Electroceramics

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Lecture - 4

So, this is the class in which we will start our discussion on some other structures. In the last class, we studied about remaining structures based on FCC packing of anions and some other structures like Perovskite structure, Cesium Chloride structures and so on. In this class, we will take on some of the structures which are technology important materials, and they are based on for instance, the perovskite packing of structures.

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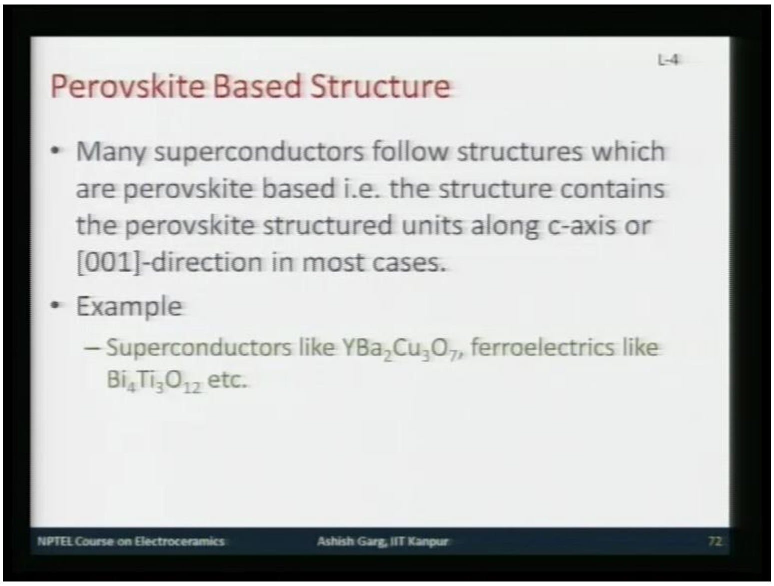

Perovskite Based Structure

- Many superconductors follow structures which are perovskite based i.e. the structure contains the perovskite structured units along c-axis or [001]-direction in most cases.
- Example
  - Superconductors like $YBa_2Cu_3O_7$, ferroelectrics like $Bi_4Ti_3O_{12}$ etc.

So, in this they are not exactly perovskites. But what happens is a structure looks like as if you know, perovskite units are tagged on top of each other. This happens typically along C axis or the enter tuning of perovskite structure with some other structure such as Sodium Chloride. So, mostly these structures, I showed by materials like super conductors, such as YBCO or ferroelectrics like Bismuth Titanate. We look at only some of the examples and rest of them, if you want to study, then you can go through them in the books.

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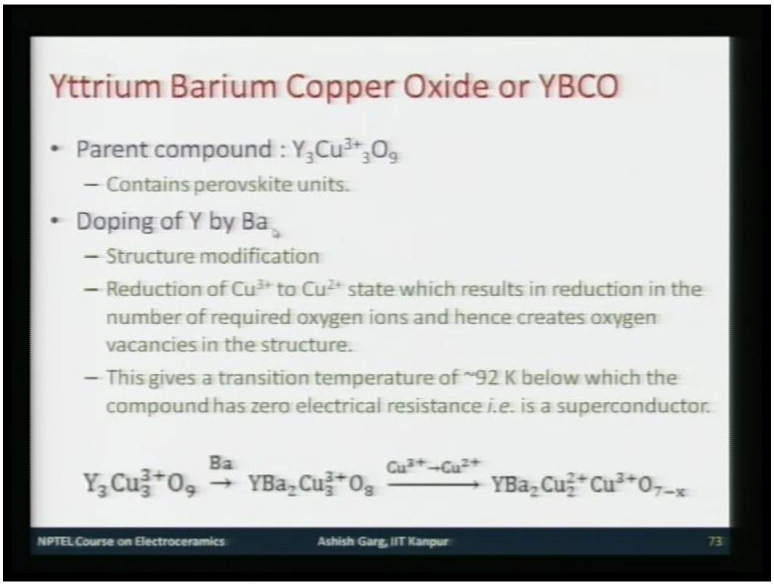

Yttrium Barium Copper Oxide or YBCO

- Parent compound : $Y_3Cu^{3+}{}_3O_9$
  - Contains perovskite units.
- Doping of Y by Ba
  - Structure modification
  - Reduction of Cu^{3+} to Cu^{2+} state which results in reduction in the number of required oxygen ions and hence creates oxygen vacancies in the structure.
  - This gives a transition temperature of ~92 K below which the compound has zero electrical resistance *i.e.* is a superconductor.

$$Y_3Cu_3^{3+}O_9 \xrightarrow{Ba} YBa_2Cu_3^{3+}O_8 \xrightarrow{Cu^{3+}\rightarrow Cu^{2+}} YBa_2Cu_2^{2+}Cu^{3+}O_{7-x}$$

So, for instance in YBCO, YBCO the parent compound is Yttrium Copper Oxide, where copper is in plus 3 state and this contains the stacking of YCUO 3 perovskite units along the C axis. So, as you can see, if you multiply YCUO 3 by 3, it becomes 3 perovskite units.

So, now it is made super conducting by converge by substitution of 2 of the yttrium ions by Barium, which modifies the structural little bit and followed by reduction of CU 3 plus to CU2 plus, which creates some oxygen vacancies as well as number of the reduction in the number of required oxygen atoms. Or basically, CU3 plus CU2O reduction requires less number of oxygen as atoms in the structure.

So, parent structure remains same, but some of the oxygen atoms from the previously occupied sites become weakened sites. This kind of doping gives rise to super conducting state in which material has 0 resistance and the temperature below which this happens is 92 kelvin or so. So, the final formula of the compound becomes YBA 2 CU 2 2 plus CU3 plus. So, one copper remains in CU3 plus state, two coppers become 2 plus state. So, Stoichiometric formula should be YBA 2 CU3O7. But super conducting state requires some more deficiency of oxygen as resulted in CUCY BA 2 CU3O7 minus X where X is a very small number like 0.15.

So, what it how it happens is, you have Y3 CU3O9. Dope it with varium and substitute for 2 yttrium. So, naturally if you substitute for 2 yttrium, you have requirement of 1 your requirement of oxygen goes down by 1. So, it becomes YBA 2 CU3O8. Now, CU3 atoms reduced from plus 3 state to plus 2 state, two of them. So, the formula now becomes YBA 2 CU2 2 plus CU1 3 plus O 7 minus X or if you do not count X, you can take it as 7.

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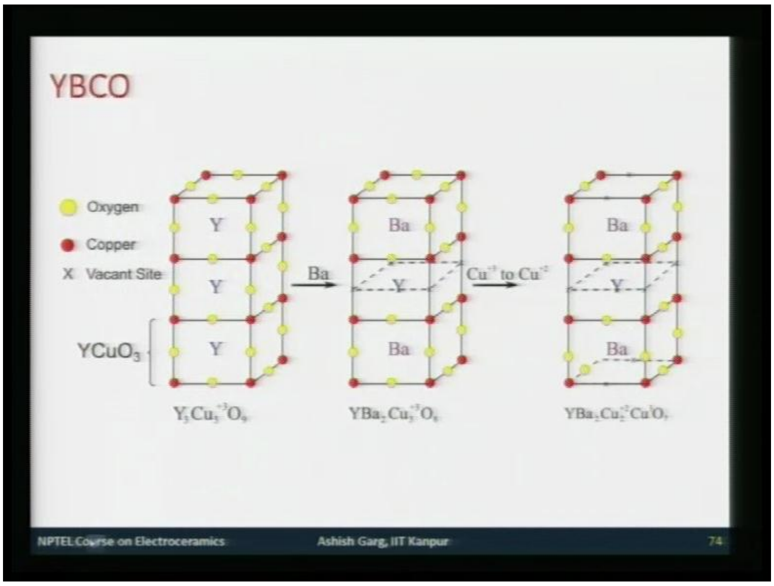

YBCO

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So, this is how the structure is going to look like. So, this is the three perovskite units stacking along 001. You replace 2 yttrium ions on the top and the bottom unit cell by barium. As a result, some oxygen is not required.

So, to count for requirement of less oxygen, you have these vacant sites of oxygen which was previously occupied. Now, further when CU3 plus, some of the CU3 plus reduce to CU2 plus, then also the requirement of oxygen goes down and you have some more oxygen vacancies created at this position for instance.

