z is equal to 0. Second layer of zinc goes at z is equal to 1 by 8. Third layer of oxygen goes at z is equal to half and the next layer of zinc goes at 5 by 8 and then again oxygen at z is equal to 1. So, this is how you are going to have these unit cells.

So, this is the smaller unit cell with 4 of these light blue atoms which are at the edges and the one which is sitting in the middle is the tetrahedral atom. So, this is basically the way

you can draw the tetrahedral sorry a hexagonal close packed Wurtzite structure with tetrahedral sites filled up to 50 percent.

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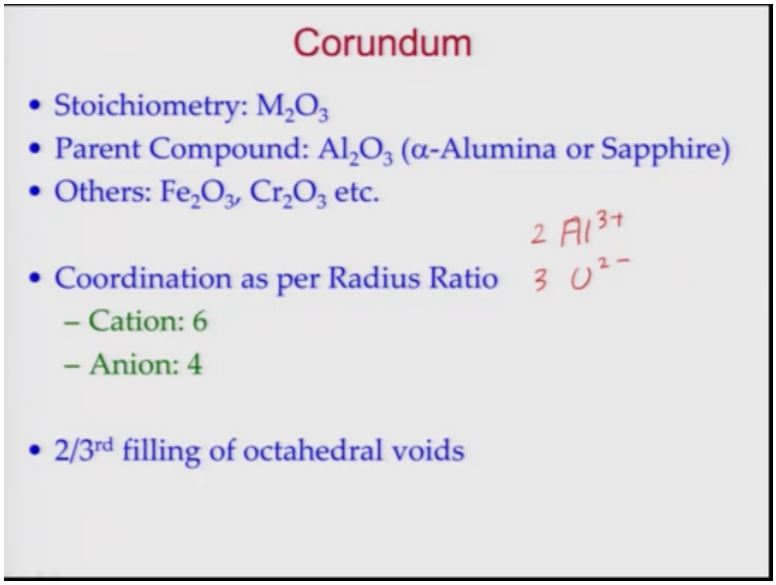

The next structure in this category is Corundum. Corundum is again a mineral name it is a mineral name of alumina very well known compound. The stoichiometry of materials which are based on the structure have M 2 O 3. So, for every 2 M there are 3 Os; so 2 cations 3 anions. So, the parent compound of this is alpha alumina which is also called a sapphire. Al 2 O 3 and there are other compounds which follow the structure such as Fe 2 O 3 or Cr 2 O 3.Iron oxide which is hematite Cr 2 O 3 chromite. The coordination as per radius ratio works out to be such that, so that cations have 6 fold or octahedral coordination.

So, to maintain the bond valence, bond strength; to maintain the electrical neutrality the anions are surrounded only by 4 cations. So, that you have, because here right now you have if its Al 2 O 3 then its Al 3 plus 2 and you have 3 O 2 minus. So, to maintain the electrical neutrality you end up with a 6 neighbors for cation and 4 neighbors for anions. And as you can see since you have hexagonal close packed cell, which has 3 oxygen atoms per formula unit.

So, hexagonal close packed cell has only one octahedron indices per atoms which means only two-third filling of interstices is going to happen. So, only two-third of the octahedral voids are filled in this structure.

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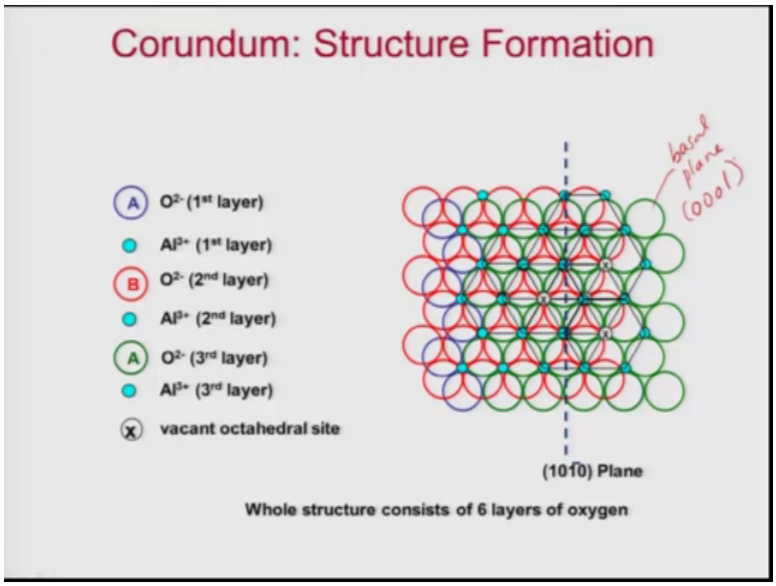

So, let us see how the structure is made in this case the oxygen layer is the first layer. So, this is the A layer of oxygen. And then you have aluminum going to the octahedral voids in the 1st layer. So, this is let say the octahedral void of the 1st layer.

