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

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Lecture - 25
Ionic Solids (Ceramics)
Remaining Cubic Structures
Non- Cubic Structures

So, today we start a new lecture 25.

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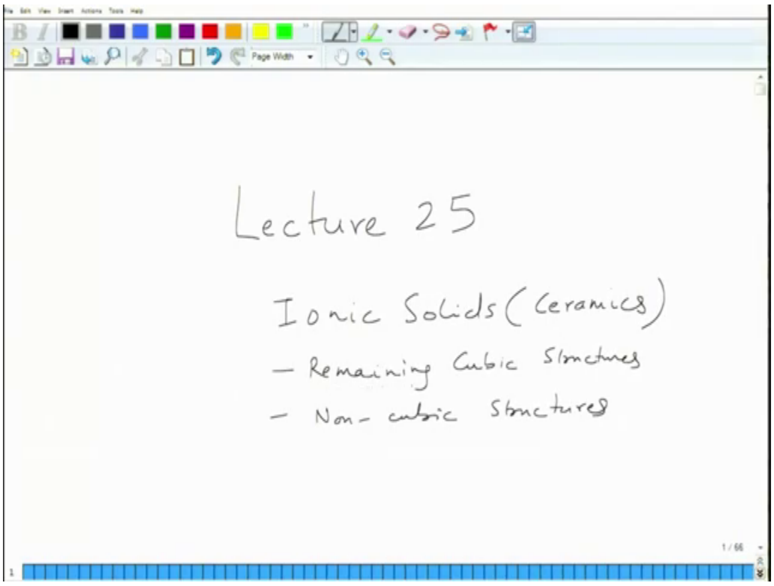

Lecture 25

Ionic Solids (Ceramics)

- Remaining Cubic Structures
- Non-cubic Structures

So, in which we will discuss the remaining part of ionic solid structures and it is large anything with ceramics. So, we will talk about remaining cubic structures and non cubic structures. So, let us just the recap about the last class.

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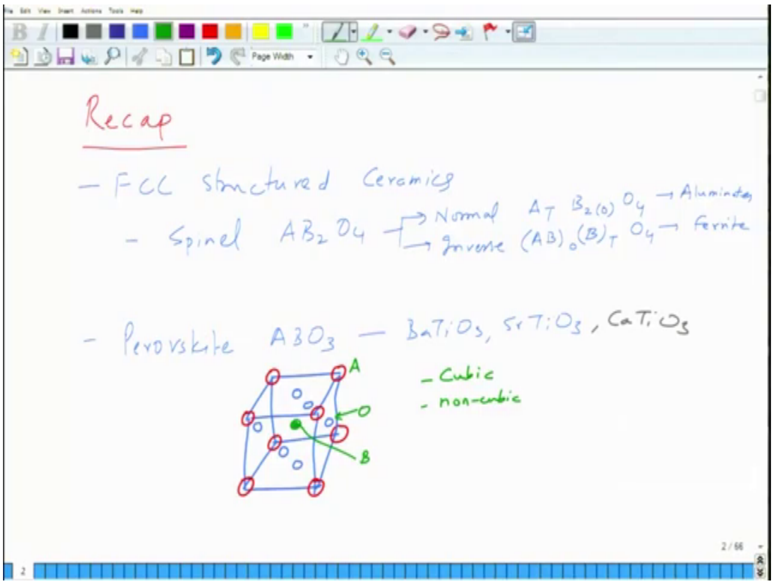

Recap

- FCC Structured Ceramics
  - Spinel AB_2O_4 → Normal $A_T B_{2(O)} O_4$ → Aluminates
    → Inverse $(AB)_O (B)_T O_4$ → Ferrite
- Perovskite ABO_3 — $BaTiO_3$, $SrTiO_3$, $CaTiO_3$
  - Cubic
  - non-cubic

Last class we did; so, in the last class we talked about FCC structured ceramics that is we talked about mostly spinel structures which are based on AB 2 O 4 kind of compounds. And these spinels are in two forms one is normal spinel and second is inverse spinel.

So, normally spinel A goes to tetrahedral B goes to octahedral and then oxygens are make FCC lattice. In case of inverse your A B go to octahedral sorry and one B goes to tetrahedral and oxygen makes FCC lattice. So, normally why spinel structures import important because many eliminate; so, many ferrites make this structure.

So, typically eliminates will make normal spinel structure typically and typically ferrites will make inverse a spinel structure. So, this is the difference between the two and then we looked at the perovskite structure which is based on AB O 3 formula unit and this is compounds such as barium titanate, strontium titanate it is thickened strontium titanate, calcium titanate and so, on and so, forth they follow this kind of structure.

And this is basically based on a non FCC packing. So, here in the unit cell oxygen goes to oxygens go to face centered sites, barium goes to corners cell corners and titanium goes to the center of the B goes to the center of the cell. So, this is A, this is B and this is O this is typically now it exists perovskites exist in both cubic and non cubic forms.

What I have shown you here is too big. So, it is basically it is a primitive cubic lattice, but many of these materials are ferroelectric in nature. So, they undergo your curie car transition at a temperature called as T C. So, let me now come to that particular aspect.