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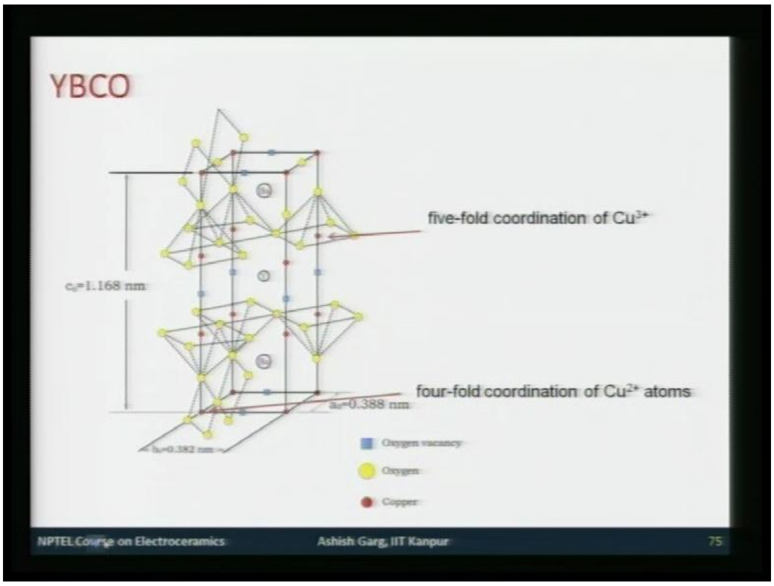

YBCO

five-fold coordination of Cu^{3+}

four-fold coordination of Cu^{2+} atoms

c_0=1.168 nm

a_0=0.388 nm

b_0=0.382 nm

🟦 Oxygen vacancy

● Oxygen

● Copper

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So, this is how the structure looks like. The correct form, the structure, this is the whole unit cell of YBCO. If you look at the co-ordination of copper atoms, this is the interesting thing about the structure, that copper has fivefold co-ordination in these locations.

So, you can see 1 2 3 4 and one here. In these positions, copper has fourfold co-ordination. So, copper tends to have threefold and fourfold co-ordinations in various positions. So, CU3 plus typically has fivefold co-ordination, CU2 plus will typically have your fourfold co-ordination.

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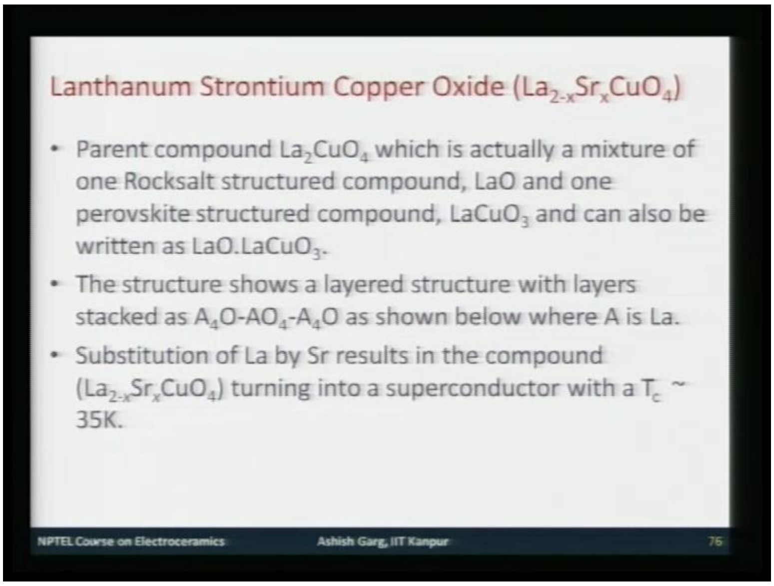

Lanthanum Strontium Copper Oxide ($La_{2-x}Sr_xCuO_4$)

- Parent compound La_2CuO_4 which is actually a mixture of one Rocksalt structured compound, LaO and one perovskite structured compound, $LaCuO_3$ and can also be written as $LaO.LaCuO_3$.
- The structure shows a layered structure with layers stacked as A_4O-AO_4-A_4O as shown below where A is La.
- Substitution of La by Sr results in the compound ($La_{2-x}Sr_xCuO_4$) turning into a superconductor with a T_c ~ 35K.

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So, another structure, which is interesting is Lanthanum Strontium Copper Oxide, for which the parent compound is Lanthanum Copper Oxide. So, in this Lanthanum Copper Oxide, which is actually a mixture of Rock salt structure compound LAO and 1 perovskite structured compound LACUO 3. You can for convenience, you can write it as LAO dot LACUO 3. So, what happens here is, when you dope this material with strontium replacing some of the lanthanum ions, this again becomes a super conductor and it gives a transition temperature of about 35 Kelvin. The structure shows basically a layered structure, in which you have A 4 O layers, which means one oxygen is surrounded by 4 A’s followed by A O 4 and then CUO 2.

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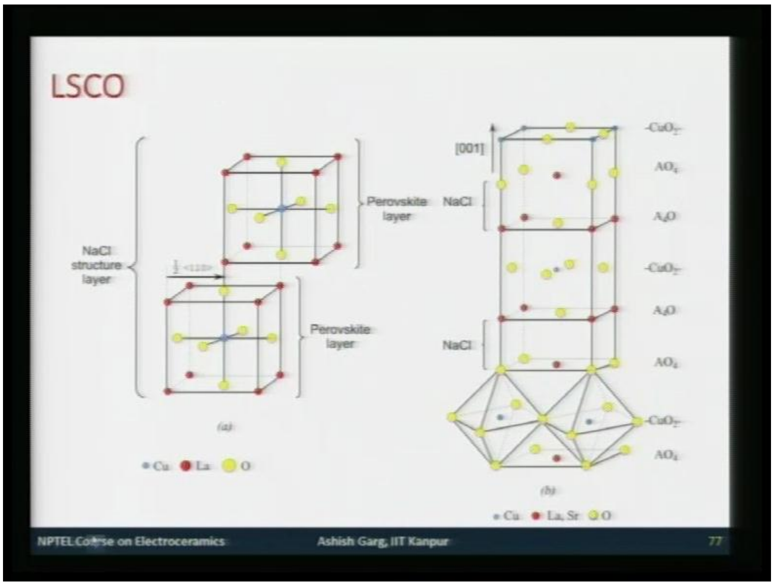

LSCO

So, this is how the stacking continues. I will show you in the next slide. So, if we go to the next slide, if we look on the left, you have these two perovskite layers which make, which together make NACL structure layer. Now, if you look at top NACL layer, sorry, perovskite layer, top perovskite layer, it is shifted with respect to the bottom perovskite layer Y by the vector half 110. So, basically the origin of the bottom layer is here and I have shifted the origin of the top layer to the, on top of phase center, on the top of, top phase center of the bottom unit cell.

So, this has gone from this position to that position, which is actually along 110 direction in the X Y plane. If you look at the structure it looks like, so you have CUO 2 layers which are these. CUO 2 layers followed by A O 4 layer, where each A atom, which could be Lanthanum or Strontium surrounded by 4 oxygen followed by A 4 O layers. Then again followed by CUO 2 layers and if you look at the CUO 2 layer, the configuration has changed from here to here little bit. So, that you have to remember. As a result, the structure continues itself. So, CUO 2, AO4, A4O, CUO2A4, OAO4, and so on and so forth, it keeps going down in the same fashion.

So, this would be your Lanthanum Strontium Copper Oxide structure, which is super conductor. So, it looks bit complex, but if you look at the structure in a different way thinking that it is a mixture of NACL and perovskite structures, the understanding becomes more clear. This is how most of the complicated structures are made of, especially in super conductors and in ferroelectrics.

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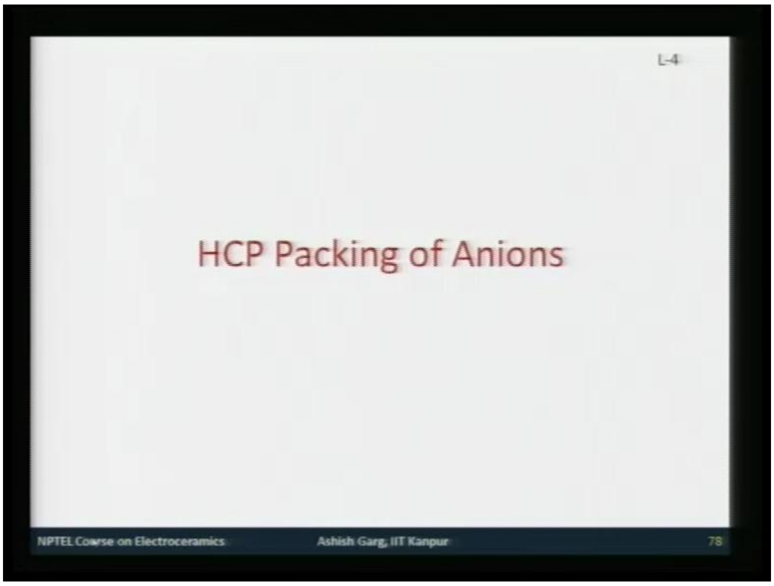

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HCP Packing of Anions

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Now, we will look at the structures, which are based on HCP packing of anions. So, here anions are typically oxygen. They make a HCP lattice and cations occupy either tetrahedral or octahedral sites depending upon the radius ratios.

