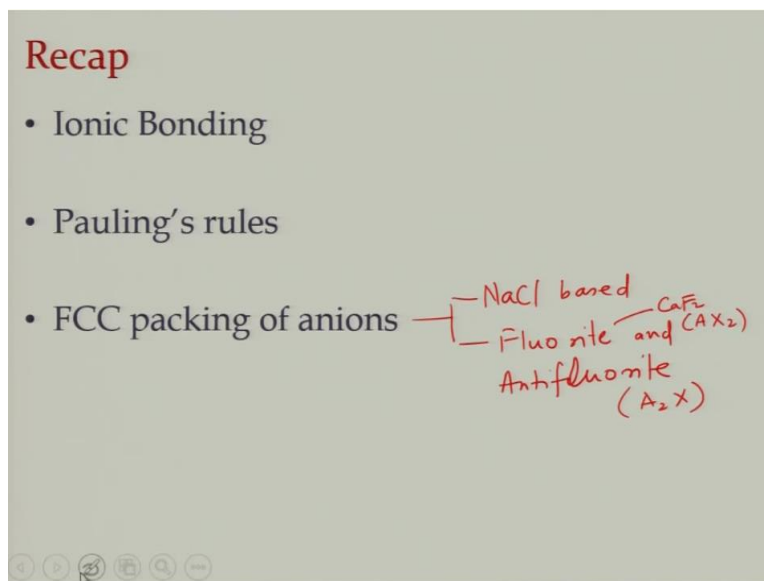


Fundamentals and Applications of Dielectric Ceramics
Prof. Ashish Garg
Department of Material Science and Engineering
Indian Institute of Technology Kanpur

Lecture No 07
Ceramic Materials: Crystal Structure

So, welcome again to the new lecture of Fundamentals and Applications of Dielectric Ceramics. So, let us just recap the previous lecture.

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The slide is titled "Recap" in red. It contains a bulleted list of topics: "Ionic Bonding", "Pauling's rules", and "FCC packing of anions". To the right of the third bullet point, there are handwritten notes in red ink: "NaCl based" with a line pointing to the bullet, "Fluorite and Antifluorite" with a line pointing to the bullet, and "CaF₂ (AX₂)" and "(A₂X)" written below.

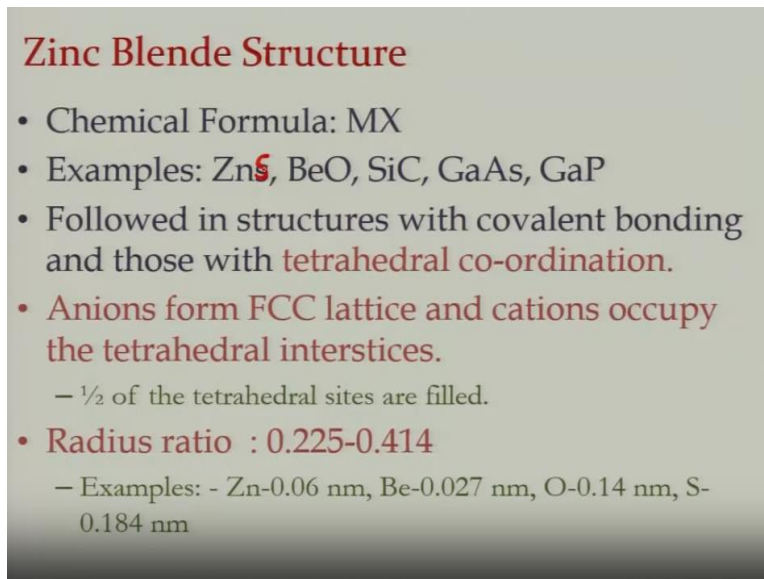
So, in previous lecture, we started our discussion on ionically bonded solids. So, we talked about the energetics of ionic bonding, and then we looked at Pauling's rules, which are basically guidelines to facilitate the formation of structures, which are primarily based on radius ratio and keeping the electrostatic repulsion minimum and so, according to radius ratios, anions make certain polyhedra, and then cations occupy the interstices in them.

So generally, as a thumb rule, when smaller the size cation is, lower the number of neighbors that are going to be, which means the polyhedra is going to be smaller. And generally for bigger size cations, you have bigger polyhedras. And then we looked at structures, we started beginning to look at structures based on FCC packing of anions, so we looked at sodium chloride, which is rock salt based structure and then we looked at fluorite and anti-fluorite structures.

So fluorite is basically CaF₂ kind of structure, so basically you can say AX₂ and this would be

A₂X kind of structures, so A is the cation and X is the anion here.

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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

So, next we look at now, following the, continuing the discussion on FCC packing of anions, the third structure that we would like to discuss is Zinc Blende structure. Zinc Blende has a chemical formula of MX, which means for every anion, you have one cation. So stoichiometry is 1:1 and examples of these compounds are basically you have zinc sulfide, beryllium oxide, silicon carbide, gallium arsenite, gallium phosphide.

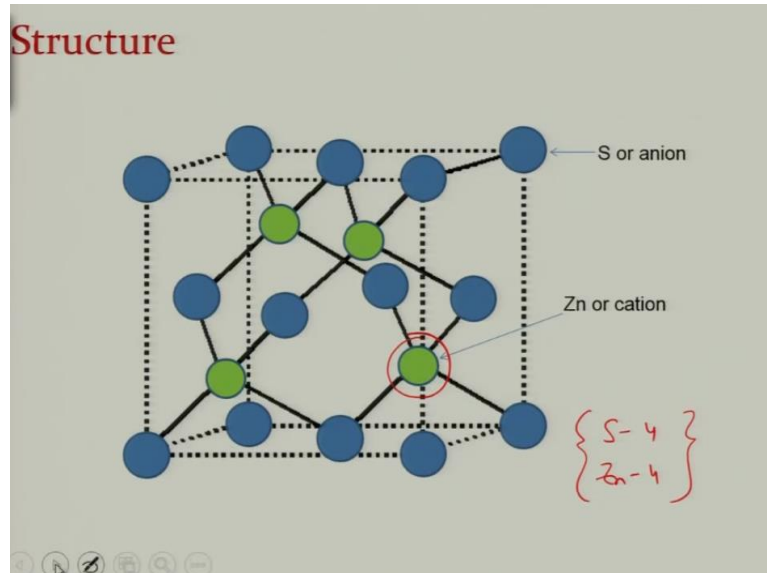
Many materials especially these group 4 semiconductors, when they make compounds and even 3, 5 kind of semiconductors, they make these Zinc Blende structure and generally this is followed in materials with covalent bonding and where you have tetrahedral coordination of atoms. So here, anions form the FCC lattice, so basically whether it is sulphur or oxygen or anything else, they form FCC lattice.

And the cations occupy the tetrahedral interstices and as a result, we can determine that only 50% of the tetrahedral sites are filled, because in FCC lattice for every atom you have two tetrahedral sites and stoichiometry is 1:1, as a result only half of the tetrahedral sites are filled. And given the fact that the stoichiometry is 1:1, to satisfy the bond strength, bond strength of cations and anions have to be equal.

The anions are also tetrahedrally coordinated. So the coordination of both anions and cations is tetrahedral or four fold coordination. And the radius ratios for these kind of materials fall in this range, so, 0.225 to 0.414. So, zinc has 0.06 nanometer, you can determine all these radiuses

and then determine the radius ratio. Sometimes, there may be some off radius ratio structures, which still show Zinc Blende, but that is determined more by the bonding than by the radius ratio. So, it does happen in some cases, but by and large they do fulfill the criteria.

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So, this is the kind of structure, this is very similar to covalent diamond structure, except that in diamond all the eight sites, four FCC and four tetrahedral are filled by carbon atoms. Here, four FCC sites are filled by sulphur atoms and four tetrahedral sites are filled by zinc atoms or any other cations. So these are all tetrahedrally coordinated cations and these are all anions, which make FCC lattice, but even anions are tetrahedrally coordinated, so both of them have tetrahedral coordination.

So, this is called as sphalerite or zinc sulfide structure. So, this is a very simple structure, there is nothing very complicated about it. So, Sulphur also has four fold coordination and zinc also has four fold coordination.

