Electroceramics
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Lecture - 3

Okay, so in this third lecture we will just review the last lecture, and then we will start on some of the new structures which you could not cover in the last lecture. So, in the last lecture we covered various ceramic structures which were derived on the rules made by Pauling which are five of them and those rules are as I said they are not fixed set of rules but are the guidelines which help in formation of ceramic structures. And as a result we divided the ceramic structures in three broad categories. The first one was the structures which were based on FCC packing of anions.

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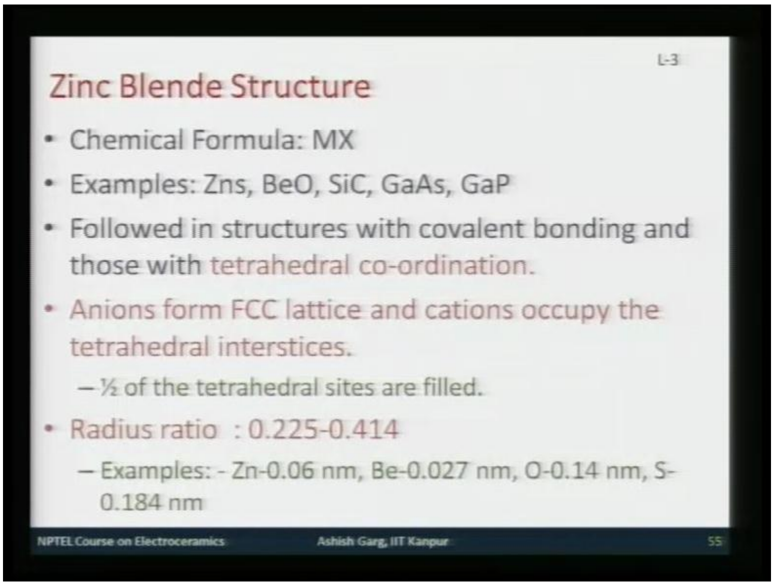

L-3

Zinc Blende Structure

- Chemical Formula: MX
- Examples: Zns, BeO, SiC, GaAs, GaP
- Followed in structures with covalent bonding and those with tetrahedral co-ordination.
- Anions form FCC lattice and cations occupy the tetrahedral interstices.
  - ½ of the tetrahedral sites are filled.
- Radius ratio : 0.225-0.414
  - Examples: - Zn-0.06 nm, Be-0.027 nm, O-0.14 nm, S-0.184 nm

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And second group would be non FCC but is still orthogonal or cubic structures and the third would be xcB packing of anions. So, in the FCC packing we looked at structures like your sodium chloride based structures or which are called as rock salt structures. Then second set of structures we looked were fluoride and anti-fluoride structure, And now we will look at other important FCC structure which is zinc blend structure. Now in this structure the chemical formula would be MX. So, you have for each cation you have an anion. So, valence of both cation and anion is equal and the examples of such ceramic materials could be zinc sulfide or barium oxide, zinc sulfide or zinc oxide, silicon carbide.

Now presence of silicon carbide here gives you a clue as to what kind of structure would be because remember when we discussed diamond-cubic structure we said that from the diamond-cubic structure you could also form silicon-carbide structure except that FCC positions were filled by silicon and that tetrahedral positions were filled by carbon and other compounds which shows structures like gallium arsenide and gallium phosphide, etcetera. In this case this S would be capital sulfur, okay. Now this is a structure which is followed in compounds which have some covalent character. For examples zinc oxide, zinc sulphide has this character, and as a result of covalent bonding not only radius ratio predicts tetrahedral coordination but also covalent bonding requires the tetrahedral coordination. So, you might find in some cases that radius ratio could be slightly off, the predicted radius ratio for tetrahedral coordination is between 0.225 to 0.414.

So, for instance in case of zinc and beryllium oxides or sulfides this is pretty much in line but for some compounds this may be slightly off and that is because the requirement of tetrahedral coordination due to covalent bonding. So, all the Pauling rules are obeyed in this case in most cases, but there may be some deviations due to requirement of tetrahedral coordination by bonding. And here again the anions form the FCC lattice and the cations occupy tetrahedral interstices. Now to maintain the stoichiometry you can see because for each cation you have one anion or vice versa; only half of the tetrahedral sites can be filled because in FCC structure there are two tetrahedral sites per atom. So, as a result only half of the tetrahedral sites are filled. So, now we will look in the next slide what the structure is.

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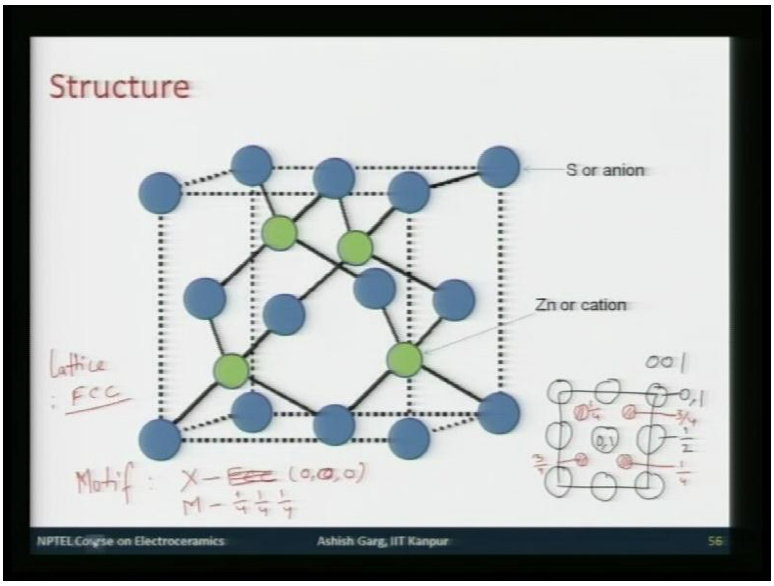

Structure

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Now the structure is. So, you have FCC structure made by these blue anions which could be for example in case of zinc sulfide sulfur atom and tetrahedral sites there could be 8 of them and only 4 of them are filled. So, the arrangement of filled tetrahedral sites is very similar to actually what you have in diamond. So, for instance you have two tetrahedral sites filled in the top half of the crystal and another two filled in the bottom half of the crystal which is rotated by 90 degrees. So, if these two tetrahedral sites were in the location for instance if you make a plan view. So, this is let say the plan view, this is 0 0 1 structure. So, these would be my sulfur atoms. So, this would be all the corner ones would be of 0 1 and this would be 0 1 as well and all these edges one would be at half and x y is self explanatory.

So, tetrahedral positions if in the top half of the crystal let me just change the color. So, if in the top half of the crystal the atoms were interstitial atoms were at 1 by 4 1 by 4 position, z is equal to 1 by 4, x y is self explanatory and the bottom half of the crystal these would be at 3 by 4. So, this is what it is shown in this three dimensional structure. So, this would be as well zinc sulfide or zinc oxide zinc blend structure is very similar to diamond cubic structure except the fact that that tetrahedral and the face centered cubic lattice ions are different. Now again in this structure the corner of the lattice can be put on sulfur iron and the corner of the lattice can also be put on the cation, so which is zinc. So, no matter where you put the corner of the unit cell, the unit cell will always remain as FCC.

So, in this case also the motif, so lattice type would be FCC because both cation and anion sub lattices are FCC in nature and motif would be if your anion is at FCC site then cation would be at 1 by 4 1 by 4 1 by 4 which is let us say 0 0 0. Once you define FCC lattice 0 0 would as I said many times it will fill all the FCC sites. Similarly, if you define 1 by 4 1 by 4 for m this is sufficient to fill all other tetrahedral sites which would be all the four tetrahedral sites not all the 8. So, this is zinc sulfide structure and next structure which is again based on FCC packing of anions is spinel structure.

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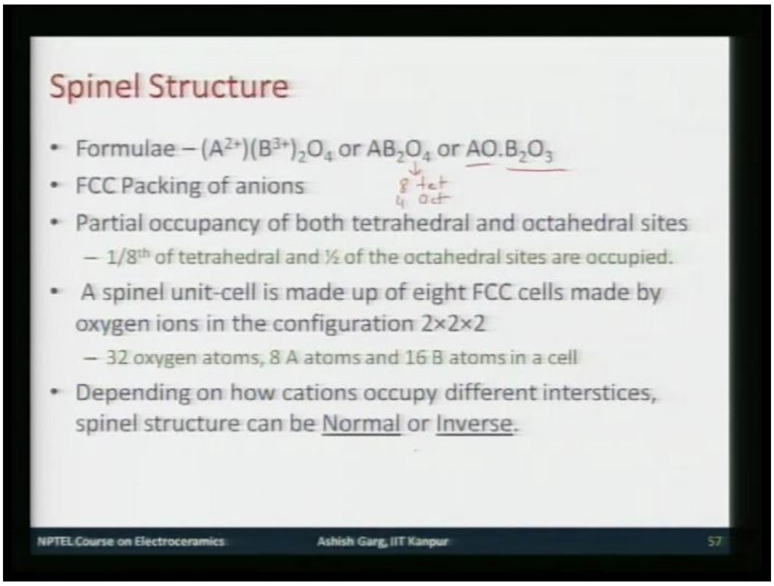

Spinel Structure

- Formulae – $(A^{2+})(B^{3+})_2O_4$ or AB_2O_4 or $AO.B_2O_3$
- FCC Packing of anions

8 tet
4 oct

- Partial occupancy of both tetrahedral and octahedral sites
  - 1/8th of tetrahedral and ½ of the octahedral sites are occupied.
- A spinel unit-cell is made up of eight FCC cells made by oxygen ions in the configuration 2×2×2
  - 32 oxygen atoms, 8 A atoms and 16 B atoms in a cell
- Depending on how cations occupy different interstices, spinel structure can be Normal or Inverse.