Then of course, all of them are not filled you can see that every third octahedral void is empty. So, if you look at this row for example, first two are filled, third one is empty. Similarly here before the two, third one is empty. So, this goes on in every row.

This octahedral void would move to next position in the next layer. So, when you put the next oxygen layer you can see the next oxygen layer has 3 atoms on top of this. So, these three on top, these three at the bottom will make a octahedral void. So, it has gone to octahedral void. Then the next oxygen layer; next aluminum layer goes to the other position ok. So, the 1st oxygen layer, this is the 2nd sorry this is the 2nd aluminum layer. So, now, the 3rd aluminum layer will move in such a fashion so that vacant side goes here ok. So, oxygen 3rd layer goes on top of the bottom layer, aluminum 3rd layer goes to this position and to make a repeatable structure you need to repeat it once more. So, basically you will have total of 6 layers. And the cross in this case determines the vacant octahedral site.

So, this is how you formulate a Corundum structure, which is basically alternating layers of oxygen in between you have aluminum atoms, and aluminum items in each layers arranged in such a fashion so that only two-third of sites are filled one-third are empty.

So, for every 3rd octahedral site will be empty, and you have to arrange them in a periodic fashion so that you make a repeatable structure.

So, if you want to look at the structure in a more clear manner, we draw a cross section. So this is the b plane right a plane or b plane. This is the basal plane. So, this plane is basically the basal plane, which is basically 0 0 0 1 plane. All right, I think it is moved again. So, this is the 0 0 0 1 plane. So, if I draw a cross section, if I draw a vertical plane across on this plane I can see this little bit more clearly.

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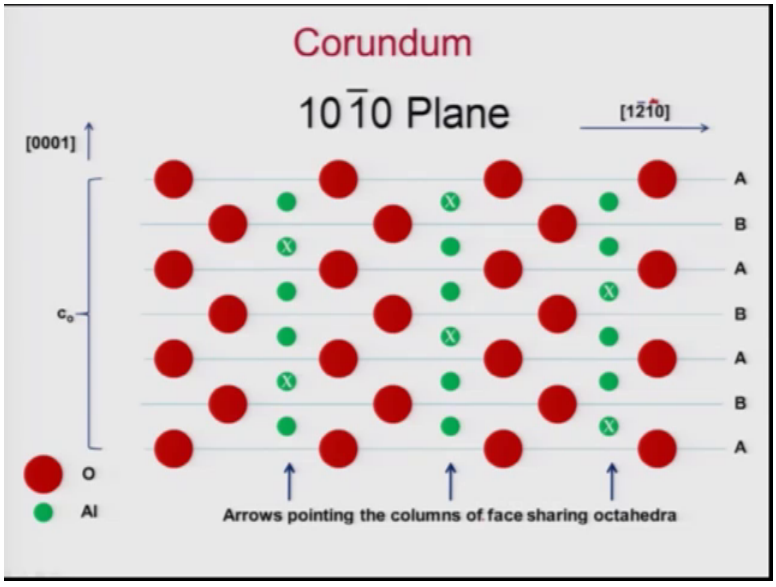

So, this will be 10 bar 10 plane. So, 10 bar 10 plane will be like this. So the 1st layer of oxygen atoms, then we have octahedral voids, you can see two empty third, two filled third empty ok. Then you have B layer again you have first empty other two filled. And we have another layer of oxygen, then the middle one empty and this goes on, until you have the 6th layers. So, you have every; you can see that both within plane and out of plane every 3rd octahedron empty and that is how you make a aluminum structure.

So, this is the c naught parameter of the unit cell which is a c parameter, and this axis is 0 0 0 1 axis which is the perpendicular to 0 0 1 plane. And this direction would be in this case 1 0 1 bar 21 01 bar 2 sorry; this bar will not be there this would be 1 bar 2 1 0 direction. So, 1 bar 2 1 0 will mean that u plus v plus t is equal to 0 and the dot product of the two is equal to 0. So, if you take the dot product of two that is equal to 0.

So, this is the Corundum structure and these are the arrows. So, this column is basically as if you have the columns of face sharing so the octahedra share the faces in this case. So, these arrows point out the columns of face sharing octahedra. So, if you look at their structure in a polyhedral view, you will see that these are octahedral voids so obviously they are octahedras, and these octahedras share each other at the faces.