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Spinel Structure

40 → 4 Oct → 2 filled
8 tet → 1 filled

- Formulae - $(A^{2+})(B^{3+})_2O_4$ or AB_2O_4 or $AO \cdot B_2O_3$
- FCC Packing of anions
- Partial occupancy of both tetrahedral and octahedral sites
 - $1/8^{\text{th}}$ of tetrahedral and $1/2$ of the octahedral sites are occupied.
- A spinel unit-cell is made up of eight FCC cells made by oxygen ions in the configuration $2 \times 2 \times 2$
 - 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.

And next we move on to what we call as a spinel structure, spinel structure materials are basically AB_2O_4 kind of materials. So, here generally, you have this kind of formula AB_2O_4 and this AB_2O_4 is represented as A is 2+, B is 3+, and then remaining 4 are oxygen atoms. So, there is one of A atom of 2+ valence, there are two of B3+ and then 4 oxygen atoms. You can also write this in such fashion so that it is a mixture of two sub lattices one of AO and second is of B_2O_3 .

This is another way of representing this, so it is a mixture of two oxides, $AO \cdot B_2O_3$. This again is based on FCC packing of oxygen or anions and in this structure, you have partial occupancy of both tetrahedral and octahedral sites. You can see that you have 4 FCC, 4 oxygen atoms. So for four oxygen atoms, you will have four octahedral voids and eight tetrahedral voids, but you have only three cations, okay.

So, the way it happens is you have one eighth of tetrahedral sites which are filled, so which means out of eight, only one is filled and out of four, basically two are filled, okay. So depending upon how cations arrange themselves in these interstices, it could be normal inverse, but the filling pattern is one eighth of tetrahedral sites and half the octahedral sites are filled, which make up three cations that are present in the formula.

So, basically, what happens is that, in a spinel unit cell, essentially you have eight FCC unit cells, so you have four unit cells at the bottom, four unit cells at the top. So, so 8 into 4 will make 32 oxygen atoms. So, for 32 oxygen atoms, you will have eight A atoms and 16 B atoms in the unit cell. This is how the unit cell looks like basically for a spinel structure. And then,

depending upon how cations occupy different interstices, whether tetrahedral or octahedral, the structure may be called as normal or inverse and we will look at both the examples in a short while.

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Normal Spinel

$\begin{matrix} \text{tet} & \text{oct} \\ \downarrow & \downarrow \end{matrix}$

- Chemical formula: $(A^{2+})(B^{3+})_2O_4$
- Examples: ZnFe₂O₄, MgAl₂O₄, MCr₂O₄
- All the A²⁺ ions occupy the tetrahedral sites and all the B³⁺ ions occupy the octahedral sites.
- Apply bond strength rule to verify the stoichiometry

$$\begin{array}{ccc} A^{\text{tet}} & B_2^{\text{oct}} & O_4 \\ \hline \frac{1}{8} & \frac{1}{2} & \end{array}$$

Normal spinel structure is again the chemical formula is same, it is A²⁺ B³⁺ 2 atoms of B and then O₄. The examples which follow the structure amongst ferrites, it is zinc ferrite that follows this structure, because zinc has a tendency to go to tetrahedral sites, otherwise, many ferrites follow inverse spinel structure, but then you have aluminates and chromates which follow this structure normally.

So, magnesium aluminate and metal chromates, variety of metals you can put in there, they all follow normal spinel structures. So, essentially what happens in this structure is, the A atom goes to tetrahedral site and the both the B atoms go to octahedral sites. So you can write this structure as, so A tetrahedral, B₂ octahedral O₄, that is how can write this structure. And again, you can see only one atom goes to tetrahedral site, so one eighth filling of tetrahedral and then then half filling of, 50% filling of octahedral sites.

You can apply the bond strength rule to verify the stoichiometry as well as the coordination of oxygen atoms that I will leave it to you as a home exercise.

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Inverse Spinel

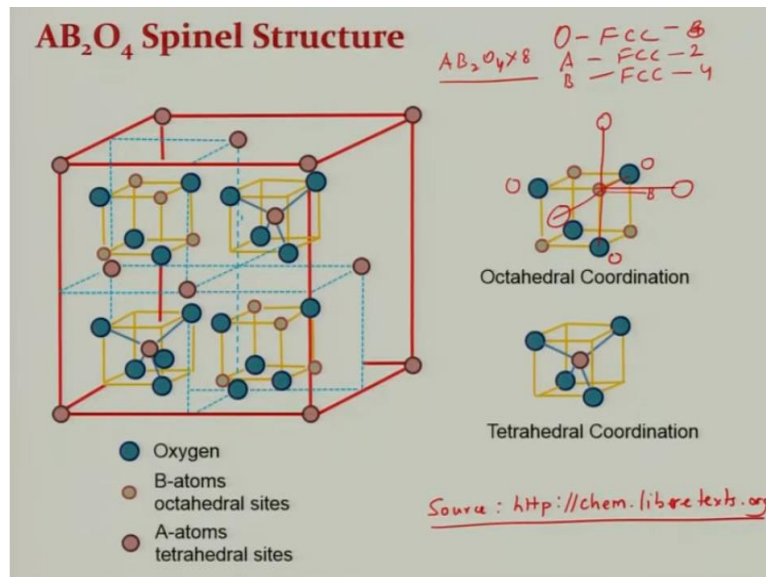
- Chemical formula: $(A^{2+})(B^{3+})_2O_4$ but can be more conveniently written as $B(\overset{\downarrow}{\text{tet}}A\overset{\downarrow}{\text{oct}})O_4$.
- Most ferrite follow this structure such as Fe_3O_4 (or $FeO \cdot Fe_2O_3$), $NiFe_2O_4$, $CoFe_2O_4$ etc.
- $\frac{1}{2}$ of the B^{3+} ions occupy the tetrahedral sites and remaining $\frac{1}{2} B^{3+}$ and all A^{2+} ions occupy the octahedral sites.

So and the inverse spinel structure is again the same formula, but it is conveniently written as $BABO_4$. So, essentially what happens here is, the B atom goes to tetrahedral sites and one A and remaining B go to octahedral sites, that is how the structure is written as inverse. So, it is B, one B goes to tetrahedral site, another B goes to octahedral sites, and A goes to octahedral site. So, here you can see that B divides itself into tetrahedral and octahedral sites and A goes to octahedral site.

Most of the ferrites with the exception of zinc ferrite tend to follow this structure, so iron oxide Fe_3O_4 , nickel ferrite, cobalt ferrite etc., they all follow this inverse spinel structure and depending upon the arrangement of, so all of these ions, you can see nickel, iron, cobalt, they all have magnetic moments. So, depending upon their distribution on these tetrahedral and octahedral sites, they carry certain magnetic moment, which is outside the scope of this lecture, but it is an interesting exercise to do for you.

So, essentially here half of the B^{3+} ions occupy the tetrahedral sites and remaining B and all of the A, occupy the octahedral sites, this is how the inverse spinel structure is.

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So, this is the structure, which is of AB₂O₃ type. This is basically taken from, let me just tell you, you can look at the details of the structure, so basically it is adapted from a chemistry website, which is chem dot, it has some very nice structural illustrations. So, you can go to this website and look at these structures, but it has been redrawn to. So, you can see that, this is one FCC cell and within one FCC cell you have certain tetrahedrally coordinated atoms and some of the octahedrally coordinated atoms.

So, this is the first cell on top, then you have another cell on the back. So, you have eight cells on top of each other. So, all the atoms have not been drawn for the sake of simplicity, but for example, this is one oxygen atom. So, these are all oxygen atoms okay. So, this is one oxygen atom, which tetrahedrally coordinates these A atoms, okay. And then, so the lattice you can see is made up of A atoms, but I mean, if oxygen makes FCC lattice, then A and B will also make FCC lattices.

