Lecture No. – 04
Arrangement of Atoms in Crystal Lattice

Welcome again to the new lecture of fundamentals and applications of dielectric ceramics. So, we will just briefly recap what we did in the last lecture.

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In the last lecture, we looked at the concepts related to Bravais lattices, 14 Bravais lattices, basically, which is a combination of primitive and non-primitive lattice of seven crystal systems. And then, we looked at briefly what planes and directions are in the crystals which basically follow Miller indices convention. And then, we just introduced what kind of bondings we have, as it happens in dielectric ceramics, most of the ceramics are ionically-bonded materials.

Partially, they could be covenant in certain cases, but by and large they are predominantly ionic in character. And this ionic bonding provides them strong bonds. As a result, they are very strong materials. They have low coefficient of thermal expansion. They have high melting points generally, but they are also brittle. And it is also because of the same reason that they also have low electrical and thermal conductivity, and that is why they are dielectrics.

And then we looked at packing of atoms because in solids, quite important role in determining the structures of these materials. So, we looked at packing methods which can lead to simple cubic structures, body-centered cubic structures, then we looked at hexagonal close-packed structures, and then we looked at cubic close-packed structure considering that all the atoms are spherical in nature.

So, these are not close-packed, but loosely-packed structures, but these packing sequences are possible, and they are observed in some solids and these are basically closed packed, okay? So, the packing ratio increases as you go from simple cubic to body-centered cubic to hexagonal cubic close-packed, but assuming that they are all same atoms, monoatomic crystals. If you have non-monoatomic crystals, then the packing density will change depending upon the size of atoms.

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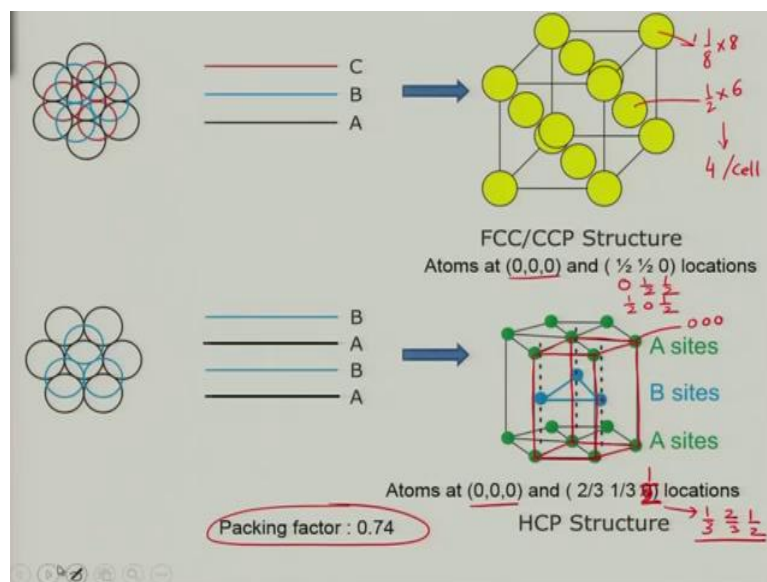
So, ABC, ABC kind of packing sequence, as we have drawn on the left, can be best described in terms of symmetry by a face-centered cubic structure. Crystallographically speaking, the cubic close-packing structure is also called a face-centered cubic structures, although here we have shown these atoms a little bit far from each other, in reality they are touching with respect to each other. And this is basically FCC/CCP structure where atoms are placed at (000) kind of positions and (1/2,1/2,0).

(1/2,1/2,0) will basically mean you have (1/2,1/2,0), (0,1/2,1/2), (1/2,0,1/2). So, you have eight atoms at the corners which means 1/8*8. You have face-centered six atoms which means ½*6 because each face is shared by two unit cells and each corner is shared by eight unit cells. And

this will give rise to a total of four atoms per unit cell. ABC, ABC kind of packing gives you a different structure.