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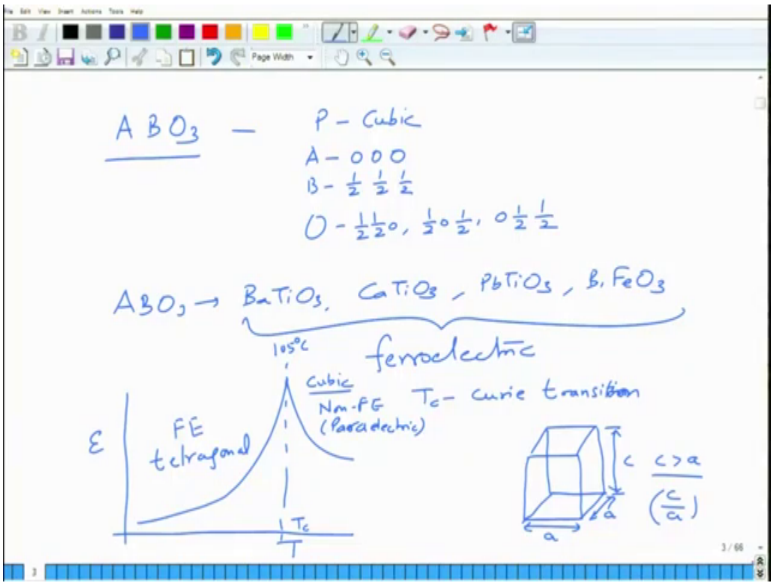

ABO_3 — P – Cubic

A – 0 0 0

B – $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

O – $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$

$ABO_3 \rightarrow \underbrace{BaTiO_3,\ CaTiO_3,\ PbTiO_3,\ BiFeO_3}_{\text{ferroelectric}}$

T_c – curie transition

So, what we talked last time was that AB O 3 is primitive cubic with motive being at a at 0 0 0 B at half and oxygen at half of 0 half 0 half and 0 half half.

But many of these compounds AB O 3 based compounds such as barium titanate, calcium titanate, lead titanate etcetera if not and bismuth ferrite; many of these are ferroelectric in natures these are all ferroelectric ok. Now ferroelectric materials have a property which is called as they undergo a curie transition that is their dielectric constant varies as a function of temperature at it undergoes through a maxima enamel is increased at a temperature called as T c this T c is called as curie transition.

A typically ferroelectric this in this diagram below T c these materials are in ferroelectric state and above T c they are in non ferroelectric that is called as para electric state. Now what happens is for example, in case of barium titanate at about 105 degree centigrade or. So, I cannot exactly remember it is about 100 it is above 100 it is above between 105 and 111 and 20.

So, above this 2D temperature of barium titanate its structure is cubic. So, what we followed is a perfectly replicated there, but below T c the material has a tetragonal structure. So, the unit cell which is a cube now converts into a. So, below T c this length is slightly larger than these two lengths.

So, this is a this is a this is c; so, c is greater than a there is some c by a ratio which unit cell will have. So, many of these peroskites in the ferroelectric state in fact, all of them they are non cubic which is required by which is which is necessitated by the requirements of electricity for electricity cannot occur in cubic compounds, but at higher temperature they become cubic.

So, this is a difference between perovskite and a cubic perovskite and non perovskite cubic perovskites.

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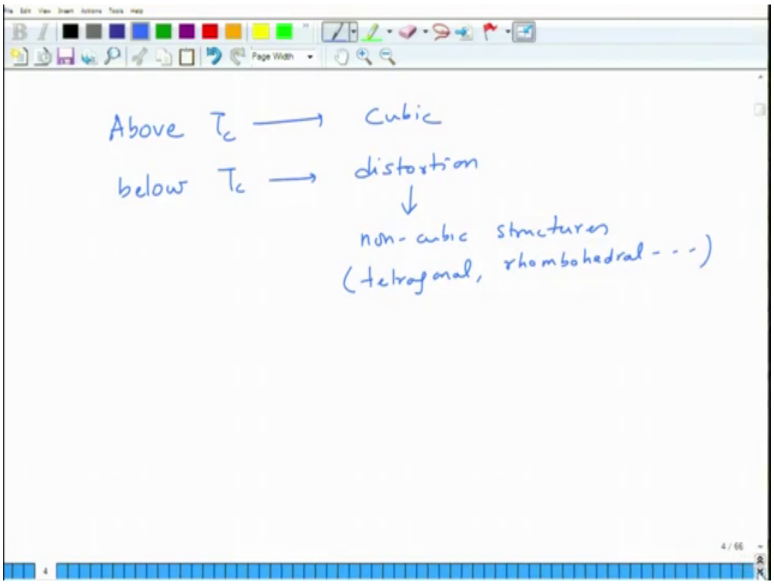

Above T_c ⟶ Cubic

below T_c ⟶ distortion

↓

non-cubic structures

(tetragonal, rhombohedral - - -)

So, many of them; so, cubic perovskites above T c the structure will be typically cubic below it T c; there will be some distortion it is a very minor distortion in the unit cell and this minor distortion leads to non cubic structures. So, these could be that tetrgonal rhombohedral and so, on and so, forth is just a slight distortion in the unit cell which makes the cubic symmetry to go away.

So, there is no cubic symmetry; so, this is the perovskite structure.

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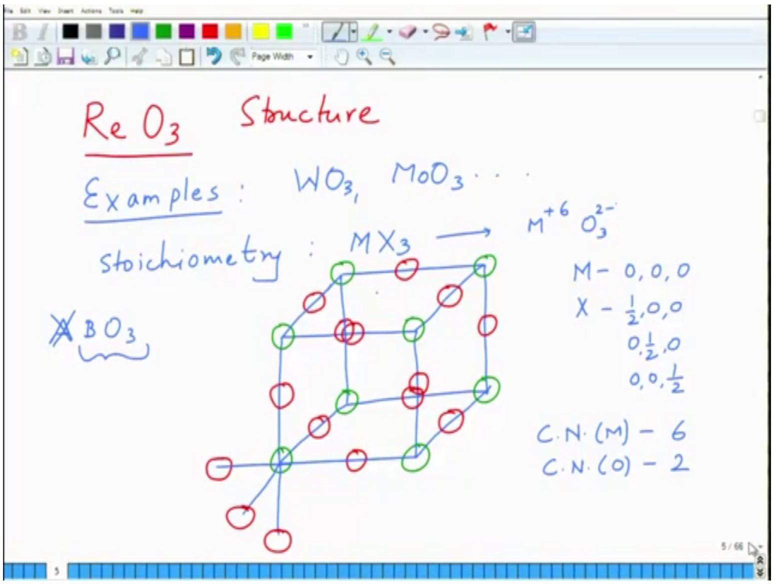

