Electroceramics
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Lecture - 1

So, welcome to you for this NPTEL course of electro ceramics. My name is Ashish Garg and I am an associate professor at the Department of Material Science and Engineering at IIT Kanpur. So, before we go for formal lecturing, I just give you a brief introduction about the course, why this course is important?

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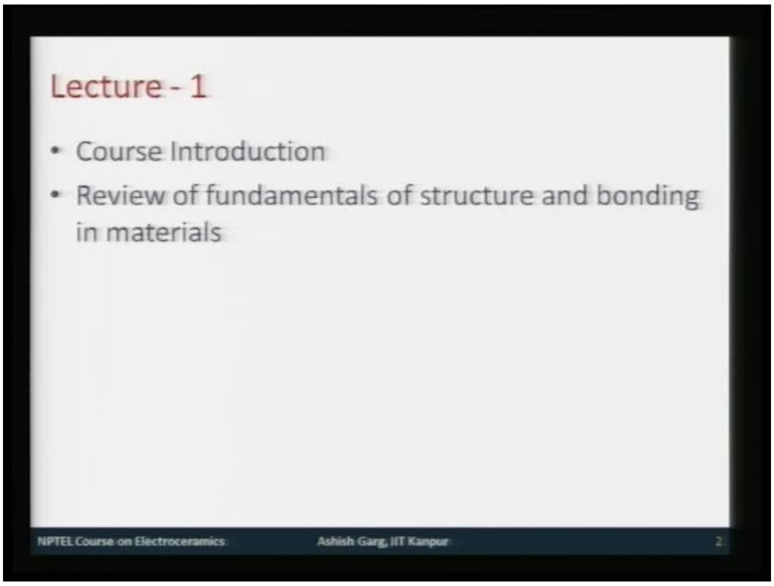

Lecture - 1

- Course Introduction
- Review of fundamentals of structure and bonding in materials

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So, in the, in this lecture I am going to give you the introduction about the course and some review of the fundamentals of things like structures and bonding in materials, which form the basics of structures for these kind of materials.

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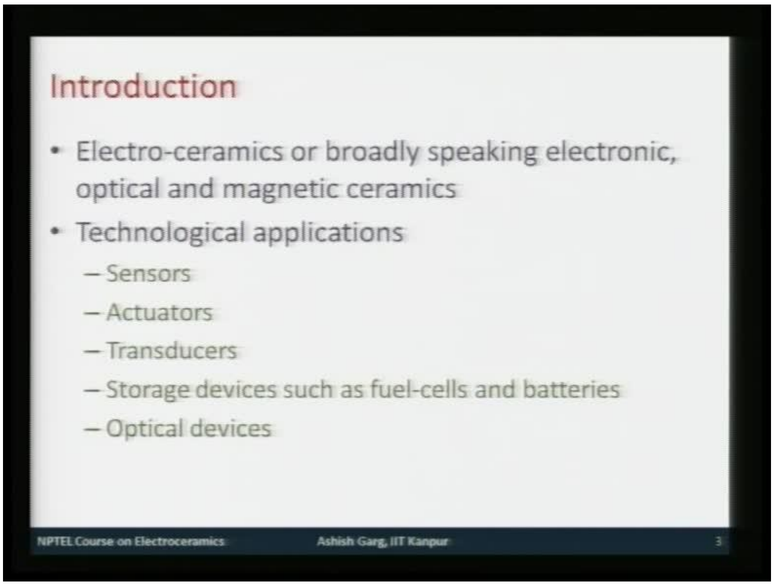

Introduction

- Electro-ceramics or broadly speaking electronic, optical and magnetic ceramics
- Technological applications
  - Sensors
  - Actuators
  - Transducers
  - Storage devices such as fuel-cells and batteries
  - Optical devices

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So, why electroceramics are important because electroceramics are important because there are used in many technological applications like in sensors, actuators, various kind of transducers devices, they can also be used there also used for a storage devices like fuel cells and batteries and even for data storage and many optical devices are made from this materials as well. Broadly speaking, there are you can define these differentiate these ceramics in electronic ceramics, optical ceramics and magnetic ceramics.

However, the fundamentals of these ceramic materials are closely related to each other. So, these are the technological importance of these materials make it important to understand there fundamentals, such as structure, the defect chemistry, how can we tell the properties. So, these are important aspects to understand these materials

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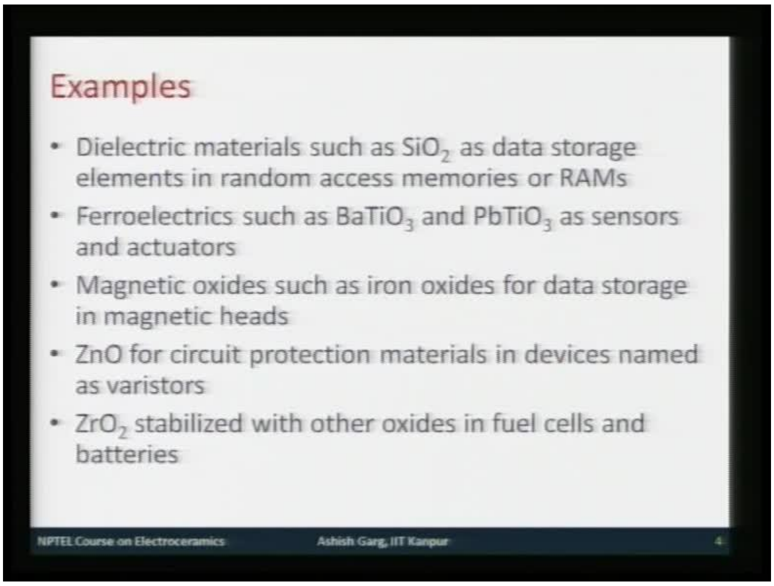

Examples

- Dielectric materials such as SiO_2 as data storage elements in random access memories or RAMs
- Ferroelectrics such as $BaTiO_3$ and $PbTiO_3$ as sensors and actuators
- Magnetic oxides such as iron oxides for data storage in magnetic heads
- ZnO for circuit protection materials in devices named as varistors
- ZrO_2 stabilized with other oxides in fuel cells and batteries

Some of the examples you can take, for example, silicon oxide which is the dielectric well known dielectric, it is used as a data storage element in your memories like random access memories, materials like barium titanate or lead titanate are used as sensors and actuators, they are also called as ferroelectric materials. Oxides such as iron oxides, which are basically magnetic in nature are used for data storage in magnetic heads materials like, for examples zinc oxide. They are are used as materials to protect the circuit and there are also called as, devices called as varistors.

Materials like zirconium oxide, which are stabilized with other oxides, so we will see how this stabilization is done in the course, but these are used in application likes fuel cells and batteries which are nothing but storage applications. So, these are the some examples of technological important applications, where these typically you see that most of these are oxides. Although some of them can be carbides etcetera and this is this explains the importance of electro ceramics and technological applications and why we need to study them? They are also used in bulk form thin frame form, depending upon the requirement and both of these forms required very good understandings of fundamentals of these materials.

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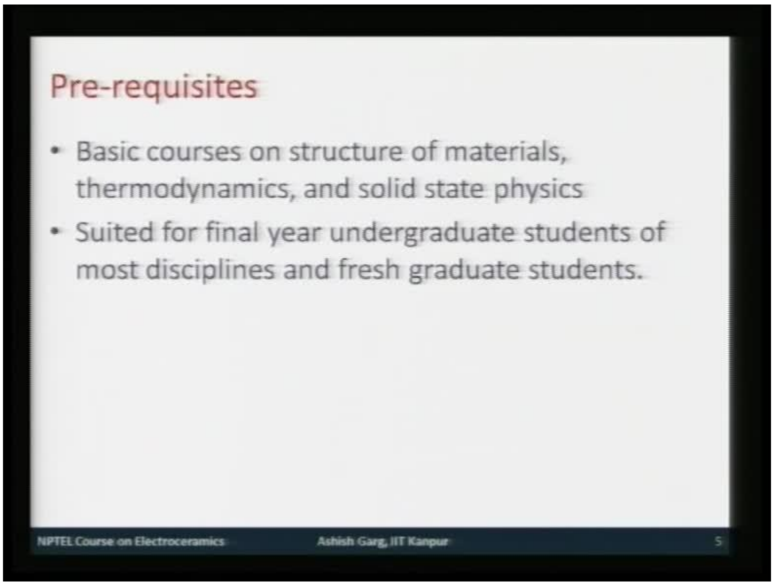

Pre-requisites

- Basic courses on structure of materials, thermodynamics, and solid state physics
- Suited for final year undergraduate students of most disciplines and fresh graduate students.

Now in order to understand the scores properly you need to know basics of structure of materials, thermodynamics and solid state physics. I have recommended some books in the bibliography of this course, which I will show you in couple of slides. I am, but you need to know these topics, because I am not going to go through these topics in detail. This course is very well suited for final year undergraduates, of most discipline. Typically I would say it is really, it would be quite easy for or quite well suited for undergraduates from material science, physics or chemistry. However, other discipline also can do that and also for fresh graduate students, those who are taken just admission into master courses.