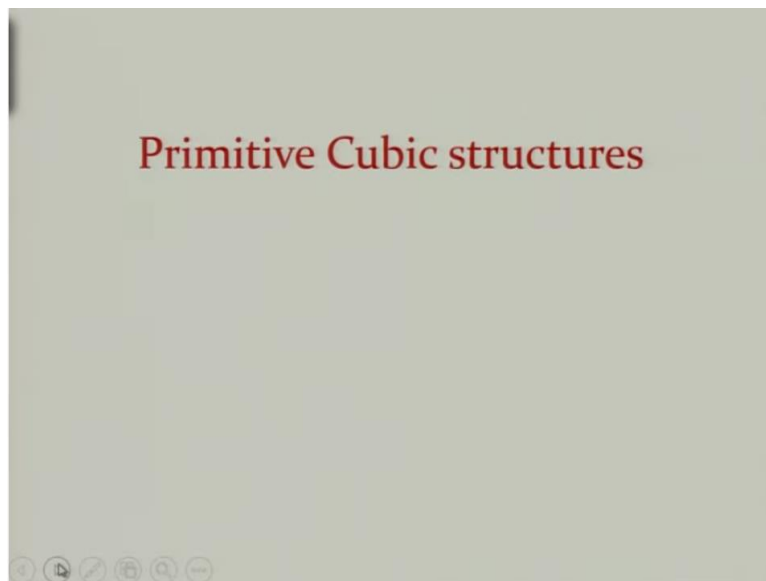
So, essentially, that is something which they have to follow. Otherwise it will not remain like a FCC lattice. So, basically you will have eight FCC lattices of oxygen, so it is AB₂O₄ right, multiplied by 8, so eight FCC lattices of oxygen, you will have eight atoms of A, so two FCC lattices of A and you will have four FCC lattices of B. So, each of these will make FCC lattice in itself, that is a crystallographic requirement for it to be FCC. So, here you can see that these are A atoms, these are tetrahedrally coordinated, the B atoms are sitting here.

So, B atoms are sitting here, so, you can see this is B atom, I have taken it out here. So, this is B, you have one A here, you have another A here, sorry another, this is oxygen, this is oxygen,

this is oxygen, you will have one oxygen here, you will have another oxygen here, and you will have another oxygen here. So this will be octahedrally coordinated. So this is octahedrally coordinated B atom, this is tetrahedrally coordinated A atom.

You can swap these positions depending upon whether it is normal or inverse, but this is how the structure will be. It is a little complex structure, so you will have to do a little bit of hard work to visualize it.

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So these are four basically most common structures based on FCC packing of anions. There are certain other structures, where the structure looks like FCC or BCC, but it is not FCC, BCC, it is based on primitive cubic arrangement.

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CsCl Structure

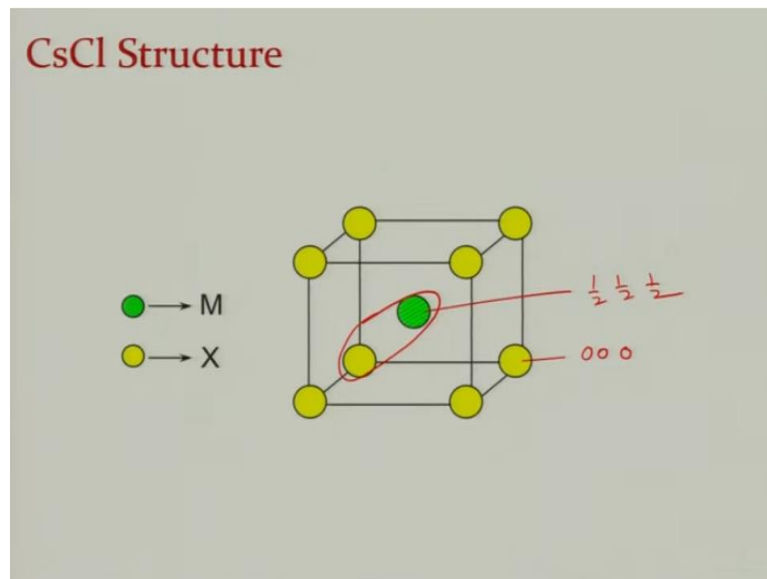
- MX type compounds, parent compound being CsCl.
- Examples: Halides such as CsCl, AgI, AgBr etc
- Radius ratio governs cubic co-ordination of both cations and anions
- Lattice type: Primitive cubic lattice
- Motif: Anions (X): 0 0 0, Cations (M): 1/2 1/2 1/2
- One formula unit per unit cell.

$\frac{r_c}{r_a} > 0.732$

So for example, the first one is caesium chloride type of structure. Basically, again, it is a MX type of compound, 1:1 stoichiometry and it is called as caesium chloride structure because the parent compound is caesium chloride. And there are many halides, which follows this structure such as caesium chloride itself, and then silver iodide, silver bromide, etc., all of them follow this structure. The radius ratio governs in this case, so r_c/r_a is such that, r_c/r_a is greater than 0.732.

So, which means, basically cations are bigger in this case, so as a result, there is a cubic coordination of both cations as well as anions because of stoichiometry and a lattice type is primitive cubic in this case and the motive will be, now if it is a primitive cubic lattice, so when you define the motive, you will have to define both the ions then. Anions will be at (0,0,0) and cations will be at (1/2,1/2,1/2). A sort of BCC structure because both the lattice points are different and there is one formula unit per unit cells.

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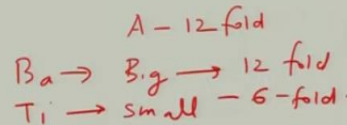


So, this is the structure like, so you have X atoms sitting at the (0,0,0) kind of positions and M atoms sitting at (1/2,1/2,1/2) kind of position. So, this is a caesium chloride structure, which is, a lot of people conceive it as BCC structure, but in BCC structure, the center and the corner atoms have to be the same. In this case, it is different, that is why it is. So, you can consider this as a molecule of this and that. So basically one molecule is turning on a lattice point. So it is a molecular structure with a primitive cubic lattice.

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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.



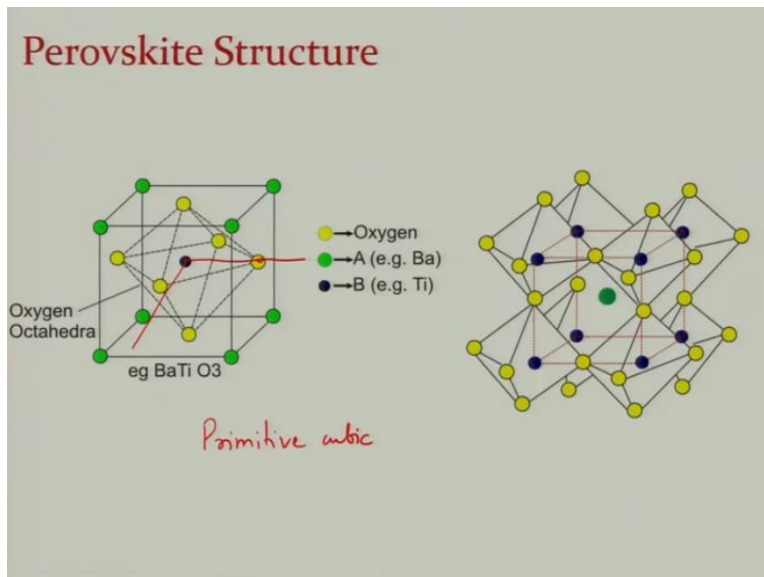
The next very important structure in this series is perovskite structure which many of the dielectrics follow, especially nonlinear dielectrics, and these perovskites are basically ABO_3 kind of compounds. So you have two A and B, and three oxygen atoms. And there are plenty of examples of these materials such as barium titanate, strontium titanate, lead titanate, potassium iodate, bismuth ferrite, a lot of these follow these perovskite structures.

In fact, many of the materials which do not have simple formula even they tend to follow perovskite unit as building blocks. So for example, materials such as $Bi_4Ti_3O_{12}$, it is a very tall structure, but it tends to follow perovskite unit cell, because perovskite units are present as building blocks in these materials. So, it might have multiple units of perovskites. So, these are very important materials, because many of the perovskites are dielectrics and ferroelectrics and piezoelectrics.

