Fundamentals and Applications of Dielectric Ceramics
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Lecture No. – 02
Basics of Crystal Structure

Welcome to this new lecture of fundamentals and applications of dielectric ceramics. So, let us just briefly review the last lecture.

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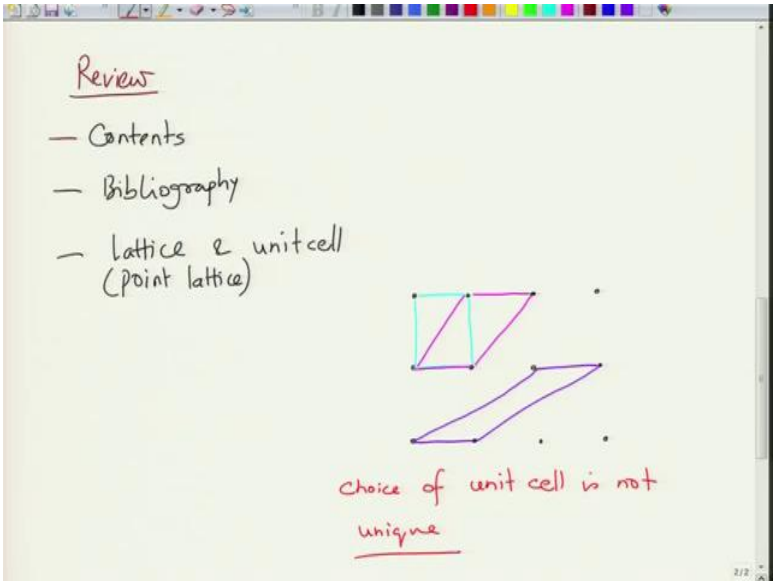

In the last lecture, we basically narrated the contents. So, we looked at the contents of the course, and then we looked at the bibliography, the kind of books that you need to read, and then we introduced some concepts related to structure. So, we started with the concept of lattice and unit cell. So, basically, we talked in the framework of point lattice, okay? So, what happens when you have points present in space.

So, depending upon arrangement of points in the space you can construct a body which is called as point lattice, and within this point lattice you can construct the smallest repeatable unit which is named as unit cell. So, basically, a point lattice is a regular periodic arrangement of points in space with identical neighbourhood of points, and then you can construct a unit cell within the lattice which is the smallest possible repeated unit.

So, for example, if you have this kind of arrangement of points in the space this is the simplest possible arrangement. So, we are drawing this in 3D, but you can draw this in 2D as well. So,

the unit cells that you can draw could be like this. So, this is a repeatable unit. You can also draw this as a unit cell as well. This is also a repeatable unit.

And, mind you, all of these unit cells have areas which are similar and the number of lattice points is basically the number of corners divided by four. So, you can see that each of these consist of one lattice point and they have similar area. So, choice of unit cell is not unique. So, basically, the message was that the choice of unit cell is not unique. You can make several shapes, and as a result, there are various possible combinations.

The question is how do you reduce the number of choices or how do you put in a framework which allows you to simply distinguish between various shapes, and this is what is called as crystal systems that will we come to later on. So, this is about the point lattice. So, point lattice means construction of lattice with the use of points in space. The second thing is called as motif.

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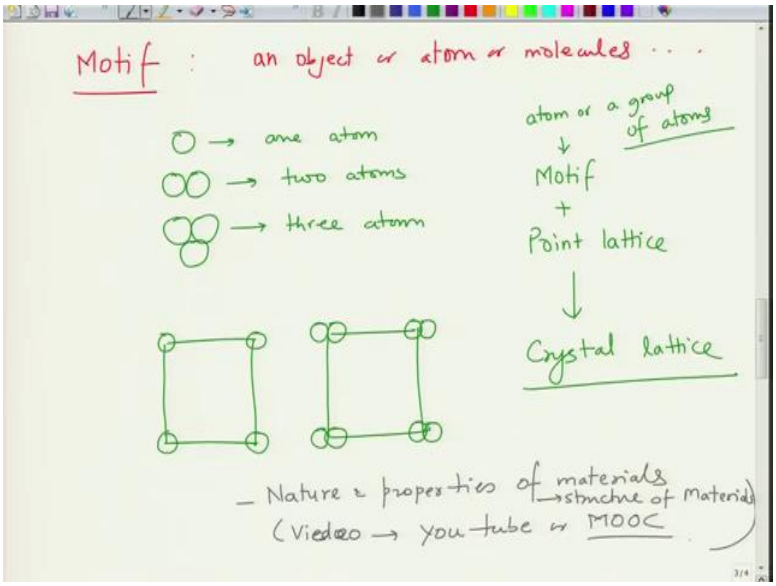