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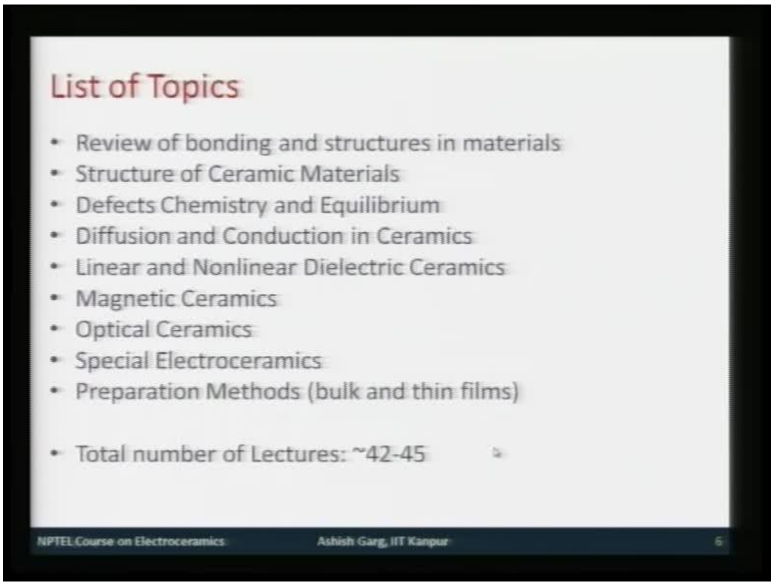

List of Topics

- Review of bonding and structures in materials
- Structure of Ceramic Materials
- Defects Chemistry and Equilibrium
- Diffusion and Conduction in Ceramics
- Linear and Nonlinear Dielectric Ceramics
- Magnetic Ceramics
- Optical Ceramics
- Special Electroceramics
- Preparation Methods (bulk and thin films)

- Total number of Lectures: ~42-45

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List of topics that we will cover in this course are we will first very briefly review the bonding and structures in materials. So, I will just devote may be one or two lectures on this topic, because this forms are basis of the next topic, which is the structure of ceramic materials, which is quite an important topic. Because the structure of ceramic materials is indeed formed on certain basis and this is where you to know little bit about the bonding and structures.

Then we will move on to structure of ceramic materials, which are again different kind of structures depending upon what kind of elements they contain and we will look at basis first of all how there structures are formed? Then we will look at the various different kinds of structures. A third topic would be, defects chemistry in equilibrium, so we will look at how the defects are formed. In various ceramics materials and we will look at bit of thermodynamics of them.

Then we will move on to more applied topic, which is well fundamental applied in in some sense, both we will look at how these defects which are formed in various materials defuse and from, the bases for conduction and ceramics, which is actually a quite important topic. Then we will look at the properties of these some of these electro ceramic materials, so we will first look at linear and non-linear dielectric ceramics.

Then we will look at magnetic ceramics materials and then couple of lectures on optical ceramics and then some special electro ceramics, which are not included in previous categories such as multi ferroics and super conductors. Finally, we will look at very briefly on preparation methods for both bulk and thin films, because these oxides have to be formed in such manner, so that there are useful in device forms. That is where preparation is very important. Total number of lectures that we will devote to this course is about between 42 and 42; that will depend how we go in the course.

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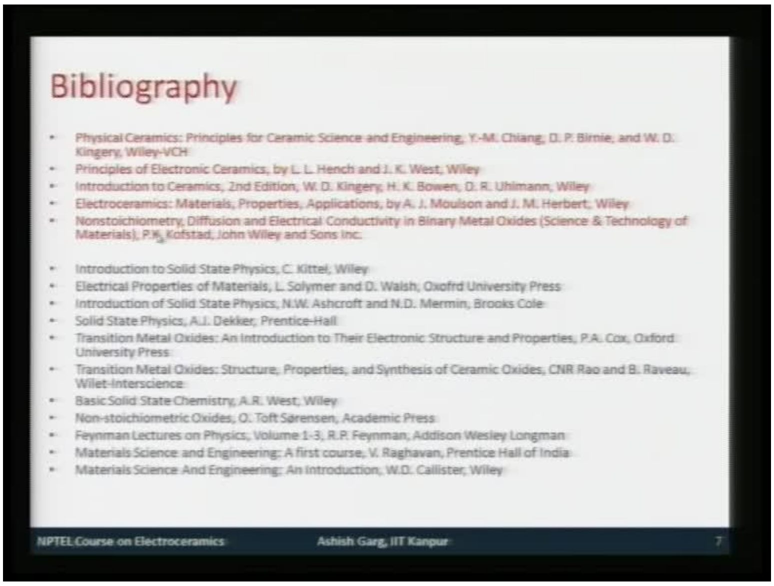

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Bibliography, this is so the books, which are on top and red they are very important books for this course. So, the first one is physical ceramics by Chiang Birnie Kingery and the second one is principles of electronic ceramics by Hench and West and the third one is introduction to ceramics it is really a classic book by Kingery Bowen and Uhimann. Then you can also go through electroceramics by Moulson and Herbert, this is a good book from the point of you of applications and processing and while previous three talk mostly about the fundamentals and properties, and this bottom book is basically non stoichiometry diffusion and electrical conductivity in binary metal oxides.

Although it talks about binary metal oxides, this is a good book from the point of view of understanding defect chemistry and equilibrium. Other books are supplementary books, solid state physics, you can go through. For example, Kittel. Solid state physics which is a very classic book on solid state physics, then electronic properties of materials by

Solymer and Waish. Solid state physics by Ashcroft and Mermin, solid state physics by Dekker ,any of these books is good enough to give you good understanding of solid state physics. Then there are some other books specialized books, for example, transition metal oxides by Cox and then CNR Rao and Raveau also written a book on transition metal oxides emphasizing on the structure properties and synthesis of these materials.

Then some other books like basic solid state chemistry non stoichiomestry oxides Feynman lectures on physics. These are very good actually, I mean for fundamentals of physics, they are really good lecture books. Then for basic materials science you can refer to material science and engineering by Raghavan or material science engineering by Callister. So, I guess the books in the blue or as it looks black are mostly a supplementary books, if you want to enhance your understanding of certain things, which you do not know before, but the top five books are actually redirectly useful from the point of view of this course. So, this is about the introduction. Now I will give you a brief over view of structure and bonding in these materials.

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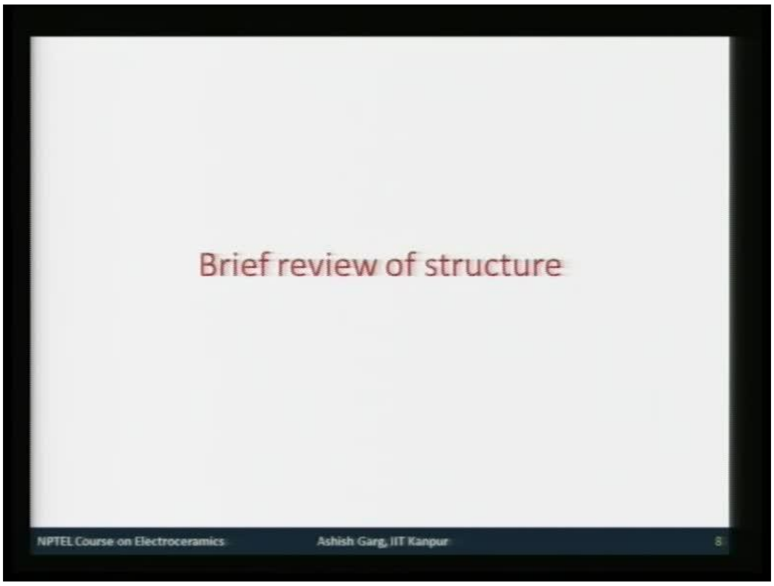

Brief review of structure

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So, first we will go through a review of structures.

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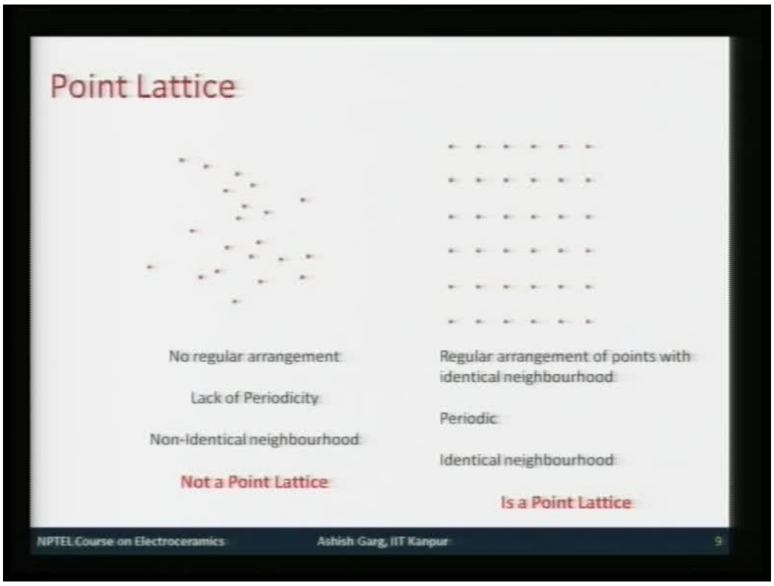

Point Lattice

No regular arrangement

Lack of Periodicity

Non-Identical neighbourhood

Not a Point Lattice

Regular arrangement of points with identical neighbourhood

Periodic

Identical neighbourhood

Is a Point Lattice

Now, in the structure, we all often talk about lattice. What is a lattice? Now, what is a lattice? Now, we do not start with atoms directly, we start with other points, distribution of points in a space. So, a points can be distributed in a space in a haphazard manner as shown on the left or in a in a ordered manner as shown on the right. Now, the ordered distribution of points in the space forms a lattice which is called as a point lattice, where you have periodic distribution of points and each point has identical neighborhood on the in contrast.

If you look on the left, no two points have similar neighborhood. So, no two points have similar neighborhood and as a result it, is not called as a periodic lattice. So, in summary you can say a point lattice is basically you have a regular invent of points with identical neighborhood periodic and each point has an identical neighborhood and if you do not have that, it is not a point lattice.