The radius ratio is such that, that A atom is bigger as a result, A atom is 12 fold coordinated, so which means it is a cubic coordination and six fold, sorry, it is FCC kind of coordination, and then B atom is six fold or octahedrally coordinated in this case. So B is the smaller one, A is the bigger one. So for example, if you look at barium titanate, barium is big and titanium is small. So, this has 12 fold and this has six fold and here, oxygen atoms form FCC like cell, it is not FCC cell, it looks like FCC, but it is not FCC.

Because there is no atom at the corner of the unit cell. So, for the sake of simplicity, the way it is represented, oxygen atoms are present only at the face centers.

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So, the way the structure looks like is something like this, you can always apply the bond strength to satisfy the chemical stoichiometry and charge neutrality. So, what you have here is these yellow ones are oxygen atoms. So, all the oxygen atoms occupy this face centers. So, ideal structure is a cubic structure, but really speaking, most of them are not cubic, especially in the ferroelectric state.

So, these oxygen atoms occupy the face centers, the titanium occupies the body center, which then becomes octahedrally coordinated by oxygen atoms and the barium atoms go to the corner. As a result, this although looks like face centered cubic kind of structure, but it is not face centered, because the corner atoms are different to face centers and then it is also not body centered because body centered atom is a different, so as a result this is a primitive cubic lattice, it is a primitive cubic lattice.

And you can also represent this structure a little differently, if you put the lattice corners at titanium, then titanium becomes the corner atom, in those cases barium comes to the center, but then oxygens are distributed in such a fashion so that oxygens are present at the edge centers, okay. So edge centers will become oxygen atoms. So basically, it is like this, if you put your corner here, so you will have one direction going like this, so this will come to edge center, okay, so that is how you could concert the lattice.

You can see that these are all octahedras, at the center of whose you have titanium atom and then within the center of these eight octahedras, you have this titanium, barium atom, which is surrounded by 12 of oxygen atoms. There are 12 edges to 12 of these oxygen atoms that is

surrounded by 12, so. So, this is the simple perovskite structure, it is followed by many technically important ceramics.

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Perovskite Structure

- Lattice type: Primitive Cubic (NOT FCC!)
- Motif
 - A ion - 0 0 0, B ion - 1/2 1/2 1/2, O ion - 1/2 1/2 0, 0 1/2 1/2, 1/2 0 1/2
- 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

So, the way you define lattice type is, it is primitive cubic lattice, it is not FCC. So, as a result, the motif is A is at (0,0,0) B is at (1/2,1/2,1/2) and oxygen is at (1/2,1/2,0), (0,1/2,1/2) and (1/2,0,1/2). You will have to define all the positions for a primitive cubic structure, so basically it is a molecule, right. One molecule is sitting at one lattice point. So, you have one formula unit per cell, that is why one formula unit is one lattice point, okay.

And coordination is B surrounded by oxygen octahedral and A surrounded by oxygen dodecahedra, which touch faces of the octahedral.

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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. $Pb(Sc_{1/2}Ta_{1/2})O_3$

And these perovskites are not only ABO₃ kind of perovskites, they can also be mixture of cations of different types. So, not only you have BaTiO₃, PbTiO₃, etc., you can also have A₃B₃ kind of combination, so A³⁺ B³⁺, so in this case, you can have lanthanum aluminate, you can have lanthanum gallate, bismuth ferrite. So here you can see the valence of cation is 2+ and 4+. In the second case, you have 3+ and 3+. So this is 2+ 4+ and this is 3+ 3+.

You can also have mixed perovskites, such as A²⁺ and B atom can be mixture of 2+ ion and 5+ ion, such as lead magnesium niobate, it is a relaxer material. Similarly, you can have a mixture of, so basically solid solution in such a fashion so that B site is partially doped by 2+ or 5+ atom, okay. And then we have, we can have A²⁺ B³⁺ and B⁵⁺ in the stoichiometry of half half. So, you can lead scandium tantalate kind of materials.

So, variety of these materials have these partial substitutions of sites by different ions, of course you will have to maintain the stoichiometry in such a fashion, so that it may charge neutral, but mixed perovskites are there, they have different properties as you will see later on in the material section.

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Distortions in Perovskite Structure

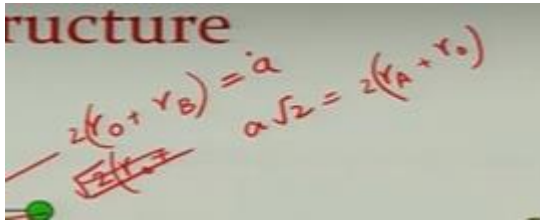
- "Tolerance Factor (t)"

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$
 - $t = 1$ 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 BaTiO₃ 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.

One of the important things that we need to know about the perovskite structure is that tolerance factor. Tolerance factor (t) is basically

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

And you can see that very clearly, this is very simple to derive. You can see that this is what is r of $2r_O + 2r_B$, right. Okay, if it was a cube, what would this be?



This would be to 2 of $r_O \sqrt{2}$, so this will be basically, this is equal to a and

$$a\sqrt{2} = 2(r_A + r_O)$$

And then you can just eliminate ' a ' and so for ideal material this ratio should be equal to 1, you are just equating the ' a ', okay. So, that is how you find out tolerance factor. So, tolerance factor will be 1 for a perfectly cubic perovskite, but if it is not cubic, which it is not in most materials, it tends to deviate from 1, generally it tends to be lower than 1.

But generally you have tetragonal distortion or rhombohedral distortion, so and this cubic structure changes to tetragonal at room temperature, for example for barium titanate. So, many of these materials have transition temperatures, above certain temperature they are cubic and below that temperature they are non-cubic structured. So, we will see that when we learn about the ferroelectric materials.

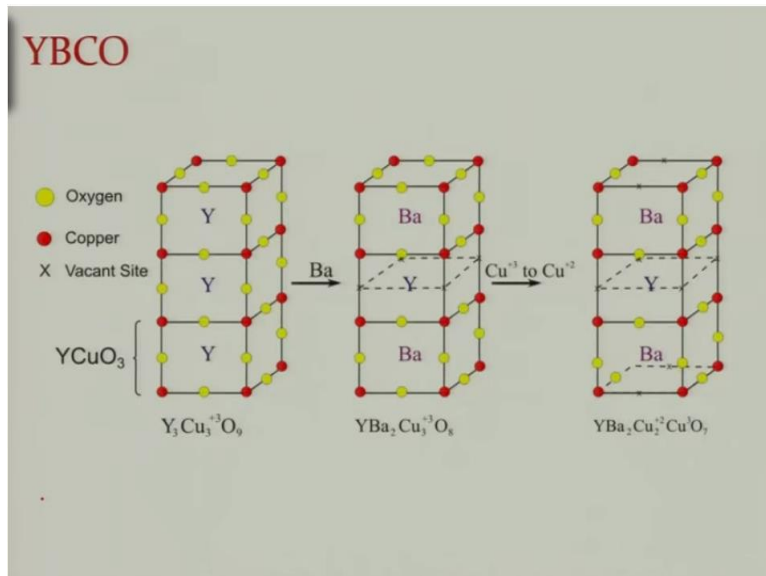
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Perovskite Based Structure

- 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 $\text{YBa}_2\text{Cu}_3\text{O}_7$, ferroelectrics like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ etc.

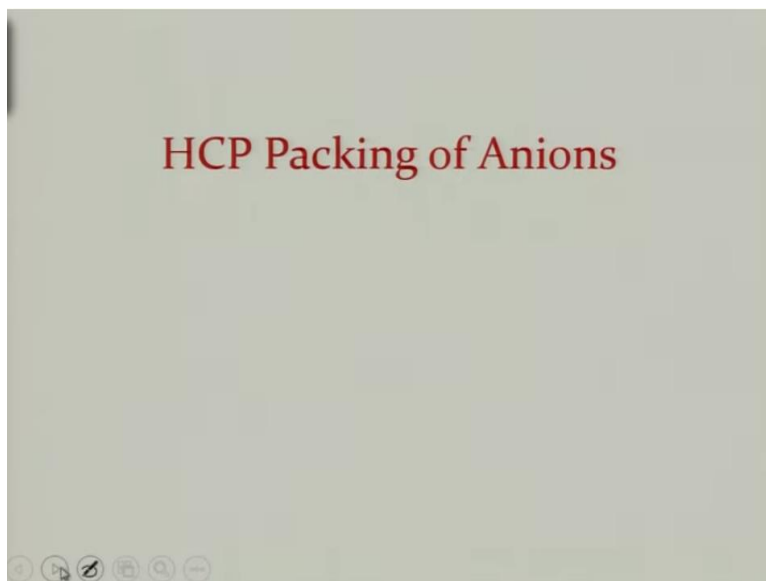
And then there are other materials such as yttrium barium copper oxide, bismuth titanate etc., all of these are based on perovskite based structures.