The second concept that you require is that of motif and motif is nothing but an object or an atom or molecule which could be group of atoms and so on and so forth. When these motif or units they replace the points in the unit sell. So, it could be one atom, it could be group of atoms, two atoms, it could be something like this, and so on and so forth. And there is a possibility to make a variety of shapes.

So, on this unit cell I can construct using the first one a unit cell like this or I can have a unit cell in which I can put the atoms like this provided they are put in such a manner so that the

neighbourhood remains identical and the arrangement remains periodic. They will all make what we call as a lattice. So, when you put this motif plus point lattice, then what we make is called as a crystal lattice. So, basically, a crystal lattice is nothing but a combination of point lattice and motif which in the case of solid is nothing but atoms or a group of atoms.

So, this motif is basically atoms or a group of atoms, okay? If you want to learn the details of this thing, then I would say you should look at the course on nature and properties of materials. The videos are available on YouTube or MOOC site. This is nature and properties of the materials, basically structure of materials. So, this is a course in which I have discussed what is the meaning of motif in a very detailed manner.

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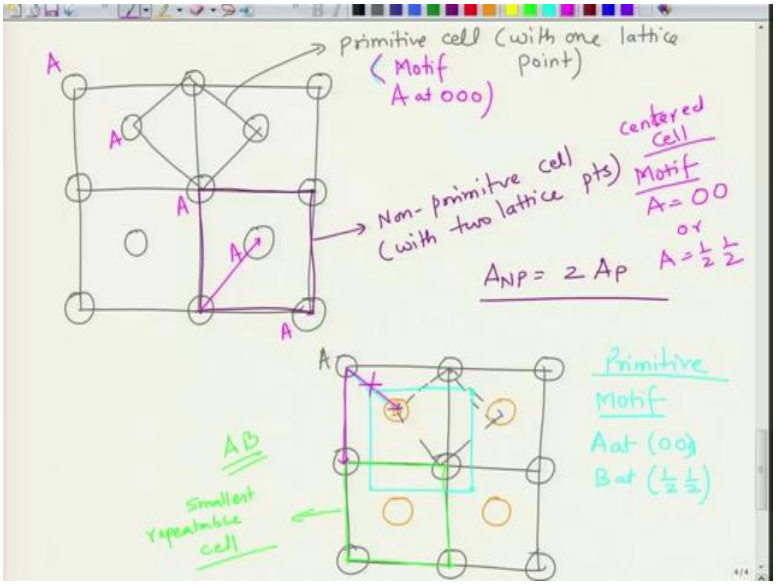

So, I will just give you one example and rest you can do by yourself. So, let us say if I construct this kind of lattice, okay, so this is just a monoatomic lattice, okay. In this case the smallest repeatable unit is this, okay. So, the smallest repeatable unit is called as primitive cell with one lattice point, okay, and then you can construct a non-primitive cell which is this cell which is called as a non-primitive cell with two lattice points, okay?

So, you can see that the area of non primitive cell is twice the area of primitive cell, okay? That is very obvious and it contains two lattice points. So, it basically scales with the number of lattice points. Suppose in the similar cell if I construct another similar cell and then I put another atom here which is like this.

Now, what happens is, basically, I can see that while this atom has a neighborhood which is made of these four, so, let us say this is A and this one is B, okay? So, B atom neighbourhood is four A atoms, whereas neighbourhood of A atom is 4 B atoms. So, both of them have different neighborhoods. So, that is why they are not separate lattice points.

So, what you have in this form now, if you now construct this as a lattice unit cell, this is not the smallest unit cell because you have different neighbourhood of different points, instead the lattice now becomes this particular body which is the repeatable in the space. So, this is the smallest repeatable cell that we will make in this unit cell, and this will have one of A atom and one of B atom. As a result, a formula will be AB in this case.