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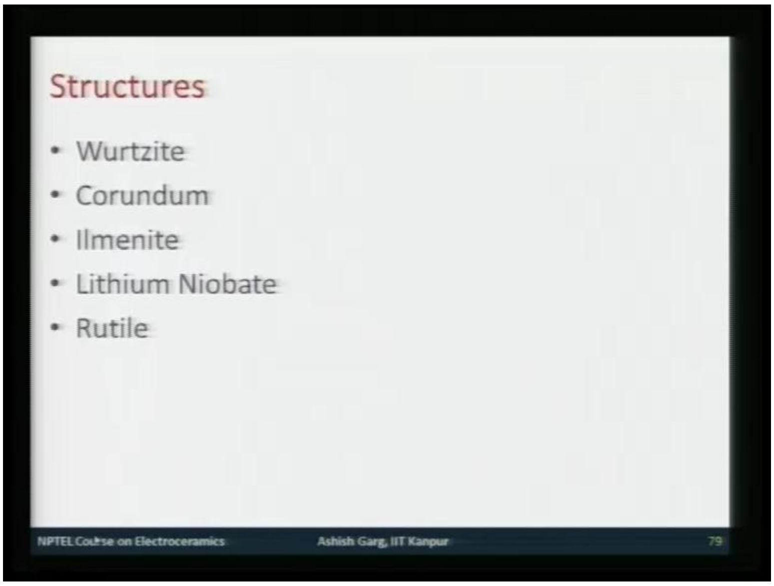

Structures

- Wurtzite
- Corundum
- Ilmenite
- Lithium Niobate
- Rutile

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So, the structures in the series are Wurtzite, Corundum; Wurtzite is your typical zinc oxide kind of structure. It is a polymer of previously studied sphalerite zinc; zinc sulphide or zinc blend structure. You have Corundum, which is the parent structure of alumina, alpha alumina. Then you can have Ilmenite, Lithium Niobate and Rutile.

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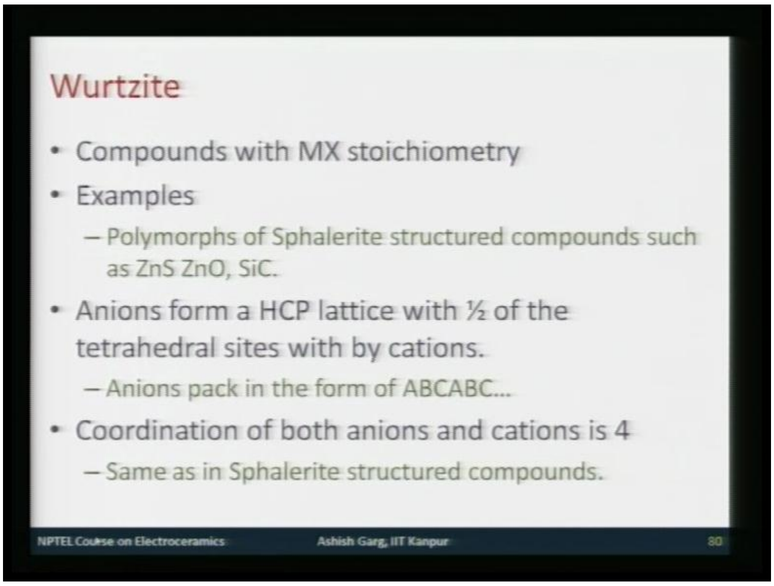

Wurtzite

- Compounds with MX stoichiometry
- Examples
  - Polymorphs of Sphalerite structured compounds such as ZnS ZnO, SiC.
- Anions form a HCP lattice with ½ of the tetrahedral sites with by cations.
  - Anions pack in the form of ABCABC...
- Coordination of both anions and cations is 4
  - Same as in Sphalerite structured compounds.

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So, we will go through these one by one in this lecture. So, Wurtzite. We will start with Wurtzite. Wurtzite structured compounds have a stoichiometry of 1 is to 1 for cation and anion. They are referred by formula, general formula m X. The examples, as I just now I mentioned, these are polymorphs of sphalerite or zinc blend structured compounds, which are zinc sulphide or zinc oxide or silicon carbide etcetera. Here, in this structure, what happens is, the anions which could be sulphur or oxygen atoms, they form a HCP lattice. Right?

Now, since they are polymorph of zinc blend structure, if you remember in zinc blender structure, we had FCC packing of anions with half of the tetrahedral sites occupied. Same happens here. It is just the structure is different. So, packing sequence of anions changes from A B C A B C to A B A B. But still, the bounding covalent, bounding contribution requires the material to have tetrahedral co-ordination as well as radius ratio in these compounds. So, half of the tetrahedral sites will be now occupied by cations.

So, whereas, anions form in the sequence, it should not be A B C A B C. It should be A B A B A B A B C A B C A B C would be true for Zinc Sulphide Sphalerite structure. The co-ordination of both anions and cations, just like in zinc blend structure would remain 4. So, there is no change in terms of packing and interstitial site occupancy with respect to zinc sulphide, which is zinc blend structure or sphalerite structure. The only change is that the anions packing is now A B A B A B instead of A B C A B C A B C.

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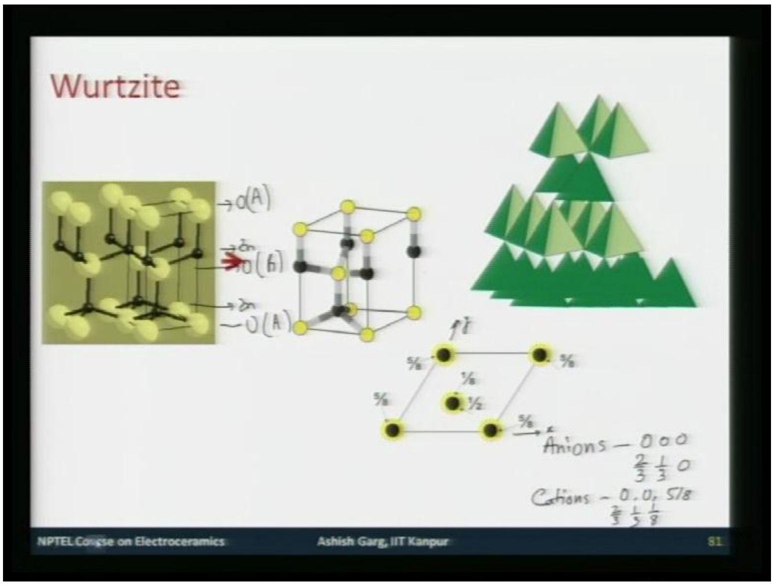

Wurtzite

Anions – 0 0 0
$\frac{2}{3}$ $\frac{1}{3}$ 0

Cations – 0, 0, 5/8
$\frac{2}{3}$ $\frac{1}{3}$ $\frac{1}{8}$

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So, the structure is something like this. So, you have, this is the layer of oxygen atoms. This is the layer of zinc atoms. Again, you have a layer of oxygen atoms. Again, you have a layer of zinc atoms followed by oxygen atoms. So, this would be A layer. This would be of B layer for anions and again, this would be of A layer. If I zoom this particular part, which is the drawn unit cell, then it looks something like this. So, you have these top oxygen atoms, bottom oxygen atoms and the central oxygen atom, this makes one hexagonal unit cell and these are the tetrahedral sites which are occupied.

So, these are and if you count the number of atoms, total, it would be 2 per unit cell of both types. So, you can see here that in this; if you draw the plan view perpendicular to parallel to c plane or perpendicular to c axis, you can note the positions of both cations and anions in this fashion. So, cations... So, your anions will be at 0 0 0 and if I consider this as X and this as Y, then my anion would be, it would be 2 by 3, 1 by 3, 0 depending on how we look at it. It could be 1 by 3, 2 by 3, 0 or 2 by 3, 1 by 3 0 and cations will be at the edges.

So, this would be at 0 0 5 by 8 and 2 by 3, 1 by 3, 1 by 8. So now, if you look at the structure, only half of the tetrahedral sites are filled. If you remember from HCP packing, in HCP packing, you have tetrahedras which are pointing downwards and tetrahedras which are pointing upwards. So, in this structure, what happens is, the structure is such that that all the tetrahedras are pointing upwards or all the tetrahedras, which are pointing in one particular direction are filled by cations. This is the polyhedral model. Of course, you can invert it. You can you can put it upside down and you can show that it is all, but the point is, they are all pointing in one direction. You can say up or down depending upon your frame of reference.