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Another formula for this spinel structure is AB 2 O 4, typically the A ion would be a ion with plus 2 valence and B would be anion with plus 3 valence. Another way to represent this formula is to consider this as a mixture of two oxides one of them would be AO and second one would be B 2 O 3. So, you could consider this as a mixture of two sub lattices AO sub lattice and B 2 O 3 sub lattice. This is what some people like to think in terms of. This is a very important structure because many engineering materials like iron oxide Fe 3 O 4, nickel iron oxide, cobalt iron oxide many magnetic materials, they follow this structure.

So, in this structure now since you have FCC packing and two different kind of anions both the anions both the cations cannot go in two different kind of cations, sorry not anions. So, both the cations cannot occupy the same interstitial site. So, radius ratio predicts that one of them goes to tetrahedral and another of them goes to octahedral. So, you have in this structure since you have FCC packing of anions. So, 4 oxygen atoms will give you 8 tetrahedral and four octahedral sites. Now 1 unit cell of spinel is made up of 8 FCC cells which mean total one big unit cell will contain 32 atoms out of which 8 will be 32 oxy. So, one unit cell will contain 32 oxygen atoms, 8 A type atoms and 16 B type atoms. So, total it would be 32 plus 24 anions plus cat ions.

Now in this structure you can see from the stoichiometry that not all interstitial sites can be filled. So, as I said in one type of spinel structure one particular site is filled by one cation and another particular site is filled by another cation. In another kind of spinel structure there is mixed occupancy at one site not on the other site but on one site and we will see how it changes in two spinel structures. So, basically in this structure you have a partial occupancy of both tetrahedral as well as octahedral sites, and no matter what type of spinal it is and how these are filled, you have one 1 8 filling of tetrahedral site. So, in one formula unit out of 8 only one tetrahedral site is filled and octahedral site you have 4 per formulae unit out of 4 two are filled. So, in a unit cell if you have 8 unit cells 8 FCC cells which means 8 formula units; 8 formula units is going to give you 64 tetrahedral sites and 32 octahedral sites in total.

So, out of 64 tetrahedral sites in one big unit cell of its spinel structure you have 8 tetrahedral sites which are filled and out of 32 octahedral sites 16 are filled, and we will see how cations arrange themselves in these 64 tetrahedral and 32 octahedral sites. And these two forms of spinal structures depending upon the distribution of cations in the interstitial sites define either a normal spinel or an inverse spinal. So, in case of normal spinel you do not have intermixing of cations in the interstitial sites whereas in case of inverse spinal you have intermixing of cations in one of the interstitial sites.

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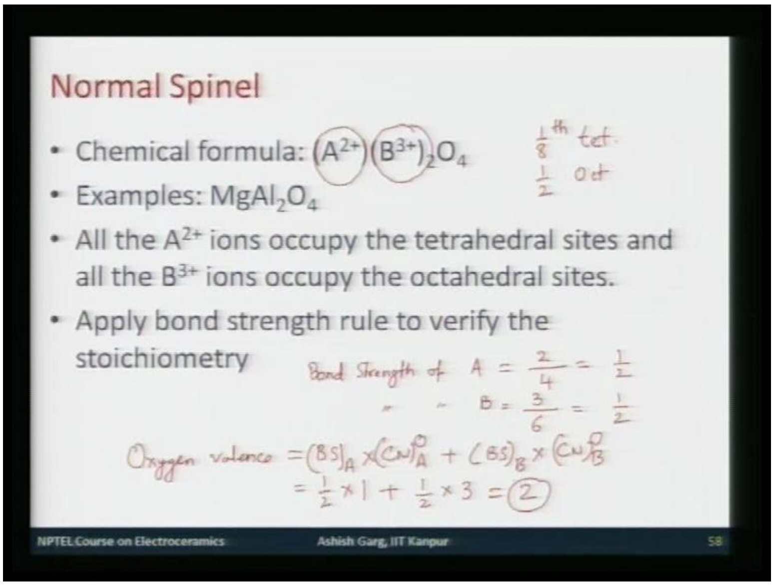

Normal Spinel

- Chemical formula: $(A^{2+})(B^{3+})_2O_4$
- Examples: $MgAl_2O_4$
- All the A^{2+} ions occupy the tetrahedral sites and all the B^{3+} ions occupy the octahedral sites.
- Apply bond strength rule to verify the stoichiometry

$\frac{1}{8}^{th}$ tet.

$\frac{1}{2}$ oct

Bond Strength of $A = \frac{2}{4} = \frac{1}{2}$

" " $B = \frac{3}{6} = \frac{1}{2}$

$$\text{Oxygen valence} = (BS)_A \times (CN)^O_A + (BS)_B \times (CN)^O_B = \frac{1}{2} \times 1 + \frac{1}{2} \times 3 = \boxed{2}$$

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So, we will see what these are. So, in case of normal spinel chemical formula can be represented as A in one bracket and both the B’s in one bracket. What this means is that all the A’s occupy one interstitial site one type of interstitial site and all the B’s occupy another type of interstitial site. Now if you go back to my previous statements in which I said that one-eighth of tetrahedral are filled, so one-eighth tetrahedral and half octahedral. So, now you can understand one-eighth tetrahedral would mean you have all the A ions going to tetrahedral sites in the normal spinel structure and all the B ions going to octahedral sites occupying half of them in the normal spinel structure, and you can very well apply the bond strength rule to verify the stoichiometry, how do you do that?

So, bond strength would be for instance bond strength of A it would be valence of A which would be 2 and the coordination of A which is 4 and this gives you 1 by 2. Similarly bond strength of B is valence of B which is 3 and coordination of B which is 6 octahedral coordination, this is 1 by 2. Now how do you make it equal to how do you verify the stoichiometry from this? Now to work out the bond strength of oxygen for both of them is slightly tricky. So, what I am going to do is that I going to work out the bond strength of I am going to work out the valence of oxygen; if I get minus 2 which means the coordination which I am calculating are correct, and if I am not doing it properly then value then the valence of oxygen would not be correct.

So, oxygen valence in terms of both the bond strength would be. So, bond strength of A multiplied by how many oxygen's are surrounded by A type of atom which means coordination of oxygen by A plus bond strength of B multiplied by coordination of oxygen by B, okay, so OA or OB. Now bond strength of A is half and in spinel structure what happens is oxygen is surrounded by 1 A atom and 3 B atoms. As a result the answer that you get is 2. So, this is two. So, oxygen valence is 2 which mean the coordination's that we are talking about are correct.

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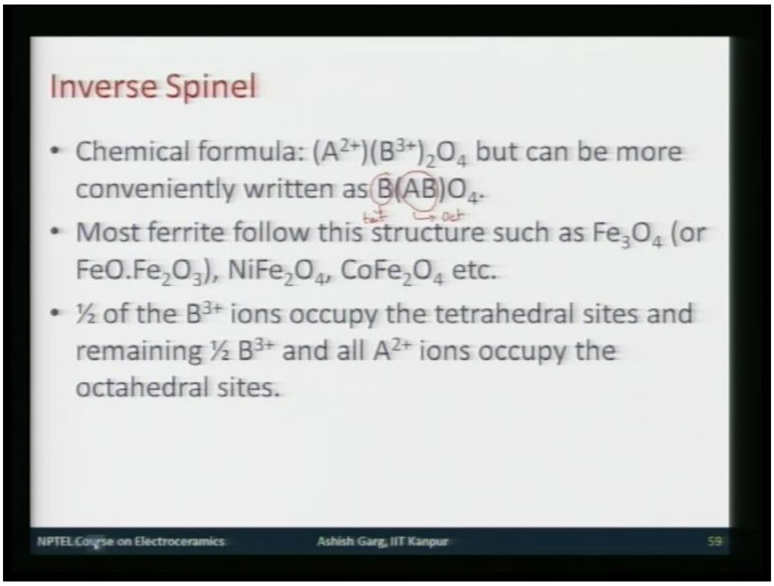

Inverse Spinel

- Chemical formula: $(A^{2+})(B^{3+})_2O_4$ but can be more conveniently written as $B(AB)O_4$.

tet → oct

- Most ferrite follow this structure such as Fe_3O_4 (or $FeO.Fe_2O_3$), $NiFe_2O_4$, $CoFe_2O_4$ etc.
- ½ of the B^{3+} ions occupy the tetrahedral sites and remaining ½ B^{3+} and all A^{2+} ions occupy the octahedral sites.