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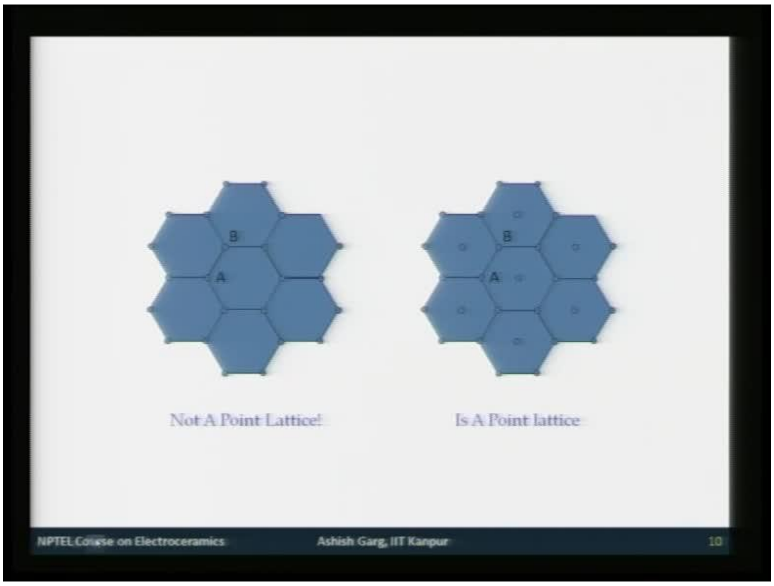

Not A Point Lattice!

Is A Point lattice

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For example, there are you can have now, even if you have that definition, let us say this is a periodic pattern, right? It looks like a periodic pattern, but what I have done is I have put hexagons together, with points denoted as circles at the corners of hexagons. Now, if you look at now a cursory look tells you in most cases that it is a periodic structure. However, if you compare point A and point B, point A has three neighbors point B also has three neighbors, that is fine, but the arrangement of nearest neighbors around point A is not similar to that of point B.

Point A has two neighbors on the right and one on the left, while B has two on the left and one on the right. as a result this is not a point lattice, on the other hand if I modify a little bit by putting another point in the center of the each of the hexagon. Then I see that both point A and point B have identical neighborhood, number of neighbors as well as the pattern of neighbors are similar. Hence, this is a point lattice, so I hope you understand the concept of point lattice.

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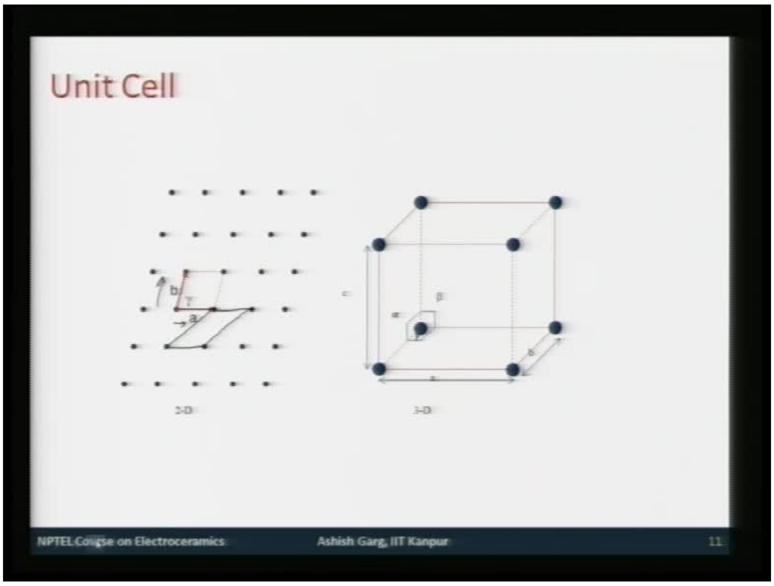

Unit Cell

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Now, in the lattice, in the point lattice, the smallest repeatable unit is called as a unit cell. From this two-dimensional picture, I can make parallelogram by connecting these four points and this would be called as a unit cell. Like you see the choice of unit cell is not unique, you can make unit cell like this, you can also make a unit cell like this. So, choice of the unit cell is not unique, but all of these unit cells which contain only four points at the corners will have same area and the dimensions of this unit cell in this case you have, A in this direction B in this direction and the angle between A and B is common.

These three parameters is called as unit cell parameters in the 3 dimension. It would look something like this, this is a, for example a cube. It does not need to be a cube, it could be anything it could be a cuboid. But, the point is the translation in from one point to another in x direction will be called as A and in the y direction it could be B and in the z direction it would be C. The angles alpha, beta, gamma between A B, B C or C A would be, all these six will make as lattice parameters.

So, A B gamma would be lattice parameter for 2 D structure, A, B, C and alpha, beta, gamma would be lattice parameters for a 3 D structure. As I said that the choice of unit cell is not unique, you must remember that. So, the question now arises, how many choices are possible? Well we can have many choices, but we can define some of these choices into certain systems, which will form the later, which will form bases of later what we will see as crystal systems.

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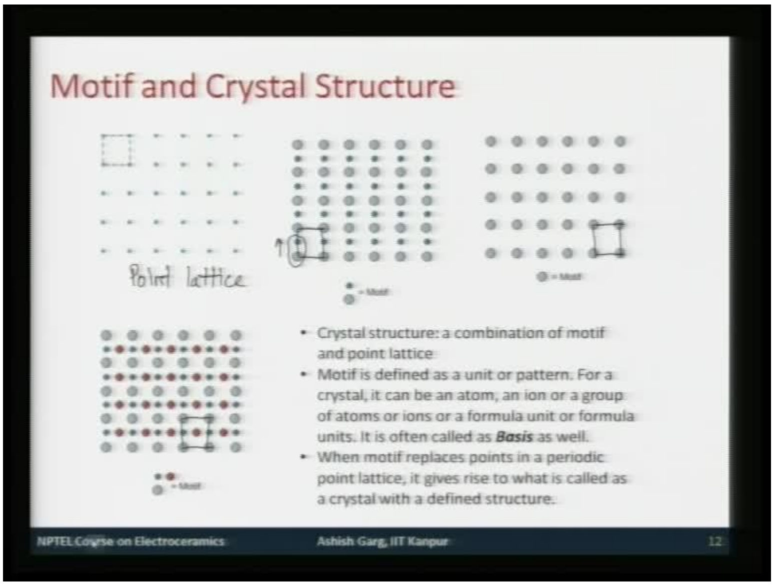

Motif and Crystal Structure

- Crystal structure: a combination of motif and point lattice
- Motif is defined as a unit or pattern. For a crystal, it can be an atom, an ion or a group of atoms or ions or a formula unit or formula units. It is often called as ***Basis*** as well.
- When motif replaces points in a periodic point lattice, it gives rise to what is called as a crystal with a defined structure.

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Now, when now so far we have been talking about the point lattice, now if u replace these points by certain objects in the lattice, what it makes is a crystal structures. So, combination of what is called as motif which as, let us say an atom or a group of atoms or a formula unit and a point lattice makes a crystal structure. So, for instance in this top left picture, you have these little blue atoms, which is a single atom. I have replaced each point with this blue atom and then I can draw a unit cell. Now, do not worry about the shape because shape could be anything.

So, this is a unit cell. This is a, this is called as a crystal structure, a smallest unit of crystal structure consisting of one atom per unit cell, in this picture on the right, okay? So, this is basically your own point lattice. So, in this point lattice, I have replaced each point by for an example this kind of motive, which is nothing but a black or gray circle, when I do that, I get the same pattern as on the left. But with each point replaced by this sphere or circle gray circle.

So, this will be a crystal structure consisting of these gray atoms and each unit cell will contain only one atom. Similarly, if instead of taking, now instead of taking one gray atom if a take a group of two atoms, I can put them anyway I want, but that wouldn't make a periodic lattice necessarily. So, what I have to do is that I have to put this group of atoms in an identical fashion at each and every point. So, for instance, if we look this group of atom is pointing a words here placing. For example, this point, so all other group of atoms are replacing all other points in the identical fashion and this again makes a periodical lattice.

So, I can connect for instance these corners and this makes a again lattice crystal lattice consisting of one gray and one blue atom. Now, one gray and one blue is you can consider as a group of atom or a formula. So, this would be more true about, for example, for a metal or single element material this would be true for a multi element or compound. Similarly, instead of two atoms a compound can have three atoms and again you replace each of these point by three of these atoms, making sure there are oriented in one direction and each unit cell consist of one formula unit.

So, if I again connect these, this will contain one formula unit. So, one red, one blue and one gray atom. So, motif you can define it as a pattern and if you combine this is point lattice it will make a crystal structure.

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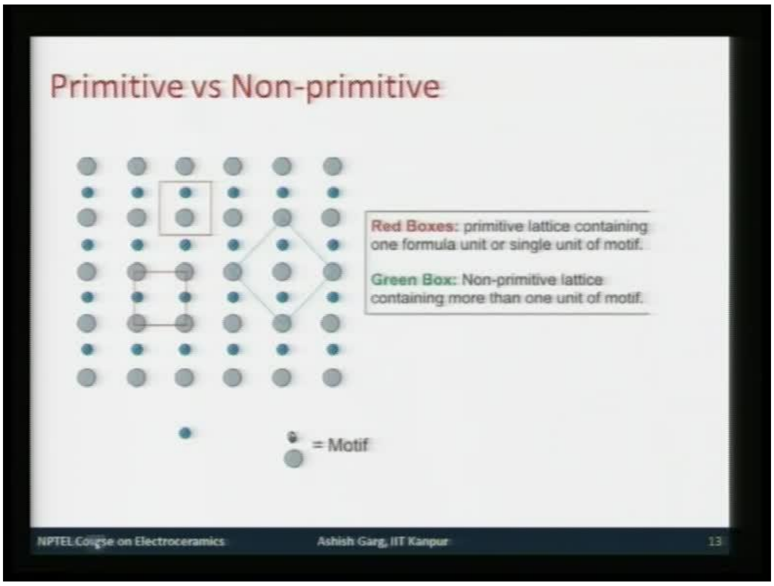

Primitive vs Non-primitive

Red Boxes: primitive lattice containing one formula unit or single unit of motif.

Green Box: Non-primitive lattice containing more than one unit of motif.