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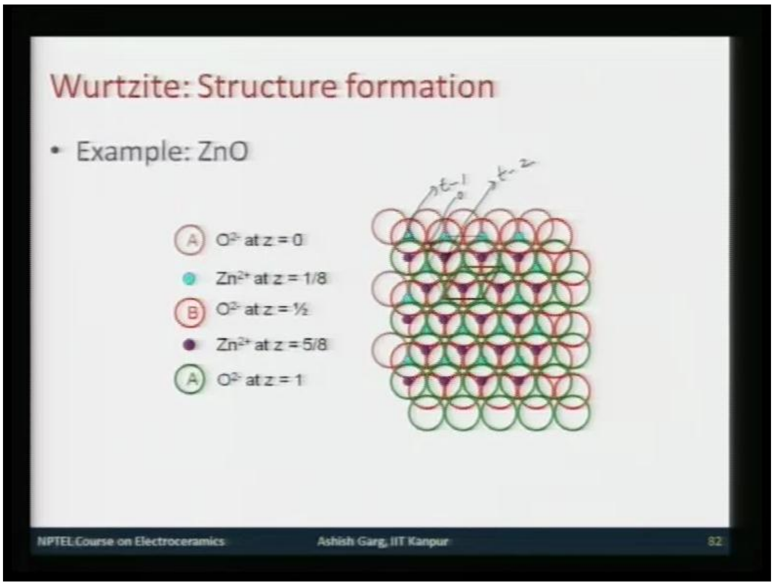

Wurtzite: Structure formation

- Example: ZnO

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So, the way it is made, the structure, you make first layer of oxygen atoms. So, this is the closest packed layer C plane. Now, the interstitial sites are either these or these. Any of these could be filled. So, let us see the second layer. First interstitial layer goes on in these sites. I have chosen to put it there. You can put it here.

Now, the second layer of oxygen atoms goes on top of these, which I have chosen to fill. This I have left it empty. Now, in this case, it would make octahedral site. So, octahedral is not filled. We leave it empty. We filled only tetrahedral site. Now, what will be the other tetrahedral site? Other tetrahedral site is this. So, this would be tetrahedral of one type, this is the tetrahedral of second type and this would be octahedral which is empty. So, these sites are labeled as T 2 will remain empty. So, when I put the next layer of zinc atoms, where are they going to go? They are going to go into positions where tetrahedras are pointing in one particular direction.

So, we will see. So now, I put the second layer of zinc and oxygen atoms and they go in the positions which are again pointing upwards. So, these are the ones which will be pointing upwards. On the other hand, if you look at for if you look at the… So, in the first layer, one particular type will not be filled. In the second layer, another particular type will not be filled, which will be both pointing upwards or pointing down. So, this would be your formation of zinc oxide structure and this would be one unit cell. This brown one would be one unit cell of zinc oxide containing 2 atoms.

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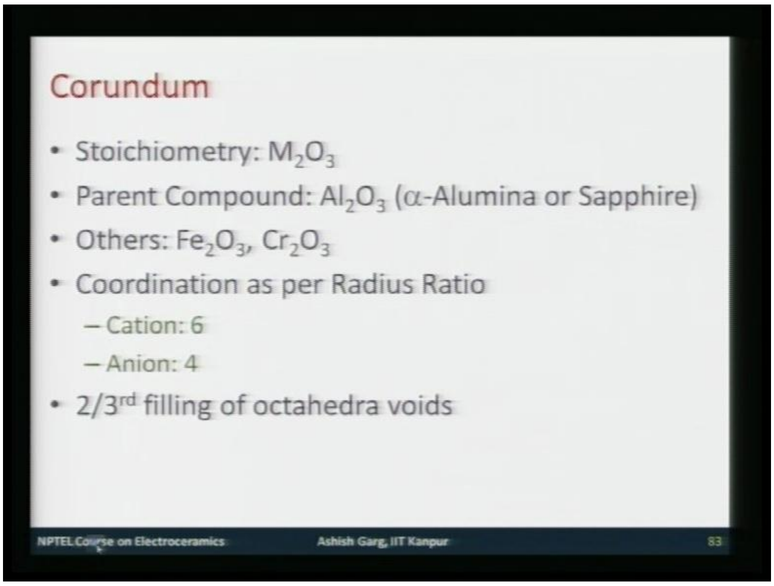

Corundum

- Stoichiometry: M_2O_3
- Parent Compound: Al_2O_3 (α-Alumina or Sapphire)
- Others: Fe_2O_3, Cr_2O_3
- Coordination as per Radius Ratio
  - Cation: 6
  - Anion: 4
- 2/3rd filling of octahedra voids

So, this is how Wurtzite structure is formed. Second structure in this series is Corundum structure. Corundum is based on parent compound L2O3 or alpha alumina. This is the Corundum is the mineral name stoichiometry of this compound as a result is M2O3. So, 2 anions are therefore, 3 cations and 3 anions form this formula unit. Parent compound, as I said is alpha alumina or sapphire. The other compound, which follow the structure are, for example, alpha iron oxide or chromium oxide. As for the radius ratio in this structure, the cations, the anions form FCC packed structure, which is AB AB kind of packing. But the cations in this structure based on the radius ratio occupy octahedral sites. Not the tetrahedral sites. As a result, the cation coordination will be 6.

Now, you can work out yourself from the bound valence rule, which I, or bound strength rule, as we saw in the previous cases, to fulfill the stoichiometric requirement. The anion co-ordination has to be 4. So now, as a result, since you have now A B C A B A B packing and for 3 anions, you have 2 cations, which means only two third octahedral voids will be filled because in a closed pack structure, there is one octahedral site per atom. So, you have three atoms of oxygen, which means only two of octahedral voids will be filled. So, you have two third filling of octahedral voids.

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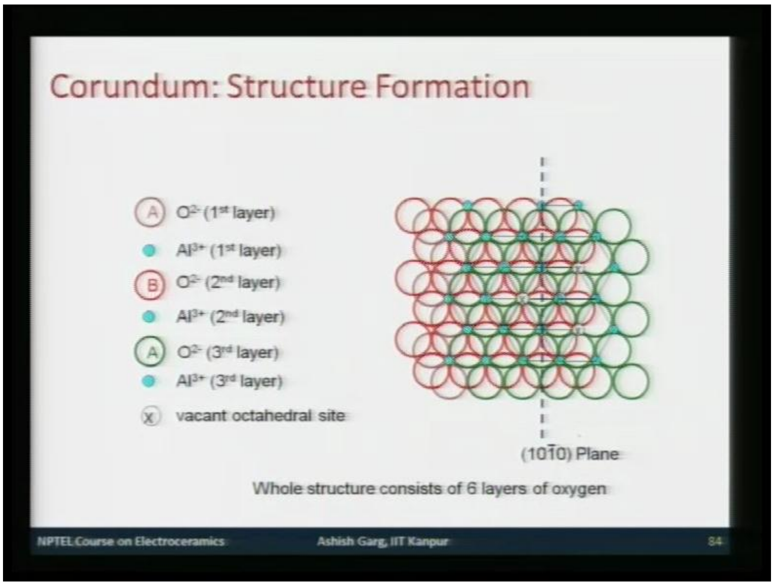

Corundum: Structure Formation

Ⓐ O^{2-} (1st layer)

● Al^{3+} (1st layer)

Ⓑ O^{2-} (2nd layer)

● Al^{3+} (2nd layer)

Ⓐ O^{2-} (3rd layer)

● Al^{3+} (3rd layer)

ⓧ vacant octahedral site

Whole structure consists of 6 layers of oxygen

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So, the structure is formed in the following manner. In this animation, I put the first layer, which is oxygen and I put the second layer, which is the aluminum first layer and the aluminum arranges itself in this kind of fashion. So, since you have one third sites, octahedral sites empty, these crosses show the empty sites and other atom show the filled sites. Now, second layer, when the second layer is formed, this vacant site will move from this position to that position in the next layer.

So, let us see. This is the second layer of oxygen atom. So, naturally this is the octahedral site between the first and second layer of oxygen. In between, you have aluminum atom and if you put the second aluminum layer, so you had the cross in this position. Now, the cross is gone there. So, this is the vacant site which is moved along a particular axis. In the next layer when you put, in the third layer, it will come back again here. So, it goes in this fashion and then comes back here.

So, when you put the next layer, this is the next layer of oxygen atom and the next layer of aluminum atom goes there. If we keep doing this and you stack 6 layers of oxygen on top of each other, then you form the whole unit cell of alpha alumina or corundum. You can look at the cross section of the structure, which explains the structure in slightly better way.