It is called as hexagonal close-packed structure. So, this is the bottom layer which is the A side, and the light blue color is the B side atoms, and then you have A side again on top. This is how ABAB stacking takes place in one unit cell which is this one unit cell here, the one drawn in the red. So, in this case, the atoms are located at (0,0,0). So, these are (0,0,0) kind of positions.
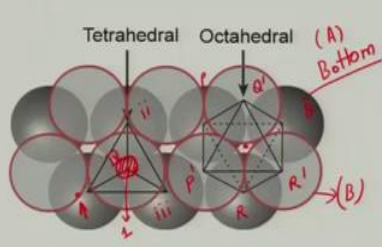
And then you have another atom sitting here which is 2/3, 1/3 and 1/2, not 0, but it is 2/3, 1/3 and 1/2 locations. So, all these corner atoms can be depicted at (0,0,0) and one in the centre can be depicted as (2/3,1/3,1/2) or you can also write it as (1/3,2/3,1/2) depending upon how you look at the unit cell, but both of them are identical sort of situations, okay?

So, these are the two structures that you find when you have close-packed structures and this packing factor, if you have monoatomic crystal, is about 0.74 and this can be found out easily by looking at the volume of atoms, all the atoms in one unit cell divided by the volume of the unit cell and you will easily find the packing factor which is a trivial exercise.

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Now, since you can see that all of these structures they do not fill the space completely, simple cubic has a lot of gaps in it, body-centered cubic has a lot of gaps in it, face-centered cubic crystals have a lot of gaps in it, which means you have holes in them. And what are these holes

useful for? These holes are called as voids or interstices. They are useful because often they contain impurities. There are smaller impurities such as carbon in iron.

They can go and sit in there, and this is useful because carbon in iron is the one which provides strength to iron, otherwise, iron will be very weak. So, these interstices or something and these interstices are even more important in case of oxides in case a dielectric materials because in dielectric materials what happens is that dielectric materials is a combination of cations and anions which are ionically bonded.

Generally speaking anions are bigger as compared to cations, so what happens is that anions generally form the base lattice and the cations sit in the interstices which are present in these base structures and that is why the concept of interstices is very important and you need to understand what these interstices are. So, in a closed-packed structure, if you put a layer of atoms like this, so this is the bottom layer, let us say A, and this is B, at the top, okay?

So, you can see that depending upon how the layers are formed, in the configuration that I have shown here, if you look at, for example, the first layer is covering. You can do this experiment at home. You take several marbles, okay? You put the marbles on a plane, just fill it completely, and then take another layer of marbles and put on top of the first layer of marbles, what you will see is that, for example, if you pick one marble in the top layer, the marble in the top layer will sit on a vacant space which is lying at a lower position than the top surface of the atoms in the bottom layer.

Let us say this was the point 1 that we described earlier, okay. So, this vacant space between the three atoms in the bottom layer and the one atom which is resting on top above these three atoms is called as, so you can see that this point here is coordinated by the atom, I cannot write, A may be, maybe I can write roman letter i, ii, iii, and iv on the top. So, these four items surround this little void in the centre of this polyhedron that I have formed.

This polyhedron is called as a tetrahedra and this void which is present in this is called us tetrahedral void because it is surrounded by four atoms. So, this is a tetrahedral void which has for coordination, which has 4-fold coordination or four atoms surrounding it. And, of course, you can make a small atom sit inside it and you can easily calculate using the geometry of tetrahedra, the size of this atom will be 0.225 of the host atom.

So, if r is the radius of host atom, then the maximum size you can accommodate inside this hole or void without displacing the host atoms will be 0.225 r. So, if you have an atom of radius, let us say, 0.3 r which means you will have to displace the host atoms a little bit, okay? In the same structure you form another void as well. So, if you look at this configuration now, here you have, let us say, P, Q, R, okay, and secondly we have P prime, Q prime, and R prime.

