An Introduction to Materials: Nature and Properties (Part 1: Structure of Materials)

Prof. Ashish Garg
Department of Material Science and Engineering
Indian Institute of Technology, Kanpur

Lecture – 24

Ionic Solids

Spinel Structure

Other Cubic Structures

So, we start again with the new lecture that is lecture 24. We will again continue about the structure of ionic solids. In the previous lecture, we looked at structures of fluoride structured compounds basically and fluoride structures compound basically Ca F 2 a structure or A 2 x kind of structure where there is a difference in the coordination of cations and anions because of different valances.

So, as a result your cation is coordinated by 8; anions in Ca F 2; and anion is coordinated by 4 cations and converse is true for A 2 x kind of compound anti fluorite structured compounds. And that unit cell as we do was a little complicated unit cell, but it is not very difficult I mean once you draw the top view and one from top view you draw the three d view its it becomes very clear.

So, now we will look at the remaining we started with the spinel structured compounds which is AB 2 O 4. But we look at this in detail and there are some other cubic structures in which anions are arranged in cubic fashion and anions go to the interstices they look very similar to FCC in certain cases or bcc in certain cases, but they are not FCC and bcc structure, but they are cubic.

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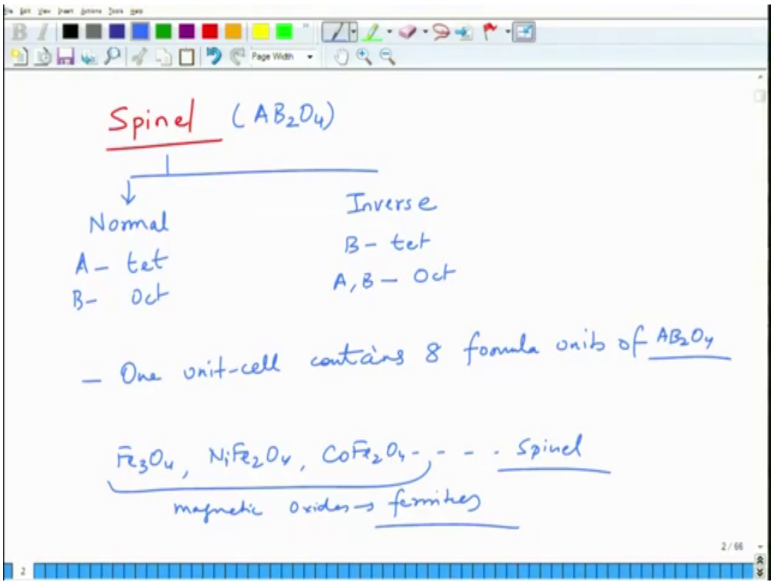

Spinel (AB_2O_4)

Normal
A – tet
B – Oct

Inverse
B – tet
A, B – Oct

– One unit-cell contains 8 formula units of AB_2O_4

Fe_3O_4, $NiFe_2O_4$, $CoFe_2O_4$ - - - - spinel

magnetic oxides → ferrites

So, let us continue discussing our spinel structured materials. So, spinel as we discussed in the last lecture there are two variants one is normal, second is inverse. Both are AB 2 O 4. In this case, A goes to tetrahedral sides, and B goes to octahedral sides. In this case one of the B goes to tetrahedral sides and A and remaining B goes to go to octahedral sides. We can see that there are now the unit cell in this case is typically made of 8 a formula units.

So, one because to accommodate these inter; these interstitial atoms in a regular periodic arrangement man so that you can form a lattice. The lattice does not come in one formula unit. You have to you have to put an eight formula units of Fe AB 2 O 4 to put these atoms in interstitial positions in a repeatable manner ok. So, the lattice is little bigger that one unit cell contains eight formula units of basically AB 2 O 4, it is a bigger unit cell. And we will see how that structure looks like just in the different slight.