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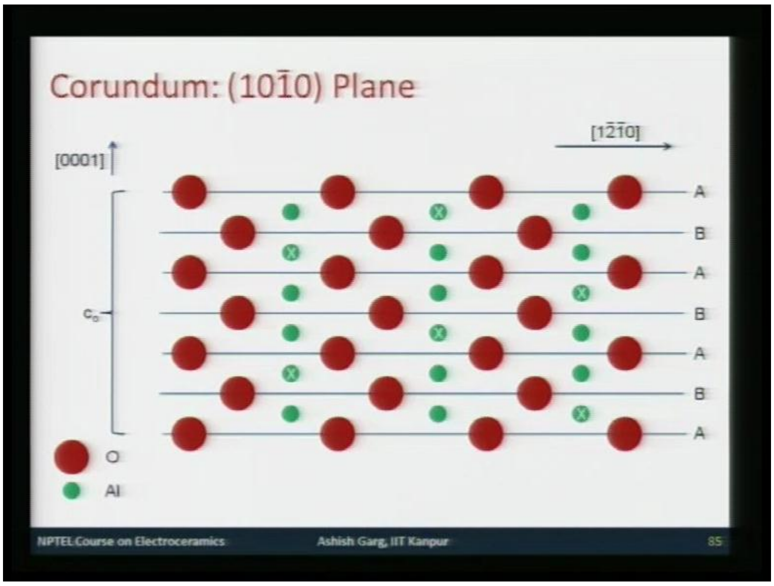

Corundum: (10$\bar{1}$0) Plane

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So, let us say, if I look at 1 0 bar 1 0 plane, which is this plane, then this is how it looks. So, you have this first layer of, A layer of, let us say oxygen followed by octahedral site filling. So, you have two filled and one empty site. Followed by second layer of oxygen atom and followed by again two by third filling of octahedral site. But if you notice that the position of octahedral site is changed and then you fill the third layer of oxygen A layer, then again the cation layer, then again you see that the site changes in a sequential manner. So, first this one goes empty, second this one goes empty and now, this one is empty. You could have made this one empty, that one empty and that one empty. So, does not really at all.

So, if we just keep doing it six times, so you have a first layer, second layer, third layer, fourth layer, fifth layer, sixth layer and this makes the whole unit cell. This would be your c parameter of alpha alumina. You can label the directions and this would be C axis 0001 direction and this direction would be 1 bar, 2 bar, 1 0. You have to make sure that the dot product of, since this is 1 0 bar 1 0 plane, the dot product of this plane, with these two directions has to be equal to 0.

So, this is how you stack two different kinds of atoms while you form this corundum structure. As you can see, these are the columns of filled octahedras; alternatively filled. So, these arrows point out these columns of octahedral, which share each other's faces.

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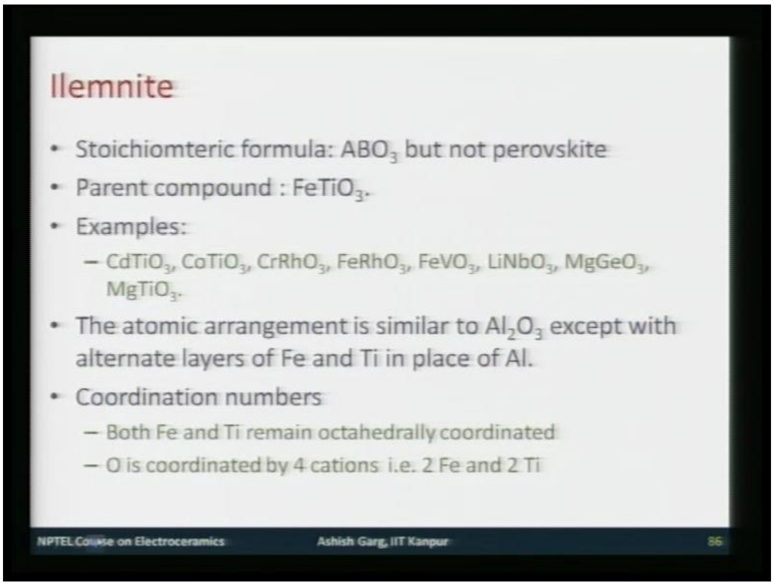

Ilemnite

- Stoichiomteric formula: ABO_3 but not perovskite
- Parent compound : $FeTiO_3$.
- Examples:
  - $CdTiO_3$, $CoTiO_3$, $CrRhO_3$, $FeRhO_3$, $FeVO_3$, $LiNbO_3$, $MgGeO_3$, $MgTiO_3$.
- The atomic arrangement is similar to Al_2O_3 except with alternate layers of Fe and Ti in place of Al.
- Coordination numbers
  - Both Fe and Ti remain octahedrally coordinated
  - O is coordinated by 4 cations i.e. 2 Fe and 2 Ti

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Now, the second structure, which is important in this series is Ilmenite structure. Now, Ilmenite structure has same formula as perovskite structure that is ABO 3. But it is not a perovskite structured compounds, rather it is based on the corundum structure. So, it is a hexagonal closed pack structure in a similar fashion as AL2O3. Except that, the difference is in the AL2O3. You have for 3 oxygen, 2 aluminum atoms and here for 3 oxygen atoms, you have 1 A atom and 1 B atom.

Now, the common example for this common compound or parent compound for this structure is FETIO3, iron titanate. Other examples are, for example, cadmium titanate, cobalt titanate and many other materials which follow the structure. However, iron titanate is the most commonly known compound for this structure. So, atomic arrangement is similar to AL2O3, except that in one layer you have iron and in the second layer, you have titanium. The site filling sequence is similar to as you have in aluminum oxide.

So, coordination numbers, both iron and titanium, since the filling is according to aluminum oxide structures, site filling remains same. So, iron titanium, both remain octahedrally coordinated. However, the coordination of oxygen now changes. It is coordinated by 2 titanium and 2 iron atoms, but it still it is coordinated by 4 cations.

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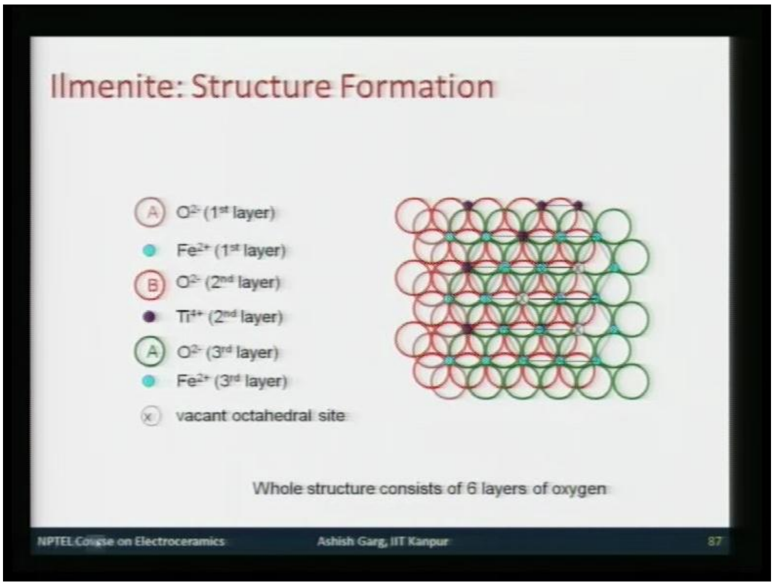

Ilmenite: Structure Formation

- Ⓐ O^{2-} (1st layer)
- ● Fe^{2+} (1st layer)
- Ⓑ O^{2-} (2nd layer)
- ● Ti^{4+} (2nd layer)
- Ⓐ O^{2-} (3rd layer)
- ● Fe^{2+} (3rd layer)
- ⊗ vacant octahedral site

Whole structure consists of 6 layers of oxygen

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So, the structure, the way it forms is, you have first layer of oxygen followed by second, first layer of iron atoms in the octahedral sites followed by, then this arrow again shows how the vacant site will move in the next layer and then this is the second layer of oxygen atom.

So, this is A layer, this is B layer followed by and now next layer will be titanium. So, this would be your titanium layer. But if you notice, the vacant site position is same as in aluminum oxide structure. Then you will have next layer of oxygen atom, which will be again A layer followed by next layer of iron atom, which would go right on top of the first layer of iron atoms. Then you will have the structure formed, if you keep doing it six times.