So, basically, it is like saying I have a unit cell which consists of a molecule AB. So, you can keep the corners of this unit cell here. It can consist of corners here or here. So, if you construct unit cell here, then basically what I am saying is that this dumbbell-shaped molecule AB is the motif or the unit that is placed at the lattice point. So, this is the motif. So, motif in this case is A at, for the sake of simplicity you put the corner on one of the atom, so A at 00, and B at half half.

Whereas in this case the motif for this cell it would be, and this would be a primitive cell, okay, whereas in this case the motif would be A at 000, there is no B atom, it is just A atoms all of them. So, it is all of them A. If it is a primitive cell, then you have to define the position of both the atoms. But if you want to define non-primitive cell let us say, for this non-primitive cell, I say this is a non-primitive cell, let us say it is a centered cell.

So I define this as a centered cell. And in this case the motif would be, you can say, A is equal to 0 or you can say A is equal to half half. So, the moment you say it is a centered cell, the motif at A = 0 will automatically mean that you have one at 00 and one at half half or if you say A is that half half, it would automatically mean that there is another one at 00 because the translation vector in this case is this translation vector.

So, the lattice translation vector in this case, in the case of compound, lattice translation vector is not this but this. This is not the lattice translation vector. This is lattice translation vector. So, it would go from same atom to another atom to complete the lattice translation and it should

be repeatable in space. You can make it more complicated if you have asymmetric molecules and stuff like that, it becomes more complicated.

So, for details, I would say that you should go to the first module of nature and properties of materials course, that is structure of materials, and look at the first module based on structure. So, there I have discussed this concept of motif in detail. Motif is also called as basis. So, motif or basis when you combine with periodic point lattice it makes what is called crystal lattice or crystal structure. So, what do you know now?

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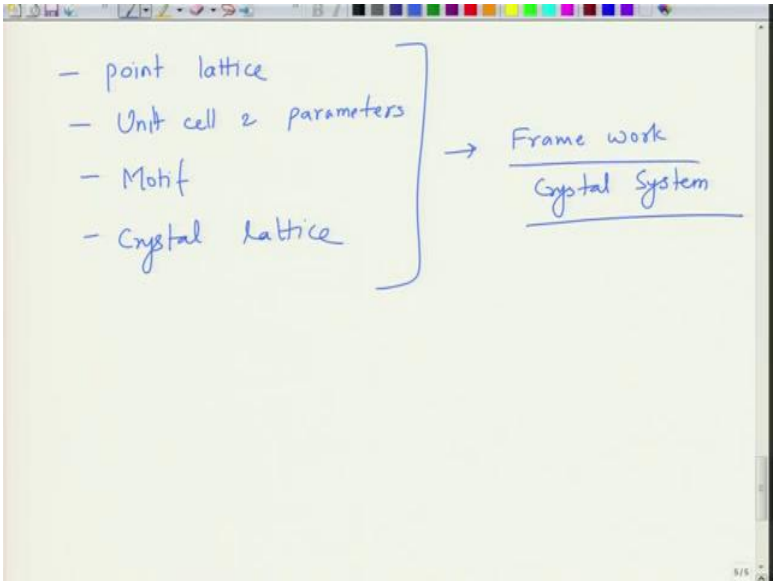

You know what is point lattice, you know what is unit cell and parameters, we also know what is motif and we also know what is crystal lattice. Now, to distinguish between various shapes and possibilities based on the symmetry arguments, people have evolved what we call as crystal system. So, these had been put in the framework of crystal system because we have multiple choices of unit cell logical fashion**,** not to have millions of choices. We have defined a framework which is called as crystal system.

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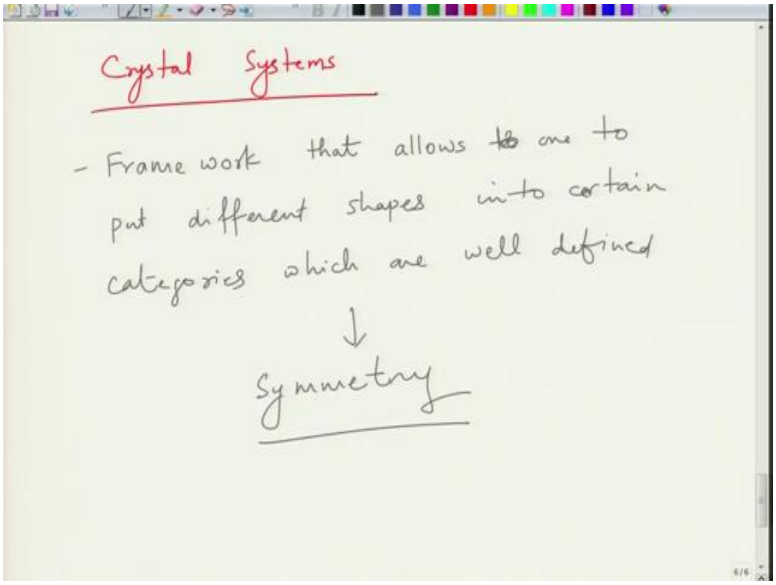