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On the other hand in inverse spinel structure what happens is the chemical formula is written as B AB O 4. Now it is again AB 2 O 4, but the way A and B occupy these interstitial sites changes the order. So, what I have done is I have put B separately and another B and A together. What this means is that one B which means 50 percent of total B ions occupy tetrahedral sites. So, this B will go to tetrahedral site and these two will go to octahedral which means A and remaining B will go to octahedral site. Example of this many ferrites follow this kind of structure such as Fe 3 O 4 which can be conveniently written as FeO dot Fe 2 O 3 or Ni Fe 2 O 4 which is also a mixture of Ni O and Fe 2 O 3 or Co O cobalt ferrite which is Co O dot Fe 2 O 3 or Co Fe 2 O 4. So, many of these materials follow this inverse spinel structure and these are all engineering materials because they are used in magnetic applications.

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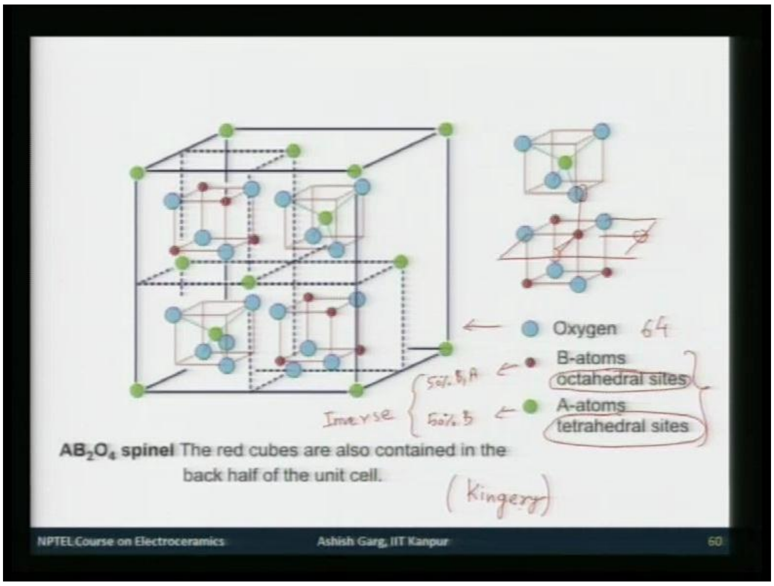

AB_2O_4 spinel The red cubes are also contained in the back half of the unit cell.

So, how does the structure look like? The structure is rather complex. So, you have this cubic unit cell a big cubic unit cell which contains 8 of these little FCC unit cells made by oxygen atoms. So, total 64 oxygen atoms would be present in one big unit cell of spinel structure, okay, and as a result now you can work out the B and A numbers. Now here if B goes to octahedral site for the sake of convenience and A go to tetrahedral sites.

So, this is basically a normal spinal structure. So, these are the. So, this is for example your oxygen and you can see that how many. So, the green atoms are A atoms, red atoms are oxygen atoms, and the blue atoms are your oxygen sorry red atom are B atoms, and blue atom is your oxygen atom, and this is a very complex structure. It is rather easy to visualize the tetrahedral site coordination, but it is a little tricky to visualize the octahedral coordination of B.

So, you can see in each layer for example, you see here that each of these is surrounded by 3 of them on one site, but it is also surrounded by other 3. So, if two B are on this side there will be another two B on this side. So, if you draw adjacent unit cell and then another adjacent unit cell on this side you will have one of them here and another one of them here and there will be another one on top. So, this will make an octahedral coordination of B, and in case of inverses spinel these red ones will be half B and A, and this would be half of B; half B means 50 percent B. So, let me just modify this a little bit.

So, this would be 50 percent B, 50 percent B in case of inverse, and here in this case it is normal, okay.

So, this is a ceramic structure. If you want to learn about how would this structure is formed from layer to layer I would suggest that you look at the book of Kingerry which is science of ceramics and where the layer by layer formation of this structure is explained in a very nice manner. So, what you would do is that you would first fill one particular site then second particular site and this goes in a sort of helical kind of manner, so that you get the repeatability of the structure, okay. Now this takes us to the end of most common structures which are based on FCC packing of anions. So, we had discussed rock salt structures, fluoride structure, zinc sulfide structure or zinc blend structure and spinel structures. This is followed by structures which are not based on exactly FCC kind of packing of anions; there is some similarity with respect to previous structures, but the structure itself is not a FCC. It is more or less its primitive structure; it could be primitive cubic or it could be a primitive tetragonal or primitive auto rhombic structures. So, we will look at this some of the structures in the subsequent slides.

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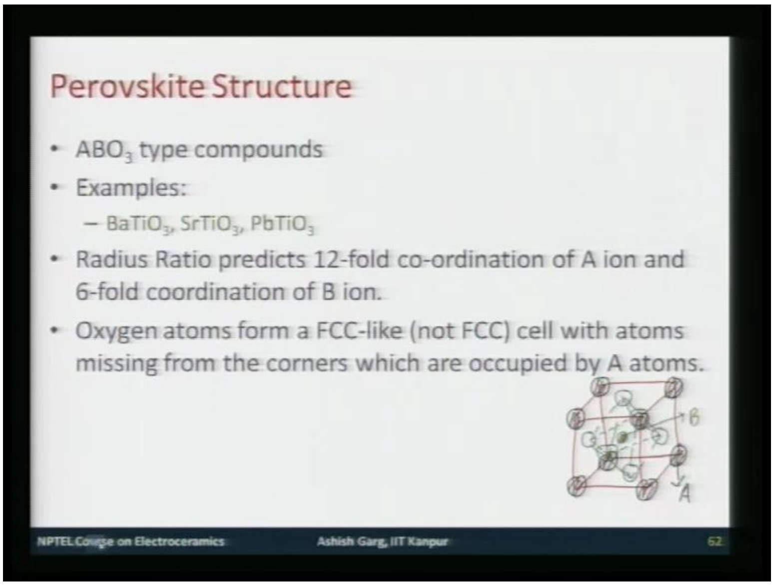

Perovskite Structure

- ABO_3 type compounds
- Examples:
  - $BaTiO_3$, $SrTiO_3$, $PbTiO_3$
- Radius Ratio predicts 12-fold co-ordination of A ion and 6-fold coordination of B ion.
- Oxygen atoms form a FCC-like (not FCC) cell with atoms missing from the corners which are occupied by A atoms.

So, the first in the series is perovskite structure. Now this perovskite structure is a very important structure because many engineering materials follow this kind of structure and most of many ferroelectric or manganite kind of materials, they follow this structure, and the formula for this particular structure are the compounds which follow the structure as

ABO 3. So, where two cations are A and B an anion is of course the oxygen, and the most common examples of materials which follow the structure are barium titanate, strontium titanate and lead tiatanate, and there are many other compounds which I will show whose names I will give it to you in the subsequent course of time. Now how this structure is formed? Again Pauling's rules apply and based on the radius ratios one predicts 12-fold coordination of A ion and 6-fold coordination of B ion. So, naturally you can see since you have 12-fold coordination of A ion the A ion tends to be much more bigger as compared to B ion which is octahedrally are 6-fold coordinated.

In this structure the difference with respect to previous structure says here oxygen atoms form a FCC like lattice but not all the FCC positions are occupied. So, you can consider this structure as you make a cube here, okay, and what you do is that if I change the color then all the face centered positions are occupied by oxygen all the face centers but I leave the corners empty. Now this does not make a FCC lattice but a FCC like lattice whose crystal system is again primitive cubic. Now what I do next is I fill the empty site which is the corner site with another kind of atom. So, I choose the bigger atom which is the barium in barium titanate.

So, this would be your A atom or barium in barium titanate. Now where does the titanium go? I am saying it should go to 6-fold coordination; 6 fold is octahedral coordination, where is the octahedral coordinated sight in this kind of structure? It would again be at the center of the unit cell. So, I will have the center of the unit cell and if you want to draw the octahedral, octahedral would be this. If you connect these oxygen atoms and then connect with the top oxygen atom and the bottom oxygen atom, so this is an octahedral right in the middle of the unit cell. So, you can see this would be your B atom and all this blue ones are oxygen atoms. So, this is how the structure is formed.