= Motif

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The now the unit cell the lattice can be your primitive lattice or non primitive lattice. So, far we have seen only primitive lattices where each of these squares as you see in the red here on the left. So, the first one the most basic is this where you connect the corner of each of these atoms. So, if you look these look at this no matter where you put this red square, it would always contain only one unit.

So, if it is at this position it has four gray atoms at the corners and two blue atom at the center of these edges, this which you shared by two neighbors. So, 4 divided by 1, 4 divided by 4 will be 1 and 2 divided by 2 will be 1. So, 1 plus 1, so group of 2 atoms, no matter now you can you can change the position of this is square, I can change the position of this square in such a manner it will still contain a group of atom. So, this will be called as a primitive lattice.

Primitive lattice would be a lattice, which can operate a unit cell is a unit cell which contains only one formula unit or single unit of motif. It could be a single atom for a single elemental material or it could be a formula unit for an compound, for a compound. Now, if you look an if you look at this green box.

This green box, it is slightly bigger and if you now count, it contains two gray atoms and two blue atoms. It contains two formula units, so this is called as a non primitive lattice. Since, it contains two formula units the area of this unit cell is exactly twice to that of the primitive unit cell. So, this is called as a non primitive unit cell. So, a motif in this cases this is your blue, I think this is moved little bit in the power point, do not worry about that.

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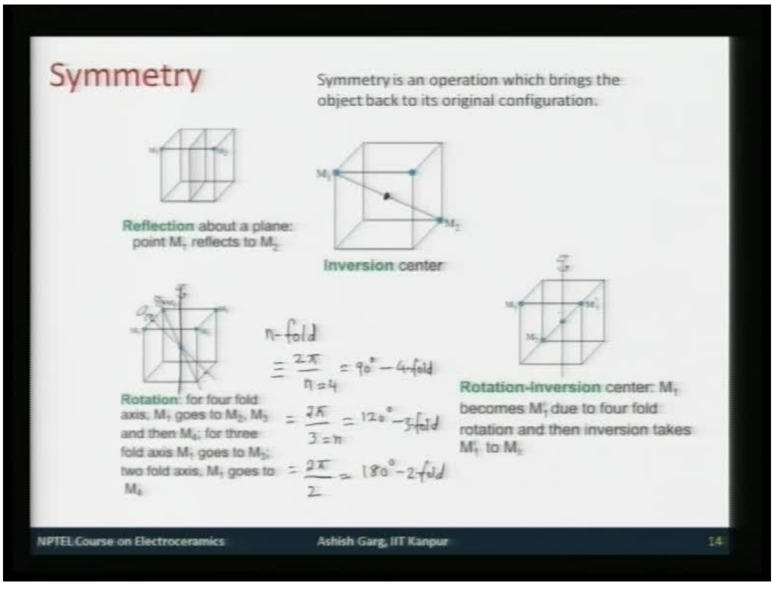

Symmetry

Symmetry is an operation which brings the object back to its original configuration.

Reflection about a plane: point M_1 reflects to M_2

Inversion center

Rotation: for four fold axis, M_1 goes to M_2, M_3 and then M_4; for three fold axis M_1 goes to M_3; two fold axis, M_1 goes to M_4

n-fold

$$= \frac{2\pi}{n=4} = 90^\circ - 4\text{-fold}$$

$$= \frac{2\pi}{3=n} = 120^\circ - 3\text{-fold}$$

$$= \frac{2\pi}{2} = 180^\circ - 2\text{-fold}$$

Rotation-inversion center: M_1 becomes M_1' due to four fold rotation and then inversion takes M_1' to M_2

Now, another consideration in forming crystal systems and the vice lattices concept of symmetry. Symmetry is basically an operation, which brings any object back to its original configuration. There are four basic symmetry operations; the first one is called the reflection about a plane in a unit cell. So, here what happens is basically u create a plane in the middle of this unit cell and the point M 1, for example in this case, across the plane on the left is reflected by another identical point on the right, which is M 2. It is like looking at yourself in the mirror.

So, mirror plane is basically mirror plane is nothing but reflection across a about a plane. So, here M 1 is reflecting to M 2 and second one rotation is if you rotate a point about certain access by a certain angle the configuration that at achieves after rotation is identical to a previous rotate configuration. For example, if you take a cube this is the most simplest case you can have. For example, I start with point M 1, so or for 4 4 rotation you can have this point M 1 going to M 2, right?

Just considered what would be the 4 4 rotation, this is the cube if I put this the line that you see this line this is the, so this is the line going through the center of the face of the cube to the other opposite center of the face penetrating through the cube. If you rotate around by 90 degrees, this point M 1 will move to pint M 2 and if all these points are identical, you can say that, the position at this point position, you can say the look of lattice in this position is identical to the look of the lattice in when the point M 1 goes to M 2.

It does not chase the configuration of the lattice, so this is your 4 4 rotation. 3 4 rotation would be the rotation in which rotate by 120 degree. So, basically if you say n fold, what it would be equal lent to is that 2 pi divided by n. So, 4 4 n will be 4 give rise to 90 rotation for 3 fold 2 pi divided by 3 that would give rise to 120 degree as so on an so fourth. So, 3 fold would be allowed the body diagonal at this cube, so the point M 1 will become M 3 keeping the configuration of the lattice similar.

Similarly, you can have a 2 fold access as well, 2 fold would be the face diagonal, so you connect basically access connect this point and this point and rotate around this access, so that point M 1 will become M 4. This will be 2 4 rotation, so any of these three operation if you perform, the configuration of lattice is not change. So, your 3, so this is 4 fold this is 3 fold and 2 fold will be 2 pi divided by 2 would be 180 degree. You can also have 6 fold, which is nothing but 160 sorry, 60 degree rotation and that is possible in, for a example in a hexagonal case.

If you have a hexagon, now it is up to you I leave it to you to show that, why do you not have 5 fold and 7 fold rotation. Third one is inversion center, so inversion center is basically a the point M 1 becomes M 2. So, this across the body diagonal here inversion center would be somewhere here. So, point M 1 will look whether you look at point M 1 or M 2 the configuration of the lattice would be same across this center of inversion.

Now, a finally, you will have rotation inversion center where M 1 becomes first M 1 prime due to 4 fold rotation around this access. This M 1 prime will then become M 2, if it was followed by any inversion across this center. So, this should be rotation in version. So, you have 4 basic material rotation and many more symmetry operation, which we are not going to details of this. But if will combine these three symmetry operations with the previous definition of lattice, then we come to crystal system. We have said that choice of unit cell is not unique, but you cannot have infinite combination.

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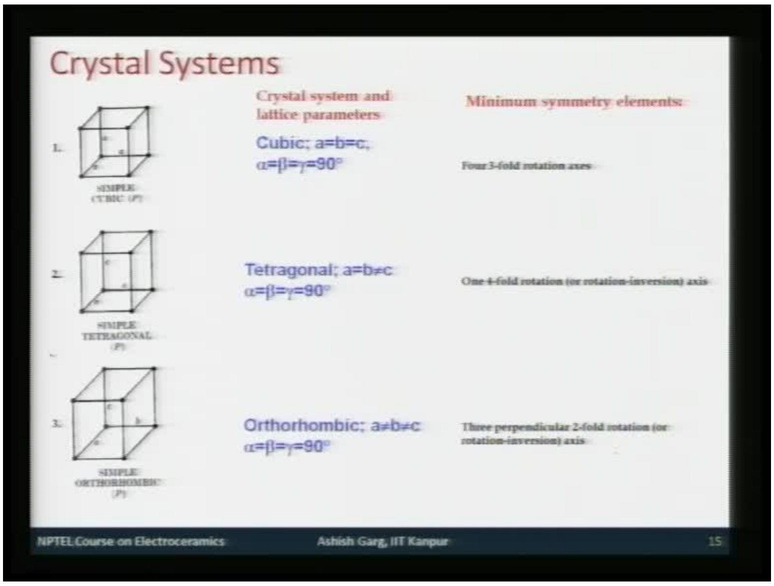

Crystal Systems

	Crystal system and lattice parameters	Minimum symmetry elements:
1.	Cubic; a=b=c, $\alpha=\beta=\gamma=90°$	Four 3-fold rotation axes
2.	Tetragonal; a=b≠c $\alpha=\beta=\gamma=90°$	One 4-fold rotation (or rotation-inversion) axis
3.	Orthorhombic; a≠b≠c $\alpha=\beta=\gamma=90°$	Three perpendicular 2-fold rotation (or rotation-inversion) axis

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So, it would be hard to remember, so what people that was they divided these unit cells based on certain criteria’s into 7 crystal system to make our life easier. The first one is simple cubic which is where A is equal to B equal to C an alpha, beta, gamma equal to 90 degree and the minimum symmetry element for this is A 4, it has 4 3 4 rotation access, which is along the body diagonals. Similarly, you can all now in the second combination would be A is equal to B, but not equal to C, but all three angels is equal to 90 degree this will make a tetragonal structure.

So, here the C parameter is different from A and B and this must have 4 full rotation or rotation inverse access, which would be along 4 full rotation would be along here parallel to the C access going through the center of this face. c So, point M 1 will look whether you look at point M 1 or M 2 the configuration of the lattice would be same across this center of inversion. Now, a finally, you will have rotation inversion center where M 1 becomes first M 1 prime due to 4 fold rotation around this access.

This M 1 prime will then become M 2, if it was followed by any inversion across this center. So, this should be rotation in version. So, you have 4 basic material rotation and many more symmetry operation, which we are not going to details of this. But if will combine these three symmetry operations with the previous definition of lattice, then we come to crystal system. We have said that choice of unit cell is not unique, but you cannot have infinite combination.

Center of the bottom face and the third one would be your orthorhombic crystal were, A is not equal to B is not equal to C, an alpha, beta, gamma all three are equal to 90 degree. It is a orthogonal system with un equal lattice parameter that is translation parameter not the angels. So, this must have 3 perpendicular 2 fold rotation or rotation inversion access.