So, based on this, people have defined various crystal systems which are, essentially it is a framework that allows one to put different shapes into certain categories which are well defined. And for this we take the help of symmetry. Now, for a lattice there are certain symmetry operations that one must be able to perform.

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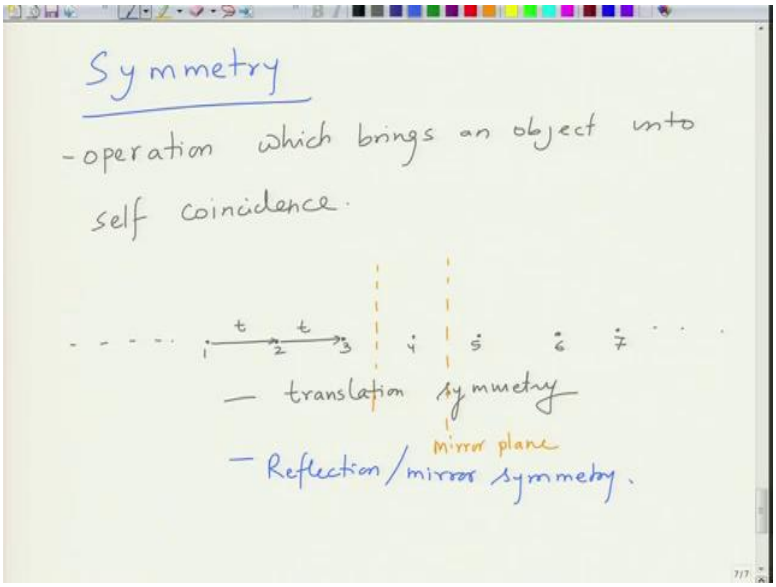

What is symmetry? Symmetry is basically an operation which brings an object into self-coincidence, okay. So, let us say if I have this array of point in a space, okay? For array of points in space, if these are all identical points and if you have an infinite array let us say, then this point is identical to this point if this point is identical this point provided they have this translation t which is similar.

This is 1, 2, 3, 4, 5, 6, 7, 8 and so on and so forth, okay. So, whether you are at 1, whether you are at 2 or 3, or 4 or 5 or 6, it does not matter because the translation of all the points around is similar, as a result this is called us translation symmetry. So, this must have symmetry for any kind of object.

Now, another thing that you can have here is, basically the idea is to bring the object into self-coincidence. So, there is a possibility that if you put in a mirror plane here, reflection, then 3 looks similar to 4, if you put a mirror plane here, and 4 will look similar to 5 or 6 will look similar to 3 and so on and so forth. So, you can have mirror plane and this is called as reflection symmetry or mirror symmetry. So, this is about 1D, all right?

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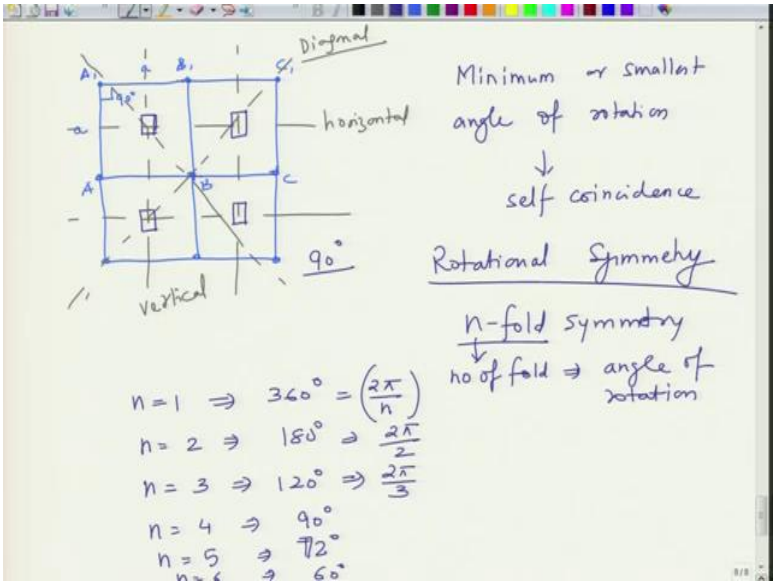