ReO_3 Structure

Examples : WO_3, MoO_3 . . .

stoichiometry : $MX_3 \longrightarrow M^{+6}\, O_3^{2-}$

$\cancel{A}BO_3$

M - 0, 0, 0

X - $\frac{1}{2}$, 0, 0

0, $\frac{1}{2}$, 0

0, 0, $\frac{1}{2}$

C.N. (M) - 6

C.N. (O) - 2

Now, next in the series is called as Re O 3 structure now Re O 3 is the parent compound other compounds which follow this structure, for example, oxides such as WO 3 MO 3 they tend to follow this. So, in this compound the stoichiometry as you can see is MX 3.

And basically this structure is like this you can see that here M is a in this kind of structure M is plus 6 iron and you have 3 oxygen which are 2 minus and there are 3 of them. The atomic positions happen to be M at 0 0 0 and X at half 0 0 kind of positions have 0 0 0 half 0 and 0 0 half type of positions it is a primitive cubic lattice.

So, this is M again this is now we will see the coordination; I have not told you the coordination this is the position of. So, what is the coordination of M in this case? M's coordination is if you go in this direction, if you go in this direction, if you go in this direction you will have one O here, here and another O here it will be 6 fold coordination.

So, coordination number of so, what is the coordination number of oxygen in this case? You can do the bond strength check, but you can see the stoichiometry is 3 times N X 3 1 is to 3; it is got to be 2. So, can you correlate this structure with AB O 3 structure we can correlate with that this structure is very similar to AB O 3 with. So, if you look at AB O 3 we drew AB O 3 in this form right.

So, where is now A? A is missing here; So, this A is missing it is a perovskite it can be considered as a sort of profit structure with A atom missing. So, it is just BO 3 alright just BO 3. So, this is what the structure is like; so, coordination of M is octahedral coordination of oxygen is linear ok. So, this is the coordination.

And the examples I have given to you and this is an important these are all important materials because you can see the structure is very open now right. You can see that there is a big void at the centre of the unit cell and this big void in the centre of the unit cell allows these materials to carry on defects and they provide good defect migration and they can also carry out they can also consist of impurities.

So, these materials for example, tungsten oxide is used as a sensor; it is used as a electrochromic material ahmaterials which change their color when they applied electric field. So, similarly maury oxide is used for lot of electronic applications. So, this the structure or the open structure of this material helps in that achieving those attributes.

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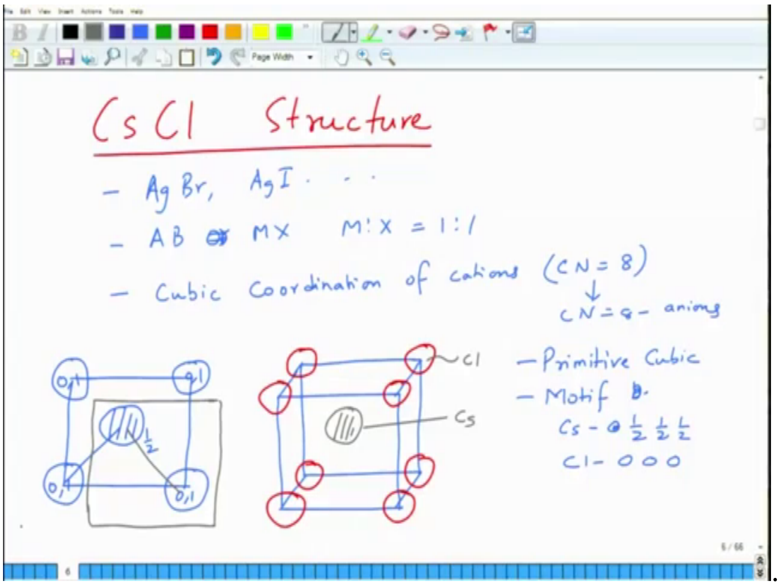
CsCl Structure

- AgBr, AgI . . .
- AB or MX M : X = 1 : 1
- Cubic Coordination of cations (CN = 8)
  ↓
  CN = 8 - anions
- Primitive Cubic
- Motif B.
  Cs - $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$
  Cl - 0 0 0

So, now let us look at another structure which is again cubic based structure which is called as C s C l structure. And this structure is followed by cesium chloride is a parent compound, but it is followed by compounds such as silver bromide or silver iodide and so, on and so, forth. So, again you can see it is a B stoichiometry where or MX you can write MX where M is to X is 1 is to 1 which means both of irons will have similar coordination that is for sure.

So, these materials also turn into rock salt structure at higher pressures, but at lower pressures they remain as a cesium chloride structure. And lot of halides adopted this kind of structures bromides iodides and chlorides of basically larger ions and ions which are bigger which require larger coordination they require they adopt this structure. So, in this structure the structure is; so we basically have based on radius ratio, we have cubic coordination of cations which means coordination number is 8 this also results in coordination number of 8 for anions.

If you apply the bond strength rule; so, the structure is something like the following and these are chlorine atoms and the cesium atom goes right at the center of the unit cell. So, this is chlorine, this is cesium; so, these are all of course, when you make the ball model they touch each other, but for the sake of clarity we have to draw them as separate.

