

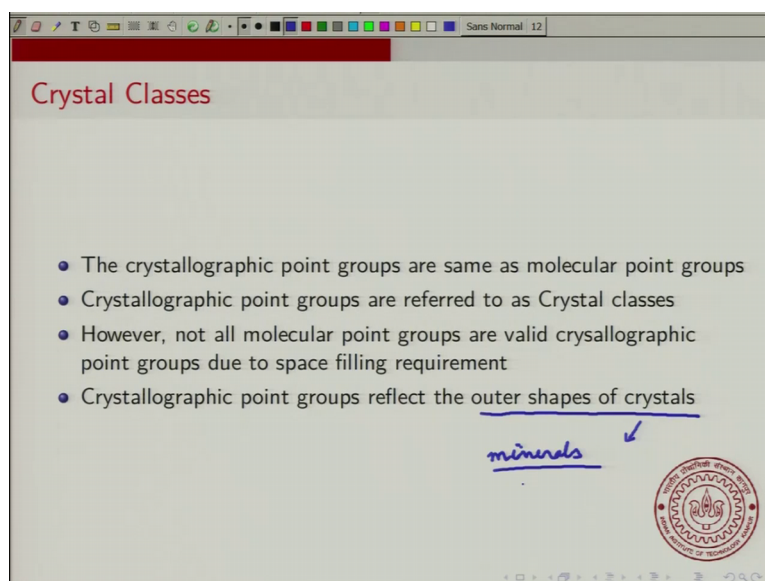
**Solid State Chemistry**  
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**Lecture – 26**  
**32 Crystal Classes Based on Symmetry**

Now, I will start week 6 of this course. And in this week, we will discuss the commonly used crystallographic notations for point groups and space groups. As I had said earlier there are two notations that are common: one is called Schoenflies symbols, and the other is called the Hermann Mauguin conventions. So, we will discuss both of these, but it is the Hermann Mauguin that is more commonly used in crystallography.

So, before we go to the actual notations, let me tell you about how you get 32 crystal classes. So, in the first lecture we will talk about crystal classes. So, week 6, lecture 1 will be on Crystal Classes Based on Symmetry.

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The screenshot shows a presentation slide with the title "Crystal Classes" in red. Below the title is a bulleted list of four points:

- The crystallographic point groups are same as molecular point groups
- Crystallographic point groups are referred to as Crystal classes
- However, not all molecular point groups are valid crystallographic point groups due to space filling requirement
- Crystallographic point groups reflect the outer shapes of crystals

Handwritten in blue ink, the word "minerals" is written below the underlined text, with a blue arrow pointing to the underlined text. In the bottom right corner, there is a circular logo of the Indian Institute of Technology Kanpur.

So now, what are crystal classes? These are the crystallographic point groups. And these are actually very similar to molecular point groups; the point groups of molecules. In fact, in fact they are identical to point groups of molecules. These crystallographic point groups are referred to as crystal classes.

Now you may have seen, you may have learnt about molecular point groups in a course on group theory in chemistry and so crystal crystallographic point groups are basically shapes of crystals, ok. So now, not all molecular point groups are valid crystallographic point groups ok, because only those shapes that satisfied the space filling requirement are valid crystallographic point groups ok.

So, what I mean to say is that the number of crystallographic point groups is much smaller than the number of molecular point groups. Now there is another point which I am not going to talk too much about. But basically these crystallographic point groups reflect the outer shape of crystals. And this has to do with a rather subtle theorem regarding the shapes of crystals.

So, if you take a finite sized crystallite then the shape of that crystal will be reflected in the, it will actually reflect the shape of the unit cell ok; and so the outer shapes of crystals will actually carry information about the point group of the unit cell. And historically this was a very powerful idea in the development of crystals, because many of these crystals were actually the early crystals that were discovered were minerals.

And while if you look at shapes of these mineral samples ok, you will often find that they have exquisite crystalline shapes ok. So, there are fairly large crystals and these are fairly exquisitely shaped ok. And so you can look up shapes of crystals of especially minerals ok.