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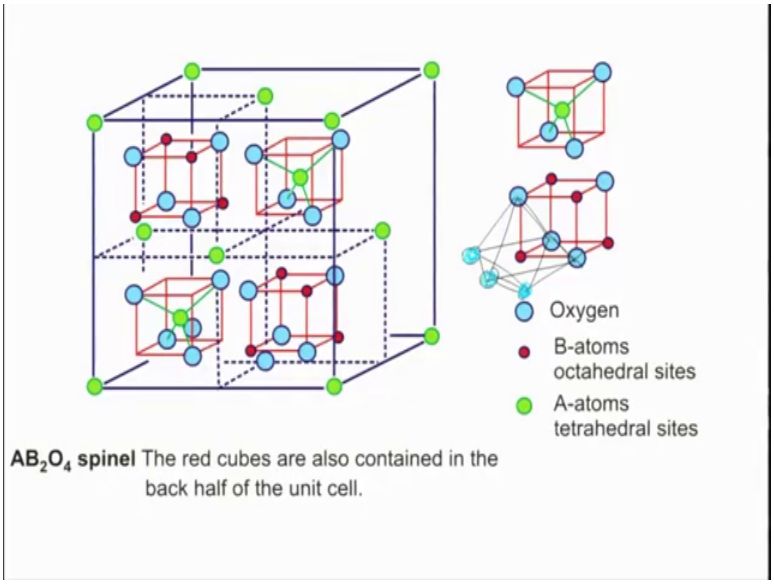

AB_2O_4 spinel The red cubes are also contained in the back half of the unit cell.

So, this is how the structure looks like in case of A B 2. So, now since it has since it has a FCC symmetry FCC lattices made by cations and anions both, then only it is a FCC lattice. So, here you can see the lattices drawn in such a manner, so that lattice corners have put on the A atoms. This is for AB 2 O 4 normal spinel. So, A atoms occupy the tetrahedral sides and you can also build a FCC lattice based on that; and the B atoms are go to octahedral sides, and oxygen basically other cations and anions.

So, this is the tetrahedral coordination where each A atom is surrounded by four oxygen atoms, and this is the octahedral coordination in which in this what will happen is that, so if you have one blue atom there if you have one blue atom there you will have another blue atom here. You will have another blue atom here and you will have another blue atom here. So, this will make a octahedra right all right. You can see that this is my blue atom, this is my blue atom, this is my blue atom. All of these are oxygen atoms right they make a octahedra and within these octahedra you have this cation sitting.

So, only half of them are filled they are filled in such a fashion, so that you can see this is that unit cell bigger unit cell and these are all oxygen atoms placed at various locations, and within them you have at some locations A atoms, some location B atom. So, this looks very complicated. So, how to comprehend this well to you can comprehend this if you look at the structure in a little different manner.

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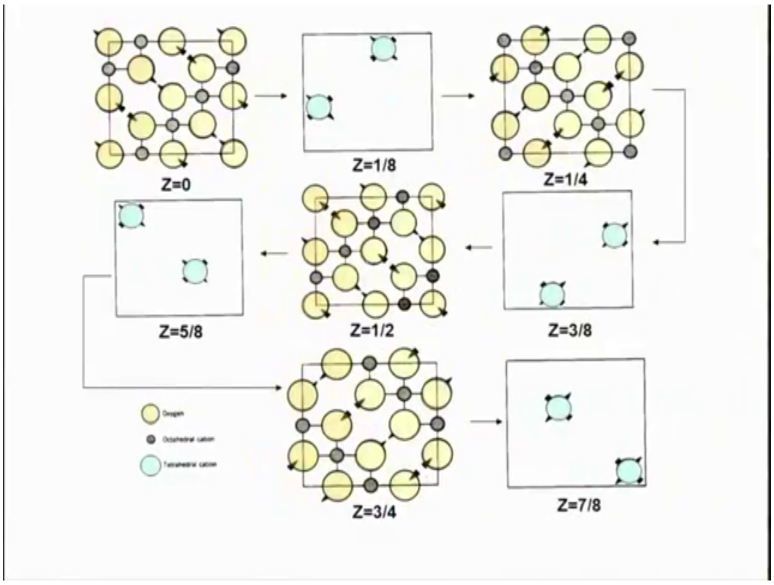

So, let us see, so this is sort of this filling sequence and these in this structure. So, if you see at z is equal to 0, I start with the layer of oxygen atoms, these orange one are the oxygen atoms ok. Now, you can see that there are four squares all right. So, this is the bottom half of one unit cell FCC unit cell, this is bottom half of another FCC unit cell, this is another FCC unit cells, you can see that you have basically four FCC unit cells right , but this is at z is equal to 0, you are going to have eight of these. So, four on the top, four on the bottom; four on the bottom, four on the top.