Now, in case of 2D, if you have a 2D object like this, and if you go on like this, okay. So, let us say these are 4 squares put in such a fashion so that this is A, this is A, this is 90 degrees, alright? So, we have translation symmetry whether you are at this point or this point or each point. So, A, B, C all these are identical points. So, whether are you at this point A1, B1, C1 and so on so forth. It doesn't matter because translation symmetry even permit to have identical neighborhood. So, the translation is there. You have mirrors which are there. So, if you draw a mirror which is, for example, at this position, then we have mirrors in this fashion, we have mirrors in this fashion also, and we have mirrors in this fashion also.

So, we have horizontal mirror, we have vertical mirror, and we have diagonal mirror. So, we have translation as well as reflection symmetry. Now, another thing that is possible is what will happen if you rotate it, for example, at this point by a certain angle. So, we can bring this

object, if this is a square shaped body, we can bring this into self-confidence only if you rotate by 90 degrees. The minimum angle by which we can rotate is 90 degree. Of course, if you rotate it by 360 degrees will come into self-confidence.

But what is the minimum angle by which you rotate it so that it comes into self confidence. So, minimum or smallest angle of rotation which will allow you to have self-coincidence, this is called a rotational symmetry. So, in this case, you can rotate it by 90 degrees. But how do you evolve a general framework? In this case, we define what we call as n-fold symmetry and this n is the number of fold or rather defined as the angle of rotation.

So, n = 1 will mean 360-degree rotation. So, basically, what it means is that it is a rotation by $2\pi/n$; n = 2 will mean 180 degrees which is $2\pi/2$; n = 3 will mean you will have $2\pi/3$ that is 120 degrees rotation; and n = 4 will mean 90 degrees; n = 5 will mean 72 degrees; and n = 6 will mean 60 degrees. So, various possibilities are there.

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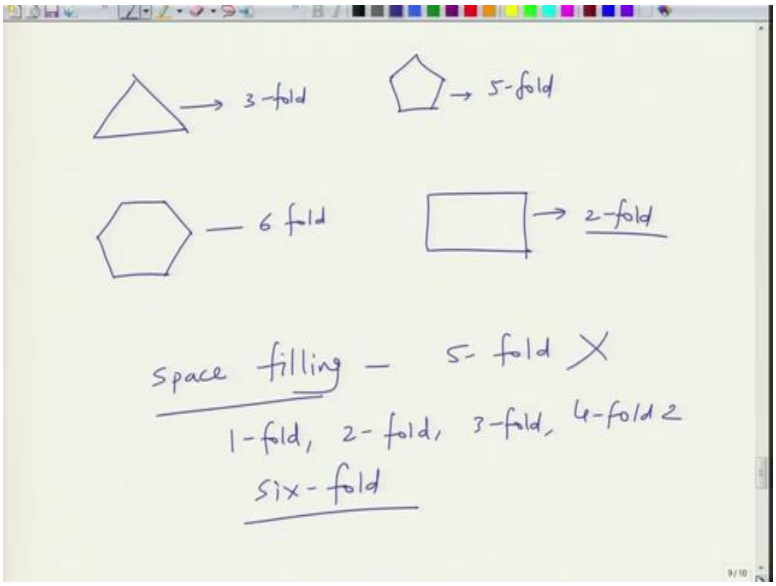

So, for shapes like triangle, anything triangular will have 3-fold, a pentagonal thing will have 5-fold, then you have hexagonal things will have 6-fold, and rectangular objects will have 2-fold. So, from the perspective of space filling without any gaps 5-fold is not possible. So, the only possible symmetries are 1-fold, 2-fold, 3-fold, 4-fold, and 6-fold, and you can try this on various objects of different shapes and see which symmetries they follow.