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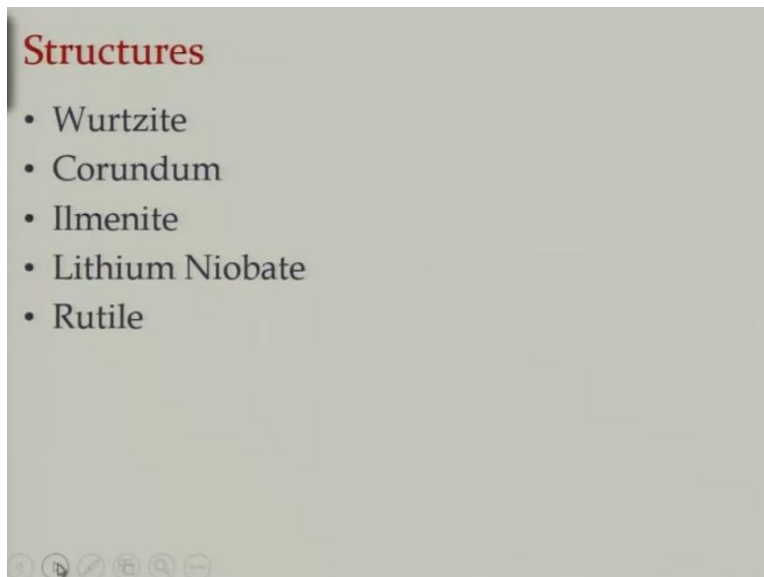
So, this is for example, yttrium barium copper oxide, which has these units of perovskites staggered on top of one on other.

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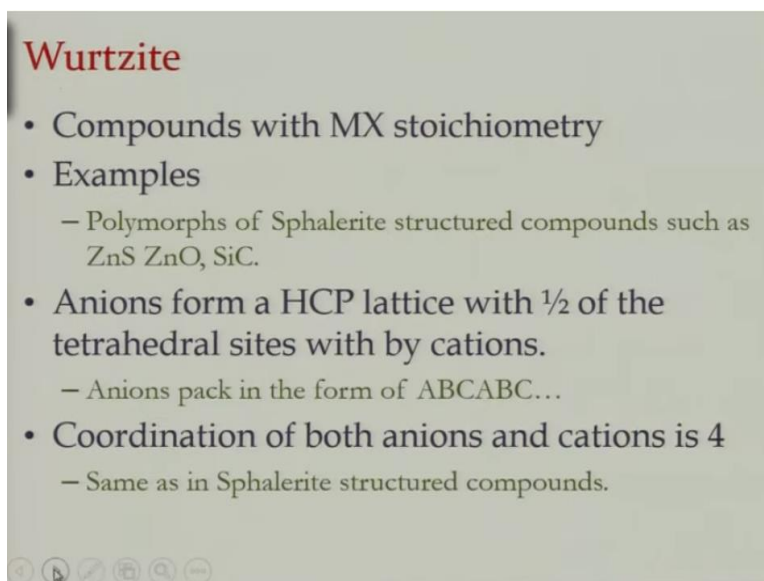
So, I will skip this for the sake of time. So, let us move to now next final part of this, that is HCP packing of anions, where anions pack themselves in HCP fashion and the cations occupy the interstices.

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So the structures that we will consider are wurtzite, corundum, ilmenite, lithium niobate, and rutile. Many of them are similar, but we will see how the deviations take place.

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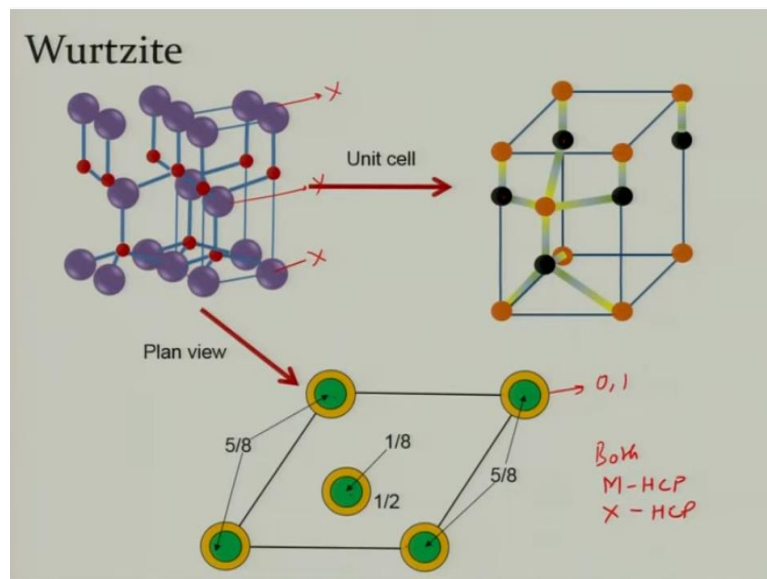


So Wurtzite is basically a compound with MX stoichiometry, $M:X = 1:1$, the materials which follow this structure are basically zinc sulfide, zinc oxide, silicon carbide etc. So again, zinc sulfide, zinc oxide etc., they also follow cubic structure and the polymorph structures follow this wurtzite hexagonal structure. So here anions form HCP lattice, with half of the tetrahedral sites filled by cations. So again, it is tetrahedral site filling, but in hexagonal form.

And here, anions pack in the form of, sorry, AB AB it is no ABC ABC it is AB AB sort of packing and tetrahedral sites are occupied by the cations. Coordination of both anions and cations by stoichiometry will have to be similar, so as a result, it is for and it is similar to what

we saw in a sphalerite structure compounds.

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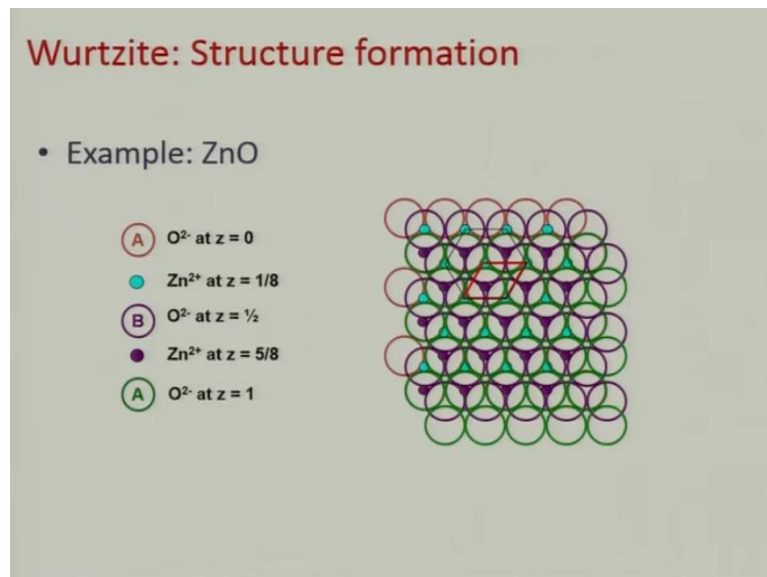
This is what the structure will look like, this is the first layer of X atom, this is the second layer of X atom, so this is X, this is X, this is X and the tetrahedral sites in between them are occupied by cation, but only half of the tetrahedral sites can be filled, not all of them because for each iron, you have two tetrahedral sites. So, if you make a unit cell in this, the unit cell will look something like this.