Now within these you start filling the octahedral sides first. So, you can see that this is an octahedral side it centers on octahedral sides right, but you do not feel all of them you feel only half of them, because octahedral side occupancy is only 50 percent. So, this is octahedral side you fill you cannot put them randomly, you have to put them in a fashion, so that you are you end up making a periodic unit cell. So, the way it fills it, it turns out two atoms go there, four atoms go there, this row remains empty, this row remains empty ok.

The next row at z is equal to 1 by 8 will be tetrahedral, because now you have two unit cells, so that 1 by 4 in normal FCC unit cell becomes 1 by 8 right. So, 1 by 8 position is a tetrahedral position. So, you put two tetrahedral atoms which is the A atom. So, this is the these are the octahedral atoms ok, these are FCC unit cells. So, when you go to z is equal to 1 by 8, you go to the plane in which tetrahedral interstices are there. So, tetrahedral interstices you fill only two of them you do not fill all of them because you cannot fill all of them you have only one-eighth occupancy.

So, you fill you have filled two of these tetrahedral sides in this fashion then you go to next layer which is at z is equal to 1 by 4 which is the middle part of the next FCC layer right. So, this will become, so this is the bottom part of first FCC layer, this is the middle part of the bottom FCC cell. So, you can see that here the atoms over here on the corners and the face center, now here they have become so here they have come at the face centers ok. So, face centers on the sides. So, these are all oxygen atoms. And you again fill that at octahedral sides in such a fashion. Now, you fill the octahedral sides in a rotated fashion. So, here they were going all along in this direction, this direction, now they have rotated by 90 degrees.

So, this is the next layer of octahedral atom. So, this row is filled, this row is empty, this row is filled, this row is empty, then again this row is filled ok. Then you come to z is equal to 3 by 8 ok, which is the again tetrahedral plane of the bottom half of the FCC unit cell. So, again you have filled the first two layers here first layer of tetrahedral side here now you fill that a tetrahedral side here. And then again you go to z is equal to half. When you go to z is equal to half you come at a position which is same as it is equal to 0, because it stops top surface of the bottom FCC unit cell.

So, the oxygen atoms are arranged in the same fashion; however, the octahedral sides are now filled in different manner instead of keeping these empty and these empty you shift the octahedral sides by another vector in the 1 1 0 direction. So, you can see that this layer is now empty this row is filled this row is empty and this row is filled. And then again you go to tetrahedral plane you rotate now the tetrahedral interstices position. Now, in that tetrahedral sides which are filled are those which is which are along this axis.

Then you go to z equal to 3 by 4, again you go to the similar structure of as you have here, but again you rotate the position of filling. So, now, the tetrahedral sides are filled octahedral sides are filled in this fashion. This row is empty, this row is filled, this row is filled, this row is empty, this row is empty alternate filling of rows. Finally, you come to z is equal to 7 by 8 where you have filled two tetrahedral interstices.

Now, you can see that these are shifted with respect to what you have at z equal to 5 by 8. So, these are shifted to the next available corner. Then at z is equal to 1, you will same you will have the arrangement which is same as z is equal to 0. So, this is how you arrange cations and anions cations in a periodic in a in a 8 FCC unit cells so as to achieve a unit cell which is periodic in nature which is repeatable in nature ok. This is a complicated lattice you have to go layer by layer filling off cations in the anion lattice, and this will make a big unit cell of spinel structure.

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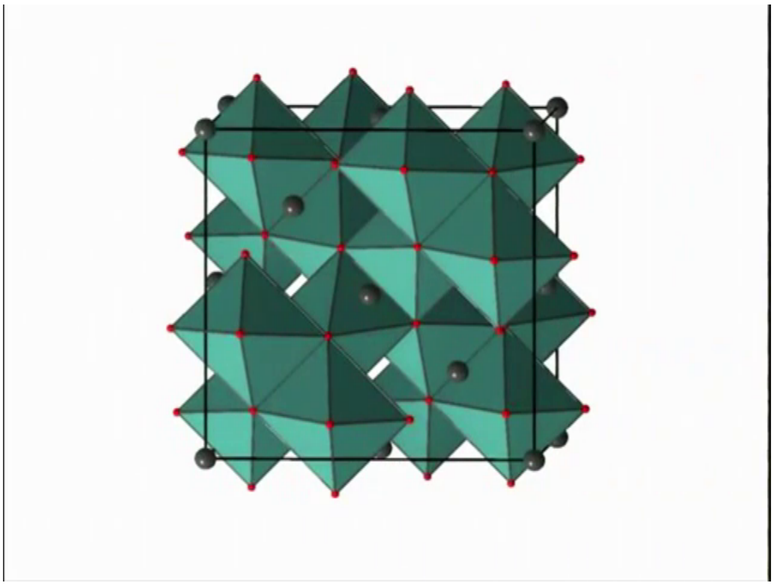