So, this is a primitive cubic lattice with motive being as cesium at sorry cesium at half half and chlorine at you can write the other way around as well. You can write the motive as chlorine at half of half and cesium at 0 0 0 because you can put the unit cell wherever you want. So, if you draw the plan view it will look something like that and this will be your; so, this is at half this is at 0 1.

So, you can consider each of these being connected to this ion. So, it is kind of dumbbell shaped structure; so, we can make them unit cell let us say if you make the unit cell here it will consist of one number off one of these right. So, maybe you can consider this create the bond between this and that ok.

So, let me see if I have a picture to show you. So, this is how rhenium oxide structure would look like.

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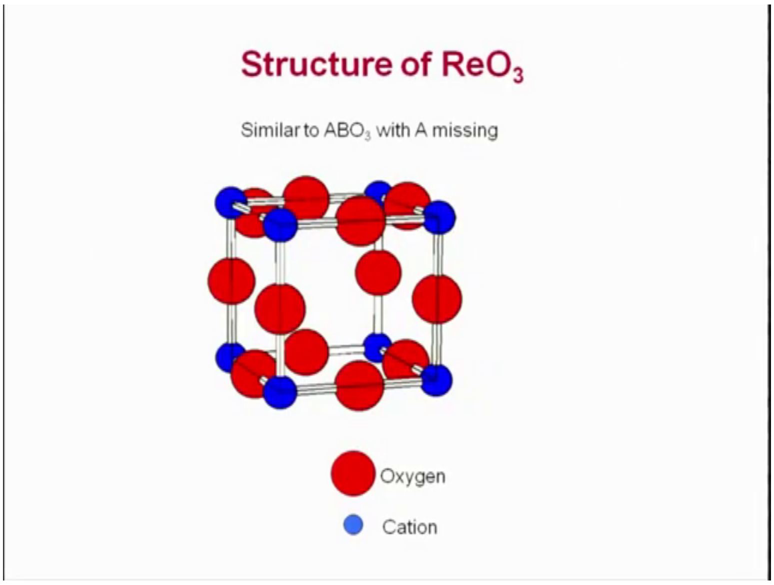

Structure of ReO_3

Similar to ABO_3 with A missing

🔴 Oxygen

🔵 Cation

So, this is the first representation and which you have B B atoms in the oxygen.

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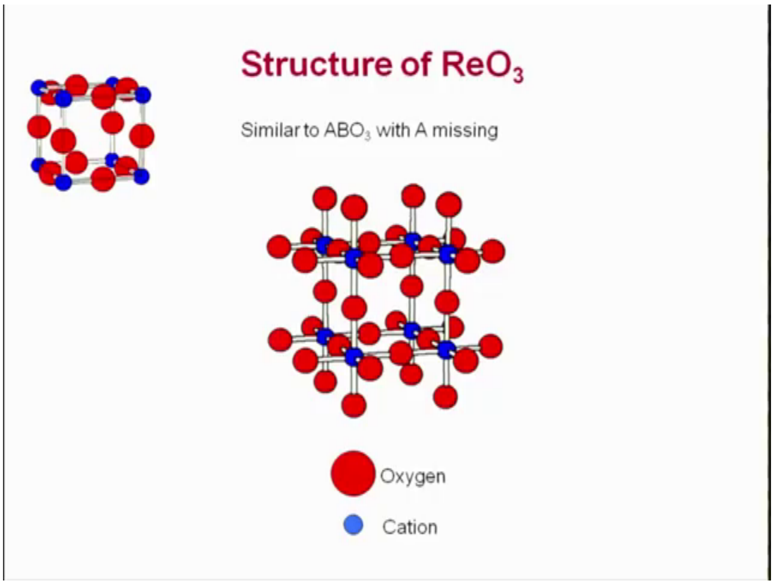

Structure of ReO_3

Similar to ABO_3 with A missing

🔴 Oxygen

🔵 Cation

You can make slightly elongated structure show the octahedrals clearly.

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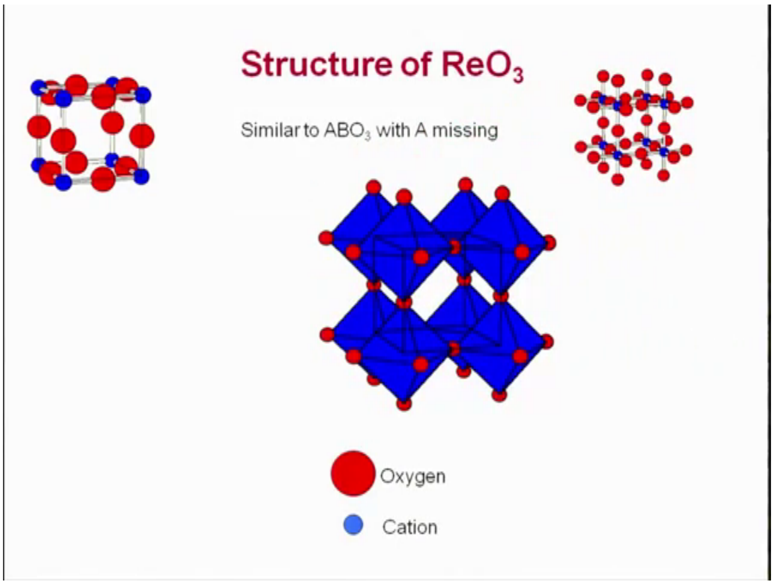

Structure of ReO_3

Similar to ABO_3 with A missing

● Oxygen

● Cation

And if you make the polyhedral view it looks like as if this is the polyhedral view of reo 3 structure.