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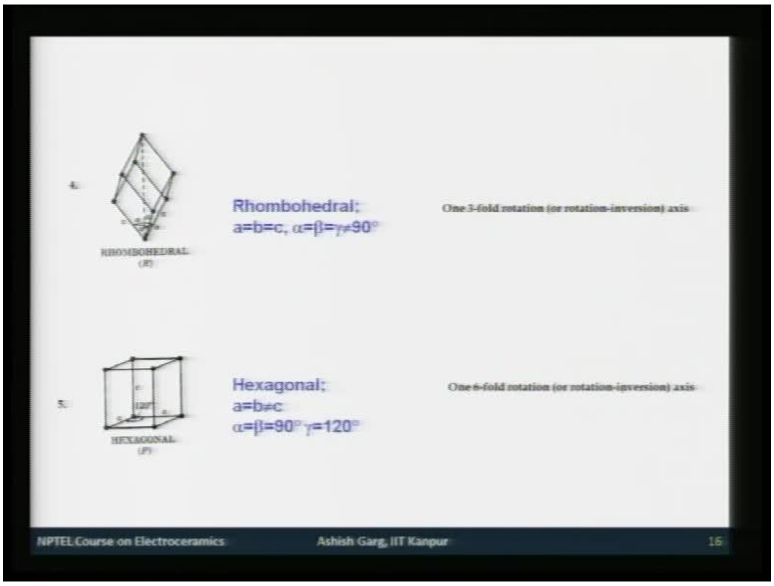

Rhombohedral;
a=b=c, $\alpha=\beta=\gamma\neq90°$

One 3-fold rotation (or rotation-inversion) axis

Hexagonal;
$a=b\neq c$
$\alpha=\beta=90°$ $\gamma=120°$

One 6-fold rotation (or rotation-inversion) axis

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So these are three crystal systems will have four more. Fourth one rhombohedral, which is where A is equal to B is equal to C alpha, beta, gamma are equal, but not equal to 90 degree. So, this is the different, this is the deviation from the cubic crystal and this must have a 3 fold. Similarly, now number 5 face hexagonal here A is equal to B is not equal to C alpha beta are equal to 90 degree gamma is 120 degree and this must have 6 4 rotation access. Remember, we I talk about 6 fold rotation, which is by 60 degree are on certain access.

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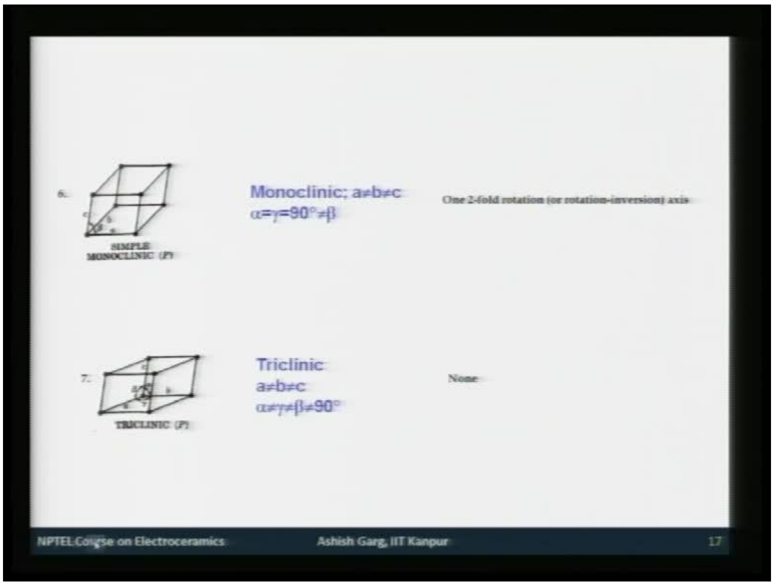

Monoclinic; $a\neq b\neq c$
$\alpha=\gamma=90°\neq\beta$

One 2-fold rotation (or rotation-inversion) axis

Triclinic
$a\neq b\neq c$
$\alpha\neq\gamma\neq\beta\neq90°$

None

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Two more 6 1 is monoclinic. this is basically we are increasing the level of difficulty. So, here A is not equal to B is not equal to C and alpha is equal to gamma is equal to 90 degree is not equal to beta. So, alpha gamma are equal to 90 degree beta is different. This must have a 2 fold rotation access and seventh is the triclinic, which is the most difficult one. But not the most common one, triclinic has it has all three A, B, C has different in this structure. An alpha, beta, gamma are all different and none of them are equal to 90 degree as well and this does not have a minimum symmetry, any minimum symmetry element, this is most unsymmetrical structure.

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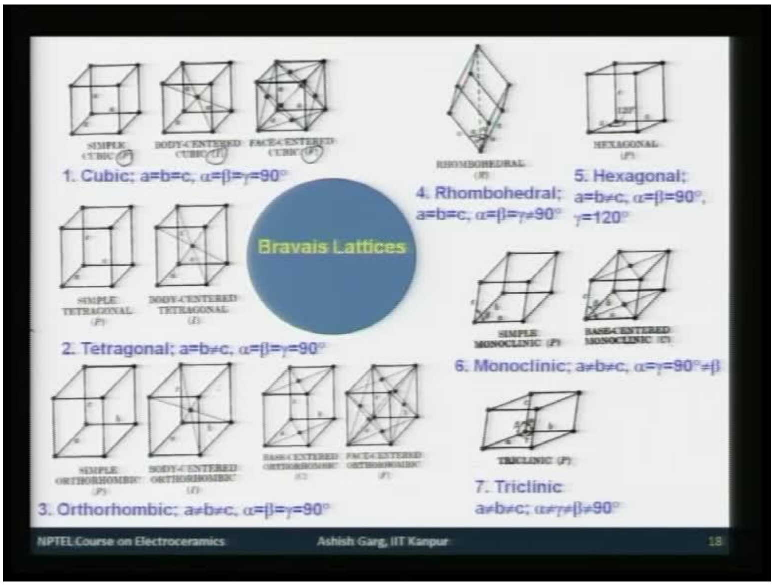

Bravais Lattices

1. Cubic; $a=b=c$, $\alpha=\beta=\gamma=90^\circ$

2. Tetragonal; $a=b\neq c$, $\alpha=\beta=\gamma=90^\circ$

3. Orthorhombic; $a\neq b\neq c$, $\alpha=\beta=\gamma=90^\circ$

4. Rhombohedral; $a=b=c$, $\alpha=\beta=\gamma\neq 90^\circ$

5. Hexagonal; $a=b\neq c$, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$

6. Monoclinic; $a\neq b\neq c$, $\alpha=\gamma=90^\circ\neq\beta$

7. Triclinic $a\neq b\neq c$; $\alpha\neq\gamma\neq\beta\neq 90^\circ$

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Based on and these crystal system can further be classified into Bravais lattice, there are fourteen kind of Bravais lattices. So, a cubic structure can further be divided into simple cubic structure as we have learnt. Body centered cubic structure, which has an extra atom of the center of the unit cell an face centered cubic structure where atom atoms occupy the center of the 6 faces. So, naturally as u can see body centered and face centered structures are non primitive structures and simple cubic is a primitive structure.

Primitive is always defined as P and in non primitive body centered is defined as I and face centered is different as F. This is useful in writing in space group, which will not considered in this course, for that definition of crystals. Similarly, tetragonal is defined as it has two variation; one is simple tetragonal, which is primitive and another is body centered tetragonal, which is non primitive, were an atoms is sitting in the center of the unit cell.

Now, you can ask question, why do not you have other variations of face centered cubic face, centered tetra, why do not you have other variation tetragonal lattice? That is because, if you have other variation you can always reduce them to one of the exiting 14, the Bravais lattices. Similarly, orthorhombic; you have simple orthorhombic, body central orthorhombic, base centered orthorhombic and face centered orthorhombic. So, these are the variation of orthosembic or orthorhombic one is primitive and three are non primitive.

In case of rombohedral, there is no other variation is only rombohedral hexagonal does not have any variation as well. So, you only have primitive lattice. In case of rombohedral, hexagonal all the rombohedral is referred as R in case of crystallographic rotation. Monoclinic has simple monoclinic and it also has a based centered monoclinic defined as C and in triclinictriclinic, you have only one variation, which is primitive triclinic.

So, you have total of 14 arise lattices, if you want to a along the details about, how these Bravais lattice are formed in? What is a bases you need to learn a bit more about crystallographic and you can read any crystallographic book of or you can go to the NPTEL course on the structure of materials that would be useful to enhance the understanding of structure.