So, this is how it is going to look like when you make. So, these are various octahedral is stacked up octahedrons will consist of basically cations B cations, and tetrahedral sides will contain the A cations. So, this is basically the spinel structure as I was talking. So, you can see here it, this contains eight unit cells or formula units of AB 2 O 4. So, essentially if you if you look at the top view, you are going to have so just like we drew 8 unit cells of fluorine in Ca F 2 structure here you again draw eight unit cells of oxygen, but they are not cubic cells. Now, they are FCC cells and then you fill the interstices in a layered fashion so as to make a periodic structure. So, what I showed you just now was a spinel structure compound.

And this is of a lot of importance because lot of engineering oxides such as you know materials like Fe 3 O 4, Ni Fe 2 O 4 Co Fe 2 O 4 all of them they follow basically spinel structure. And these oxides are interesting because they are magnetic oxides and they are called as or ferrites. They are used for lot of magnetic applications so that is why it is important to know how the sides are filled in these structures and based on the side filling they show some interesting magnetic phenomena ok. So, now let us let us move on to the next structure which is called as so this is these are all these are the structures which were based on FCC packing of anions.

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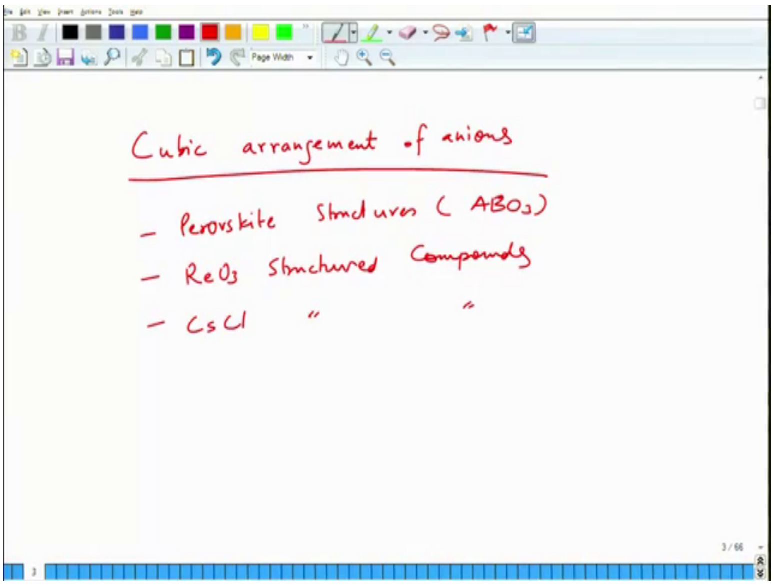

Cubic arrangement of anions

- Perovskite Structures (ABO_3)
- ReO_3 Structured Compounds
- CsCl " "

There are certain structures which are which look as if there is a bcc or FCC packing of anions, but if you look at the lattice carefully it is just a simple cubic lattice. So, in this category let us give the lets categorize as a cubic arrangement of anions. So, in this we look at first perovskite structures perovskite is known as A B O 3 structured compounds, then we have Re O 3 structured compounds , and then we have Cs Cl structured compound cesium chloride ok.