And if you take any one well-formed crystal piece, the shape of that crystal will be reflected in the crystallographic point group. But in any case we will not talk too much about the outer shapes of crystals here.

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**Crystal System classification based on symmetry**

- Triclinic : None
- Monoclinic : One two-fold axis or mirror plane
- Trigonal : One three-fold axis
- Hexagonal: One six-fold axis
- Orthorhombic: Three mirror planes or three two-fold axes
- Tetragonal: One four-fold axis
- Cubic: Four three-fold axes

So, let us get back to the crystal system based on symmetry. We already saw that there are seven crystal systems: a triclinic, monoclinic, trigonal, hexagonal, orthorhombic, tetragonal, and cubic. And this is based on symmetry triclinic has has no essential symmetry, whereas monoclinic has 1 two-fold axes of mirror plane; trigonal has 1 three-fold axes, hexagonal has a six-fold axes, orthorhombic tetragonal cubic, ok. Now, let us now look at these in terms of let us see how these lead to various crystal classes.

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**Crystal Classes - Most unsymmetric**

- Triclinic : 1 - Pedial
- Triclinic :  $\bar{1}$  - Pinacoidal
- Monoclinic : 2 - Sphenoidal
- Monoclinic :  $m$  - Domatic
- Monoclinic :  $2/m i$  - Prismatic
- Orthorhombic : 2 2 2 - Rhombic-disphenoidal
- Orthorhombic :  $m m 2$  - Rhombic-pyramidal
- Orthorhombic :  $2/m 2/m 2/m$  - Rhombic-dipyramidal

So, let us first look at the most un symmetric crystals ok. So, if you look at the triclinic system that has the least symmetry. So, actually there is no essential requirement of symmetry ok. So, if there is only, if the only symmetry operation that is present is an identity; identity which is basically mean means doing nothing.

So, if the only symmetry operation that is present is the identity operation; that means, the crystal has no essential symmetry. Of course, it is a crystal. So, the translational symmetry of the crystal is there, but there is no other symmetry of in the crystal. Then, that crystal class is referred to as the pedial crystal class

Now the other possibility in the triclinic crystal system is where you have an inversion axes. So, you have only one symmetry of operation and that is an inversion. So, crystals that have an inversion symmetry and nothing else, their unit cells will be triclinic and they will fall in the pinacoidal crystal class. So, these are the most unsymmetric, where you do not have any symmetry. In the monoclinic you have to have at least a two-fold axes of rotation or a mirror plane ok.

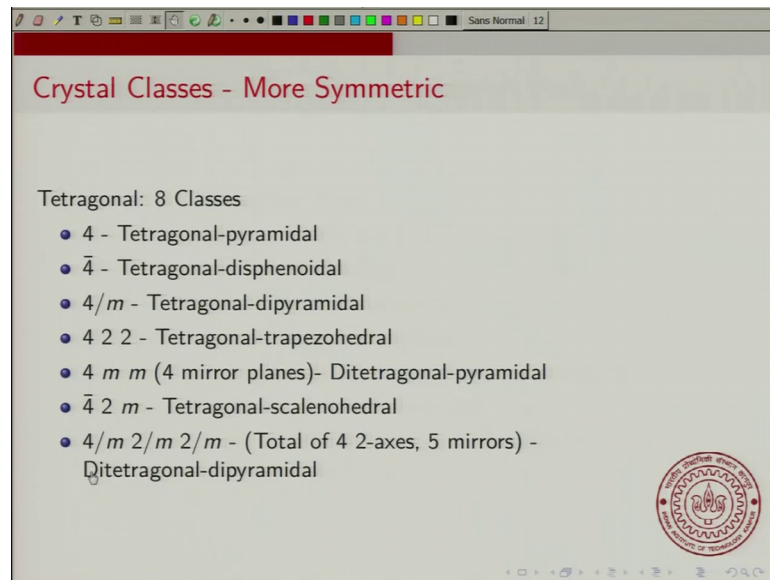
And so, there are three possibilities where if you only have a two-fold axes of rotation in your crystal then it is sphenoidal ok. And it will fall in the monoclinic crystal system it will be sphenoidal it is called the crystal classes referred to as sphenoidal. If you have a mirror on just one mirror ok, then the crystal class is referred to as domatic. Now if you have two-fold axes of rotation and the mirror perpendicular to the axes of rotation, then automatically you that implies that you have an inversion center in the crystal. And the crystals that that only have these symmetries are referred to as prismatic ok. So, the crystal class is called as prismatic ok.