They also form a void here. So, the void between these is located here and this void has now six neighbors. And the polyhedra which is formed by connecting the centers of all these atoms is called as octahedra and the void is called as octahedral void. Octahedral void basically means it has six neighbors and octahedra will mean it has eight faces, okay? So, basically it is octahedra-shaped polygon.

It has eight faces, and again you can calculate the size of the atom that will sit inside this octahedra easily using geometry, and this size will turn out to be 0.414 of the radius of host atoms. So, the maximum size you can put in there without displacing the host atom is point 0.414 of the radius of host atom, and these can be easily visualized especially in a cubic close-packed structure.

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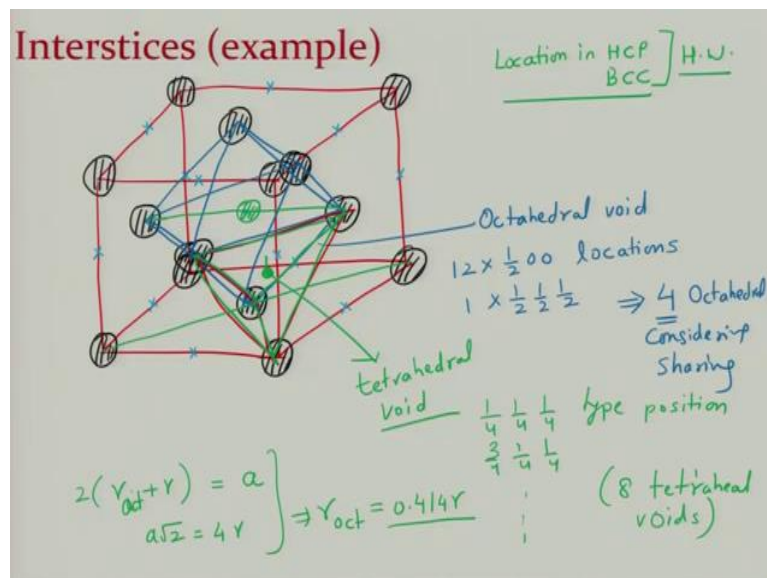
So, let us see how you can visualize them in a cubic close-packed structure. So, this is a unit cell that I am going to draw. For the sake of clarity I will not make the atoms touch each other. I will rather draw atoms which are a little away from each other. So, this is first atom, second

atom, third atom, fourth atom, fifth atom and then I will place atoms at the, so this is a face-centered cubic unit cell.

Now, in this the octahedral voids are located at positions which are marked by these Xs, okay, and there will be one at the body centre. So, the easy one is, I can draw one octahedra for the sake of illustration. So, if I connect this atom with the atom here, atom with here, the atom here, and the atom here, okay, and if I connect the dots with respect to this, that, that. So, this is the body which is called as octahedral void.

So, octahedral voids in FCC structure they are located at (1/2,0,0) locations which means edge centers and one at (1/2,1/2,1/2). So, there are 12 edges. So, 12*(1/2,0,0) kind of locations and 1*(1/2,1/2,1/2). But each edge is shared by four unit cells. As a result, there are four octahedral voids in total considering sharing, okay, all right? Now, how to draw the tetrahedra. Tetrahedra is again very simple.

Tetrahedra is basically formed by atoms. So, if I connect this atom, if I connect this atom, and if I connect this atom, and I put all of them together, then I form a body which is called us tetrahedra. So, let me just use a different colour maybe, I can use a green colour. So, this is the tetrahedra that we formed, and this atom which sits inside the tetrahedra will be tetrahedral void.

Tetrahedral voids in FCC structure are located at (1/4,1/4,1/4) type of positions. So, you have (1/4,1/4,1/4) you can have 1/4, 1/4, and various combinations. So, you will have basically eight tetrahedral voids, okay? In the previous slide we saw that maximum size of the atom that can be put inside these octahedral and tetrahedral voids is, in octahedra it is 0.414 r and tetrahedra is 0.225 r.