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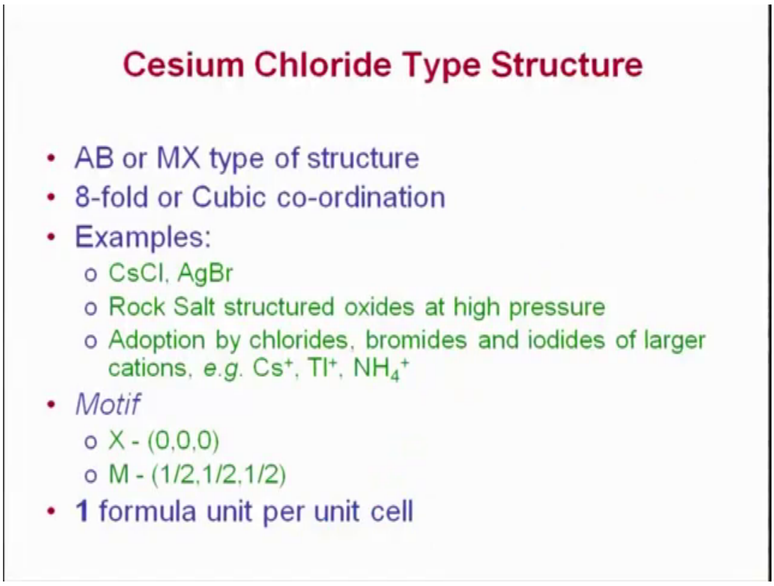

Cesium Chloride Type Structure

- AB or MX type of structure
- 8-fold or Cubic co-ordination
- Examples:
  - CsCl, AgBr
  - Rock Salt structured oxides at high pressure
  - Adoption by chlorides, bromides and iodides of larger cations, *e.g.* Cs^+, Tl^+, NH_4^+
- *Motif*
  - X - (0,0,0)
  - M - (1/2,1/2,1/2)
- **1** formula unit per unit cell

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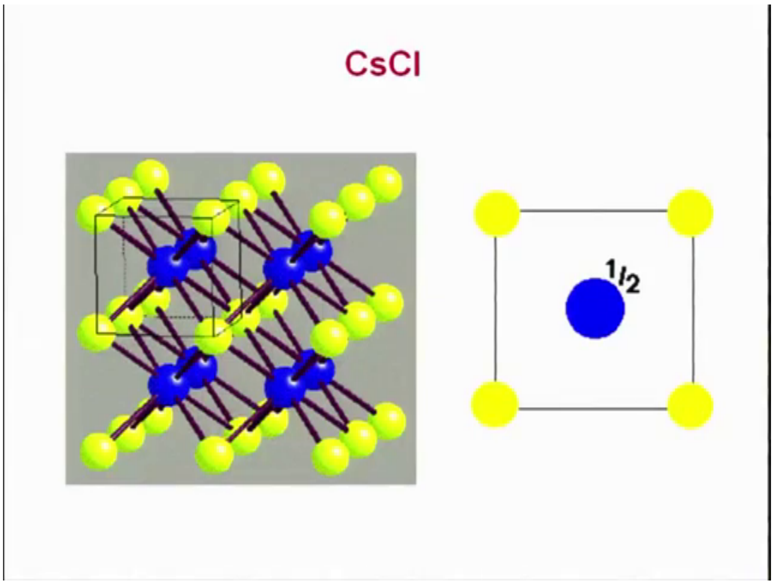

CsCl

So, this is the cesium chloride sort of structure you can say that these are the sort of dumbbell shaped structures. So, these are all chlorine atoms these are all cerium cesium atoms ok.

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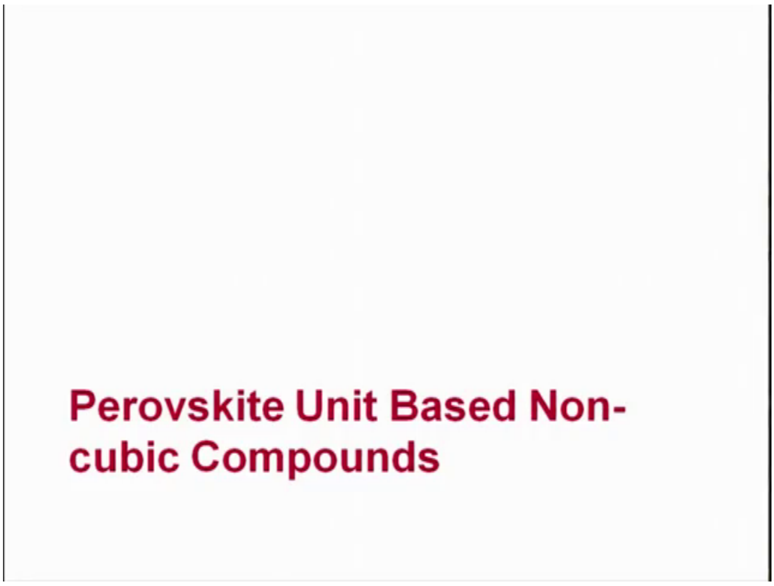

Perovskite Unit Based Non-cubic Compounds

So, now we will move on to another category of materials which are ceramics basically ionically bonded ceramics; which are non cubic compounds they are not hexagonal ah, they could be orthorhombic that would be tetragonal, but they contain perovskite units the perovskite units are inbuilt between them or they contain some other they may contained for example, sodium chloride units or so, on and so, forth.

Now, many of these compounds happen to be very important for a lot of technological applications ok.