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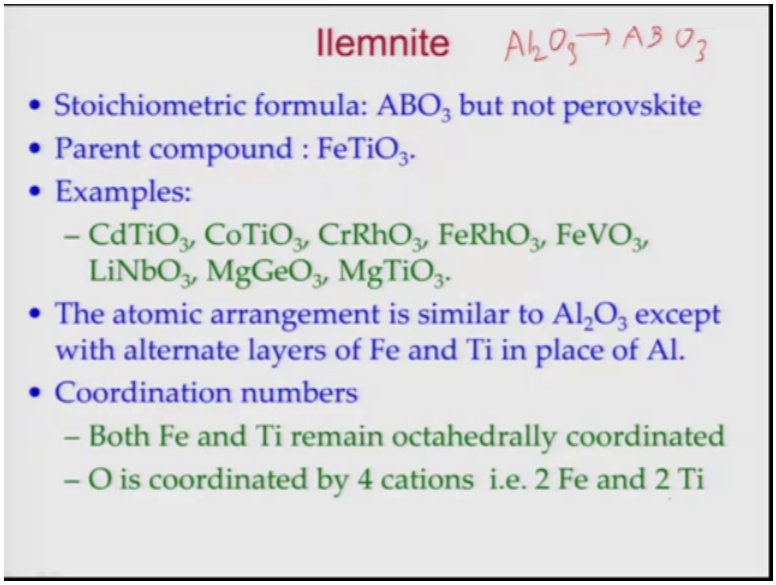

Another derivative of Corundum structure or sort of similar structure is Ilemnite. Now stoichiometry of this material is ABO 3, but it is not a perovskite structure this based on the same Corundum structure.

It is just that, so instead of having Al 2 O 3 I replace aluminum by 2 cations. So, one is A second is B and O remains the same. So essentially, for example, the parent compound in this case is Fe TiO 3 iron titanate. And there are other examples plenty of compounds are there cadmium titanate, cobalt titanate and so on and so forth. They all follow, in fact even Lithium Niobate as we will see in the next slide it comes in the same category, but its structure is slightly different.

The atomic arrangement in this structure is very similar to what you have in Al 2 O 3 ok. Except that, instead of having aluminum all over the place here you have one layer of iron and then another layer of titanium in place of aluminum. So, coordination numbers remain, same both iron and titanium remain octahedrally coordinated, but oxygen is now

coordinated by 2 iron and 2 titanium. So, it is not coordinated by 4 iron or 4 titanium it is coordinated by 2 iron and 2 titanium.

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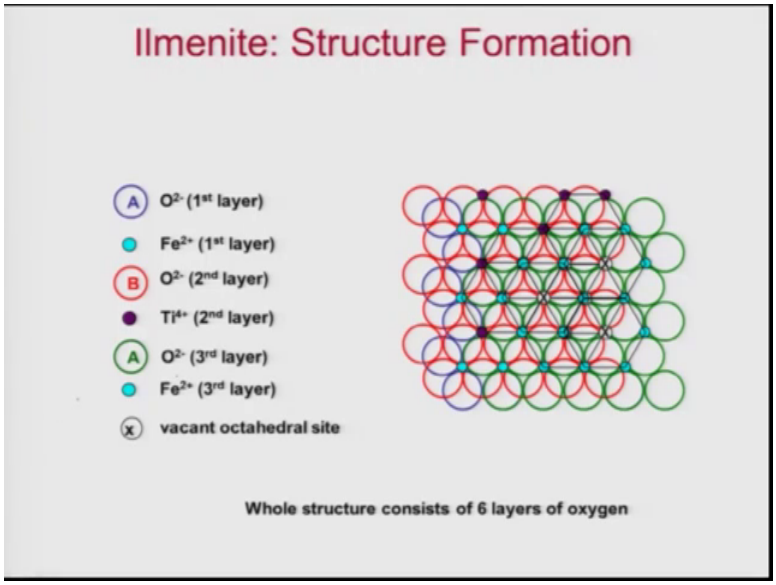

So, this is how the structure is built, if we look at the structure. So, this is the 1st layer of aluminum oxygen which is the A layer. The next layer is this your ox iron goes just like aluminum and Al 2 O 3 your iron occupies octahedral sites except that in the 2nd layer it is going to be titanium. So, the next layer is oxygen again. And in the next layer the vacant site will move to this site. So, next one would be oxygen, it goes to the B layer and then we have the next layer of titanium, so this titanium is a dark atom which is moved there. And the site in the next layer will move to this site; the vacant site. So, oxygen again will go on top of A layer sorry the A at the bottom which is the blue one; blue and green are the same it is just that they are different represented differently. Then we have again next layer of iron and so on and so forth.

So, if we just keep doing it 6 times you will have the structure of Fe TiO 3 same as what you had earlier.