This is the maximum size that you can put inside them without displacing the atoms and this can be very easily calculated. For example, for an octahedra it is very easy. For octahedra this is the size that you are putting in there. So, basically, if all the atoms are touching each other, then you can say that $2(r_i + r) = a$, okay? And what is a in terms of r, because atoms are touching each other, $a\sqrt{2} = 4r$.

And if you just substitute this, you will find r octahedra to be equal to, this is let us say r_{oct}, okay? This will be equal to 0.414 r. Similarly, you can also find out what is the tetrahedral size. So, as a home exercise, your job is to now work out what will be the locations in HCP and BCC structure. This is your homework, okay, and also you can calculate the size of atoms which are present there, okay.

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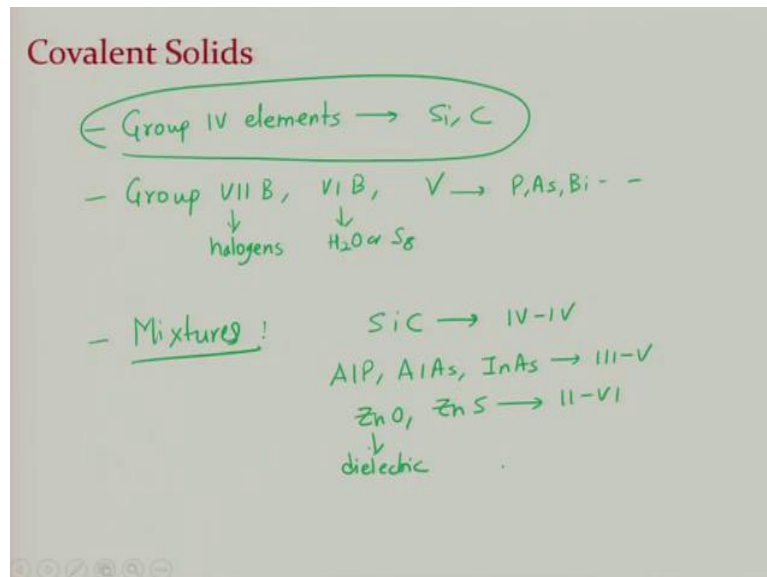
So, now, having done this interstices thing, let us just go to some of the examples of covalent solids, because now we are moving towards dielectric structures, so we will just look at some of the examples of covalent solids. Basically you can say there are group VI elements such as silicon, carbon, which are covalently bonded. Then, we have also group VII B, VI B, and V elements which are also covalently bonded.

So, VII B will be basically halogens, okay? VI B be will be basically, you can say, H_2O, or you can say sulfur S_8 molecule. And group V will mean you have phosphorus, arsenic, or bismuth, etc., they are all covalently bonded. But the most famous example of covalently-bonded solids are these group IV elements, silicon, carbon, etc. And then we have mixtures which also form covalently bonded and which are basically compounds.

And these mixtures could be silicon carbide which is a IV – IV compound. You can also have aluminum phosphide, aluminum arsenide, and indium arsenide which are also III-V compound. You have zinc oxide, zinc sulfide which is II-VI compound. Zinc oxide is a dielectric material and we will see what its structure is and so on and so forth. There are multiple examples of these covalent solids.

Oops, I think I had it written anyway.