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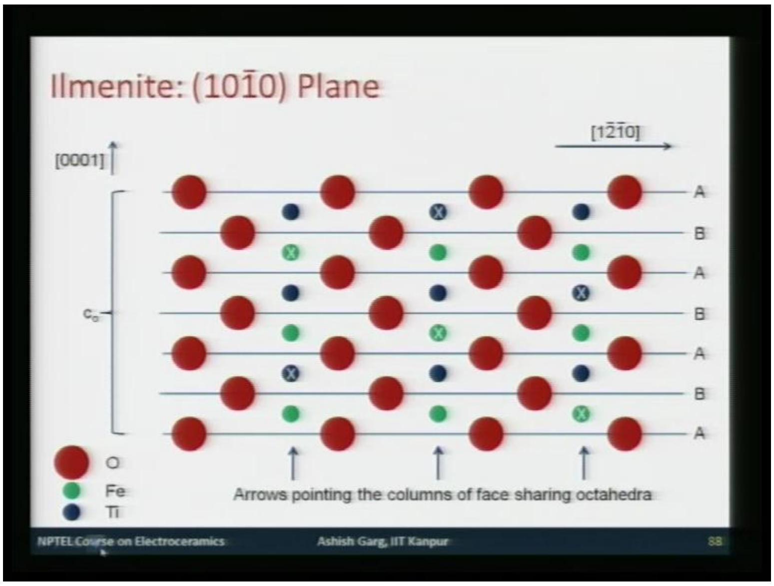

Ilmenite: $(10\bar{1}0)$ Plane

Arrows pointing the columns of face sharing octahedra

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So, the whole structure will consist of six layers of cations or oxygens and this will make a complete Ilmenite structure. Again, we can look at 1 0 bar 1 0 plane. So, first layer of oxygen, followed by first layer of iron, followed by B layer of oxygen, followed by first layer of titanium. If you notice, the vacant sites remain same. Except that, now aluminum atoms are replaced in one layer by iron and second layer by titanium. Then again, A layer of oxygen, then again first layer, second layer of iron followed by second layer of titanium, followed by again oxygen, again iron, again titanium and then oxygen. So, this will whole make one unit cell of iron titanate. Again you can mention the directions just like that. So, this is how and again these are the face sharing octahedral.

But now regularly alternatively occupied by iron titanium, vacant iron titanium vacant. So, this is how it is going to be occupancy sequence. So, this is another important structure, which is Ilmenite structure. Now, in this series, the next structure will be your Lithium Niobate structure. Now, Lithium Niobate is an important compound. It is ferroelectric in nature and it has optical properties, which are of technological importance. We will discuss that in the next slide.

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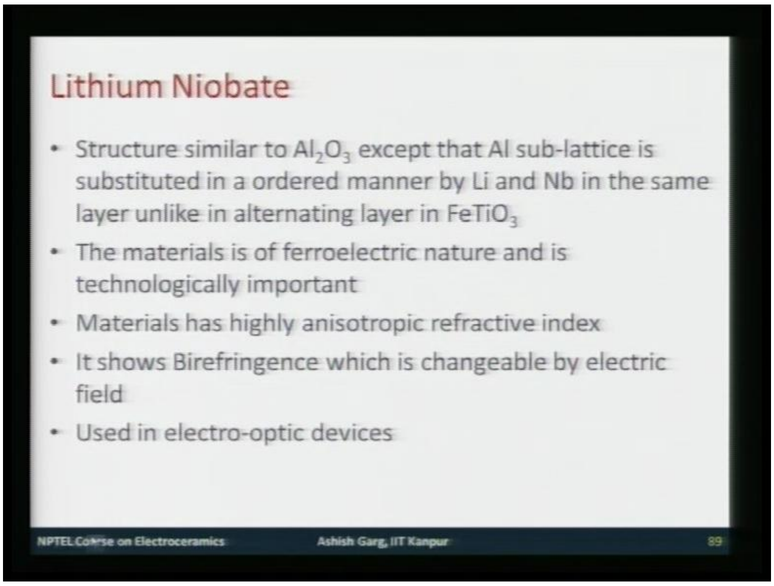

Lithium Niobate

- Structure similar to Al_2O_3 except that Al sub-lattice is substituted in a ordered manner by Li and Nb in the same layer unlike in alternating layer in $FeTiO_3$
- The materials is of ferroelectric nature and is technologically important
- Materials has highly anisotropic refractive index
- It shows Birefringence which is changeable by electric field
- Used in electro-optic devices

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So, if we go to the next slide, so again Lithium Niobate structure is very similar to aluminum oxide. By this, I mean that the anion sub lattice is same. So, anions pack in the same manner as they pack in aluminum oxide.

Now, the difference is, now in each layer where aluminum was, both lithium and niobium go, but they go in an ordered manner. So that, lithium and niobium occupy the aluminum positions in an ordered fashion, so that, the structure become repeatable. So, it is different to FETIO3, where FE and TI occupy the octahedral sites in alternating layers. Here, both the atoms stay in the same layer, but in an ordered fashion. So, this material, as I said is ferroelectric in nature, which makes it important from the point of view of technology. This also has the highly anisotropic reflective index, which is anisotropic means it is direction dependent.

So, it is high in one particular direction and low in another direction. It also shows birefringence and which can be changed by application of electric field. So, these properties make this material important from the point of view of applications, device applications and it is used in electro optic devices quite commonly.

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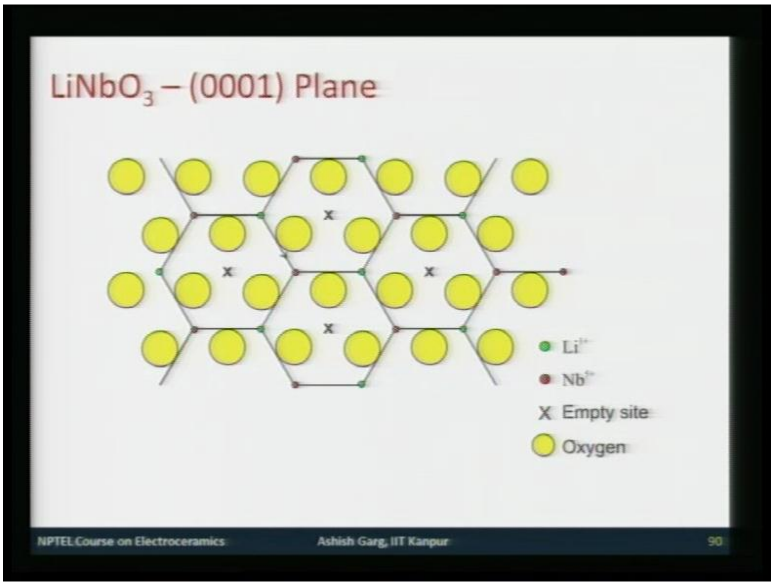

LiNbO$_3$ – (0001) Plane

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So, this is your Lithium Niobate 0001 plane. So, if you know now look at this, so the yellow atoms represent the layer of A B A layer of, let us say oxygen atoms. Now, if you look at here, these red and green atoms, red is niobium and green is lithium. They occupy the octahedral sites and the crosses represent the empty octahedral sites. So, if you look at, suppose the color of both of these small atoms was same, it would make aluminum layer in aluminum oxide. Now here, if you notice both of these are occupied in such a manner, so that, in one position lithium is surrounded by 3 niobium, and in other position, niobium is surrounded by 3 lithium. So, this is how the structure looks like or if you make a hexagon in this layer, the effects of the hexagon and the vertices of the hexagon are alternatively occupied by lithium and niobium atoms. So, this is how it is going to proceed. The new stack, the structure, I am not going to show you the stacking, because it is very similar to the previous two structures.

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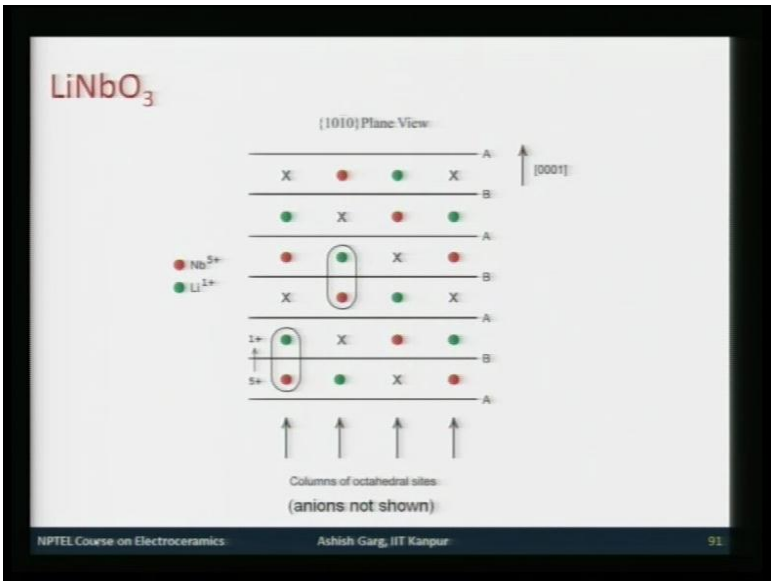

$LiNbO_3$

[1010] Plane View

(anions not shown)

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I am just going to show you the cross section of 1 0 bar 1 0 plane. So here, you have again A B A B A B layers. These are the oxygen layers. In between them, you have, so lithium niobium cross, which is the vacant site, then again lithium niobium vacant site. Then in the next layer, since the vacant position moves in this direction, in all the structures, so you will have again niobium vacant, lithium niobium and then again you will have vacant.

So, this is how it continues. Again 6 layers of oxygen atoms and this makes a lithium niobate unit cell. Again columns are columns of octahedral sites and you can again see lithium niobium vacant, niobium lithium vacant, niobium lithium vacant sites. The difference to FETI structure here is, here if you notice, this lithium and niobium atoms, they make charge dipole, which is a reason for this ferroelectric nature of these compounds. All these dipoles are pointed in one direction, which do not cancel each other. If you go back to iron titanate structure, there also you have dipole formation, but both the dipoles are oppositely oriented and they cancel each other. Hence, it is not a ferroelectric material.