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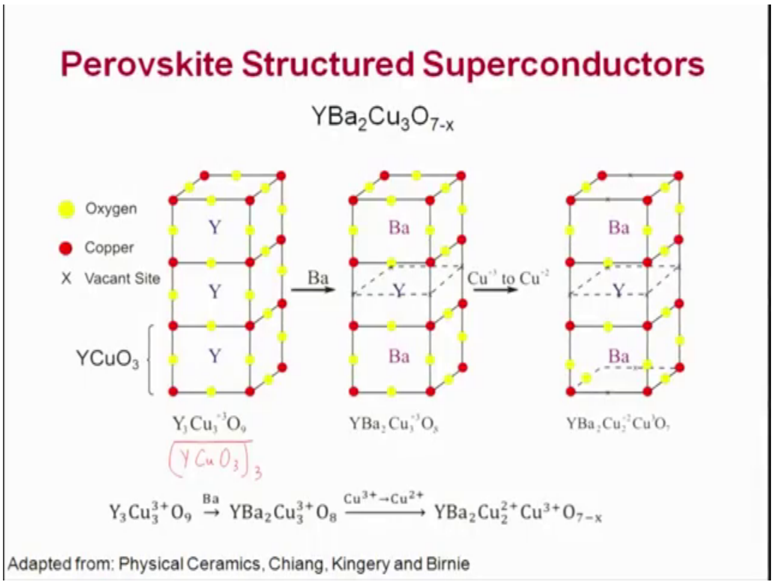

Perovskite Structured Superconductors

$YBa_2Cu_3O_{7-x}$

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

Adapted from: Physical Ceramics, Chiang, Kingery and Birnie

So, one such structure is a atrium barium copper; atrium barium oxide atrium barium copper oxide is a superconductor YBa 2 C u 3 O 7 minus x. Now this material is the basically if you look at the parent compound of this material parent compound of this material as drawn on the left is y 3 y 3.

So, the parent compound is Y 3 C u 3 O 9; it has a tetragonal structure in this unit cell you can see it is made up of 3 unit cells of Y C u O 3. So, if you can see that Y 3 C u O 3 9 or Y C u O 3 3 times right. So, your 3 unit cells stacked on top of each other whichever perovskite in nature. The way it is made superconducting is by first a doping it barium; so, what barium does is that barium replaces two of the atrium ions.

So, one in the bottom unit cell another in the top unit cell. So, this leads to YBa 2 C u 3 3 plus this is C u 3 plus by the way not C u 2 plus ok; now since barium has less oxygen with it because it has valence of only plus 2 there is oxygen deficiency. So, oxygen deficiency is now it results in O 8 ok. So, you can see that there are some vacancies of oxygen some of the oxygens had disappeared.

So, these are these oxygens which were present here they have now disappeared. So, you have oxygen vacancy, oxygen vacancy, oxygen vacancy, oxygen vacancy; it is not a vacancy in this or in the that is in the in the type of defect it is just there is no oxygen there now because of stoichiometry you further reduce C u 3 plus 2 C u 2 plus. So, that it becomes YBA 2 C u 2 2 plus C u 3 O 7.

So, you have two of C u and C u 2 plus one of C u in C u 3 plus and as a result oxygen becomes 7. So, when you do that the reduction is not complete it is sort of it is not a stoichiometry. So, you end up having 7 minus x and the 7 minus x state is the superconducting state. So, you have many more vacancies of oxygen; this is oxygen empty oxygen sites these are empty oxygen sites these are empty oxygen sites. So, this is a perovskite unit based structures structured which is modified into a superconductor. So, you still have the basis as a still perovskite it is just that it is a modified perovskite.

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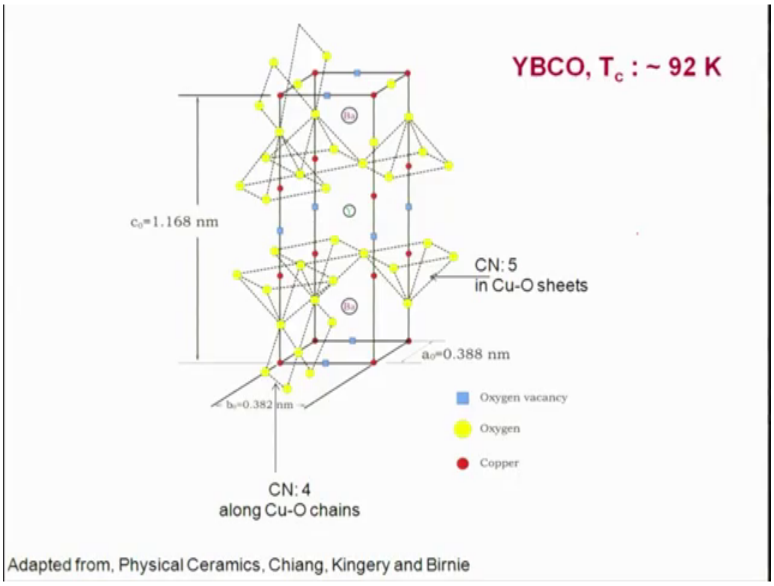

Adapted from, Physical Ceramics, Chiang, Kingery and Birnie

So, this becomes; so, it has a it does not have the typical octahedral coordination you will have. So, for example, oxygen and the copper in these positions it has five fold coordination because the one oxygen on top has gone missing which was presented here. So, instead of 6 fold coordination you end up having fivefold coordination here because you have oxygens missing on this side as well as on this side the oxygen the copper is surrounded by now four oxygen atoms.

So, you have four fold coordination you have 6 fivefold coordination instead of typical 6 fold coordination as you would have in perovskite and it is along these C u chains the super conductivity prevails. So, super conductivity is along those directions. So, this is one interesting example of perovskite based structure; it is not exactly perovskite because perovskite is just one unit ah, but it contains multiple perovskite units in it.