And again there are there are several examples for each of these, I am not going to go into the actual examples ok. Then, but these show that monoclinic there are three possible crystal classes: in triclinic there are only 2 crystal classes ok. So, we see that triclinic there are only 2 crystal classes, whereas in monoclinic there are 3 crystal classes.

What about orthorhombic? Now orthorhombic means, it should have 3 two-fold axes or mirror ok. Now, it can have 3 two-fold axes or it can have 2 mirrors and a two-fold axes or it can have 3 two-fold axes with perpendicular mirrors. And each of these falls in a different class ok. So, again there are 3 crystal classes. These are referred to as rhombic disphenoidal, rhombic pyramidal, and rhombic dipyramidal ok.

So, now, you can see that these groups have only you know 1 two-fold axes of rotation if at all ok. Some of these have no axes of rotation, like the domatic or the pedial and pinacoidal tilde, everything has at least 1 two-fold axes ok. Now let us go to more symmetric crystal classes.

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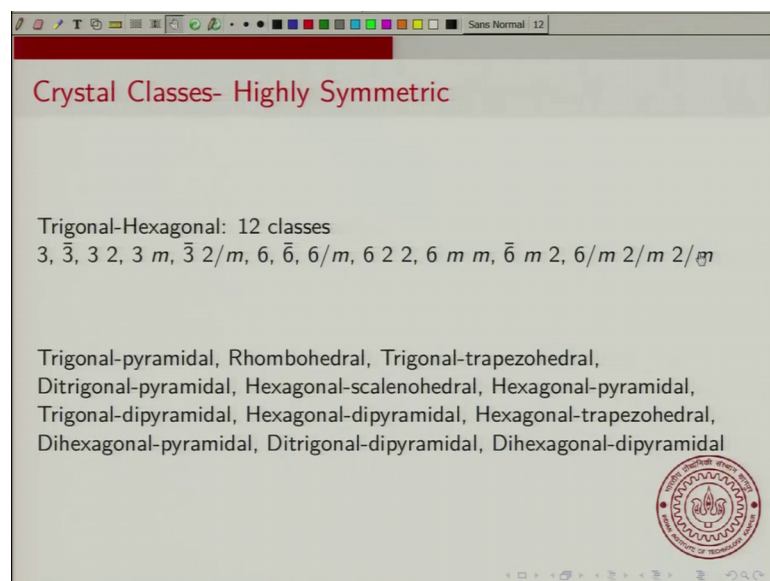
So, now we look at the tetragonal. So, the in the tetragonal there are 8 classes, ok. And these 8 classes are tetragonal pyramidal, tetragonal disphenoidal, and so on. I will not go through all the names ok, but let us see the operations.

So, tetragonal means it has to have a four-fold axes of rotation. So, if it has only a four-fold axes of rotation, then you call it tetragonal pyramidal. If it has a four-fold roto inversion axes, then you call it tetragonal disphenoidal. If it has a four-fold axes of rotation and a mirror perpendicular to it to it then you call it tetragonal dipyramidal. If it has a if it has a four-fold axes and 2 two-fold axes of rotation then you call it tetragonal trapezohedral.

Now if it has tetragonal axes and 4 mirror planes ok; now I am writing only 2 mirror planes we will see soon why we write only two ok. But basically if it has four-fold axes of rotation and mirror planes and 4 mirror planes, then you call it a tetragonal pyramidal or ditetragonal pyramidal. If it has a four-fold in roto inversion axes two-fold axes of rotation and a mirror plane, then you refer to it as tetragonal scalenohedral.