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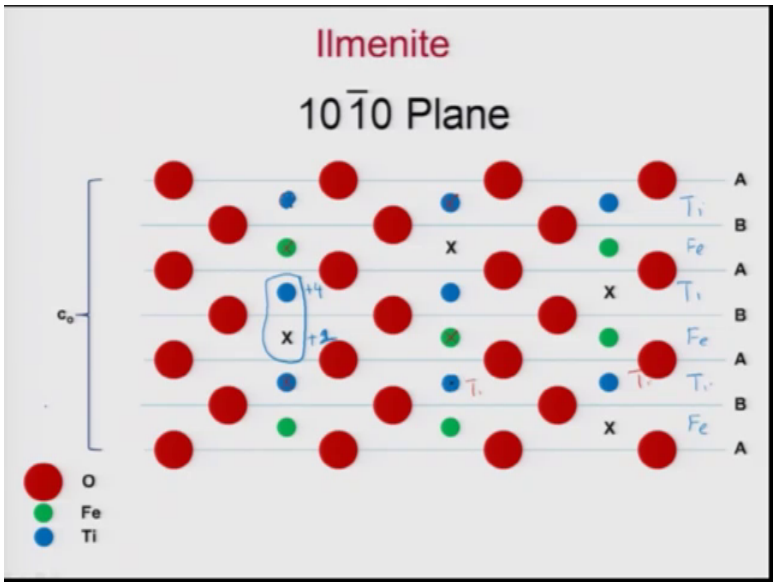

So, again if we draw the 10 bar 10 plane and just like in previous case you have first layer of aluminum oxygen. Next layer of iron all right. Next layer of oxygen, again next layer of what has happened here again this should be so; next layer of titan this is our titanium. So, I think the colors have one different, this is titanium, this is titanium and this would be empty in this case.

And then next layer of oxygen, the next layer of iron again. So, we will have this as; so in this case this would be empty. And then again next layer of so you have; in the first case this is empty, in the second case this is empty, in the third case this is empty, then again this is empty, then again you will have this as empty and then again you will have this as empty. And this would be your let me just use a different color there.

So, this is the titanium atom again. So, you can see that, what you have here is iron titanium blank, and then again you will have iron titanium blank and so on and so forth. So, this is how it is going to go. And again here you have iron titanium blank iron and then titanium iron blank and this is how it is going to go. So, you can see the 1st layer of; this is the 1st layer of iron, 2nd layer of titanium, then iron, then titanium, then iron, and then titanium.

So, you can see here other thing which is quite important is that you have plus 4 iron and a plus 3 iron here. This is plus 3 and this is plus 4 or in this case its plus 2, its iron plus 2

Fe TiO 3 its plus 2. If you have plus 2 plus 4 and plus 2 basically they make a dipole there is a charge distribution.

However, what happens is that this dipole is pointing in one direction, but on the other side the other dipole is pointing in the other direction. So, as a result they both cancel each other, so it does not have any dipole moment in the material as such. So, basically what you have is 1st layer of iron, 2nd layer of titanium with every 3rd octahedral site being empty. So, this is the 3rd layer of that the titanium atom. And then you have these blank sites all right.

So, this is what is the structure so that you can see that every; I think there is some problem in the ppt anyway do not worry about it, just one second. So, in this case what we have is,, again you can see that if you go along this column the sites are empty. So, these are all empties once right, again if you go along this the sites are empty, but these are all filled these are filled, and these are filled.

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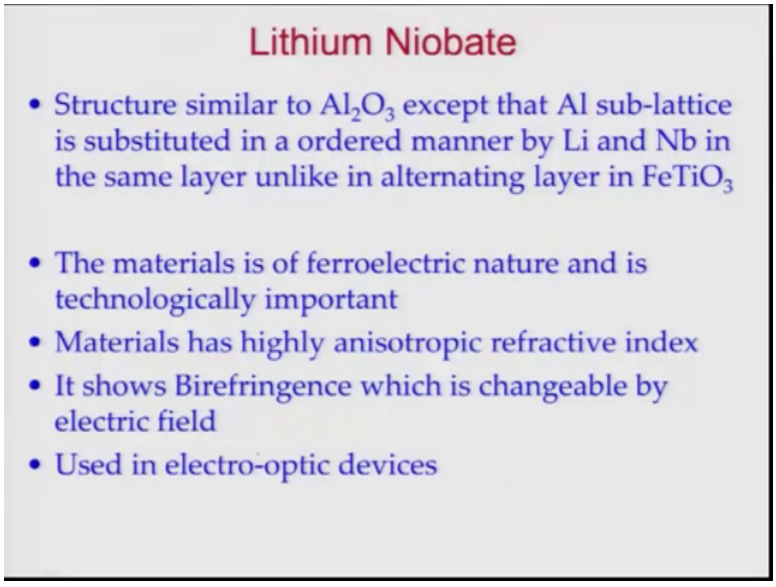

So, first column filled, second column filled, third column empty right. So, you can see these in various ways; empty site. Now let us go to the slide number 12, which is the Lithium Niobate.