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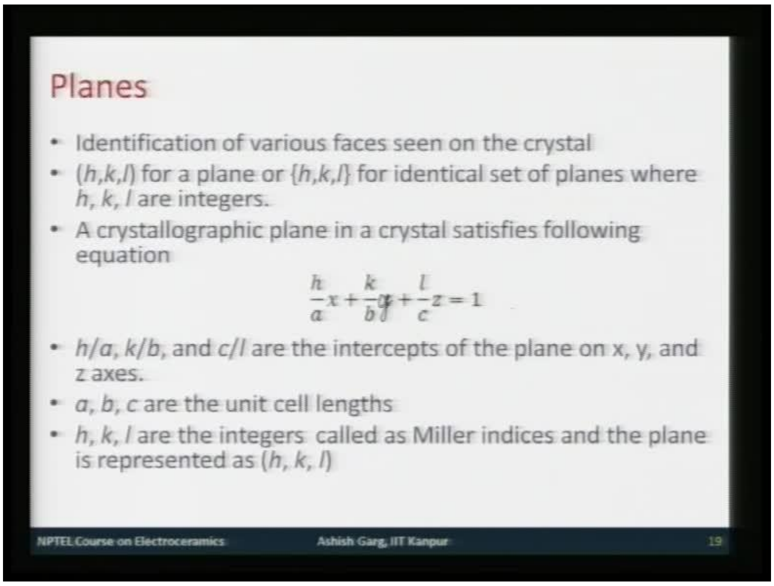

Planes

- Identification of various faces seen on the crystal
- (*h*,*k*,*l*) for a plane or {*h*,*k*,*l*} for identical set of planes where *h*, *k*, *l* are integers.
- A crystallographic plane in a crystal satisfies following equation

$$\frac{h}{a}x+\frac{k}{b}y+\frac{l}{c}z=1$$

- *h*/*a*, *k*/*b*, and *c*/*l* are the intercepts of the plane on x, y, and z axes.
- *a*, *b*, *c* are the unit cell lengths
- *h*, *k*, *l* are the integers called as Miller indices and the plane is represented as (*h*, *k*, *l*)

Now, crystal are often defined by planes and direction now these planes are nothing but a crystallographic planes are nothing but identification of various faces as seen on the crystal. There are defined by indices h k l, either in the round brackets or in curved brackets round brackets would define one plane and curved bracket would define identical set of planes and this h k l are nothing but integers and these are called as miller indices. Crystallographic you can define a plane in the crystal by this equation, were a h by a plus k by b sorry, it should be y and l by c z is equal to 1, where h y a and k by b a b d c by l are intercepts on, of the plane on whatever the plane is on x, y and z axis. A, B ,C cell are the unit cell lengths.

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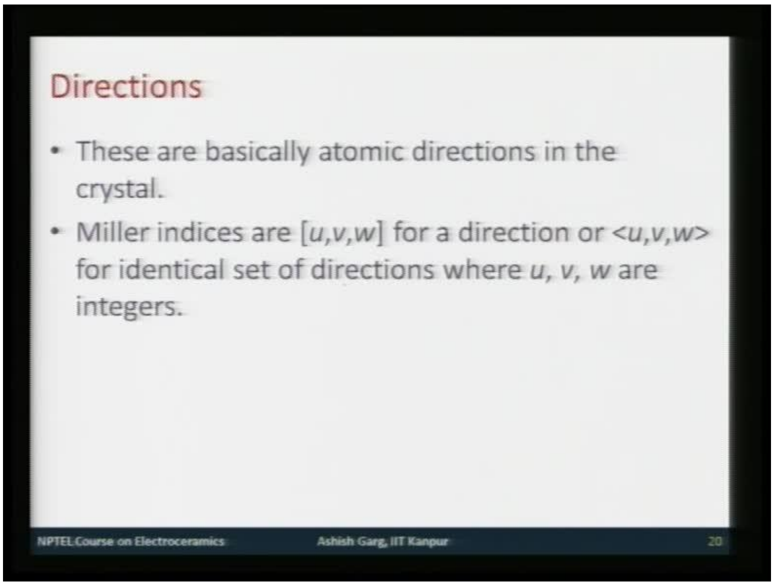

Directions

- These are basically atomic directions in the crystal.
- Miller indices are [*u*,*v*,*w*] for a direction or <*u*,*v*,*w*> for identical set of directions where *u*, *v*, *w* are integers.

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Similarly, you can defined direction, basically there atomic directions in a crystals along, but you can say there vectors basically. There also different defined by unit such as u v w or in the square brackets or in the smaller brackets u v w for a identical set of directions and the only difference with the spectro vectors is that vectors can go out of the crystal direction are usually defected inside the crystal from one side to another, but they nothing but vectors fundamentally.

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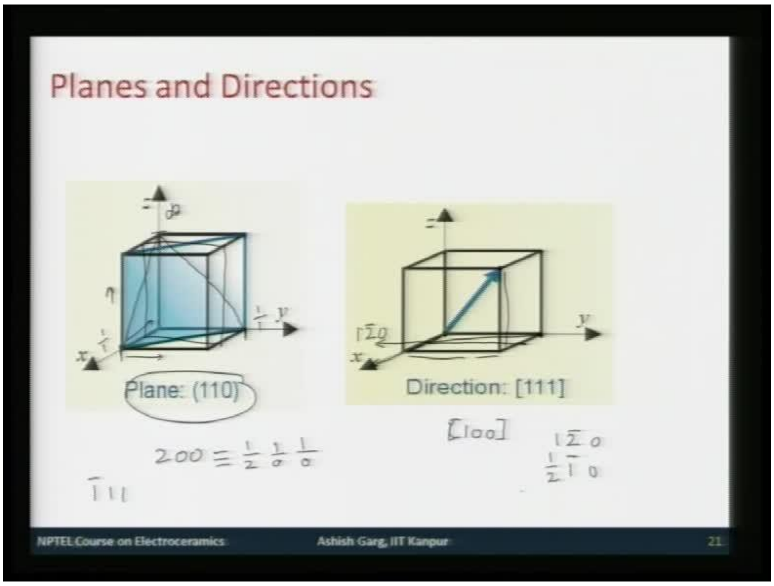

Planes and Directions

$200 \equiv \frac{1}{2}\,\frac{1}{0}\,\frac{1}{0}$

$\bar{1}11$

[100]

$1\bar{2}0$

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

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So, for example, a plane in a crystal would be this would be 110 plane. So, 110 what you have here is the intercept on x axis is 1. So, this would be 1 by 1 intercept on y is 1 again 1 by 1 and there is non-interceptor on 0 along the z axis. So, interceptor along the z would be 1 divide divided by… So, you can say its infinity interceptor infinity and then you take reciprocal of these to get the plane digit. Similarly, if you want to draw 111, 11 would be interceptors 1 on x, 1 on z, 1 on y. If you collect all these three points together you will make 111.

Similarly, you can make 2 000, 00 would be intercepts on x would be 1 by 2, interceptor y would be 1 by 0, interceptor on x z would be 1 by 0. So, there is no intercepts on y and z, which means is parallel to y and z and it cuts x on half a distance. So, this plane would be 2 00 plane often encounter negative digits as well. For example, you can have bar 11 bar, 1 is nothing but its matter of shifting the centers. So, in case of x instead of taking the center here you take the center here. So, your x become so you always travel in x this direction y remains positive z remains positive.

So, bar is handed by just the shifting the center similar direction 111 direction is nothing but you travel from this point 1 next direction 1 in y direction, 1 in z direction and combine these two points, this will make a 111 directions if you want to drive on 10100 direction, 100 would be based direction. Similarly, if you want to draw 1 bar 20 for bar 2 0, you need to again change the axis. So, bar 2 along the y direction, so instead of choosing the point center here origin, I can shift the origin here.

What I do is that basically I go half along x minus 4 along y 0 along z. So, half along x minus 1 along y I connected this two points. So, if connect these two point, this would be 1 bar 20 direction. I have, you can use 1 bar 20 as well. But you need to you need to go out of crystal. So, that is y I took a fraction basically the largest digits converted into 1 and all other digits become fraction to pet the direction in the unit cell.

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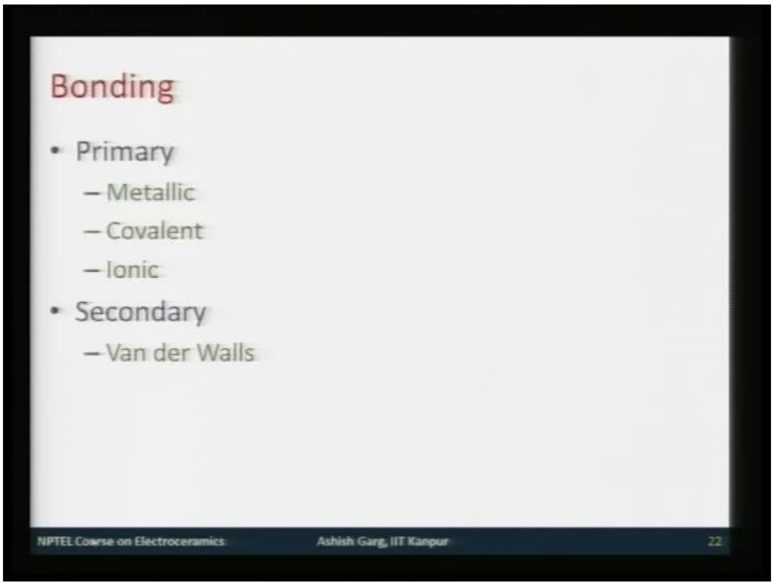

Bonding

- Primary
  - Metallic
  - Covalent
  - Ionic
- Secondary
  - Van der Walls

Now, we move on to bonding basically materials have to two kinds of bonding; one is primary on is secondary. There are three primary bonding mechanism metal metallic bonding covalent bonding and Ionic bonding and the secondary bonding is often referred as Van der walls bonding. There are other kinds of secondary bonding as well which we will not went to must details, but it is that for a review purposes metallic bonding.

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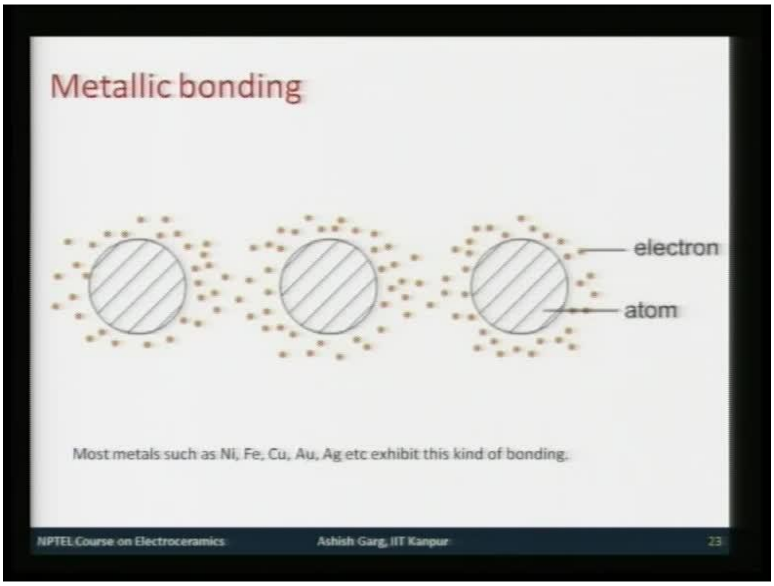

Metallic bonding

Most metals such as Ni, Fe, Cu, Au, Ag etc exhibit this kind of bonding.