And if it has a four-fold axes with perpendicular mirror and two-fold and two-fold axes with perpendicular mirrors; so actually there is a total of 4 two-fold axes with perpendicular mirrors, and there are and then and there is one mirror perpendicular to the four-fold axes. So, actually there are there are four 4 two-fold axes of rotation and 1 four-fold axes of rotation and total of five mirrors ok. Then you call it a ditetragonal dipyramidal and this is the this is the tetragonal structure with the highest symmetry. So, the tetragonal the tetragonal class crystal class with the highest symmetry is this ditetragonal dipyramidal ok.

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Next let us look at the trigonal hexagonal systems ok. We will look at both of them together, both the trigonal and hexagonal we will look at them two together ok. So now, there are a total of 12 classes, and I am not going to list all of them in detail or describe all the operations in each one of them. But basically trigonal systems are characterized by having a three-fold axes of rotation. Hexagonal is characterized by having a six-fold axes of rotation, ok. Now if you just have a three-fold axes of rotation then it is referred to as trigonal pyramidal. If you have a three-fold roto inversion axes then you refer to it as rhombohedral and so on. If you have a three-fold and the two-fold axes then its trigonal trapezohedral.

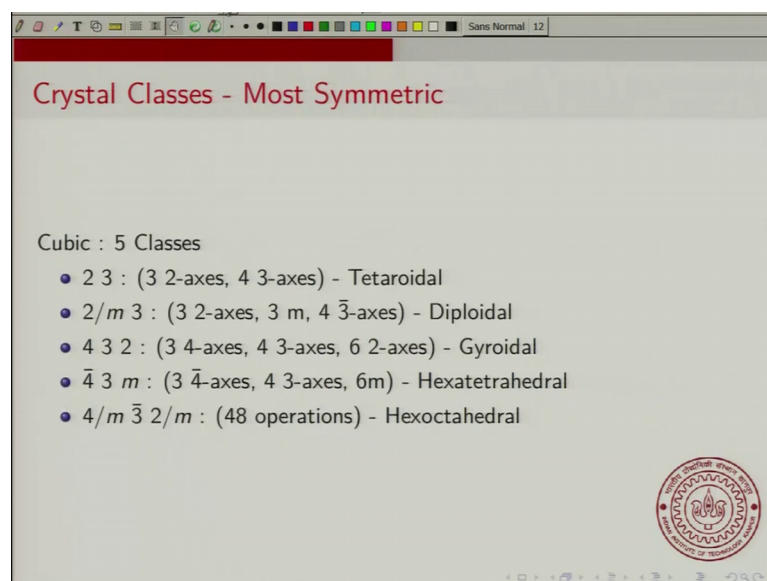
And these names of the various crystal classes are based on the on the shapes of the crystals; on the outer shapes of the crystals ok. So, these are all solid objects, these are

geometric objects that have these are shapes of geometric objects. If you have a three-fold axes and a mirror then it is referred to as ditrigonal pyramidal. So, if you have a three if you have just a three-fold axes there is trigonal it is called trigonal pyramidal. If you have a three-fold axes with the mirror its referred to as a yeah its referred to as a ditrigonal pyramidal ok.

So, similarly you can you can see if you just have a six-fold axes, then it is referred to as its referred to as hexagonal scalenohedral ok. If you have a six-fold rotoinversion axes then its hexagonal pyramidal and so on. You can you can go through the entire list of list of symmetries. Now the die hexagonal dipyramidal has a six-fold axes with a perpendicular mirror and two-fold axes with perpendicular mirrors ok.

So, here there are 12 classes in the trigonal and hexagonal systems. And these are these are in some sense highly symmetric, ok.

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But the most the highest symmetry; the crystal class with the highest symmetry the crystal system with the highest symmetry is the cubic system. And the cubic system is gives the most symmetric classes. There are five crystal classes in the cubic systems, and these have names, ok.