So, basically, in this, the covalent bonding is because of hybridization of orbitals. So, if you combine 2s orbital with a 2p orbital, you will have 2sp hybridized orbitals and, as a result, you will have different kinds of hybridization that will occur.
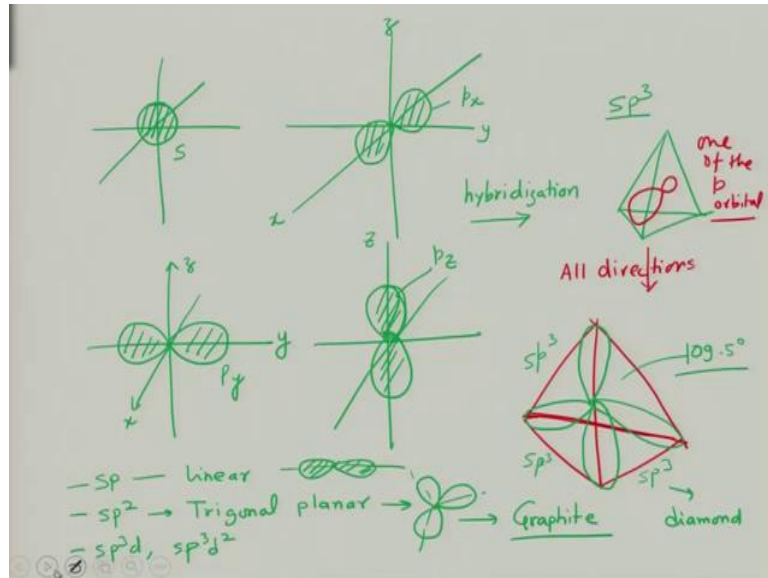
So, if you look at the hybridization schemes in covalent solids, so if you bring in s orbital, s orbital is spherical in nature, this is s orbital, okay, and then you bring in what we call as, let us say, p x orbital. So, if this is x-axis, this is y, this is z, then let us say this your p_x, okay, and p_x and you can have p_y as well. So, if you have along this axis, you will have p_y. So, this is y, this is z, this is x, this is p_y and you will also have p_z.

They are not spherical in nature. They have sort of this kind of shape. So, this is p_z and if you make them hybridize, so now let us go to process of hybridization. Hybridization normally leads to formation of structures which are a little asymmetric in shape. So, you can you can have formation of sp^3 hybridization. So, SP3 hybridization will generally lead to sort of tetrahedral kind of shapes.

In this case, what we will have scheme something like this. This is sp^3 hybridization that we will have. So, we will have sp^3 along one direction, second direction, and the third direction. Eventually, if you consider all the three directions, okay, so this is for one direction, okay, one of the p orbitals, okay? And if you consider all the three orbitals, then the shapes that you will form is basically something like this.

So, inside this you will have one like this, another like this, another like this, and another like this. So, this is how you will have sp^3 hybridization that will occur inside these materials. So, this is sp^3 along this, sp^3 along this, and sp^3 along that. So, this is how you will have all the hybridization and this hybridization also leads to angle that you will get 109.5 degrees that you get in these solids. So, hybridization can be various types.

What we have drawn is sp^3 hybridization which is basically tetrahedral kind of configuration. But, in reality you can also have sp hybridization which is a linear hybridization scheme. There is a possibility of sp^2 hybridization which is trigonal sort of planar. sp^3 what I have drawn is here and you have possibility of sp^3d, you can have sp^3d^2 as well, okay?

These are the possibilities. So, in the linear case you will have this kind of hybridization. In the planar case you will have this kind of hybridization. This is a planar one. So, sp^3 happens in case of, for example, diamond and sp^2 will happen in the case of things like graphite, okay? Graphite is sp^2 bonded and carbon diamond is sp^3 bonded.

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So, now, if you look at the structure of these materials, we have these covalently bonded solids in diamond. So, in case of diamond because of sp^3 hybridization and it is covalently bonded, it has four neighbors. So, as a result, it is tetrahedrally bonded. So, what we have is basically carbon making FCC lattice and four carbon atoms are tetrahedrally bonded, sp^3 hybridized to these atoms.

The way it happens is that each carbon atom whether you look at this atom, whether you look at face-centered atom of whether you look at the one which is sitting inside the tetrahedra, all of them are tetrahedrally coordinated, okay? So, if you look at the top view, top view is like this. This is the unit cell. This is the base unit cell. 01, 01, 01, 01 these are the corner atoms. You can see x and y.