Basically you have these atoms around, which you have these of this c of electrons which are free to roam around and this is why metals are very malleable and conducting and metals like nickel, iron, copper, gold, silver etcetera.

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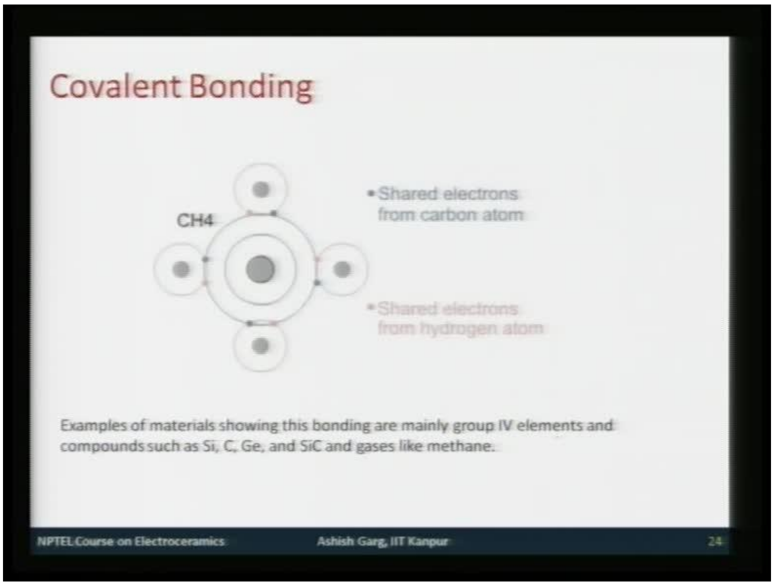

Covalent Bonding

- Shared electrons from carbon atom
- Shared electrons from hydrogen atom

Examples of materials showing this bonding are mainly group IV elements and compounds such as Si, C, Ge, and SiC and gases like methane.

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They showed this kind of covalent bonding its typically due to its due to sharing of electrons. For instance in methane you can have 1 carbon atoms shared by surrounded by 4 hydrogen atom and 1 electron so each electron carbon is shared by each of these hydrogen atom. In case of diamond you can have 4 electrons of each carbon atoms shared by 4 electron of under a carbon atom to make it to fulfill the sharing the requirements, to satisfy the periodic, to satisfy the electronic arrangement, to full to fill the orbital's. The examples of the these materials can be group mostly group four elements like carbon, silicon, germanium and materials like silicon carbide or even gases like methane and as well as glasses like silicon oxide.

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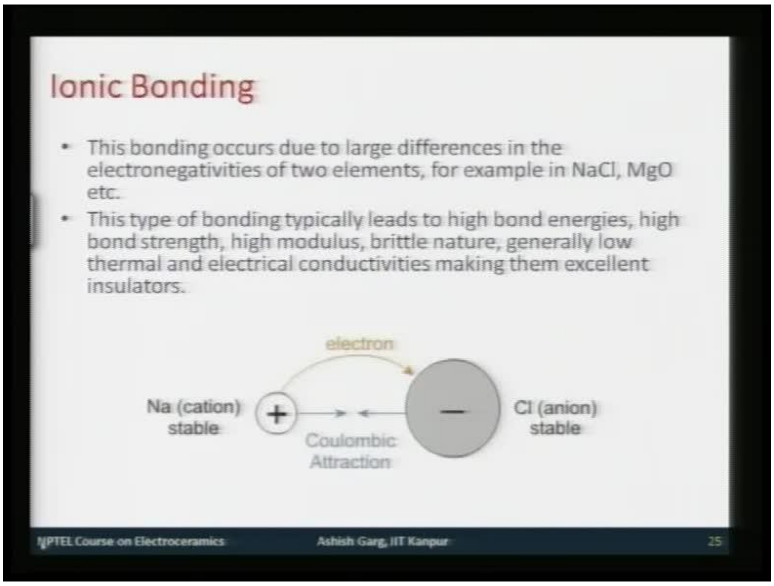

Ionic Bonding

- This bonding occurs due to large differences in the electronegativities of two elements, for example in NaCl, MgO etc.
- This type of bonding typically leads to high bond energies, high bond strength, high modulus, brittle nature, generally low thermal and electrical conductivities making them excellent insulators.

They have predominantly covalent bonding character, then ionic bonding. Ionic bonding basically due to large difference in the electronic negative in the two ions, so for example, you can have materials like sodium chloride, magnesium oxide, cation has for example, in this case plus 1 charge and anion has minus 1 charge. So, each of these both of them are either ready or ready to give are expect the electrons, so they have very strong afraid to each other sodium and chlorine.

For example, in this case sodium gives 1 electron to chlordane, which readily acceptors and so this is basically strong bond, which is formed between 2 ions two differently charged ions and this kind of bonding typically have high bond energy. I am not to fundamental bond energy, if you want to go through you need to any basic book. For example, Kittel or Ragavan or Callister, so bond energy is basically a parameter which decides how strong the bond is.

It is typically high bond energy will imply high bond strength, which typically implies high modulus, brittle nature of materials and low in generally low thermal electrical connectivity, which makes these material very good insulator. Most of the electro ceramics have very large proportion of them are ionically bonded compounds. So, this is what is going to govern the formation of the structures an many of these compounds.

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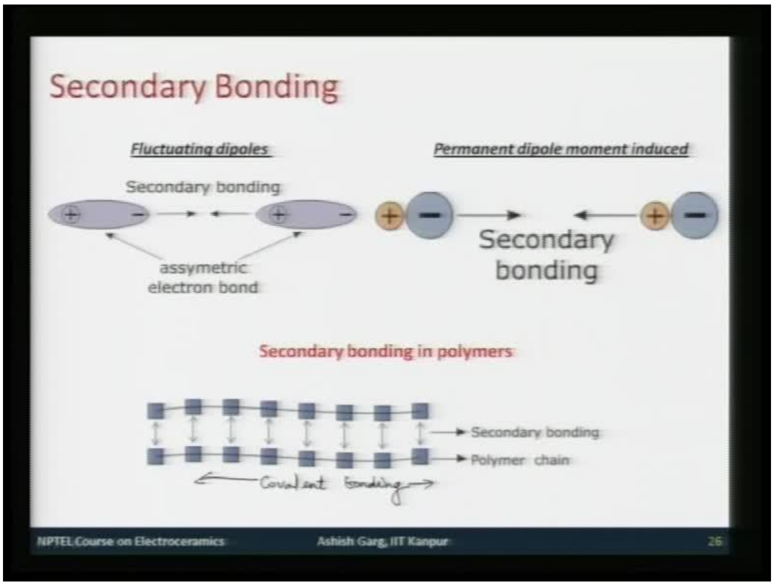

Secondary Bonding

Fluctuating dipoles

Permanent dipole moment induced

Secondary bonding in polymers

Finally, you have secondary bonding, secondary bonding can due to a symmetrical electrons clouds as a results you have fluctuating dipoles and this fluctuating dipoles lead to attraction of the ends of these entities, which leads to kind of attraction between them, this is secondary bond. You can also have a permanent dipole moment in in the act at the molecules, which gives which also gives rise to kind of attraction between two oppositely charge ends.

These are two kinds of secondary bonding, which happens in most material. Secondary bonding is very prevalent in natures like polymers, so polymers have a chain which is covalently bonded. So, in the chain, they have along so here you have covalent bonding along the chain. So, for example, could be a chain of ethylene in this, but between the chain. So, between the chain you have secondary bonding which is the one worst bonding, as a result polymer as strong along the chain, but there are flexible because of the secondary bonding between the chains.

Chains can they in terms with each other with each other when give rise to low modulus and high flexibility polymers typically. So, this is a basic review of a structure an bonding in these materials. Now, we will look at how the atoms in various structures pack against each other. So, the next topic in this lecture would be to see, if you have atoms then what are the possible fashions in which if you put these atoms in the space, in which they can pack together?

What is an and then will concentrate on what sort of wades there between this atom in which can be then filled by various other kind of atoms which are crustal in forming the ceramic structures? So, earlier we so that how the structure of what the fundamental of structure the concepts of lattice crystal system etcetera. Then we looked at the kind of different bondings. Just to emphasize, most of these ceramic material are bonded by covalent or ionic bonding typically ionic with some covalent character and as a due to due to difference in the bond energy, the covalent ionic bonded ionically bonded materials tern to be more stronger.

They have high modular's, typically low electrical in thermal conductivity and are buddle in nature. And on the other hand covalent bonding terns to be again these are be stronger, sometimes not as a stronger than ionically bond, but in terns to be very directional in nature. For instance the hybridization of a orbital's requires this bonding. The bonding to be directional as a result the bonds are stronger than the metallically bonded material and metical, metallically bonded material typically or malleable conducting and very easy to deform, either at room temperature or high temperature.

Secondary bonding is typically weaker kind of bonding such as (( )) corresponding. Now, we will see how the atoms if we take considered atom hard its fear how these atoms pack themselves in the space? So, there are three ways in which taken do, there are many various ways, there are various ways in which atoms can pack themselves in the structures.