So, this is something that you require for a 2D object. For 1D object you are okay with only translation and reflection, but for 2D objects, in addition to translation and reflection, you also

require rotation symmetry. And for 3D objects one more thing is added which is called inversion symmetry.

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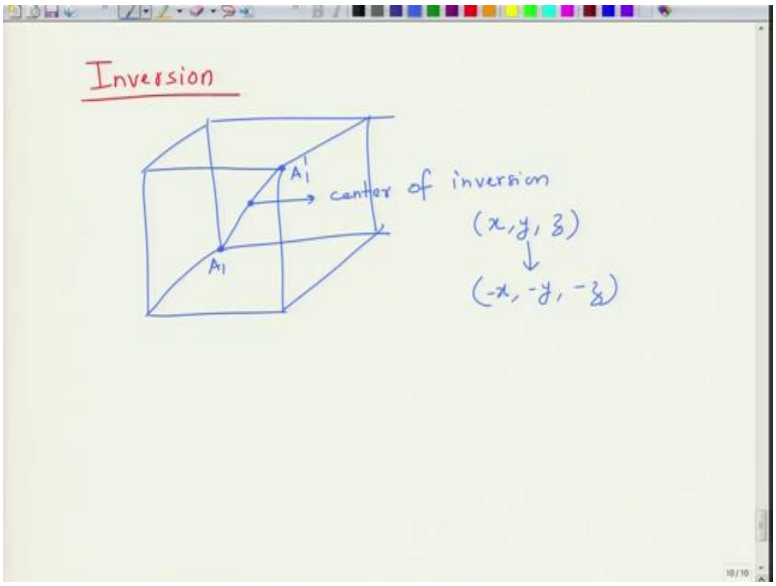

So, inversion basically is, in three dimensions, let us say you have a body like this, obviously this 3D object will have translation symmetry elements, reflection symmetry elements, and rotation symmetry elements, but in addition, it will also have inversion. So, for example, if it is a cube, then this point A1 can be brought into position A1 prime through a center of inversion which is located here. So, this is center of inversion.

So, basically, in general terms it means that anything which is at x, y, z if can be seen or if it can be brought into self-confidence at – x, – y, – z, then this is called as you are going through a process of inversion. So, what we have seen is four symmetry elements, translation, reflection, rotation, and inversions. So, in 3D it is important to consider the inversion as well, whereas inversion is not considered for 2D objects. Now, let us look at the symmetry from the perspective of 3D objects.

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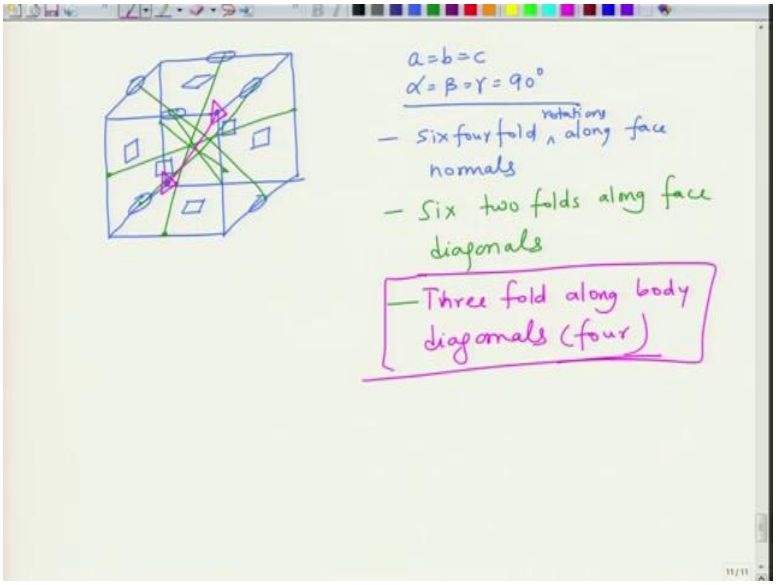

We will just consider a cube for instance, if you have a cube, alright, and why I am focusing on this a little bit, because when we learn about ferroelectricity we will need this concepts back on. So, this is a cube, okay. So, cube means a = b = c and $\alpha = \beta = \gamma = 90°$, okay. So, in this cube you will see that faces of the cube are squarish which means all of them can be rotated by 90°.