So, this is x, this is y, and the z is perpendicular to plane, right? So, x, y position is obvious, z position is written, all right? So, you can see that these are atoms at face centers. These are corner atoms. These are the ones which are tetrahedrally coordinated atoms. We can see that this atom sitting here will coordinate with one of the atoms. So, this is what is this atom. We have drawn this tetrahedral.

It is coordinating with one of these atoms, one of the face-centered atoms. On the other side, on the face-centered atom this side and one of the face-centered atom on this side. So, it is coordinating with these four atoms. Now, crystallographically speaking, even these atoms which are sitting here they are also coordinated. So, instead of drawing the lattice corner here, suppose if I draw the lattice corner here, then if I take 1/4 position as 0 position, then this will become 0 and 1.

This will become half. There will be identical atoms sitting here. This will be at (0,1). What will this convert to. This will convert to tetrahedral position that is 1/4 position. This is at half. This will convert to 3/4 position. So, basically, all the atoms are tetrahedrally coordinated, whether you look at the one that is sitting on face-centre of the corner or whether you look at look at the one which is sitting at the tetrahedral void.

So, essentially diamond cubic structure is basically a combination of two FCC lattices of carbon, one shifted by 1/4, 1/4, 1/4 with respect to other, okay? So, you have two cubes. The second cube is shifted with respect to the first one by 1/4, 1/4, 1/4, and you can see that since carbon makes FCC lattice theoretically speaking there are eight tetrahedral voids but only four of them are occupied.

You cannot make eight of them occupied. If you make eight of them occupied, the problem is one carbon atom will have four neighbors, but the second one will have eight neighbors and that will violate the bonding. So, as a result, you will have only four tetrahedral voids filled, not eight.

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Layered Structure of Graphite

(Source: Wikipedia)
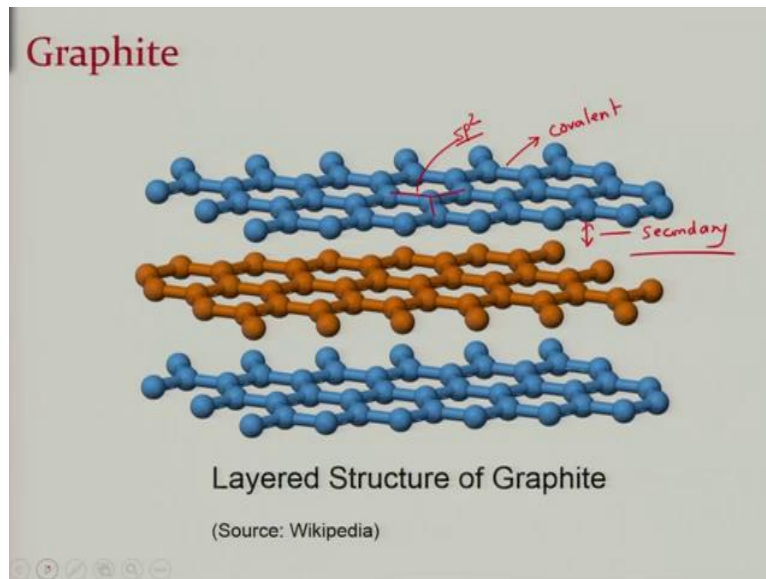
So, this is diamond structure. You can have graphite in which carbon is bonded by these three atoms, sp^2 hybridized. So, this is covalent bonding within the layer, but between these we have secondary bonding and that is why carbon is very hard because of its directional nature, it is very hard, but graphite is loose. It is a layered material. It is used as a lubricant in many cases. So, this is what we have in terms of diamond.