Now this structure is similar to Al 2 O 3 or even Fe TiO 3; except that the ordering of iron and iron Lithium and Niobium takes place within the same layer unlike in Fe TiO 3 which was in every alternate layer.

So, the structure is basically and this is why you will see that structure is ferroelectric in nature and it is technologically an important material. And that is why it also has a birefringence because it has a highly anisotropic refractive index it is a birefringence material. And the refrigerants can be changed by applying electric fields. It is a important material and that is why it is used in electro-optic devices.

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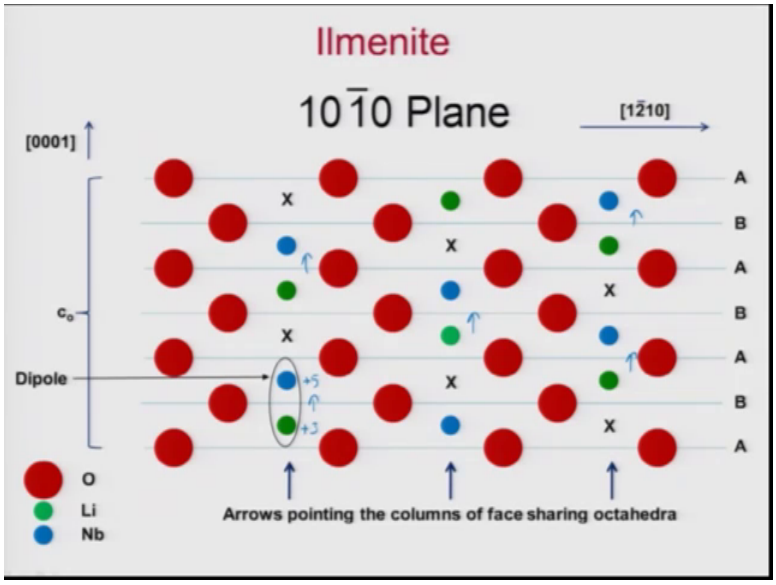

So this material again, you can see if I just fill in the blanks here, I think again this have so you can see here you have A layer, you have B layer and so on and so forth of oxygens. Now within the same layer you have Niobium you have Lithium you have Niobium then empty site. Now here, you have this empty site. So, Lithium, so this is Niobium here would have been Lithium empty and then again Lithium Niobium it will continue that way. So, within the layer you have this periodicity, perpendicular to the layer also you have periodicity you have Lithium Niobium empty, Lithium Niobium empty.

And here you see unlike Fe TiO 3 the dipole always points in the same direction, right. So, here you have this is Lithium plus 3, Niobium plus 5. So, you have a dipole here and the dipole always points in the same direction, whether you go here, here, here or here

and this is why its it has a permanent dipole moment it is a ferroelectric material in nature unlike Fe TiO 3. And this is what makes this material exciting ok. This is the c lattice parameter and there is a direction 1 bar 2 1 0.

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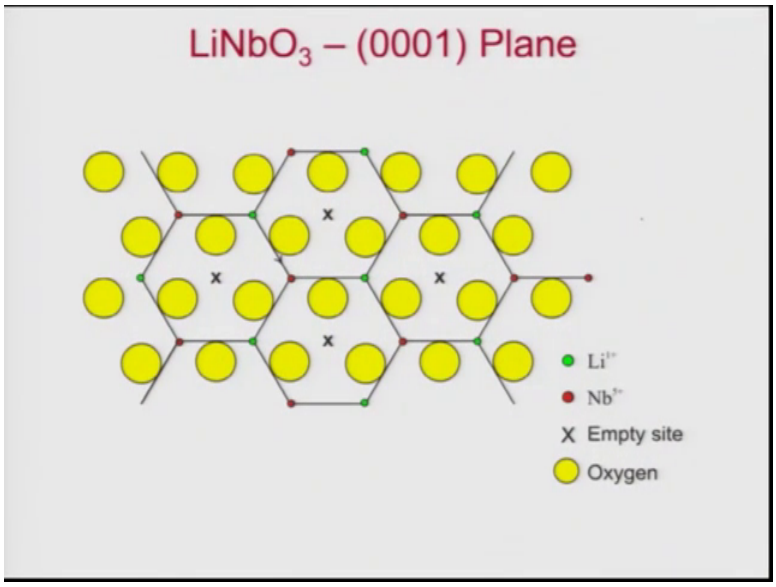

So, this is how if you look at the plane view top view it looks like this. The top view you will have the layer of oxygen and between the layer you have octahedral sites filled. So, alternating oxhahedra octahedral sites fill Lithium, Niobium Lithium, Niobium Lithium, Niobium, and in between you have one empty. So, again you can make the hexagon. So, these are all empty sites. And this continues in the same fashion as in Al 2 O 3 and Fe TiO 3. It is just that this x will move to this position and then this x will come to this position. And this will keep happening in the same manner in the whole at unit cell.