So, you have these oxygen atoms sitting at the lattice sites and then in between them, so this is a tetrahedrally coordinate metal, this is a tetrahedrally coordinated metal, so you have metals here then another metal there, okay. So, two cation and two anion will be what that will be present in a lattice and if you look at the plan view, this is how it is going to look like. You will have cations at position.

So, these are, the orange ones are anions at 01 , you have another anion sitting at the half position right in the middle of the unit cell, but then you have cation sitting at positions $5/8$ alongside c axis and another cation sitting at $1/8$, So $5/8$ minus $1/8$ will be $1/2$ right, so it is displacement of half. So, just like you have this atom displaced from this atom by half, this atom is displayed with respect to this atom by half.

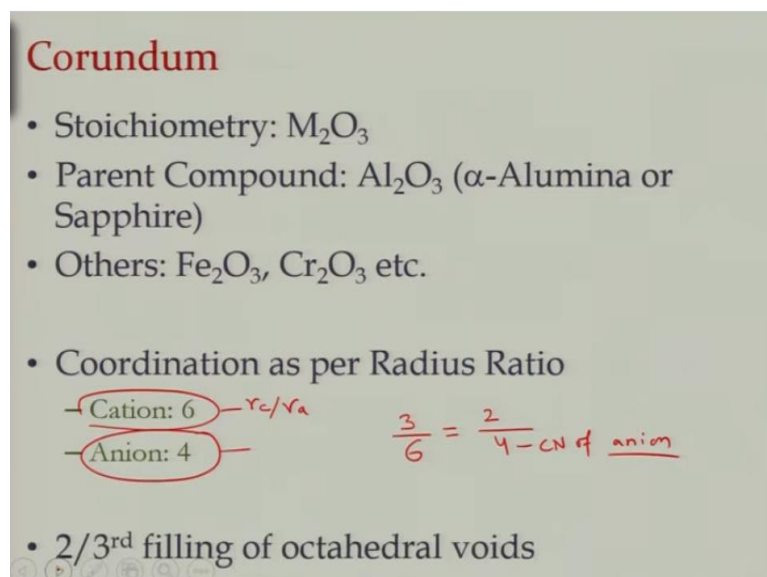
So, you can construct HCP lattice by putting corner at the green atom rather than at the, 0 position can be at the green atom instead of orange atom, because it is HCP, so both M is also HCP and X is also HCP lattice.

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So, if you look at the ZnO structure, the first layer will be this oxygen, hexagonally, then zinc atoms go to $1/8$ sites, not all of them, but only half of the sites are filled. Then again, second layer of oxygen atom and then again another layer of zinc atom, which goes somewhere then another layer of, so you have another layer of zinc atoms, another layer of oxygen atoms that is what makes a unit cell, the red one is the unit cell, which will contain these oxygen atoms and the zinc atoms, okay.

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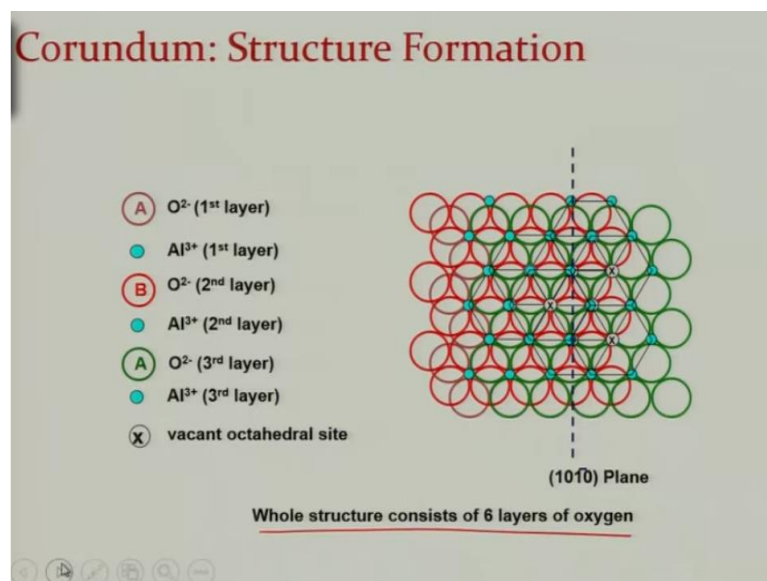


The corundum structure is now Al_2O_3 kind of structure, M_2O_3 , it is called as, so basically it is alumina based, parent compound is alumina, but there are other materials such as iron oxide, chromium oxide, variety of A_2O_3 kind of structures, they follow corundum structure. Here oxygen makes HCP lattice and metal goes to octahedral sites, okay. Now, since for each atom

you have one octahedral site, and the stoichiometry is three which means only two third of octahedral sites are filled, okay, because you have two cations for every three anions.

And as a result, because of stoichiometry, cation has six fold coordination because of radius ratio and because a bond strength, anion will have four fold coordination, right. Because cation has three valence coordination of six and the bond strength of anion has to be same as this, so which means anion is two, which means it has to be four fold coordinated. So, this is the coordination number of anion, okay. And since stoichiometry is 2:3, the octahedral site filling is two third.

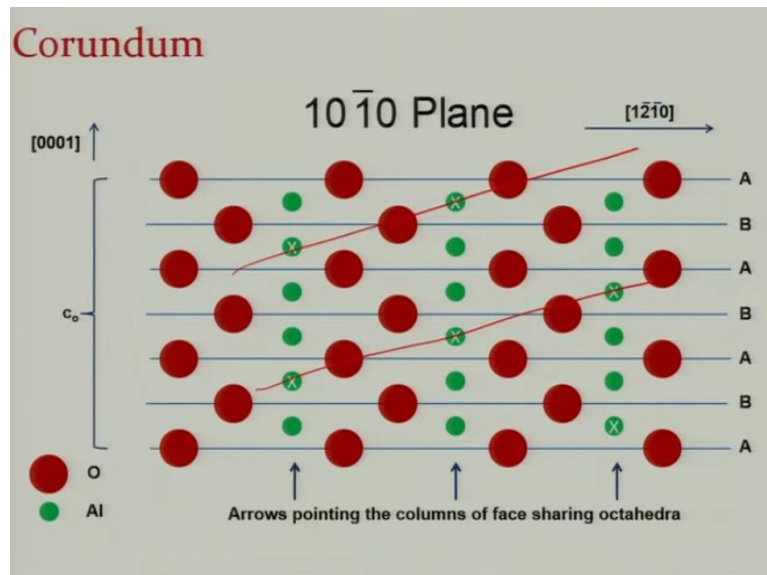
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So this is the structure, the way it is formed is, you make first layer of oxygen, then you fill in octahedral sites two thirds, okay, so every you can see for every two, one is empty. Then, this octahedral site will move to another position at the next layer to maintain the periodicity of the lattice. So, the next oxygen layer goes like this. So, you can see that this is octahedral, so three inverted and three up facing oxygen atoms. The second layer will go like this, then the next layer of, so it has to complete the triangle to make a repeatable lattice.

Then the third layer of oxygen will come, then you have another layer of oxygen, then you have vacant octahedral site again and this structure, so you have to repeat this once more to get a repeatable lattice. So, this whole structure consists of six layers of oxygen, okay. And the way you visualize this structure is, if you look at for example, cross section of this $10\bar{1}0$ plane.

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Put in first layer of oxygen, then you put in layer of aluminum, one is empty, another layer of oxygen, another layer of metal again one empty and you keep doing this, do it six times and this is what you get. So, you can see that for every three atom the third site is empty and it has to go in such a fashion so that it follows a pattern like this okay. So, these are basically you can say, the arrows which are pointing to columns of face sharing octahedra, so basically these are the octahedral positions.