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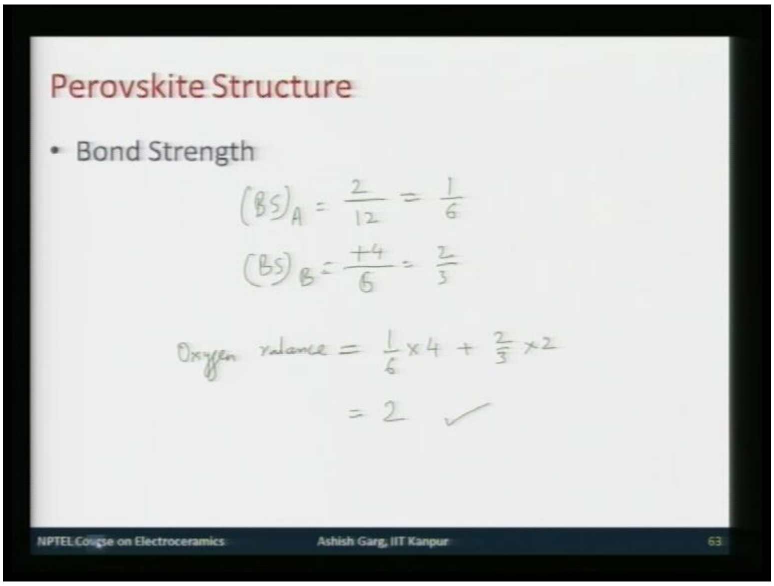

Perovskite Structure

- Bond Strength

$$(BS)_A = \frac{2}{12} = \frac{1}{6}$$

$$(BS)_B = \frac{+4}{6} = \frac{2}{3}$$

$$\text{Oxygen valance} = \frac{1}{6}\times 4 + \frac{2}{3}\times 2$$

$$= 2 \checkmark$$

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You can again apply the bond strength rule to work out the stoichiometry. So, bond strength of you can calculate bond strength of A ion. So, A ion is plus 2 divided by its coordination 12 that would be 1 by 6, bond strength of B is plus 4 in case of barium titanate and this would be divided by 6. So, this would be 2 by 3. So, oxygen valence is given as 1 by 6 multiplied by how many A ions surround an oxygen plus bond strength of B and how many B ions surround an oxygen atoms. So, this would be 1 by 6 into 4 plus 2 by 3 into 2. So, if you look at the structure there will be 4 A atoms which surround each oxygen atom, and there will be two titanium atoms which surround an each oxygen atom, and this will work out to two. So, which means your stoichiometry is correct. So, this gives you correct stoichiometry as a result of correct coordination.

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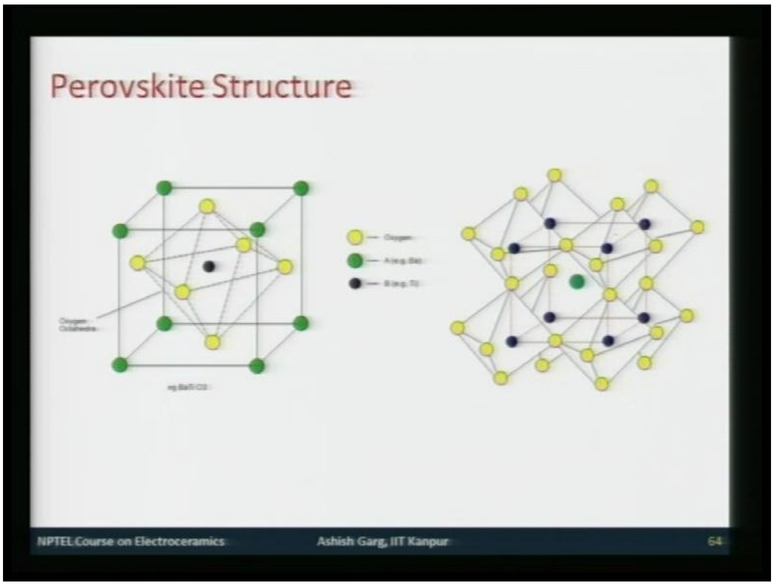

Perovskite Structure

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So, the structure looks like this. Green atoms would be A atoms or barium atom and the blue center atom would be B atom or the titanium atom and all the face centered atoms would be oxygen atoms, and you can see that all these 6 oxygen atoms make a oxygen octahedral center of which is occupy by a smaller sized atom; octahedral view would look something like this, this is a polyhedral view. So, you have 8 of these octahedral. Now in this case if you notice the corner of the unit cell has been shifted from barium to titanium atom, and now since titanium is at the corner of the unit cell the corner of the unit cell also contains these octahedral. So, 8 octahedral that 8 corners of the cell and middle of the cell is occupied by big barium atom and this barium atom is coordinated by 12 oxygen atoms making it a dodecahedra; dodecahedra is the coordination of each of these barium atom.

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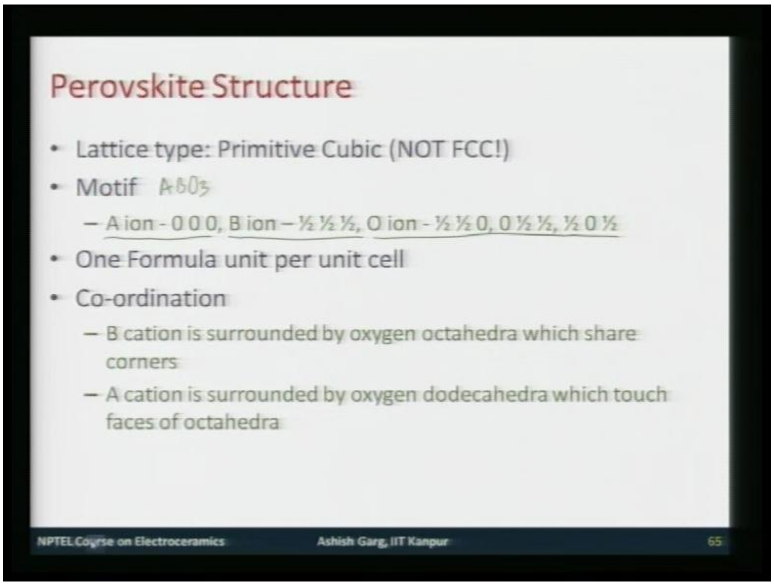

Perovskite Structure

- Lattice type: Primitive Cubic (NOT FCC!)
- Motif ABO_3
  - A ion - 0 0 0, B ion – ½ ½ ½, O ion - ½ ½ 0, 0 ½ ½, ½ 0 ½
- One Formula unit per unit cell
- Co-ordination
  - B cation is surrounded by oxygen octahedra which share corners
  - A cation is surrounded by oxygen dodecahedra which touch faces of octahedra

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So, in this case now if you were thinking that the lattice type would be FCC you are not correct, because for FCC lattice all four FCC positions must have been occupied by oxygen ion. In this case only three face centered position were occupied by oxygen, corners were empty and they were occupied by cations. So, lattice type is primitive cubic. So, you can define this structure as 5 primitive cubic lattices, 3 of anions and two of cations interpenetrating into each other. So, this is a primitive cubic lattice, and the motif or the formula unit is ABO 3. So, one unit cell contains one formula unit which means it is a primitive lattice, and A ion goes to 0 0 site, B ion goes to half half site and oxygen goes to half half 0, 0 half half and half 0 half sites.

Notice since the lattice type is primitive cubic I had to define all the oxygen positions. If it was FCC then I only need to define oxygen or any other iron at 0 0 0 and rest would be automatically formed in FCC type of manner by just translating each of these by half half 0 translation. As I said there is one formula unit per cell coordination B surrounded by 6 oxygen atoms making oxygen octahedral which are shared at the corners if you looked at the previous picture. And A is surrounded by 12 oxygen atoms which make dodecahedra which touch the faces of octahedral. So, the common point between dodecahedra and octahedral is the face. There are not only you have ABO 3 kind of compounds but you also have some other type of perovskite compounds.