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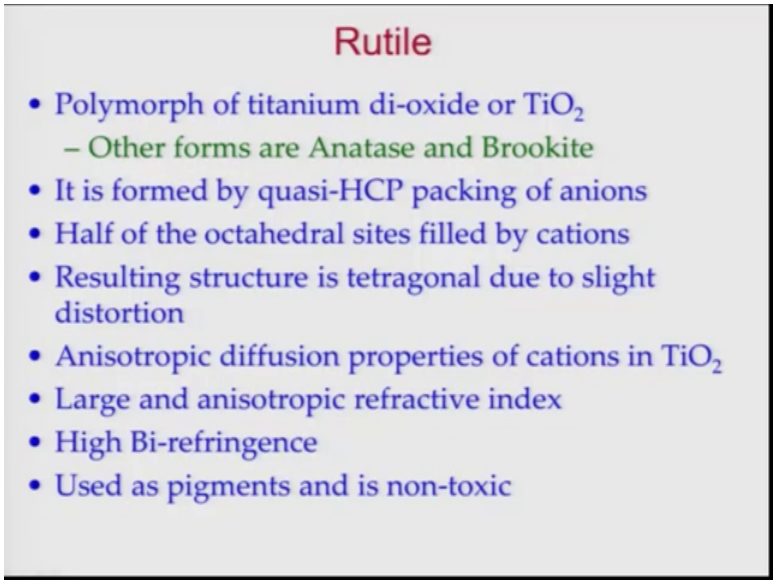

So, this is again a very important material Lithium Niobate, it is a electro optic materials used in lot of optical applications.

Finally we have called material which is again technologically important called as Rutile. Rutile is a polymorph of titanium dioxide which is a very useful material in lot of applications. There are other forms of TiO 2 which are Anatase and Brookite, but Rutile is one of the most commonly known form of TiO 2. It is formed by a hexagonal close packing of anions, but it is a quasi hexagonal close packing it is not quite hexagonal in nature, so it is like distortion in the structure.

So however, what happens here is the tetrahedral octahedral sites are filled by cations, as a result only half the octahedral sites are filled because you have 2 oxygen atoms. So, for each of them you are going to have two sites. So, only half of them are filled, because you have only 1 cation.

Slight distortion leads to a tetragonality in the structure. So, it does not look like quite as hexagonal structure it looks more like tetragonal structure. Tio 2 also has this interesting property like anisotropic diffusion. So, it has different diffusivity in different directions in the unit cell, as a result the material has different uses in the crystalline forms and it also has large anisotropic refractive index. So, it has it if a the light bends by different magnitudes in different directions. And as a result it has birefringence properties. And that is why it is used in quite in optical applications as a pigment. And it is also

advantages to use it as a pigment because it is non toxic, it is not a very sort of toxic material.

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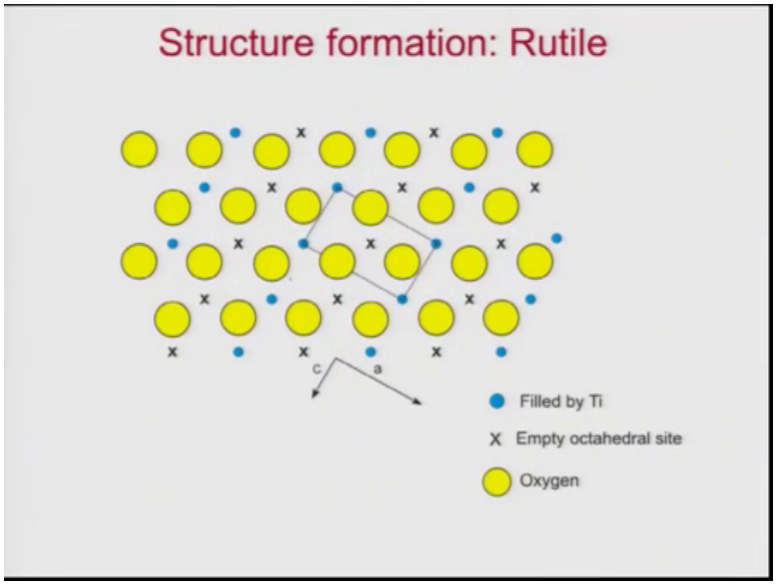

So, this is how the structure is you have sort of hexagonal arrangement of oxygen atoms, and you can see that these titanium atoms occupy half the interstices sites. So, this column is filled, this column is empty, this column is if I just use the arrow here. So, this column is filled, this column is empty, this column is filled, this column is empty. And there is a slight distortion within the unit cell which leads to formation of this as a tetragonal cell. So, this is the tetragonal cell which you can form by putting corners on the cations.