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Ilemnite

- Stoichiometric 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

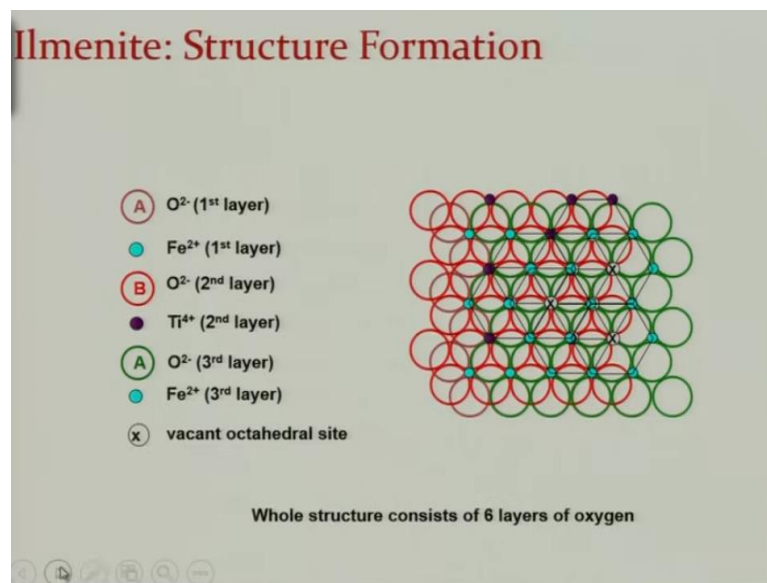
Both Fe and Ti remain octahedrally coordinated

You can make another structure based on the same thing, which is ilemnite. Ilemnite is ABO_3 , but it is not perovskite. Essentially, it is Al_2O_3 , but instead of two aluminum you have one A and one B. Same as Al_2O_3 , but you are divided two aluminum into one A and one B, parent compound is $FeTiO_3$, which is called as ilemnite mineral, that is why it is called as ilemnite, but there are a lot of other materials cadmium titanate, cobalt titanate, etc., which follow similar

structure and then they make this.

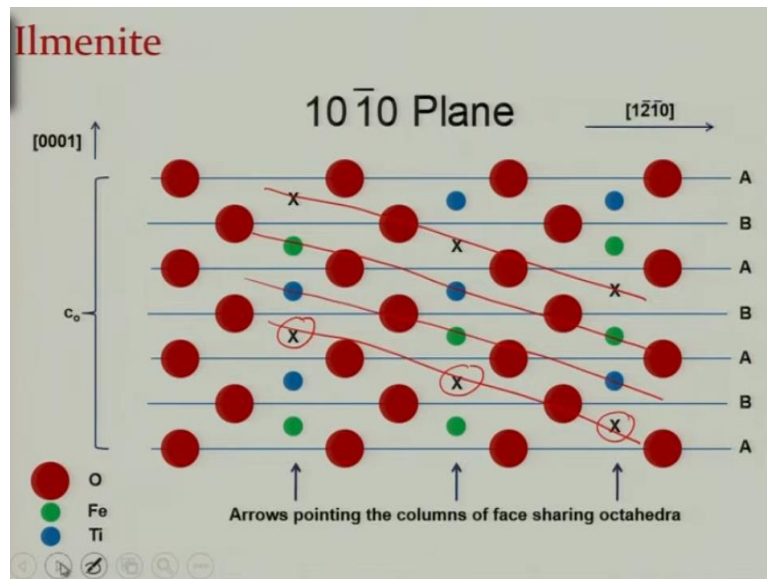
And the atomic arrangement is similar to Al_2O_3 , but the difference is, instead of aluminum being in every layer, you have alternate layers of iron and titanium. So, in one layer you will have iron second layer you will have titanium, then iron, then titanium, and then you keep continuing like that and the coordination numbers remain same, both iron and titanium remain octahedrally coordinated.

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So, the way the structure goes is, you have first layer of oxygen, second layer of iron, again the same fashion as aluminum and again you put in the second layer of oxygen, okay. Now, you put second layer which is of titanium, okay. Then you put again second layer of iron, oxygen and you keep continuing this few more times. So, again you continue for six times, basically six layers and you will get a structure.

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So, this is how it is going to go. Iron, oxygen, titanium, iron, oxygen, iron, titanium and so on and so forth. So, the way you do this structure is like this. So, you have, this is the iron layer, one empty, this is the titanium layer, one empty, this is the iron layer, one empty. So, you can see that it has to go progressively in this fashion. Even this way you can see iron titanium iron, titanium iron iron. So, it is alternatingly coming in every direction.

And this is basically similar to Al_2O_3 structure except that now you have one layer of iron and one layer of titanium. And the next variant of this is, again it is the same thing.

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Lithium Niobate

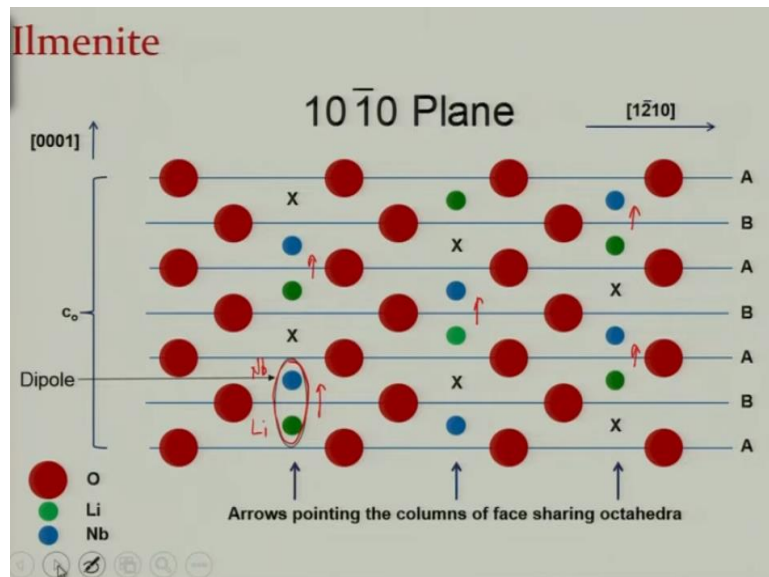
- Structure similar to Al_2O_3 except that Al sublattice is substituted in a ordered manner by Li and Nb in the same layer unlike in alternating layer in FeTiO_3
- The materials is of ferroelectric nature and is technologically important
- Materials has highly anisotropic refractive index
- It shows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

Again, another variant is lithium niobate, which is similar to the alumina structure except that in the previous case we had one layer of iron, then titanium. Here you will have in the same layer alternating lithium and niobium atoms. So the way the structure goes is, we will see in

the next slide, but this is a material which is very important, lithium niobate. Lithium niobate is ferroelectric, it is a birefringent material, it has highly anisotropic refractive index, so it is optically very important material.

So it is a birefringent material and this refringence can be changed by electric field.

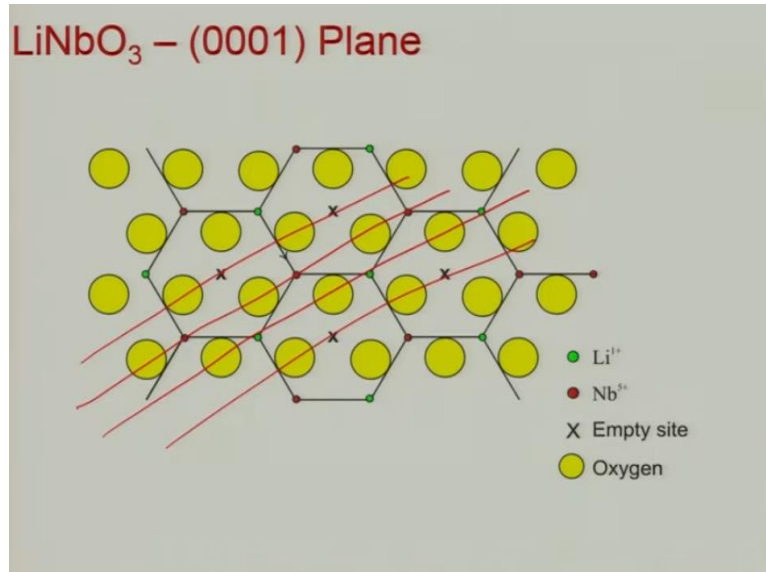
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So, in this material, we have oxygen layer, then we have second layer where we consider, so you can see this is lithium, this is niobium, this is empty. The second again oxygen, then again you follow, so again you will have, So, this is how it will be. You have lithium niobium empty, niobium empty lithium, empty lithium niobium. This is how you go, now you have alternating atoms in the same layer. This is what is lithium niobate.