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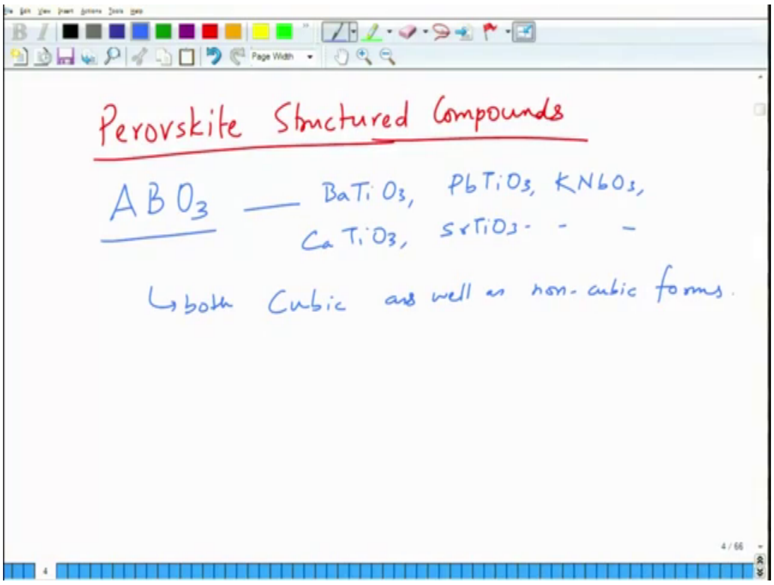

Perovskite Structured Compounds

ABO_3 — $BaTiO_3$, $PbTiO_3$, $KNbO_3$, $CaTiO_3$, $SrTiO_3$ - - -

↳ both Cubic as well as non-cubic forms.

So, let us first begin with the perovskite structured compounds. So, in this category, these the general formula of these compounds is A B O 3 ok. And this is again ionically bonded solid like the compounds that you can include in this category are things like barium titanate, lead titanate KN B O 3 potassium niobate, calcium titanate, strontium titanate various titanates and niobates they follow this kind of structure.

And although it is cubic in many circumstances at least some forms of these or these oxides are cubic, they tend to sometimes distort and they make non cubic structures. So, they exist in both a cubic as well as non-cubic forms, they are slightly distorted from cubic structures.

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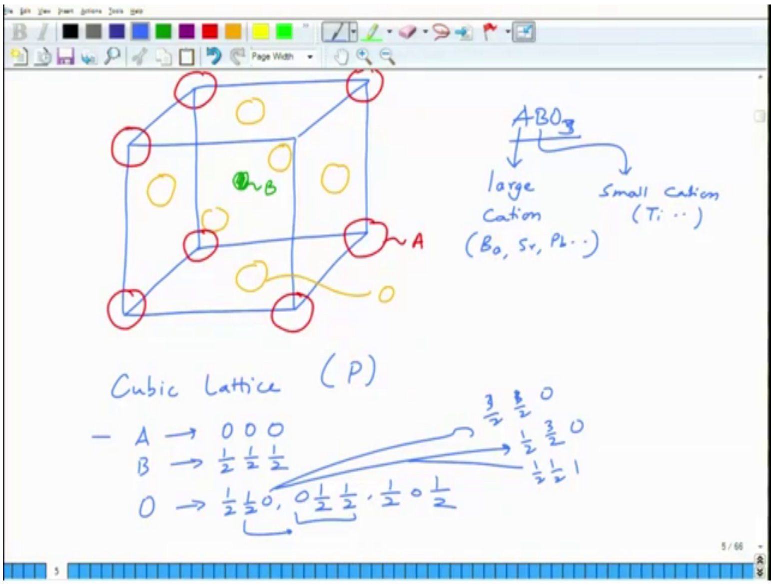

So, the way this structure is made is like this. So, in this unit cell the oxygen atoms if I refer them as orange occupy the face centers of this cube. The barium atom so let us write the formula let us say A B O 3. So, there are three oxygen atoms right, half, half, half, half, half, half, so three oxygen atoms let us say the A atom is the bigger cation, it goes at the cell corners , this is A and this was oxygen.

And the B atom is the smaller cation which is B. So, A is typically a large cation such as barium strontium, lead; B is a small cation such as titanium, many cases it is titanium, it could be zirconium and iron as well in certain cases and some of the atoms. So, you can see here it looks as if it is a FCC structure, but it is not FCC structure, because not all the sides face centered sides are filled by same atom.