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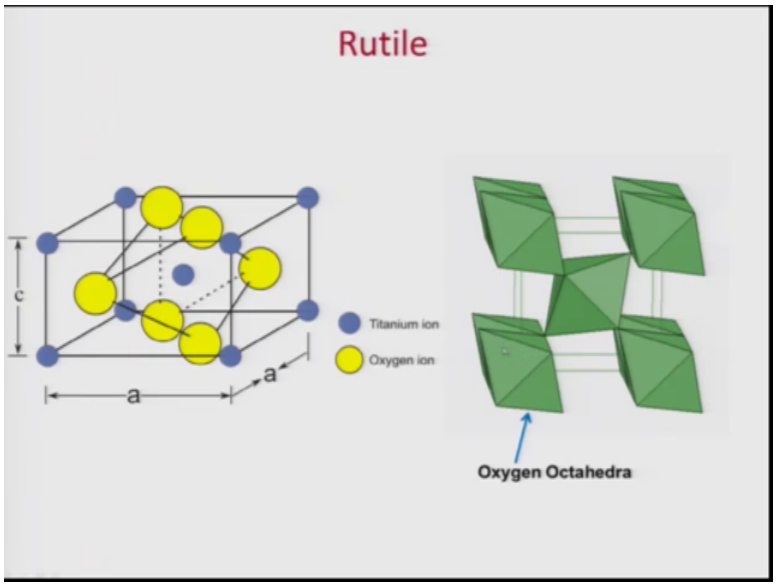

And this is how it looks like. So, you have a unit cell tetragonal unit cell which can be made by cations. And anions are located, two of these anions are located on these two faces, so you can see one is shifted by down there another is shifted up there. And the other two cations are on these two faces and they make sort of an octahedron and this is.

So, it is not quite a hexagonal structure because of distortion of oxygen atoms within the layers as a result it ends up being a tetragonal lattice. And this is how the structure would look like if you make it on the basis of oxygen, polyhedral models. So, two octahedras pointed in this direction, other octahedra would point in this direction and within the center of these octahedras you will have titanium occupied in such a fashion so that only 50 percent sites are filled all right.

So, what you see here is this octahedra the one in the center, so you will have 1 titanium atom there. But these titanium atoms are occupied in such a fashion. So, that you have one octahedra here, one octahedra here. So, you have ok. So, only those octahedras are shown which are coordinating the titanium atom.

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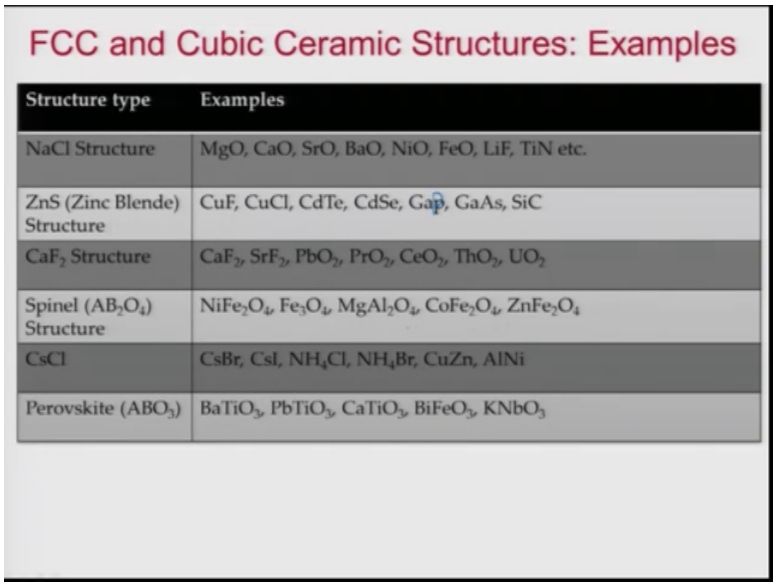

So, just to summarize now, there are a variety of these materials which we have discussed for ceramics which are ionically bonded.

So, for example, NaCl structure is followed by materials such as magnesium oxide, calcium oxide, strontium oxide etcetera. Zinc sulfide or zinc blend structure is followed by various materials copper fluoride, copper chloride CdTe, CdSe, gallium phosphide, so this p would be capital here there this is p gallium arsenide, silicon carbide etcetera. Then CaF 2 structure, calcium fluorite structure followed by CaF 2, SrF 2, PbO 2, PrO 2, CeO 2 variety of oxides also follow the structure.