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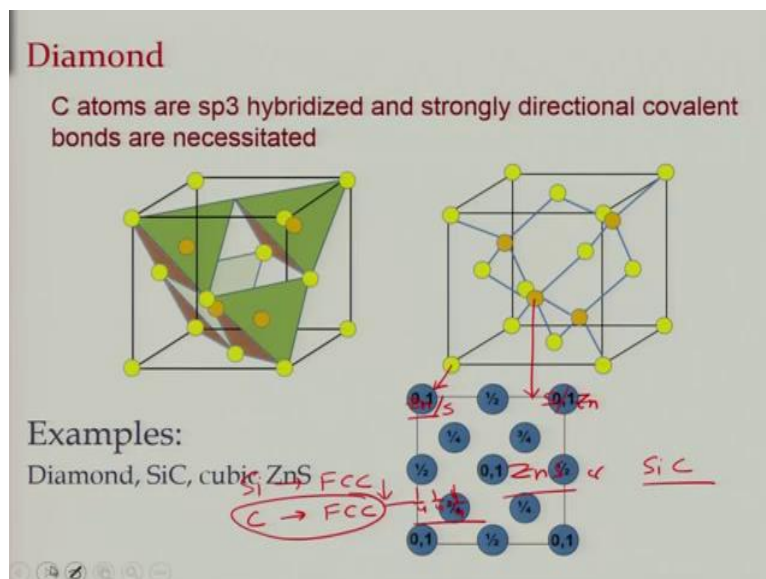
Because of its sp^3 hybridization and strongly directional covalent bonding diamond is a very hard material. So, other materials also form this kind of structure. So, if you replace this carbon sitting in a tetrahedral void by let us say sulfur and carbon by zinc or zinc by carbon, this could be zinc as well, then this makes zinc sulfide. Similarly, you can have silicon carbide. Silicon carbide and zinc sulfide also make the structure.

So, there is a one FCC lattice of silicon and second FCC lattice of carbon. So, they So, this second FCC lattice of carbon is shifted by 1/4, 1 / 4, 1/4 with respect to the first lattice of silicon and same is true for zinc sulfide. So, these are the forms of carbon that are covalently bonded forms of carbon.

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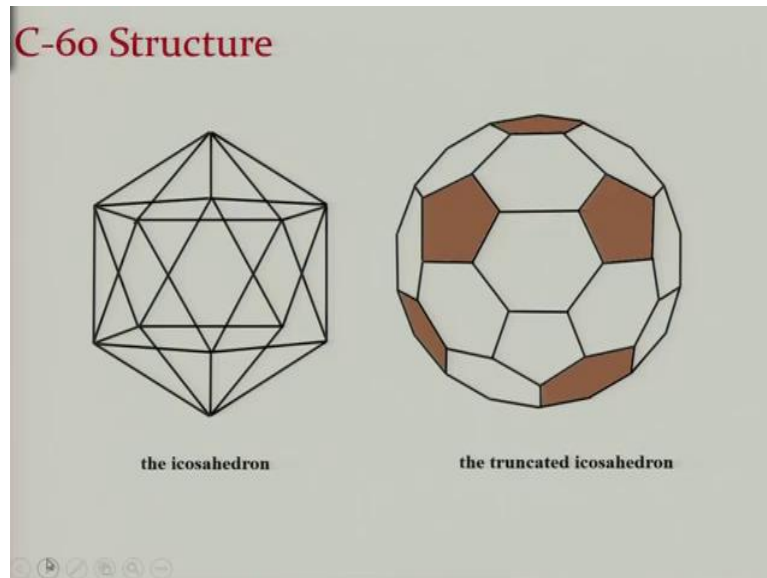
And one final one is the C-60 structure which is basically a truncated icosahedra. Icosahedron is a polyhedral drawn here and C-60 is basically, if you truncate the corners, since some of the corners have 5-fold rotation, other corners have 6-fold rotation. So, you will see arrangement of pentagons and hexagons. It is like a Bucky ball or football shaped structure. This is a C-60 structure. So, we will stop here today.

What we have discussed is the structure of these covalently bonded solids which are primarily decided by bonding, because of directionality in the bonding hybridization that is required. The dielectric ceramics on the other hand are typically ionically bonded predominantly which is based primarily on filling of ions, and so we need to understand how do they form in the next lecture. So, we will stop here. Thank you very much.