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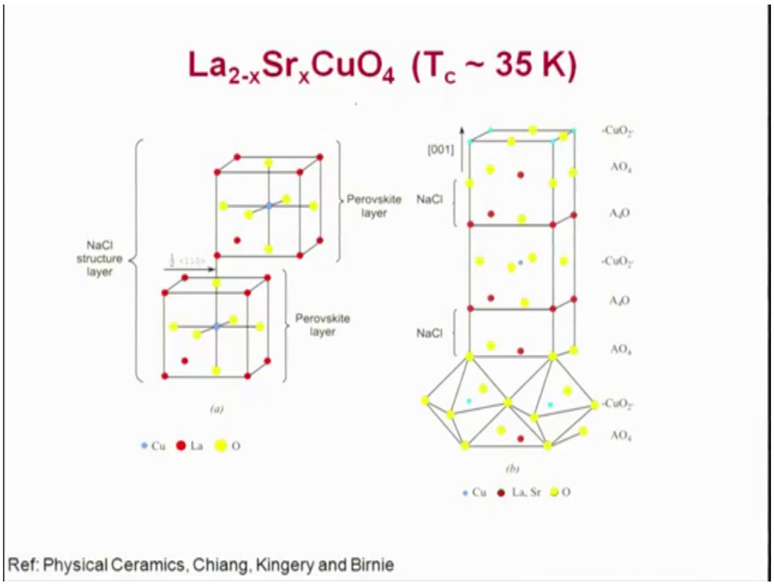

$La_{2-x}Sr_xCuO_4$ (T_c ~ 35 K)

Ref: Physical Ceramics, Chiang, Kingery and Birnie

Second structure is again a superconducting oxide which is lanthanum strontium copper oxide and this it has a now by the waste atrium barium copper oxide was a superconductor with a transition temperature of 92 Kelvin.

This was the first superconductor when it was discovered which had a transition above liquid nitrogen see most of the superconductors had transitions lower than liquid nitrogen that made that. So, if you wanted to use superconductors in any application you would have to use liquid helium. Liquid helium is far more expensive and difficult to manage as compared to liquid nitrogen which is far more cheaply available and this reduces the cost of operations.

So, this discovery was a major discovery in the area of super conductivity because 92 Kelvin was higher than liquid nitrogen. So, you could have a superconducting wire at 90 Kelvin without needing liquid helium which was a great achievement.

Student: (Refer Time: 21:38).

They are not perovskite as you see perovskite is just AB O 3 structure; this is based on AB O 3 structure, but it has a you can say it is a triple perovskite it is not a it is not a single perovskites a triple perovskite.

Student: (Refer Time: 21:54).

Many of the; I will show you I will come to some of these compounds. So, for example, lanthanum strontium copper oxide this is also a superconductor basically the parent compound is lanthanum copper oxide in which strontium is doped at the site of lanthanum. So, as a result you change the stoichiometry of this material to some extent. So, this will change the oxygen stoichiometry will change this has a T c of 35 Kelvin this again is built of a perovskite layers.

So, you can see this perovskite layer this is the copper atom, this is the lanthanum atom and this is the oxygen in copper the smaller atom lanthanum is the bigger atom and it has these zig zag kind of perovskite layers you have one perovskite layer another perovskite layer is shifted by half half of half 1 10 vector. So, it has this one perovskite layer shift another perovskite perovskite layer and so, on and so, forth.

So, overall if you look at this together they make a NaCl layer it is a very interesting structure. So, it has this layered structure the first layer is copper oxide, second layer is a 4; A could be you know a strontium or lanthanum. So, copper oxide copper oxide layer A O 4 layer A 4 O layer, C u O 2 layer, A 4 O layer, A O 4 layer it looks complicated where it is fairly simple layered arrangement.

But the layered layers are shifted the position of ions in these layers is such that that you have these alternating sodium chloride layers and in between you have these perovskite layers; we can see that perovskite layer containing C u O 6 octahedra. So, you have this copper atom and then you have these oxygen atoms surrounding in the octahedral manner. So, this is a layered structure which is a blend of perovskite and NaCl sort of structure you cannot see with what apparent when you look at the tall unit cell.

But when you look at it closely you can see that there are similarities with the perovskite structure as well as with the NaCl structure. So, some of these structures which look very difficult to just to visualize they can be remarkably simple. So, just stacking of layer Cu O 2, A O 4 A 4 A 4 U; CO O 2 A O 4 A 4 O for just go in that sequence.

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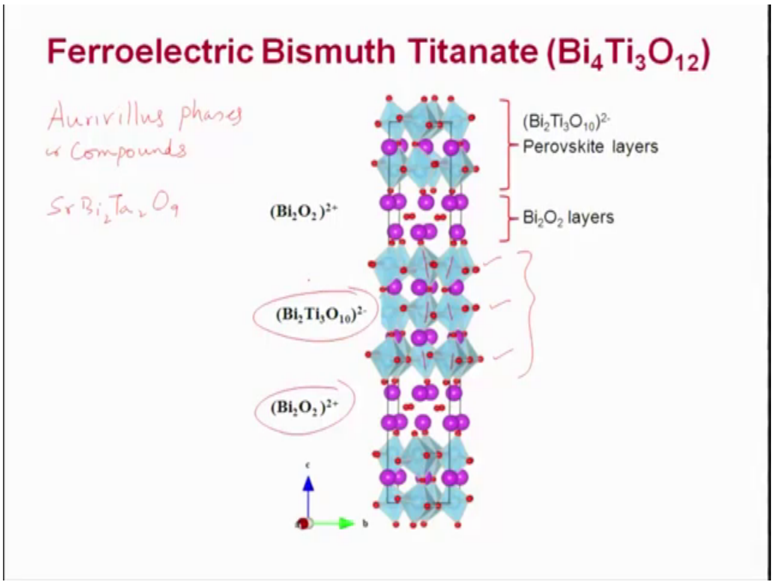

Ferroelectric Bismuth Titanate ($Bi_4Ti_3O_{12}$)

Aurivillus phases
or Compounds

$SrBi_2Ta_2O_9$

Now, third structure in this category that we will talk about is ferroelectric bismuth titanate.