And here, since you have these lithium niobium atoms stacked in this fashion, they also form these dipoles, these are permanent dipoles and all of these dipoles they point in the same direction. So this is lithium, this is niobium, there is a charge density difference, as a result you have dipoles pointing in this direction. So this is basically a ferroelectric material, because of permanent dipole moment.

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And this is how it looks like if you look at the top view, this is the oxygen layer and these are all octahedrally coordinated, there is lithium, niobium, lithium, niobium, lithium, niobium and this site is empty in the middle. So, these are empty channels, these are filled channels. So, these are filled channels of, so this is filled channel of niobium, filled channel of lithium, empty. So you can look at this in various ways. But again, you have to maintain the two third filling. (Refer Slide Time: 34:18)

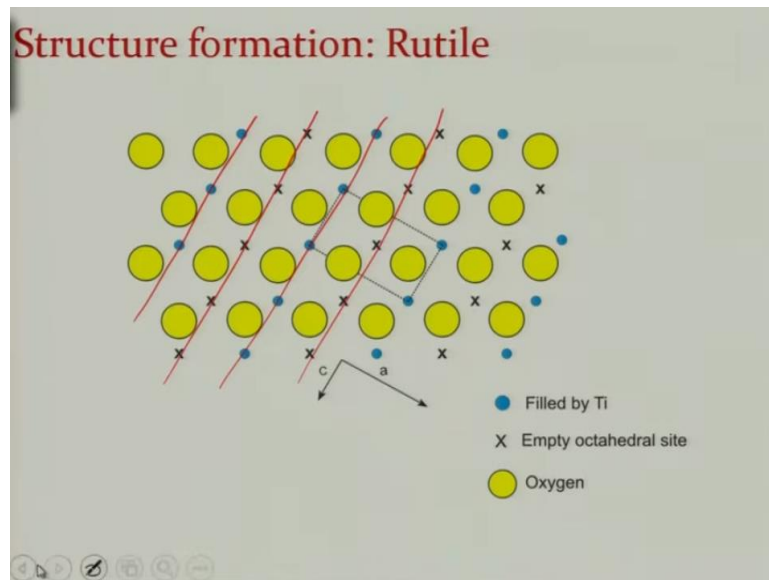
Rutile

- Polymorph of titanium di-oxide or TiO₂
– 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 TiO₂
- Large and anisotropic refractive index
- High Bi-refringence

And finally we look at rutile, which is a polymorph of titanium dioxide, which is very important material, it exists in anatase and brookite forms also but rutile is the most commonly used material and it is also again based on HCP packing. So it is based on HCP packing, but it is quite HCP, it is slightly distorted, that is why it is called as quasi-HCP packing. So, what happens here is again here half of the octahedral sites are filled by cations.

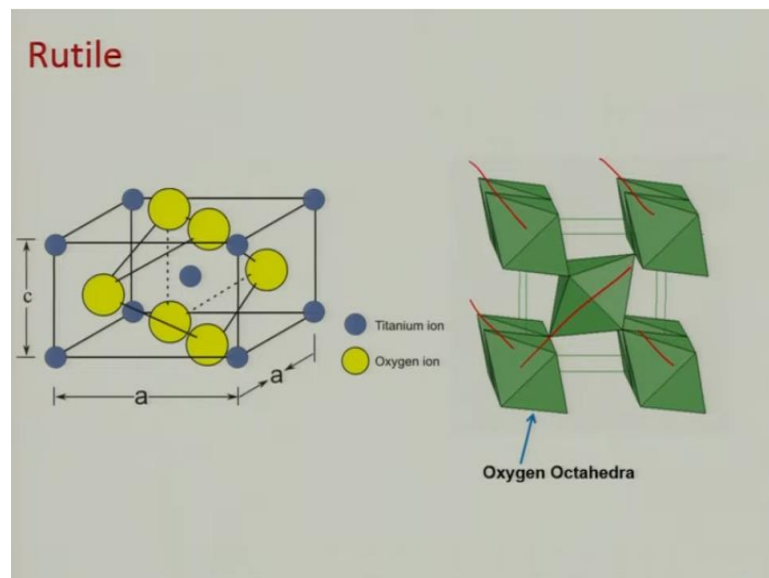
Because you have two of the oxygen atoms, only one cation, so only 50% can be filled. The resulting structure because of distortion happens to be tetragonal instead of hexagonal close packed and this material is very important because it has an isotropic diffusion properties of cations, as a result it has several technological applications. It has large and anisotropic refractive index, it also has high bi-refringence.

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So this is how the structure looks like, you have this hexagonal sort of arrangement of oxygen atoms and titanium goes to octahedral sites. So you can see that there is one channel of titanium is filled, second is empty, third is filled, fourth is empty. So only 50% filling is there.

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And when you stack it all together, the structure looks something like that. So, you make a cell, you can keep the corner at the titanium atoms. So one corner will be here and then another

will be at the center and the oxygen atoms will be like this and they make octahedral, which is not regular octahedral, slightly distorted octahedra and if you want to look at the polyhedral picture, it is like this. You have eight octahedra facing in this direction and you have this octahedra facing in this direction.

Slightly distorted structure, that is why it is tetragonal instead of hexagonal close packed.

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FCC and Cubic Ceramic Structures: Examples

Structure type	Examples
NaCl Structure	MgO, CaO, SrO, BaO, NiO, FeO, LiF, TiN etc.
ZnS (Zinc Blende) Structure	CuF, CuCl, CdTe, CdSe, GaP, GaAs, SiC
CaF ₂ Structure	CaF ₂ , SrF ₂ , PbO ₂ , PrO ₂ , CeO ₂ , ThO ₂ , UO ₂
Spinel (AB ₂ O ₄) Structure	NiFe ₂ O ₄ , Fe ₃ O ₄ , MgAl ₂ O ₄ , CoFe ₂ O ₄ , ZnFe ₂ O ₄
CsCl	CsBr, CsI, NH ₄ Cl, NH ₄ Br, CuZn, AlNi
Perovskite (ABO ₃)	BaTiO ₃ , PbTiO ₃ , CaTiO ₃ , BiFeO ₃ , KNbO ₃

So, this is where we end with this structure of ceramic materials module. We looked at FCC and cubic based ceramic structures, which consists of sodium chloride, zinc blende, fluorite structured materials, spinels, caesium chloride and perovskites. Not all of them are dielectrics, but many of them happen to be dielectric, especially the perovskite structured compounds they happen to be dielectric in nature.

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HCP Structured Compounds

Structure	Examples
Wurtzite	ZnO, ZnS, ZnSe, CdS, CdTe, AgI, AlN
Corundum	Fe ₂ O ₃ , Cr ₂ O ₃ , Rh ₂ O ₃
Ilmenite and LiNbO ₃	FeTiO ₃ , CdTiO ₃ , CoTiO ₃ , CrRhO ₃ , FeRhO ₃ , FeVO ₃ ,
Rutile	SnO ₂ , TiO ₂ , GeO ₂ , MnO ₂ , VO ₂ , NbO ₂

And then we looked at a HCP structured compounds, which are basically wurtzite, corundum, ilmenite and lithium niobate and rutile. And many of these materials are dielectric in nature, titanium oxide based materials are dielectric, ilmenite and lithium niobate are dielectric materials. So, this is a sort of summary of how the structure of these dielectric ceramics evolves. I hope you have got a fair idea of how the structure of these materials is like and how is it derived.

And in the next lecture, now, we will take up the defect chemistry of these oxides which is important from the perspective of determining their properties. So, thank you very much. This is a summary slide which you can read for yourself.

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Summary

- Most ceramic structures are ionically bonded.
- Anions form the base lattice whilst cations occupy the interstices which can be completely or partially filled depending on stoichiometry.
- Pauling's rules play important role in structure determination
- Deviations lead to structural distortions
- Most compounds follow three common structures
 - FCC packing of anions
 - HCP packing of anions
 - Primitive cubic structures

So, thank you.