So, the corner of the cube is occupied by A atom, the face center of the cube is occupied by oxygen atom, and center of the cube is occupied by B atom. So, this lattice is basically a cubic lattice p-type that is primitive cubic lattice ok. It has one formula unit of A B 2 O 3, A atom being at a at 0 0 0, B at and oxygen at. You need to define all the positions. If you are defining a primitive lattice you need to define all the positions because primitive lattice vector is only 1 0 0.

So, if you go from half 0 0, the lattice translation is only 1 0 0, it will go to 1 half 1, half 1 half 0. So, you cannot get this point. So, you need to explicitly mention this point to get this either because in FCC lattice the lattice vector is half of zero. So, you can translate each point by half 0 0, half of 0, half 0 half and 0 half half, but in this case the primitive lattice vector is one one 1 0 0, as a result 1 0 0 or 0 1 0 or 0 0 1, as a result you cannot get the other points ok. So, if you if we translate half of zero, you will get let us say if you translate half of zero by 1 0 0, you will get 3 by 2, 3 by 2, 0 right.

If you translate this by 0 1 0, you will get 0 3 by 2 sorry this will be 0 3 by 2 half zero. Similarly, if you translate this by 0 0 1, you will get half half one. So, you will again reach the same point, you will not reproduce these two points. So, in order to produce these two points, you need to explicitly mention them. So, that is why it is a primitive lattice and it is.

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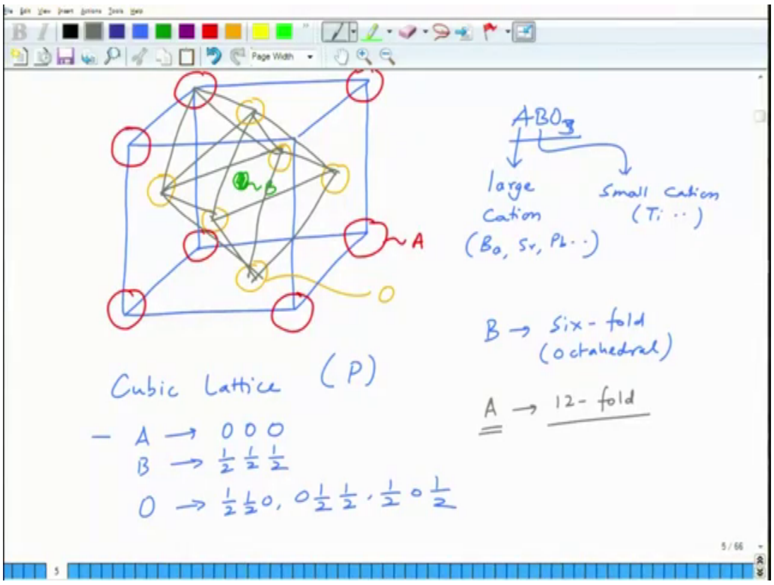

ABO_3

large Cation (Ba, Sr, Pb..)

Small Cation (Ti ..)

B → Six-fold (octahedral)

A → 12-fold

Cubic Lattice (P)

- A → 0 0 0
  B → $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
  O → $\frac{1}{2}\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$

So, now, look at the coordination here B atom is a smaller atom the coordination of this is six-fold which is octahedral. You can see the octahedra here, this is octahedra that you make ok. So, B atom is octahedrally coordinated. What about A atom, how many if you look at A atom here, let us say this A atom, it has one neighbor here, it is another neighbor, there it is another neighbor there three neighbors are present in this unit cells. And it is going to be surrounded by eight unit cell side; it is going to be shared by eight unit cells. So, but some of these atoms are shared by two unit cells.

So, it will be twelve fold coordination. And it makes sense because B is a smaller atom it recurred it requires based on radiation it has six-fold coordination. And A has a coordination which is twelve-fold because it is a bigger atom. You can represent these units in a different manner also.