So, this is one of the peculiarities, peculiar observation in this material. So, this would be your dipole. So, these are the structures, which are based on perfect HCP packing of anions. The last structure in this is going to be your titanium oxide or Rutile structure, which is based on HCP packing. But it is not exactly perfect HCP packing, rather it is called as a quasi HCP packing of anions. So, we will look at that structure in little detail and following that, we will summarize this module. In the next class, then we will start with the different module.

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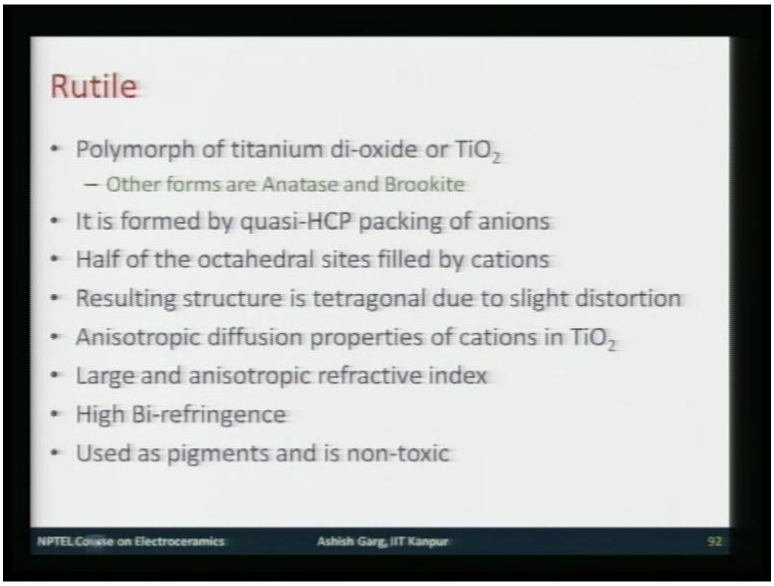

Rutile

- Polymorph of titanium di-oxide or TiO_2
  - Other forms are Anatase and Brookite
- It is formed by quasi-HCP packing of anions
- Half of the octahedral sites filled by cations
- Resulting structure is tetragonal due to slight distortion
- Anisotropic diffusion properties of cations in TiO_2
- Large and anisotropic refractive index
- High Bi-refringence
- Used as pigments and is non-toxic

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So, the next slide is on Rutile. Now, Rutile is a very well known material. It is used as pigments etcetera in applications and it is basically a polymorph of well known titanium dioxide. Other forms that can be available are Anatase and Brookite but Rutile is something which is very well known for variety of reasons. Now, in this structure, you have quasi HCP packing of anions, which means anions pack in the same fashion as in a FCC structure, but there is some distortion in terms of spacing of atoms and formation of perfect hexagon.

So, it is not exactly a hexagonal structure, but sort of quasi HCP structure. Now again, in this structure, red based on the radius ratio, you have octahedral site filling by cations, which means titanium goes to octahedral site having 6 fold coordination. Now, if titanium is occupied, if titanium is coordinated by 6 oxygens, based on the stoichiometry, oxygen will be coordinated by 3 titaniums. So, this is something or it will have triangular coordination. So, this is something which you can again verify using bond valance or bond strength rule. Since, you have for two anions one cation, only half of the octahedral sites will be filled. So, when we form the structure, the resulting structure does not have a hexagonal form. Rather, it is tetragonal in nature, because of slight distortion of the structure. So, that is why this HCP packing is referred as quasi HCP packing.

This material again, it has an isotropic diffusion properties and cation, which as titanium, it tends to diffuse, it tends to have different diffusivities and different directions and this makes this material very interesting. Also, it has very large isotropic reflective index, which is again technologically useful. This also tends to have high birefringence and this is commonly used as pigment and for some other optical applications, electronic applications and is in general non-toxic applications. Hence, it is also useful for some biological applications as well.

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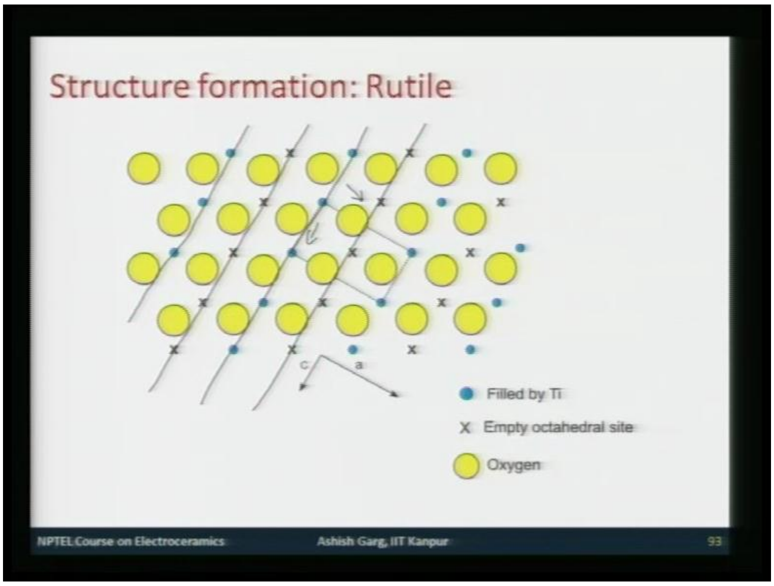

Structure formation: Rutile

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So, this is the structure. This is how the structure is formed. You have this one layer of oxygen atom, which forms itself in the same fashion as in a HCP structure. So, you can look at this hexagonal array of oxygen atoms. If you look at the structure, the octahedral sites are now filled by titanium. But you see, in this particular direction, all the sites are filled and in this particular direction, all the sites are empty and again, you have a column of filled sites and then again, you have a column of empty sites.

So, this tells you that 50 percent of octahedral sites are filled. Now, the unit cell has its corners. If you look at the unit cells on top, for example, unit cell has its corners on titanium atoms. So, it makes, this is the basal plane for example, of tetragonal structure. This would be your A axis and this would be your C axis as denoted below.

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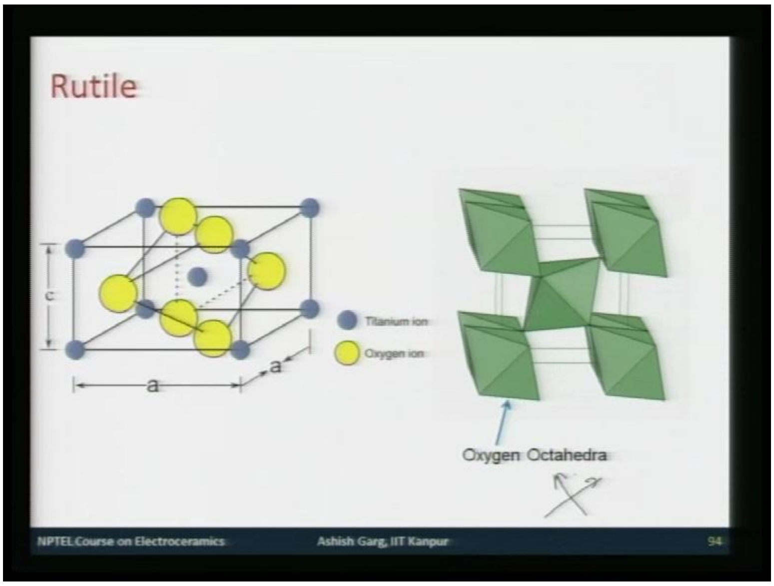

Rutile

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If you look at now the whole structure, so when you put the next structure, next layer on top of both oxygen and atom, oxygen and titanium, you see something like this. So, you have a bottom layer of titanium atoms with oxygen atom. So, if this is the whole layer of, so you have first layer of titanium, second layer of titanium, and third layer of titanium. Between them, you have oxygen, either top either below or under the layers and if you look at excuse me and if you just connect these oxygen atoms, they form an octahedra. Center of this octahedra is occupied by titanium atom. If you look at each oxygen atom carefully, each oxygen atom is occupied by, each oxygen atom is coordinated by 3 titanium atoms, because none of these oxygen atoms are perfectly within the plane. They are slightly out of or above the plane and their positions are not exactly in the center of the planes. As a result, they tend to be closer to 3 cations than anions.

If you look at the polyhedra model, the polyhedra model looks something like this. So, octahedras at the corners. So, since all the titanium atoms will be coordinated by octahedras, octahedras at the corners pointing in this direction and octahedra at the center will be pointing in this direction. So, it is a structure in which some half of the octahedras will be pointing in this way and half of the octahedras will be pointing in this way. So, this will make a, in this way and this way. So, this will make a titanium oxide rutile structure.