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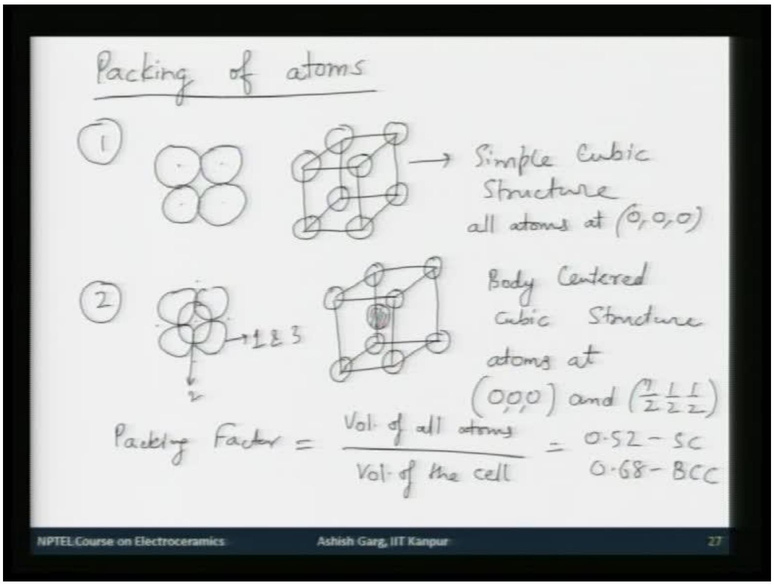

Packing of atoms

① Simple Cubic Structure
all atoms at (0,0,0)

② Body Centered Cubic Structure
atoms at
$(0,0,0)$ and $\left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right)$

$$\text{Packing Factor} = \frac{\text{Vol. of all atoms}}{\text{Vol. of the cell}} = \begin{matrix} 0.52 - SC \\ 0.68 - BCC \end{matrix}$$

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In the first, so we can say packing of atoms so the first simple way of packing these atoms in the way like this. So, you have an atom like these, you have an atom like these. So, this the first layer of atom and what I do is that if I put a another layer of atom I can put an another layer of atom right on top of it. So, the second layer will have same configuration like these and it goes on right on top of it. So, on the 3 D what you make something called as a cube, follow this atom for a same size and same type.

So, what that make us a cube an sent corner of these cubes are occupied by each atoms. This is called as a simple cubic structure, with all atoms at 0,0 and 0. Second way of packing these atoms could be you again take a layer. This is the first layer configuration, second layer shifted by if you look at in this direction in this picture, second layer first atom is like this and then second atom would be… So, if the atom center of first atom is here the second atom center would be here and third atom center would be here.

So, this is little bit shifted, since you have this kind of configuration, so the first layer is the this one. This is the second layer third layer goes right on top of first layer. So, this would be 1 and 3 when u make a 3 D structure like this, what you have is body centered cubic structure, where corners are occupied these spheres. All this spheres are identical mind you and so these are so this is first and third layer makes the simple cube and the second layer goes inside this I have dash I put a dash just to differentiates other wise these two are same.

So this will make a body centered cubic structure and atomic position would be 000, and half, half, half you can calculate the packing factor. The packing factor is nothing but volume of all atoms divided by volume of the cell and you can work it out yourself. It would be 0.52 for simple cubic structures 0.68 for BCC structure, I will leave it you to work it out. It very simple exercise, all you need to do that you considered the radius of which each atom has r and make sure make sure and consider and assume that all the atoms are touching each other and so you can determine what is the packing factor.

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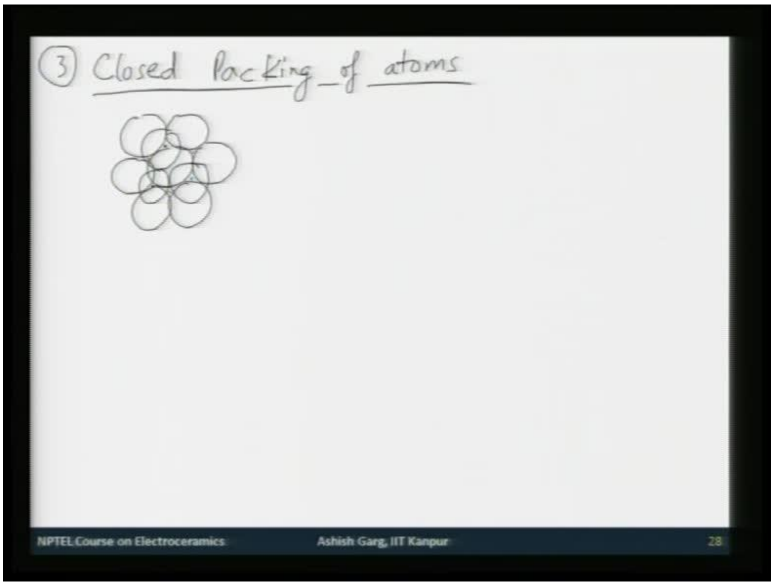

③ Closed Packing of atoms

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The third way in which atoms can pack with each other is formation of closed pack structure. So, this is closed packing of atoms. In this kind of structure, you have wave first low of atoms like this, this is the closet packing in 2 D, spheres can pack only this manner. The second layer which comes it can go right on top of this but that will not be closed packing. But the second layer you can put one atom here another here and another here. Now, so these are all empty sites it do like this or it could have gone here it does not matter there are all identical. So, if I just change in color, so you have these side and you have these sides.

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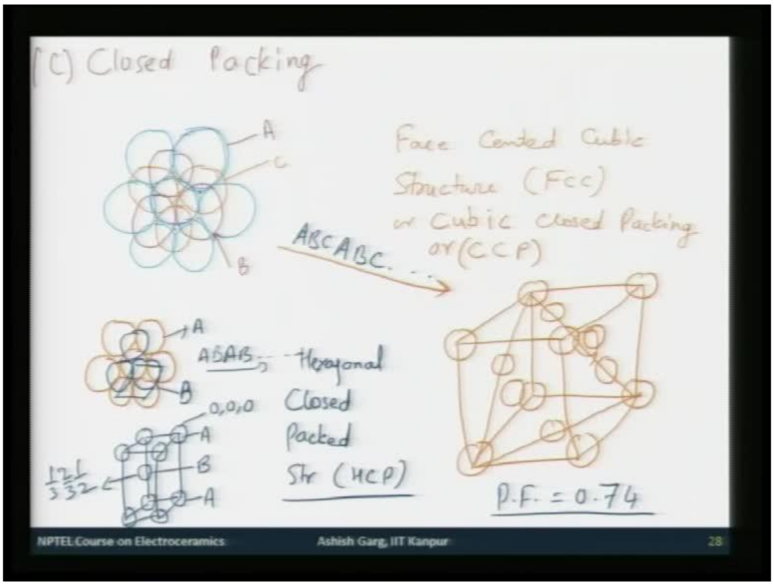

So, this is the first layer. The second layer can go either in top of these or on top of these all of them cannot be filled simultaneously because size of the atoms would not would not allow that. So, the second layer would be let us say I choose to fill this one, second layer would be like this. So, this would be second layer, let us say this I call at a layer this I call us B layer. Now, next can continue, so all the red type empty size will be covered by the second layer. On the third layer, which income it can come either on right on top of a layer, which means if I put the third layer it can go this fashion.

So, this would be my third layer going on right on top of first layer or the third layer can go in different fashion. Third layer can cover size, which will not filled previously, so the third layer can go now on the top of these, right? So, this layer has completely different orientation as compare to rest of two layer. So, this would called as A, B, C kind of stacking. So this A, B, C kind of stacking gives rights to what it called as a face centered cubic structures or FCC or often called as cubic closed cubic closed packing or CCP. So, what it looks like in a cubic form is like this. You have cube corner of cubes are filled and center of all these six faces are filled as well this will make a cubic closed pack structure all in this schematic. I have not made each atom each atom touch each other in this kind of configuration, closed packing.

They will be touching each other, so this A, B, C A, B, C is taking leads to this kind of configuration and the plane of visualization A, B, C is basically the 111 plane of FCC unit cell. You have to basically stack A,B,C A,B,C along on top of 111 plane. if you had this A, B kind of stacking A, B, A, B would be something like so you have first layer, second layer would be this layer and third layer could again be the same as first layer. This would be A, this could be B, so this is A, B, C, A, B, C and if you have A,B, A, B this would leave to something called as hexagonal structure or hexagonal closed pack, packed structure called as HCP packing.

So, you put another one on top and the, so if you put another one at top it would become just like a and the unit cell. The smallest unit cell for hexagonal is if you connect the center of these and if it is going the z direction, it would look something like this. One atom would be at center, so this would be A layer, this would be B layer and this would be again A layer. So, these all will be 000 and this would be at 1 by 3, 2 by 3 half or 2 by 3 1 by 3 half ending upon the way you look at it. So, this would be your hexagonal closed pack structure.

You can also calculate the packing factor, packing factor for these this is these are the most closed packs structures. These are these are a packing factor of about, packing factor would be 0.74. This is only the stacking sequences is difference, there is no other difference in terms of filling the voids or putting atoms top of each other because the number of nearest neighbors either in this structure or that structure both is 12, packing factor remains same. Only the sequence changes, but not the packing factors, so this is a the closest closable packing possible from only one type of his spherical atoms.

Now, once you have seen these various kind of atoms, a packing possible. The next thing is, you still see some voids inside these structures, right? So, no matter how closely you pack, you can only close you can only pack 74 percent of the space, 26 present of the states still empty. These are spaces are often as voids or interstices. Some of these voids can be filled by the foreign atoms that is why they called as interstices. These are called at interstices and the atom which filled is voids are called as interstitial atom. It is a very common phenomena most of the material, for example steal.

In a steal iron makes the bcc lattice and carbon goes to in the interstitial sites. There are typically two kind of interstitial sites its one is tetrahedral interstitial sites octahedral interstitial sites. Tetrahedral interstitial sites is the sites which contain four nearest neighbor around the interstitial atom, whereas octahedral interstitial site is the body is looks like a octahedral. The interstitial whole has six nearest neighbor around it. So, we look at the interstitial sites in the next class. And then we will move on to the material, which a ceramic material which can be formed by various kind of bonding such us ionically or covalently bonded materials.

Thank you.