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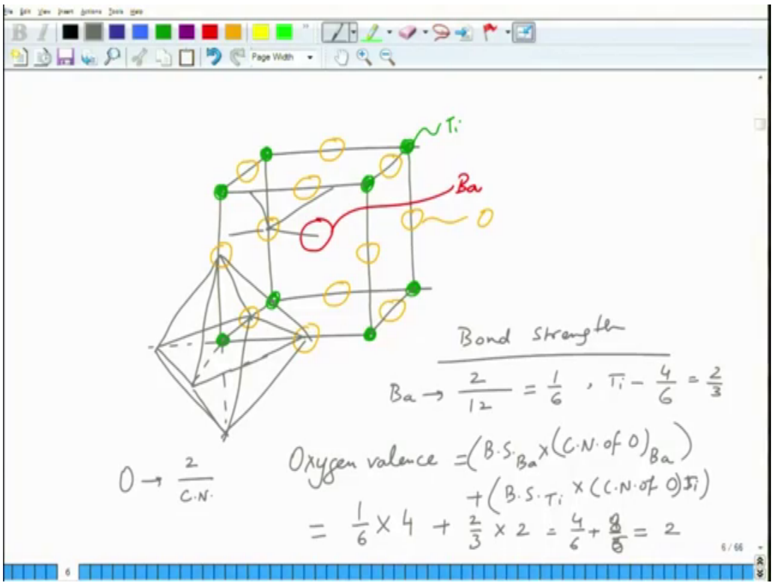

Bond Strength

$$Ba \rightarrow \frac{2}{12} = \frac{1}{6}, \quad Ti - \frac{4}{6} = \frac{2}{3}$$

$$O \rightarrow \frac{2}{C.N.}$$

$$\text{Oxygen valence} = (B.S._{Ba} \times (C.N. \text{ of } O)_{Ba}) + (B.S._{Ti} \times ((C.N. \text{ of } O)_{Ti}) = \frac{1}{6} \times 4 + \frac{2}{3} \times 2 = \frac{4}{6} + \frac{8}{6} = 2$$

If you let us say if I put the titanium atom at the, at these corners, let us say this is titanium atom. But these are titanium atoms, where does oxygen go, oxygen goes to the. And where does barium go, the barium goes to what is the color where we used to red one ok, put the red one right here. Now, you can see the twelve neighbors, four of these, four of those, four of those, the twelve neighbors to the barium atom is that clear. So, this is barium; this is oxygen. So, this is the structure which is called as perovskite structure.

So, you can see that this structure is as if you can write the, you can mark the octahedral here. So, this is the first octahedral, you will have one on the other side. There is another octahedral, and one this side. And you can connect this octahedra to these points, and the one at the bottom will be here right. So, these are all vertically stacked octahedron one octahedra here under another here, and the here, another here, another here, and there here. So, you have eight octahedral vertically stacked up.

So, this is basically the polyhedral representation of the unit cell , you can also do the bond strength check here. Now, cation for barium barium is it has a valence of two it surrounded by 12 right; its bond strength is 6, 1 by 6. Titanium is surrounded by it has a valence of 4 surrounded by 6, it has a build. Now, oxygen has a valence of two-coordination number something coordination number now either you know the coordination number, you need to get the valence out. So, what you can do is that oxygen valence in this case is bond strength of barium multiplied by coordination number of oxygen by barium plus bond strength of titanium multiplied by coordination number of oxygen by titanium.

So, it turns out you have in the first case 1 by 6, the now how many barium atoms around each oxygen atom. Let us say this is the reference oxygen atom ok, one in this, one on the back, one here and one here, four, four, one step titanium is 2 by 3. And how many oxygen, how many titanium is around the oxygen atom; now this is oxygen where on this side one on that side only two right is it right. So, this is 4 by 6 plus 4 by 3 which is nothing but 8 by 6. So, this becomes 2 and oxygen valence is 2. So, it does follow the rule of bond strength because it gives you the same variance.

So, basically solid is electrically neutral. If you get something other than 2, which means there is something wrong with the co-ordinations, because the valence of cation anion must electrically the number of atoms and the way they should be arranged in such a fashion, so that solid is electrically neutral. So, each of them have that coordination. So, this is a perovskite structure, there are a lot of compounds which are perovskite.