So, in crystal class terminology they have slightly different names then the point group names. But in any case I am just listing these for completeness ok. So, if you have so,

remember a cubic system is characterized by 4 three-fold axes of rotation ok. So, in every case you have to have 4 three-fold axes of rotation. Now if you have in addition to this, if you have 3 two-fold axes then you refer to the system as tetrahedral if you have 4 three-fold axes ok, and 3 two-fold axes and 3 mirrors then you refer to it as diploidal ok.

Notice that, the moment you have 4 three-fold axes, you automatically end up with 3 two-fold axes ok. So, now, this is another property of this. If you have 4 three-fold axes then again just based on symmetry you have to have at least 3 two-fold axes ok. So, you cannot have just 4 three-fold axes because the 4 three-fold axes will intersect some intersect at some point and usually if you take a product of two of them then you will get a two-fold axes ok.

Now this has a two-fold axes with a perpendicular mirror, and in addition to the 4 three-fold axes ok. Now notice on the left I am not writing all the symmetry elements I am just writing this  $2/m\bar{3}$ , and again this will become clear ok. So, it turns out that only this two-fold axes with the perpendicular mirror and a three-fold axes will that is sufficient; you will automatically because of this three-fold axes and this mirror you will generate you will generate a total of 3 mirrors, and actually there are 3 two-fold axes that are generated again because of this three axes ok.

In this case it is a  $\bar{3}$  axes, as opposed to a 3 axes. This is referred to as diploidal. Then you could have 3 four-fold axes, 4 three-fold axes. And 6 two-fold axes; this is called gyroidal then you could have.

So notice here there are no mirrors ok. So, in this gyroidal system there are no mirrors there are only; but there is four-fold axes, three-fold axes, and two-fold axes, but there are no mirrors ok. And again this four this 3 four-fold axes, 4 three-fold axes, and 6 two-fold axes is still this these numbers 3 4 6 are fairly standard ok.

Now in the case of hexatetrahedral you have the 3 four-fold axes, but now they are 4 bar roto inversion axes, you still have the 4 three-fold axes. And instead of having the 6 two-fold axes or the two-fold axes that you had in the case of gyroidal you have 6 mirrors ok. And this is referred to as hexatetrahedral ok.



And finally, this is the axes that we have seen before ok. So, you have a four-fold axes and a perpendicular mirror, and then you have three-fold roto inversion axes, and you have a two-fold axes and a perpendicular mirror ok. This is a 48 option operations that you saw in the case of cubics; of the face centered cube and the body centered cube ok. This is referred to as hexaoctahedral ok. And this is the highest symmetry that you can get. This is in some sense the most symmetric crystal class ok.

So, with this we complete the discussion of the 32 crystal classes, and I just want to make couple of points ok. I do not expect you to remember the names of all these 32 crystal classes. However, I do expect that you remember that the cubic crystal has 5 classes, and you should know some important crystal classes; like the hexaoctahedral or the gyroidal and so on ok.

Similarly, I would expect that you know that the trigonal hexagonal crystal class; trigonal hexagonal systems have a total of 12 classes. And that similarly the tetragonal has 8 classes, and the triclinic has 2, the monoclinic has monoclinic and orthorhombic have 3. So, some general information I expect you to know. Similarly I would expect that at least for the triclinic monoclinic and the orthorhombic you should know what are the various possibilities of to the crystal classes ok. So for example, triclinic can have only an inversion or nothing, the monoclinic can have a two-fold axes or a mirror and a mirror or both and so on ok

So, some basic information I expect you to remember. However, I do not expect you to remember the 8 classes in the tetragonal ok you should you should know that a tetragonal system has this four-fold axes of rotation ah, but I do not expect you to know all these 8 classes. Similarly I do not expect you to know the 12 classes of the trigonal hexagonal systems, but I would expect you to know the 5 classes of the cubic systems, ok. So, I would expect you to know that these are the 5 possibilities and that these are the 5 crystal classes.

So, I will conclude this first lecture of week six here, ok. Now and in this lecture I have tried to show how the 32 crystal classes can be derived based on symmetries. And I have used some part of the crystallographic notation ok, that we will discuss in more detail in the next, in the remaining part of this week ok.

Thank you.