Now, this is a ferroelectric compound B i 4 T i 3 O 12; this is not a ferrule this is not a peroxide structure, but it does contain perovskite units. Now this is this belongs to a family of what we call as aurivillus compounds aurivillus phases or compounds. So, you have bismuth titanate you have strontium bismuth Sr Bi 2 T a 2 O 9 and some other oxides which belong to this category these are mostly bismuth containing compounds.

So, in these compounds what happens is that you have the perovskite layers which are sandwiched between the bismuth oxide layer. So, in between you have Bi 2 O 2 layers. So, these are Bi 2 O 2 layers, you can see the purple bismuth and red oxygen atoms. Between the two successive Bi 2 O 2 layers you have 3 perovskite layers. So, first perovskite layers, second perovskite layer, third perovskite layer in which titanium is octahedrally coordinated by oxygen.

However these perovskite since these are in these materials this is the tetragonal structure in these materials there is significant distortion of octahedra octa hedra not all running straight; there is a bit of twisting and rotation of octahedra you can see that this octahedra is going this way this octahedra is going this way. So, there are different axis along which they tilt and twist. So, this rotation or distortion of octahedral leads to ferro electricity; ferro electricity does not occur in symmetric compounds it only occurs in non symmetric compounds.

So, these thus tilting and distortion of octahedra brings about ferro electricity; similarly the barium titrant kal and other compounds ah. Cubic does not have any dipole moment because all the vectors cancel each other it is only in the non cubic form in tetragonal rhombohedral other forms in which octahedra is slightly distorted and that distortion gives rise to ferro electricity because of finite dipole moment. So, and there are the factors as well, but that is why some. So, these are all perovskite layers 3 of them 3 perovskite layers sandwich between successive Bi 2 O 2 layers.

So, it does it is not exactly a perovskite structure is based on perovskite units. So, many of these compounds they may contain 3, 5, 7 various possibilities are there. So, it is a whole series that can be built upon these perovskite units. So, just the number of you change the number of these layers and you can make different formulas of these Euler's phases. So, these are 3 types of compounds which basically have these structures. So, let me go back to my this thing.

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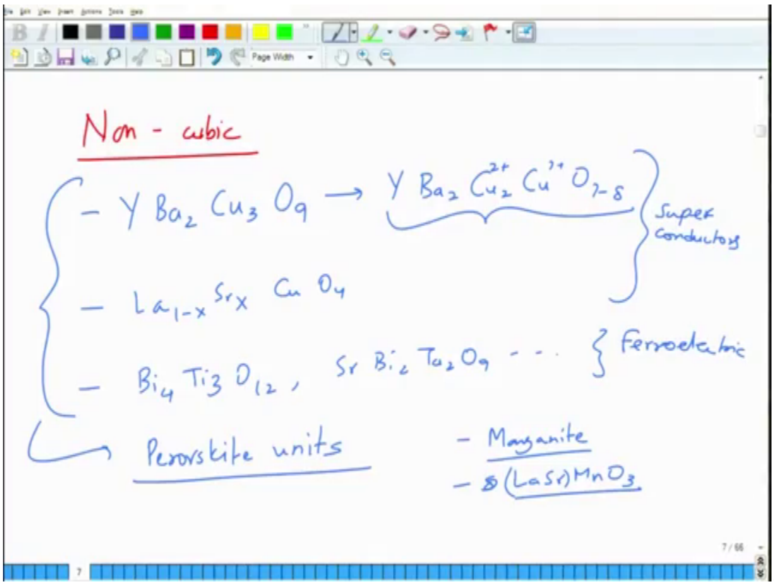
Non - cubic

- $YBa_2Cu_3O_9 \rightarrow \underbrace{YBa_2\overset{2+}{Cu_2}\overset{3+}{Cu}O_{7-\delta}}$
- $La_{1-x}Sr_xCuO_4$

Super conductors

- $Bi_4Ti_3O_{12}$, $SrBi_2Ta_2O_9$ . . . Ferroelectric

Perovskite units

- Manganite
- $(LaSr)MnO_3$

So, among the non cubic structures the first one was YBa 2 C u 3 O 9 which converts to YBa 2 C u 3 this is 2 plus this 3 plus O 4 minus delta. So, this is the superconductor this contains perovskite units then you have La 1 minus X Sr X C u O 4; this is again a superconductor. So, these two are superconductors.

Then you have compounds such as Bi 4 Ti 3 O 12; Sr Bi 2 Ta 2 O 9 these are all ferroelectric; they contain perovskite units in them ok. So, this is the there are a lot of manganites as well; for example, lanthanum strontium manganese oxide L S Mo this is also a; so, this is La Sr M n O 3; this is again a magnetic oxide, it is a colossal magnitude resistive oxide these are also perovskite structured compounds.

So, these are some of the cubic and non cubic structures in the next lecture we will look at the ionically bonded ceramics or ceramic structures which are based on hexagonal close packing of oxygen atoms and because that is also important category of materials in ceramic structures ok.

Thank you.