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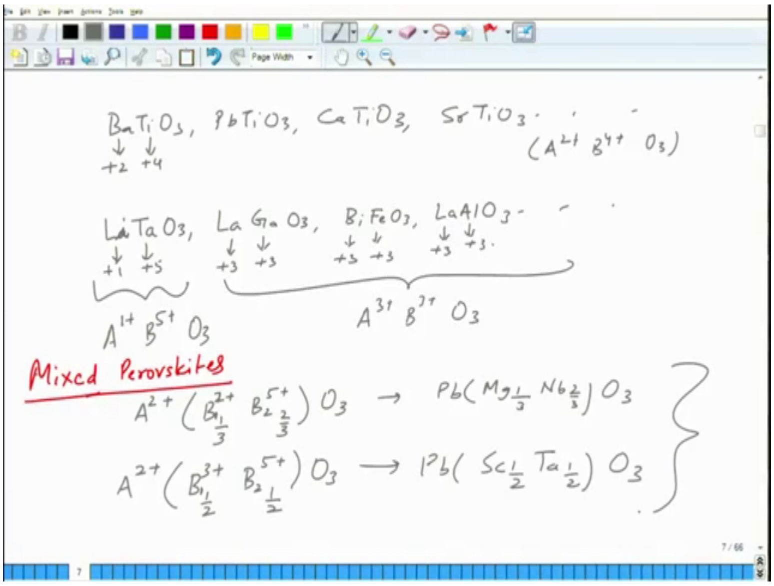

$\underset{+2}{\underset{\downarrow}{Ba}}\underset{+4}{\underset{\downarrow}{Ti}}O_3$, $PbTiO_3$, $CaTiO_3$, $SrTiO_3$.

$(A^{2+}B^{4+}O_3)$

$\underbrace{\underset{+1}{\underset{\downarrow}{Li}}\underset{+5}{\underset{\downarrow}{Ta}}O_3}_{A^{1+}B^{5+}O_3}$, $\underbrace{\underset{+3}{\underset{\downarrow}{La}}\underset{+3}{\underset{\downarrow}{Ga}}O_3,\ \underset{+3}{\underset{\downarrow}{Bi}}\underset{+3}{\underset{\downarrow}{Fe}}O_3,\ \underset{+3}{\underset{\downarrow}{La}}\underset{+3}{\underset{\downarrow}{Al}}O_3}_{A^{3+}B^{3+}O_3}$

Mixed Perovskites

$$\left.\begin{array}{l} A^{2+}\left(B_{1\,\frac{1}{3}}^{2+}\,B_{2\,\frac{2}{3}}^{5+}\right)O_3 \rightarrow Pb\left(Mg_{\frac{1}{3}}Nb_{\frac{2}{3}}\right)O_3 \\ A^{2+}\left(B_{1\,\frac{1}{2}}^{3+}\,B_{2\,\frac{1}{2}}^{5+}\right)O_3 \longrightarrow Pb\left(Sc_{\frac{1}{2}}Ta_{\frac{1}{2}}\right)O_3 \end{array}\right\}$$

For examples of perovskite is not only you have barium titanate, lead titanate, calcium titanate etcetera, strontium titanate, there are various solid solutions. So, for example, in these you see barium is plus 2, titanium is plus 4, but they do not need to be like that only. There are a lot of other cases for example, you can see La Ta O 3 sorry Li Ta O 3 lithium tantalate and then you have La Ga O 3 you have Bi Fe O 3 you have La Al O 3.

In this case, plus 1, plus 5, here you have plus 3 plus 3 here you have plus 3, plus 3, again plus 3, plus 3. So, you have possibilities or plus 3. So, these are. So, here they are A 2 plus B 4 plus O 3 this is an example of A 1 plus B 5 plus O 3, these are all examples of A 3 plus B 3 plus O 3 ok. You can also make mixed perovskite such as mixture of. So, these are mixed mixed perovskites basically solid solutions.

So, mixed perovskites will be A 2 plus let us say B one by three one plus sorry 2 plus and B 1. So, this is B 1 ok. Then you have B 2 2 by 3 5 plus O 3. So, for example, you have lead magnesium niobate they are in they are put in such a fashion, so that the stoichiometry is maintained and the charge neutrality is there. So, bismuth is 2 plus you can only put 1 by 3; B 1 is 2 plus, you can put only 1 by 3; B 2 is 5 plus, it is a strain to 2 by 3. So, magnesium 1 by 3, niobium 2 by 3 will give you 4 plus valence together ok.

Similarly, you can have A 2 plus B 3 plus half B 1, then another B 2 you can take half as 5 plus O 3. So, this says for example, lead scandium tantalate ok. So, these are certain examples of perovskite. So, we will finish here in this class where we looked at spinel structure and perovskite structures. We will do the remaining structures in the next lecture ok.