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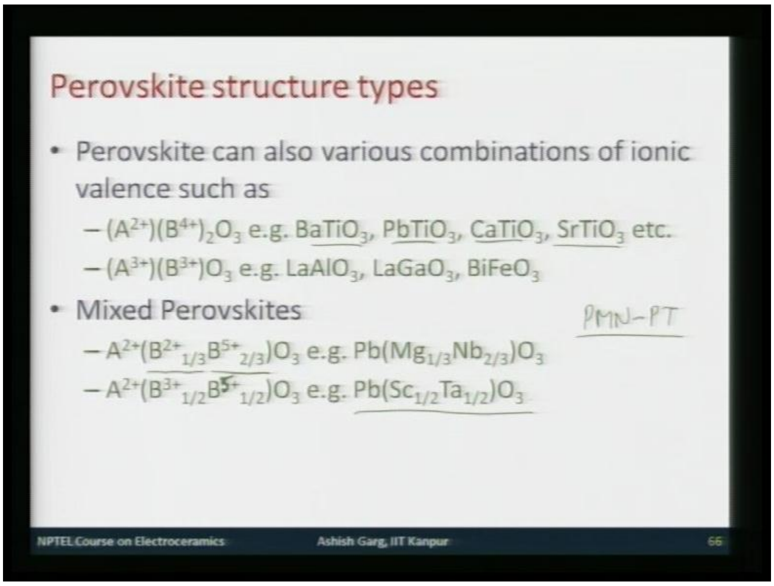

Perovskite structure types

- Perovskite can also various combinations of ionic valence such as
  - $(A^{2+})(B^{4+})_2O_3$ e.g. $BaTiO_3$, $PbTiO_3$, $CaTiO_3$, $SrTiO_3$ etc.
  - $(A^{3+})(B^{3+})O_3$ e.g. $LaAlO_3$, $LaGaO_3$, $BiFeO_3$
- Mixed Perovskites
  - $A^{2+}(B^{2+}{}_{1/3}B^{5+}{}_{2/3})O_3$ e.g. $Pb(Mg_{1/3}Nb_{2/3})O_3$
  - $A^{2+}(B^{3+}{}_{1/2}B^{5+}{}_{1/2})O_3$ e.g. $Pb(Sc_{1/2}Ta_{1/2})O_3$

PMN-PT

So, naturally if you have A 2 plus and B 4 plus it would be BaTiO 3, PbTiO 3, calcium titanate, SrTiO 3 strontium titanate; all these are very well known ferroelectric oxides, and you can also have A 3 plus B 3 plus O 3. So, here instead of having 2 by A 2 and B 4 you have A 3 and B 3. So, 3 plus valence gives rise to compounds like lanthanum aluminates, lanthanum galliate or bismuth ferrite; again very important in engineering ceramics used in many device applications either as films or substrates and then you have a mixed perovskites where one of these cations typically B can be make sure of two cations. So, for instance you can form a compound of formula A 2 plus then B 2 plus B 5 plus.

Now, to maintain the stoichiometry and the charge neutrality B 2 plus is 1 by 3. So, one-third of B sites are filled by B 2 plus and one another two-third of B sites are occupied by 5 plus cation. So, one such example is lead magnesium niobate; this is also called as PMN. PMN makes a very important material like PMN-PT in solid solution with lead titanate, so PMN-PT which is a very important very well known relaxer material. So, here you could see that one-third of octahedral sites are occupied by central one-third of octahedral sites were occupied by magnesium and two-third of octahedral sites were occupied by niobium. You can also have there is a slight mistake here; they should be B 3 and 5 plus here, that is correct.

Now, instead of having one-third and two-third occupation of B site you can have half-half occupation of B site, but rather what you will have here is you have one B cation half of the B cation B sites would be occupied by plus 3 valence cation and half of the B sites would be occupied by plus 5 cation. So, now this average of these anyway gives you 4. So, this is very much similar to A 2 plus B 4 plus O 3 except that B sites 4 is now averaged out by half of B 3 plus and half of B 5 plus cations. So, one example is lead scandium tantalite which is again a very extensively resourced material a dielectric material. So, these are some of the examples of perovskite structures. So, these are again just to reiterate these are not FCC based structure; these are simple primitive cubic structures where you can imagine the structure as being interpenetration of 3 anions sites 3 anions cubic sub lattices and two cation sub lattices.

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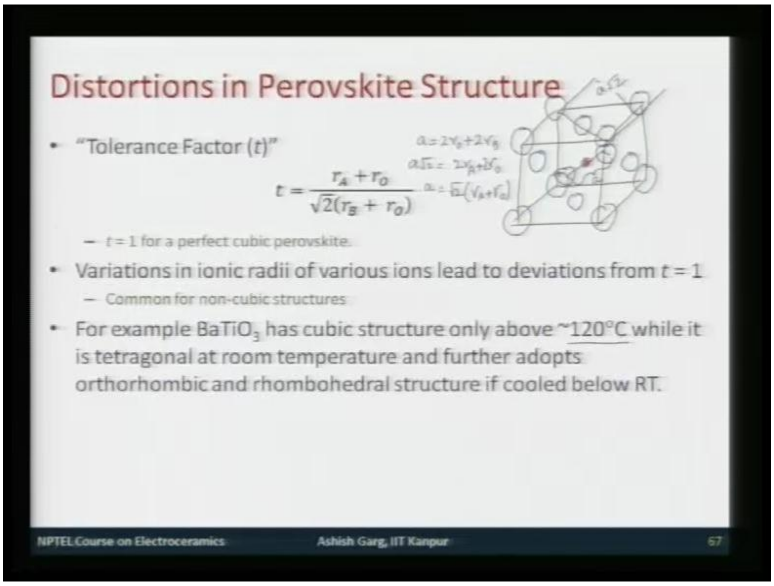

Distortions in Perovskite Structure

- "Tolerance Factor (t)"

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

  - $t = 1$ for a perfect cubic perovskite.
- Variations in ionic radii of various ions lead to deviations from $t = 1$
  - Common for non-cubic structures
- For example $BaTiO_3$ has cubic structure only above ~120°C while it is tetragonal at room temperature and further adopts orthorhombic and rhombohedral structure if cooled below RT.

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One important parameter which defines perovskite structure is tolerance factor. A tolerance factor is given as sum of radius of A ion and oxygen ion divided by root 2 of radius of sum of radius of B ion and oxygen ion. Now for a perfect cubic perovskite this would be one and you can see how, I mean if you have this kind of structure. So, if these were all anions oxygen atoms and then you will have in the center you will have the smaller atom which is like cations smaller cations such as titanium, and then you will have another one would be your bigger cation which is for example barium and barium titanate. Now imagine that all these ions were touching each other and cations were perfectly touching all the anions. Then the sum of this lattice parameter which is nothing but. So, this is your lattice parameter A.

So, A is equal to 2 r O plus 2 r B, correct, and then you have this side which is a root 2 and a root of 2 is equal to 2 r A plus 2 r O or a is equal to root 2 of r A plus r O. So, now if you divide r A plus r O by root 2 of r O plus r B you will get one for a perfect cubic perovskite, but in practice since the ionic positions are such that they never form t is equal to 1. So, most of the perovskite structure will show deviations from one, and often what happens is you may also find non-cubic structures such as distortions may happen into tetragonal or rhombohedra or orthorhombic structures, and this is specially important for because cubic structures also tend to be centrosymmetric which means they have a center of symmetry which if the case then compound not will be ferroelectric and to be ferroelectrics since most of these compounds are ferroelectric compounds it requires that structure be present in non-cubic state such as tetragonal or rhombohedra or orthorhombic. So, many of these peroxide compounds also commonly present in non-cubic forms.

So, it is very common in non-cubic structures, and in many of those cases t is never equal to 1; it is always less than 1 in most cases. For example, material like barium titanate it has a cubic symmetry only above 120 degree centigrade which is also called as Curie temperature which we will see in subsequent lectures what it is, but Curie temperature is basically transition temperature above which the material is cubic and below which when you cool it, first is it is tetragonal and then further cooling brings it down to orthorhombic structure as well as rhombohedra structures if you pull it further down room temperature. So, these are your perovskite structured compounds. So, I hope that you have been able to understand the basis of formation of these perovskite compounds.

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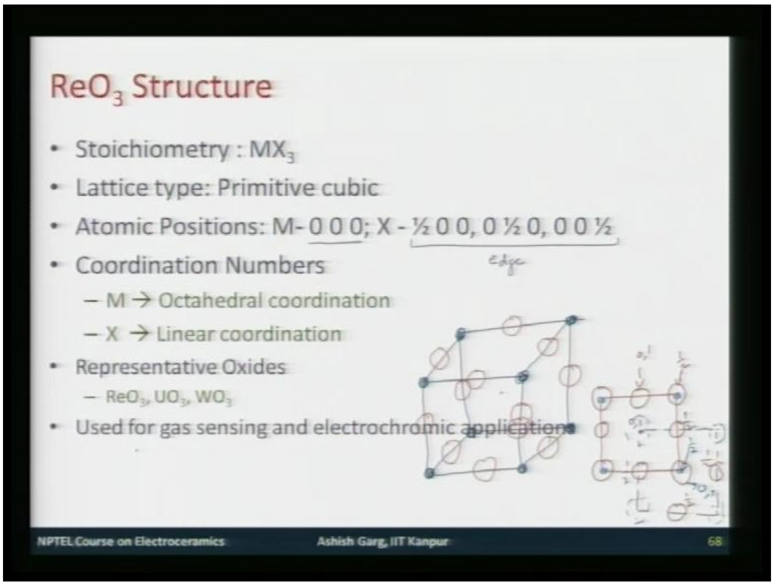

ReO_3 Structure

- Stoichiometry : MX_3
- Lattice type: Primitive cubic
- Atomic Positions: M- $\underline{0\ 0\ 0}$; X - $\underbrace{\tfrac{1}{2}\ 0\ 0,\ 0\ \tfrac{1}{2}\ 0,\ 0\ 0\ \tfrac{1}{2}}_{edge}$
- Coordination Numbers
  - M → Octahedral coordination
  - X → Linear coordination
- Representative Oxides
  - ReO_3, UO_3, WO_3
- Used for gas sensing and electrochromic applications

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The next structure in this series of structures based on non-FCC looking but not FCC structures is your rhenium oxide structure on basis of which there are some again useful compounds. So, stoichiometry here is MX 3. So, for each cation you have 3 anions. The lattice type again is primitive cubic. This structure is very much similar to perovskite structure; that is why I have put it after perovskite, but there are some differences. So, here the atomic positions are metal occupies 0 0 0 position, and oxygen occupies or the cation occupies as half 0 0, 0 half zero and 0 0 half position.