Spinel structure is followed by NiFe 2 O 4, Fe 3 O4, MgAl 2 O 4 depending upon whether it is in inverse or normal. Cesium chloride lot of bromides, halides, chlorides follow the structure, in fact, CuZn, AlNi intermetallics also follow the structure. Perovskite structure is followed by most of the ferroelectrics, dielectrics, barium titanate, lead titanate, calcium titanate, bismuth ferrite, lead diabate.

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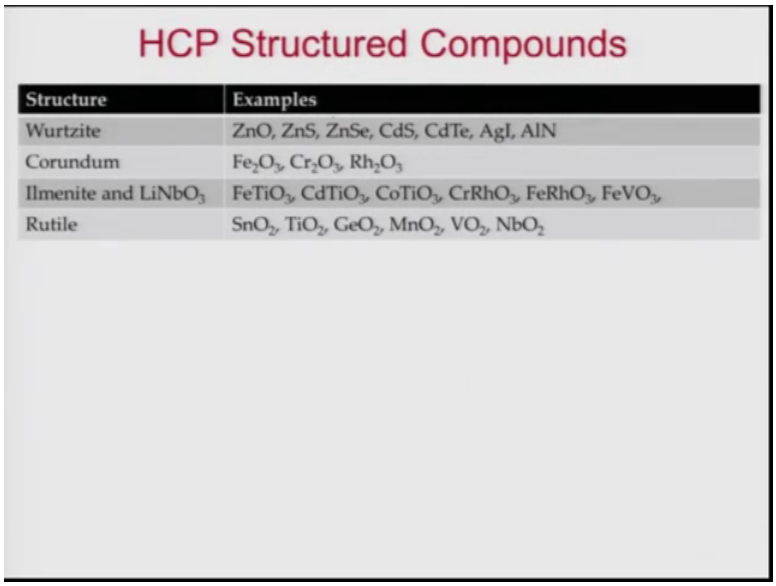

And then we have HCP structured compound: Wurtzite for example, zinc sulphide, zinc oxides, zinc selenide all these materials; corundum, iron oxide, chromium oxide etcetera. Ilmenite and Lithium Niobate, FeTiO 3, CdTiO 3, cobalt titanate and so on and so forth; Rutile bi tin oxide, titanium oxide, germanium oxide, manganese oxide, vanadium oxide, Niobium oxide many others.

So, these are the few examples of these materials.

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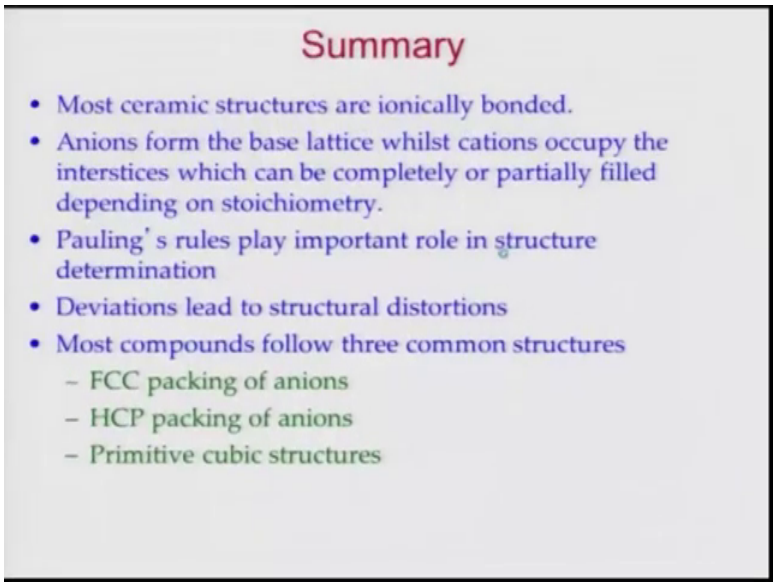

So, finally, let me summarize in this material. In this slide that most ceramic structures are ionically bonded. They follow certain rules which are called as Paulings rules in these materials anions from the base lattice, whereas the cations occupy the interstices which can be completely or partially filled depending upon the stoichiometry and radius ratio ok.

Paulings rules play important role they are not the final deciding factor. Deviations occur at times; so you have structural distortion for example, perovskite could be non cubic in many cases it could be tetragonal slightly. There are three common structures that most of the anions make: first is FCC packing of anions, second is HCP packing of anions and third is primitive cubic structure. And then there are some tetragonal orthorhombic structures as well, but many materials follow these three structures quite commonly.

So, this is where we will end the in organic materials, next we will look at the structure of some of the non-crystalline materials mainly in glasses and polymers. And then we will look at the structure determination of materials and defects in materials before we conclude this course, ok.

Thank you.