So, all the faces have four-fold symmetry elements. So, cube has six 4-fold rotations along face normals. You can also rotate cube by 180° along these diagonals. So, if you put diagonals like this, I will use a different color, so if you connect this point and this point, if you connect this point and this point, this point to that point, so you will have these diagonals connecting each other.

So, how many of these will you have? You will have one of this, one of that, then one will connect here, and then we will have, 1, 2, 3, 4 and then we will have one of these and then you will have one of these as well. So, you will have six two folds along face diagonals. And the third thing that cube must have, the defining symmetry of the cube is the three fold rotation along this axis which is the three fold along body diagonals.

So, in 3D case, the rotational symmetry often becomes the defining symmetry of 3D shapes. So, for a cube for example, it must have three fold along the body diagonals, four of them, okay. So, based on these symmetry arguments and lattice definitions people have come up with framework which is called as crystal system.

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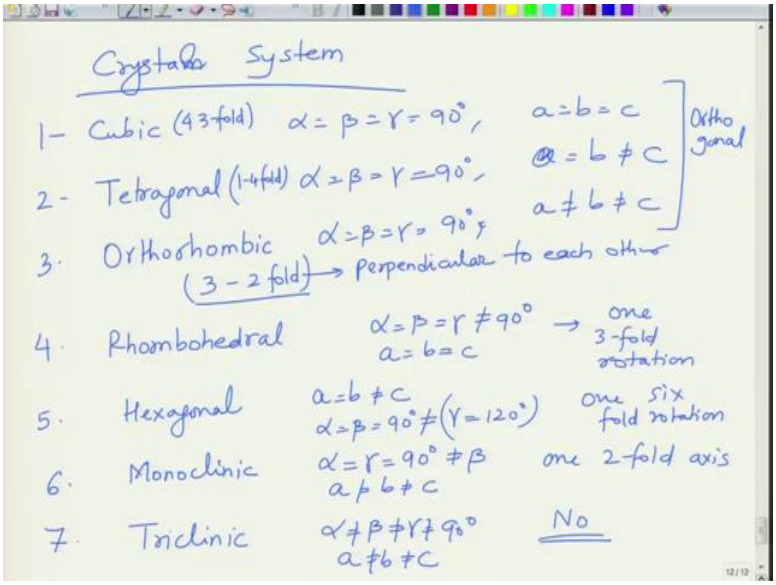

So, first of these is cubic which means $\alpha = \beta = \gamma = 90°$and is a = b = c, that is what we have seen. If it distorts a little bit, you may get tetragonal system, which means $\alpha = \beta = \gamma = 90°$, but $a = b \neq c$. So, c parameter is a little bit shorter or longer as compared to a or b. Third is called as orthorhombic wherein $\alpha = \beta = \gamma = 90°$, but $a \neq b \neq c$. These three are basically orthogonal systems, but they have different symmetry elements. Defining symmetry for a cube will be four 3-fold. For a tetragonal you must have one 4-fold. For orthorhombic you must have three 2-fold. These are the defining symmetry for the systems. These three 2-fold are perpendicular to each other, okay.

And then you have non-orthogonal systems such as rhombohedral for which $\alpha = \beta = \gamma \neq 90°$ but a = b = c and this must have one 3-fold rotation in the system, that is the definition, okay, one 3-fold rotation. And then fifth one is hexagonal. Hexagonal is basically $a = b \neq c$ and $\alpha = \beta = 90° \neq \gamma = 120°$ okay.

And for this we must have one 6-fold rotation and then finally two more choices. Sixth one is called as monoclinic for which $\alpha = \gamma = 90° \neq \beta$ and $a \neq b \neq c$. It must have one 2-fold rotations axis, okay. And then seventh is triclinic for which $\alpha \neq \beta \neq \gamma \neq 90°$ and $a \neq b \neq c$ and it does not have any symmetry elements.

So, these are the classifications which have been made on the basis of symmetry. So, although you have infinite choices of shapes, these are categorized in these seven categories of crystal systems which makes it easier to classify different solids and easy to understand categories

which are based on symmetry arguments. You will have a cube only when it has four 3-fold axes.

You will have tetragonal crystallographically only when it has one 4-fold axis and so on and so forth. So, we will stop here today. In the next lecture, we will talk more details of structures of dielectric ceramic materials. Thank you very much.