So, if you think about it these are the edge positions; if you make it huge these would be edge centers, and this would be corner of the cube. So, naturally corner of the cube 8 of these corners will give you one atom and there are 12 edges and each edge is shared by 4 unit cells. So, 12 by 4 will give you 3 anions. So, if you look at the coordination the coordination number according to radius ratio as well metal ion is octahedrally coordinated and as a result of requirement of bond strength and to maintain the stoichiometry the anion has to be linearly coordinated.

This links somewhere like M is octahedrally coordinated and X is linearly coordinated. If you go back to perovskite structure the coordination of one of the cations was octahedral, okay, and that very cation coordinated the anion in a linear coordination and that was if it was ABO 3 it was B. So, this structure you can say it is a ABO 3 structure with A missing, okay. So, I can form this structure as. Now this is what it is going to look like if

I make this structure according to what I have written. So, according to what I have written this structure is. So, I am saying that metal is at 0 0 0. So, this is metal or the cation. So, this will effectively make one cation and anion I am saying is going to these sites. So, these are 12 edges and you have 12 of these anions. Now this does not ring the bell, right.

Now what I am going to do is that. So, this sort of rings the bell that this structure is pretty much similar to what something we have seen before. So, what I am going to do is that instead of keeping the center here I keep the center here. So, I make another. So, you shift it here. So, the best way to understand that is to make a plan view. So, plan view is something like this, okay, and the previous position of atoms is. So, you have metal at 0 1 and so these are at the moment 0 1 and oxygen is at. So, you have half half. So, these would be at 0 1 all that and these would be at half positions half and 0 1 and the blue one is a 0 1. So, what I am going to do now is I am going to draw out of the one.

So, I want to draw another unit cell which is going to be here whose corner at the center of the unit cell. Now if I put the corner at the center of the unit cell then this position becomes 0 1. As a result this position which was 0 1 earlier it becomes half. This will also become half, and you will have another one here at half and you will have another one here at half, okay, and you will have these oxygen atoms at the, sorry this would be empty; these are empty, nothing, okay, and where is your cation going to be? So, these were at half and this would become at 0 1 and this cation would become at half.

So, this now looks like ABO 3 structure with these big cations missing which were supposed to be at 0 1 but they are not there, and you have these oxygen atoms which are the face centers and these are top and bottom face centers oxygen atoms and the middle you have titanium atom. So, this is going to look like ABO 3 kind of structure with A atom missing. Thus materials which form the structures are materials like rhenium oxide; rhenium oxide is the parent compound that is why it is known as rhenium oxide structure and other oxides like uranium oxide, tungsten oxide. Tungsten oxide is a very useful material; it is used for electrochromic applications and which is used also for gas sensing application.

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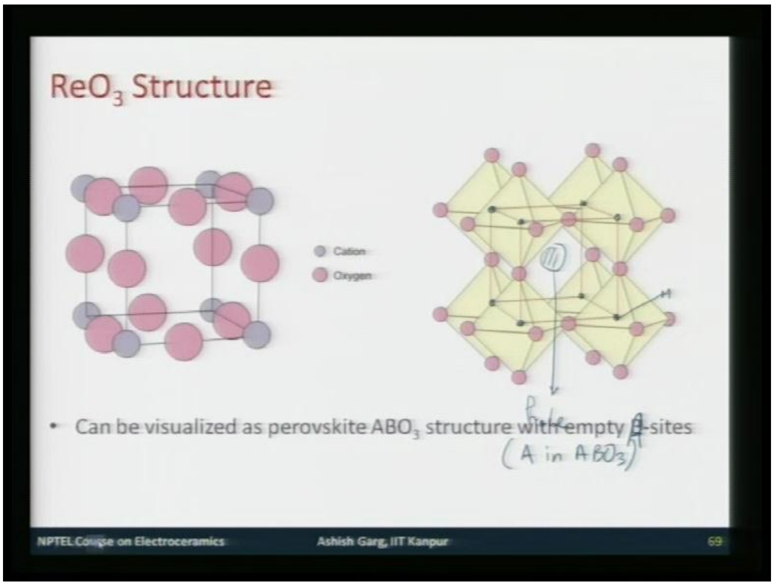

ReO_3 Structure

- Can be visualized as perovskite ABO_3 structure ~~with~~ hole empty ~~B~~ A-sites (A in ABO_3)

So, this is the structure what it looks like. This is the structure looks in the form in which I have given you the atomic positions. This is how it looks that way, but you can also say that if you remember in perovskite structure we drew the perovskite polyhedral module of perovskite structure where we put the corner of the unit cell at the central position at the corner of the unit cell at the titanium atom. So, this is in this case here you would have. So, these positions would be now metal positions and all these 8 metal positions are surrounded by 6 of these anions and the center of the unit cell which was supposed to be. So, in this case it is a hole but A in ABO 3 which is missing in this case. So, now I hope you can understand what the structure is like. So, it can be visualized as a perovskite ABO 3 structure which is empty A sites, not the B, A sites.

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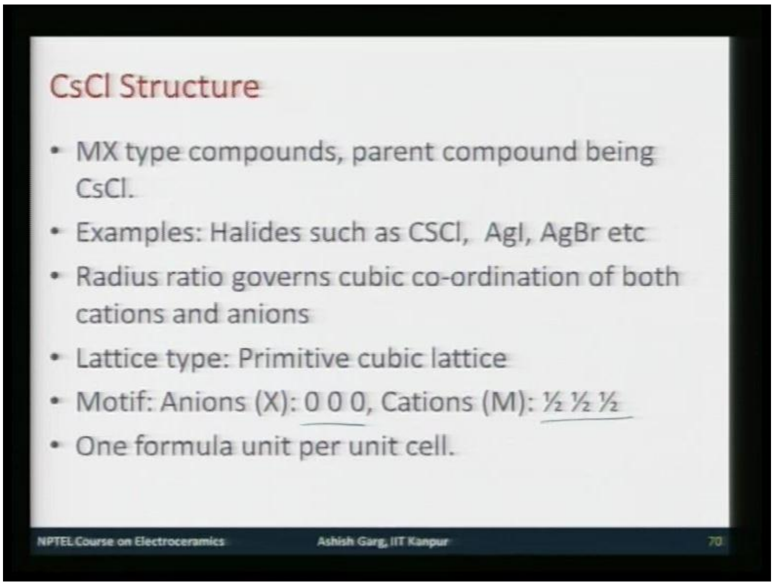

CsCl Structure

- MX type compounds, parent compound being CsCl.
- Examples: Halides such as CSCl, AgI, AgBr etc
- Radius ratio governs cubic co-ordination of both cations and anions
- Lattice type: Primitive cubic lattice
- Motif: Anions (X): 0 0 0, Cations (M): ½ ½ ½
- One formula unit per unit cell.

And another structure which is not similar to any of these which falls in the category of primitive cubic structures is cesium chloride structure. This is of MX type of compound and the parent compound is cesium chloride, and the examples of such structures materials with such structure are cesium chloride many halides like silver iodide, silver bromide, etcetera will follow this structure. The structure is very simple. The radius ratio is such that it governs the cubic coordination of both the cation as well as anions. So, which means it is big; in these structures the cation is reasonably big. Lattice type happens to be primitive cubic. Motif since it is cubic lattice; if anion you put at 0 0 0 the cation goes to half half half. It looks like a body centered cubic structure but it is not a body centered cubic structure because anions and cations are different. The two sites are occupied by two different ions, and again because of primitive structure you have only one formula unit per unit cell.