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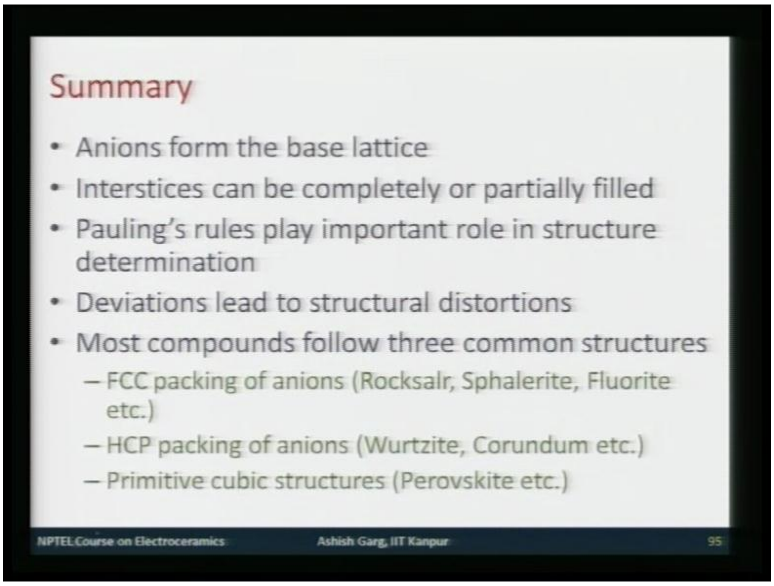

Summary

- Anions form the base lattice
- Interstices can be completely or partially filled
- Pauling's rules play important role in structure determination
- Deviations lead to structural distortions
- Most compounds follow three common structures
  - FCC packing of anions (Rocksalr, Sphalerite, Fluorite etc.)
  - HCP packing of anions (Wurtzite, Corundum etc.)
  - Primitive cubic structures (Perovskite etc.)

So, in summary, we have gone through variety of topics. We started with the discussion on lattice and bonding. We went through the concept of point lattice, what are point lattices, what is primitive lattice, and what is the non-primitive lattice. Those concepts are very important in order to understand the structures. Then we looked at what are the possible crystal systems and what are the possible bravais lattices. We saw that there are 7 crystal systems and 14 bravais lattices, which completely, in which all the possible crystal structures can be differentiated, since the choice of unit cell is not unique. As a result, you have to define certain way of categorizing them.

So, this forms a base of 7 crystal systems. Then cemetery comes into picture, which takes us to bravais lattices. So, you have for example, simple cubic body, central cubic phase, central cubic structures and then various other forms of orthorhombic and tetragonal structures, then rhombohedral, monoclinic, triclinic and hexagonal structures, so these with the structures. Then we looked at some formation of planes and directions very briefly. Then we reviewed the bonding. In bonding, we looked at metallic bonding, covalent bonding and ionic bonding. In most of the ceramic structures, tend to be ionically bonded with partial contributions from covalent bonding, since most of the ceramics are made from cations and anions, which in most cases have good difference of electro negativity. This gives rise to very strong ionic bond. As a result, they also have high modulus and high melting points and low portion thermal expansion.

Then, we moved on to understanding the ceramic structures. Before that, we also looked at how the atoms pack in metals and how the atoms pack in general, which actually form the bases or metallic structures. Voids between these spheres are interstices, which follow very good bases for filling in ionic structures. Because in anionic structures, anions being bigger, they form the host lattice and cations occupy the interstitial sites. Then we looked at various possible structures and we see that there are certain guidelines, which govern the formation of these structures, which are called as falling stools. Based on these rules, you have certain coordination of each anion or each cation and anion and the interstices based on the stoichiometry can be completely or partially occupied. Since the sizes of these atoms are often not perfect according to radius ratio, then also the shape of the atom may not be completely spherical. Often you have deviations from the equilibrium structure.

So, there are structure distortions. But in most cases, it is very easy to understand the structures. Most of the compounds follow three common structures. You have the structures based on FCC packing of anions, such as rock salt, sphalerite and fluorite structure, so most of the ceramic structures, most of the ceramic compounds follow three common structures. There are structures which were host lattices made in FCC packing by anions, so A B C A B C kind of packing of anions. Examples of which are materials like magnesium oxide, zinc oxide, (( )) oxide etcetera and these are defined by parent structures.

So, you can have rock salt structure, which is FCC based structure, where cations occupy the octahedral sites and based on the stoichiometry, all the octahedral sites are filled. You can also imagine the structure to have a intertwined structure of 2 FCC lattices made by cation and anion. Similarly, you can have sphalerite structure, sphalerite structures, zinc sulphide or zinc blend structures also often called as and compounds which follow the structure of, for example, your oxide, zinc sulphide, silicon carbide etcetera. Here again, anion make FCC lattice; however, here the cation has tetrahedral co-ordination.

Now, based on the stoichiometry, it is only, there is only 50 percent occupancy of tetrahedral sites. As a result, you have a periodic occupancy of tetrahedral sides which we looked at. Then we looked at fluorite structure, in which you can have fluorite or anti fluorite structure. So, for example, alkali oxides, like sodium oxide, lithium oxide, they make anti fluorite structure, where you have for each anion, two cations and both the cation, and the cations have tetrahedral coordination. So, oxygen makes FCC lattice and all the tetrahedral sites are filled by cations. In this case, the coordination for anion will be eightfold. So, anion will have cubic co-ordination.

However, lattice is represented by making a lattice unit cell on the anionic sites. So, it works pretty well and this structure again has FCC lattice. So, whether you put the lattice corner by unit cell corner on oxygen or any of the sodium atoms, that still makes FCC lattice. So, you can also think of this structure as 3 FCC lattices interpenetrating to each other. 2 FCC lattices of cations and 1 of anion and inverse of this structure is fluorite structure. There you have FCC lattice made by cations. This is the simplest way of understanding structure and all the tetrahedral sites of that unit cell filled by anions like in zirconium oxide

However, the correct way of understanding this structure is making the base lattice of anions. Now, since cations have eightfold co-ordination, which is cubic coordination; cubic coordination, if you just draw in a cube, it is not going to fulfill the stoichiometry because in one cube you will have only one cubic site. So, what you do is that, you make one big cube of 8 FCC 88 cubic unit cells of anions and now, you have in a big cube, you have 8 cubic voids or body centers. Out of these 8 or out of these 8, 4 are filled by cations.

So, this makes a fluorite structure or calcium fluorite kind of structures. Then we looked at the other structures like perovskite structure, cesium chloride structure, peroxide structures are very interesting structure from the point of view of applications. Many important materials like barium titanate and strontium titanate etcetera, which form perovskite structure. Typically, perovskite structure compounds are ABO 3 compounds, where you have a cube. For instance, the perfect form has a cube. The phase centers of this unit cell are occupied by oxygen and body center is occupied by the smaller atom, which is typically B and the corners of the unit cell are occupied by bigger atom, which is A.

However, most of the practical most of the materials in ferroelectric form show a non-cubic structure. It could be tetragonal rhombohedral orthorhombic depending upon the temperature and type of material, but the pattern remains same. So, that is perovskite structure. You can also have perovskite structure, where cation and anion can have plus 3 plus 3 valence and you can also have mixed perovskites, such as PM and lead magnesium niobate or lead scandium tantalite. Then we looked at the cesium chloride structure, whose parent structure itself is cesium chloride, where you have cubic coordination. Since stoichiometry is 1 is to 1, it is just formed within a cube.

So, corners of cube are occupied by 1 ion and center of the cube is occupied by another ion. It is a primitive cubic structure. So, both perovskite and cesium chloride are primitive cubic structure. Variation of perovskite structure is rhenium oxide structure. So, in ABO 3, if you remove A, then it is a BO 3 kind of structure. That makes a rhenium oxide structure such as in tungsten oxide. Then we looked at some of the special structures which are based on perovskite packing of, perovskite layer stacking such as yttrium copper oxide, which forms the bases of super conductor, super conducting compounds. Then we looked at HCP packing of anions. Examples of which were wurtzite corundum lithium niobate and iron titanium etcetera.

So here, in these structures and the cations, anions form the HCP packed layers and either tetrahedral as in wurtzite or octahedral as in corundum ilmenite or lithium niobate or in titanium oxide as well octahedral sites are occupied by cations. The occupancy is determined by the stoichiometry. So, this is very, what I can say is reasonably long discussion on the structures of ceramic materials. So, I hope you are able to understand the fundamentals. In the next class, we will move on to a different topic, which is important from the point of view of functional properties of these materials. So, in next class, we will look at what are the defects in these materials, how the defects form, how the defects are related to parameters like temperature and pressure of oxygen and so on and so forth. So, I hope that you are now able to understand the structures of these ceramic materials in a good detail.

Thank you.