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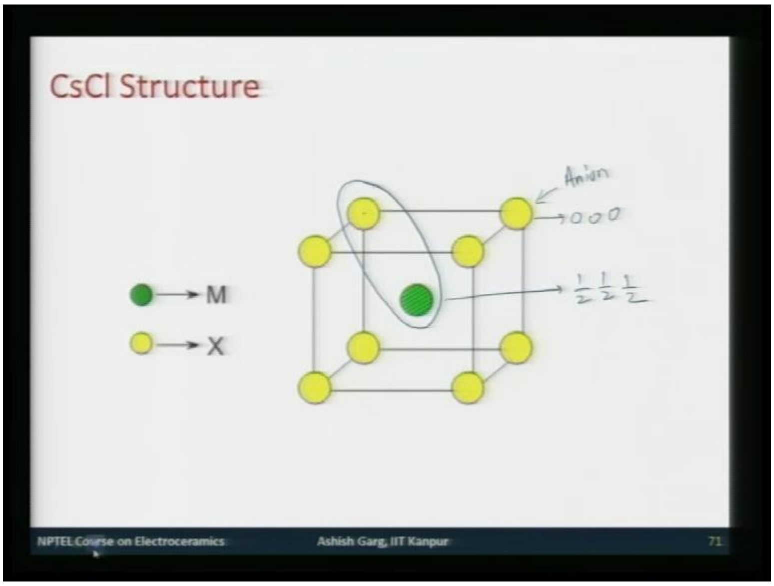

CsCl Structure

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So, this is the structure like. So, if this is your anion or X atom then the center one would be. So, this would be at 0 0 0, and this would be at half half half. So, you can consider this whole thing as formula units of. So, each of this anion is coordinated with is attached to each of this cations. So, you can say that for this also there will be one cation somewhere and so basically instead of. So, what you can see is that instead of putting one particular sphere at this position you have put a group of two spheres and both of these spheres are different.

So, it looks like a BCC structure, but it is not a BCC structure. So, you again go back to concept of motif. So, motif is not one atom rather it is a group of two atoms. So, it is again a simple primitive cubic structure. Now the structures which are going to follow are not cubic in nature rather they are perovskite based tetragonal or orthorhombic structures useful as superconductor. Superconductors are the materials which we will see in the end of this lecture series which have zero electrical resistance when they are cooled below a certain temperature which is called as a transition temperature, and they were useful because simply because they have zero resistance. So, you can draw large current densities from them.

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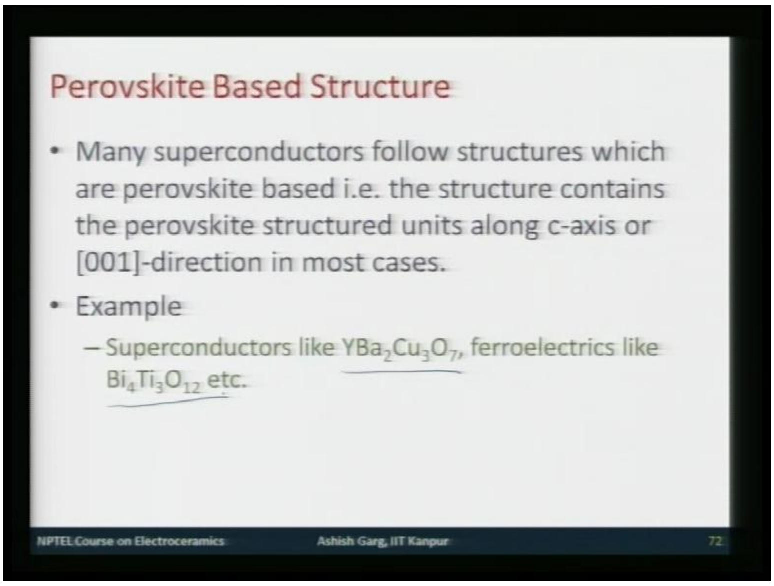

Perovskite Based Structure

- 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, these are called as perovskite based structure. Typically in these structures the perovskite units are stacked along the 0 0 1 axis of the unit cell or which is also called as c-axis, and the examples of such materials are superconductors like atrium barium copper oxide, even some of the ferroelectric materials like bismuth titanate and some manganites as well follow this kind of structure. We will look at only in the case of two materials which are rather interesting as well as little simple.

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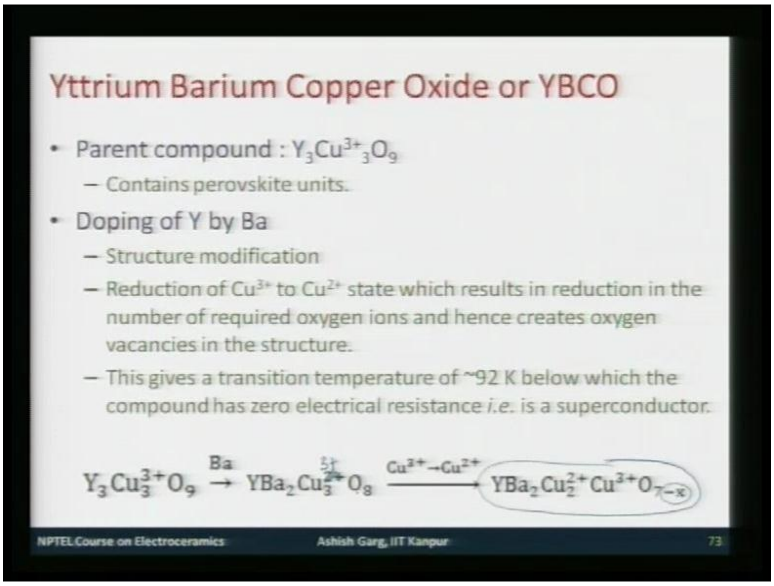

Yttrium Barium Copper Oxide or YBCO

- 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.

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

So, one of the example that we take are atrium barium copper oxide. The parent compound for this is atrium 3 copper 3 in 3 plus state O 9. This is not a superconducting material; however, this contains perovskite units. We will see how in the next slide when I show you the structure, but basically it has a structure which contains a perovskite unit stacked on top of each other. So, you have one block of. So, you have the building blocks made by oxygen atoms and within these building blocks you have atrium and copper atoms sitting in such a manner as if you see the perovskite unit is characterized by formation of these octahedral; its characteristic octahedral center of which is occupied by a small atom. So, you will see here these octahedral are stacked along c-axis.

So, it looks as if it is a sequence of perovskite series. Now in this structure what you do is that if you dope this atrium by barium atom sequentially the structure modifies itself a little bit. So, what happens is that when you start doping atrium with barium; now atrium is plus 3, barium is plus 2. As a result what happens is that to maintain the charge and charge neutrality as well as the stoichiometry you create. So, the Cu 2 plus which is derived by reduction of Cu 3 plus. So, some of the Cu 3 plus reduces to Cu 2 plus state. Now if you do that, so you have one substitution of atrium by barium which is anyway plus 2 plus followed by reduction of Cu 3 plus to Cu plus; the net requirement of oxygen goes down.

As a result in the parent structure you create some vacant oxygen sites which are called as oxygen vacancies simply because the requirement of oxygen has gone down. In this case 3 atrium atoms require atrium as Y 2 O 3 oxide. So, 3 atrium atoms would require atrium as plus 3. So, 3 into 3 is 9, so four and half oxygen atoms and remaining four and half are required for Cu 3 3 Cu 3 plus. So, total of 9 oxygen atoms are required. So, if you replace some of these by ions which are of a smaller valence in nature then number of oxygen atoms required would also be smaller. As a result you have oxygen vacancies; however, when you keep doping this structure by atrium there comes a concentration at which this material become superconducting and at 92 Kelvin it has a transition temperature below which the material at zero electrical resistance, and this is what is important about this material and the sequence is such that.

So, Y 3 Cu 3 O 9 you start doping by barium it becomes YBa 2 Cu 3 2 plus O 9, okay. So, Cu 3 now has converted into Cu 2 plus, and as a result if you notice the oxygen requirement has also gone down, and further reduction of Cu 3 plus to Cu 2 plus gives rise to YBa 2 Cu 2 2 2 plus Cu 3 plus O 7 minus X. So, some extra oxygen is missing which is what is responsible for superconducting behavior in these materials. We will not going to superconductivity reasons at the moment, but a sequence of doping is such that it become superconductor at this particular. So, X is the oxygen number is little smaller than 7 for the superconducting state, and here just a second I will just make a modification here. This should not be C; all of this should not be 2 plus. This should be so you have replaced two of these. So, there should be 3 plus, okay, because to maintain the stoichiometry because you have replaced two of the barium atoms. So, Cu will remain in 3 plus state, so that you have one oxygen less.

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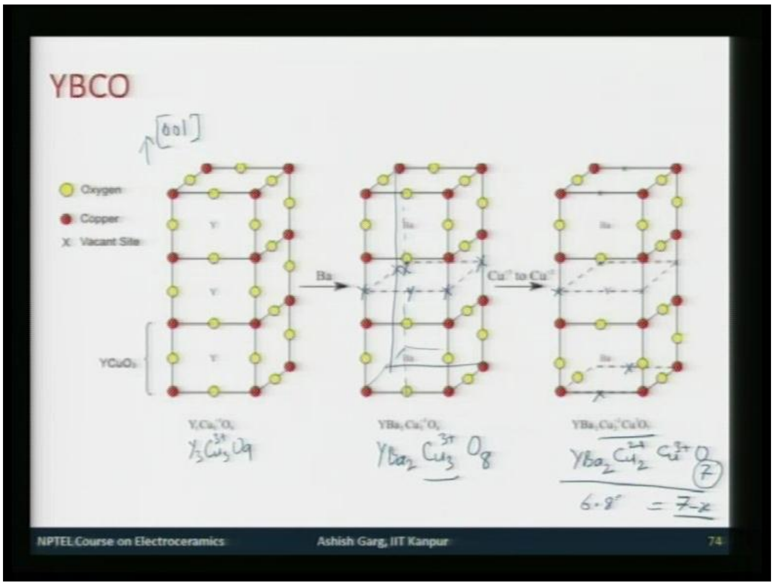

YBCO

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So, that structure is something like this. This is your Y 3 Cu 3 anion structure. Cu is in 3 plus state. So, these are the Y Cu 3 perovskite units which are stacked along the c-axis. So, this would be your 0 0 1 axis of the unit cell, and what you do now is you start replacing atrium by barium. So, two of these top and bottom atrium atoms are replaced by barium, but center one still contains atrium. So, this is your atrium. As a result you reduce the number of oxygen atom. So, this becomes Y B a 2 Cu 3 plus O 8.

So, as a result oxygen on these sites is missing. So, this would be your back site. So, if I connect these so this would be your missing sites. So, these are your missing oxygen sites and when you further reduce Cu 3 plus to Cu 2 plus. So, this becomes YBa 2 Cu 2 2 plus Cu 3 plus O 7. Some more oxygen go out; for instance these and these and part of the copper atoms become Cu 2 plus, part of them remains 3 plus. This becomes YBa 2 Cu 3 O 7 and when some more oxygen goes out when it is 7 minus x then it becomes six superconductors roughly at 6.85 or x is equal to approximately 0.15.

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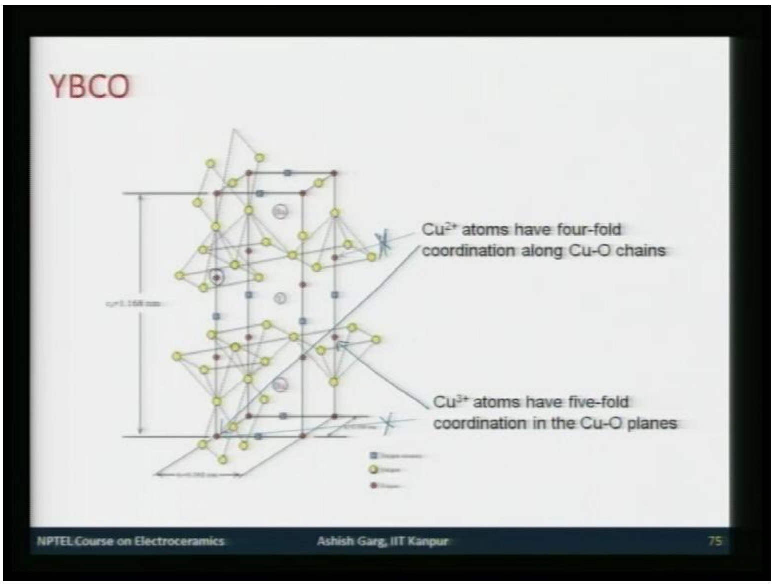

YBCO

Cu^{2+} atoms have four-fold coordination along Cu-O chains

Cu^{3+} atoms have five-fold coordination in the Cu-O planes

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So, this is the structure one unit cell. Now here the important observations are these copper atoms are fivefold coordinated 4 of these and one on top, and these copper atoms are fourfold coordinate. So, this is one of the peculiar features of YBCO structure copper atoms. So, Cu 2 plus atoms have a fourfold coordination, sorry this should be in that way; those have gone wrong, it should be this one. So, these are the correct arrows. So, Cu 3 plus atoms have a fivefold coordination, and Cu 2 plus atoms have fourfold coordination, and this is one of the peculiarities of the structure.

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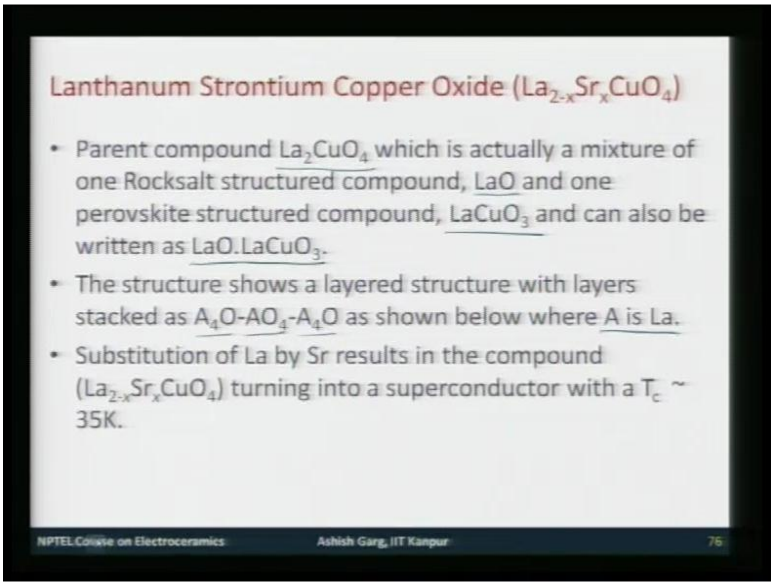

Lanthanum Strontium Copper Oxide ($La_{2-x}Sr_xCuO_4$)

- 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.

Another structure is lanthanum strontium copper oxide which is a mixture of one Rocksalt structure compound based on La 2 Cu O 4 which is a parent compound which is a mixture of LaO which is a Rocksalt structured compound and LaCuO 3 which is a perovskite structured compound. So, this is a mixture of Rocksalt and perovskite written as LaO dot LaCuO 3.Nnow when you replace some of the lanthanum by strontium ions this becomes superconducting. So, the layered sequence in the structure is such that you have A 4 O layers followed by A O 4 followed by A 4 O and where A ion is nothing but your lanthanum ion the bigger ion. Substitution of lanthanum by strontium results in a superconductor with the T c of above 35 Kelvin.

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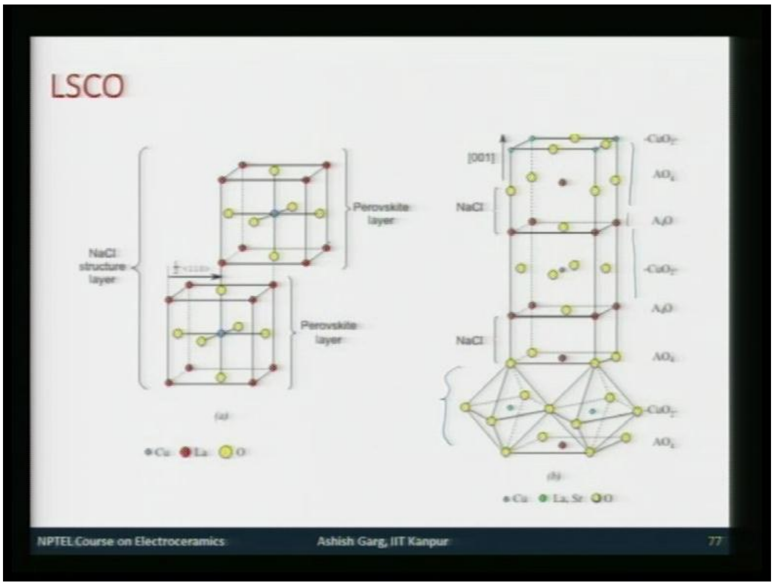

LSCO

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So, the structure is like this. So, you have this A O 4 units, then A 4 O. This is A 4 O then A O 4 A 4 O A O 4. So, this is a sequential structure. So, you have these sodium chloride units and these are the perovskite units. So, this is one perovskite layer; this is other perovskite layer shifted. If you look in front one of them is on the back of the front one, and the whole unit will be NaCl structure. So, these are some of the specialized structure which we are not discussing in much of detail just to give you an idea that if you apply the principles of simpler structure well enough you can conceive even the complex structure with the other with relative ease, so that they will not appear as complex as they look in the pictures. So, if you want to go into details I would recommend you to read the books and understand how these structures are formed.

So, in the next class we will look at the HCP packing of anions, and we will look at the oxides which follow ceramic materials which follow which are based on HCP packing of anions.

Thank you.