Fundamentals and Applications of Dielectric Ceramics
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Lecture No. – 03
Basics of Crystallography and Bonding

Okay, so, welcome to this new lecture of fundamentals and applications of dielectric ceramics. Let us just briefly recap yesterday's lecture.

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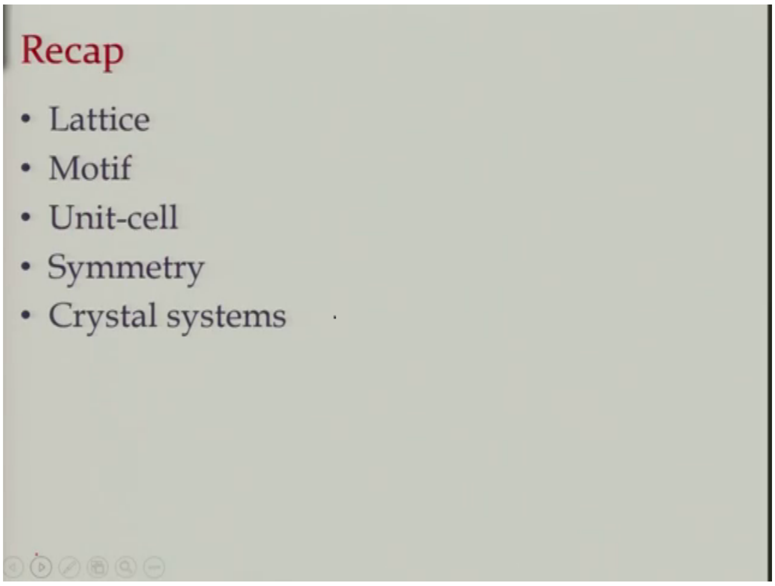

Recap

- Lattice
- Motif
- Unit-cell
- Symmetry
- Crystal systems

So, we learned about the concepts of lattice; what a lattice is, basically point lattice. And then we also looked at the concept of motif which is basis which could be an atom, group of atoms, molecular unit, etc., and when you combine point lattice and motif you will make crystal lattice. And then we also briefly looked at what a unit cell is, what symmetry operations are in space, and when you put the constraint of the symmetry operations you derive what we call as crystal systems.

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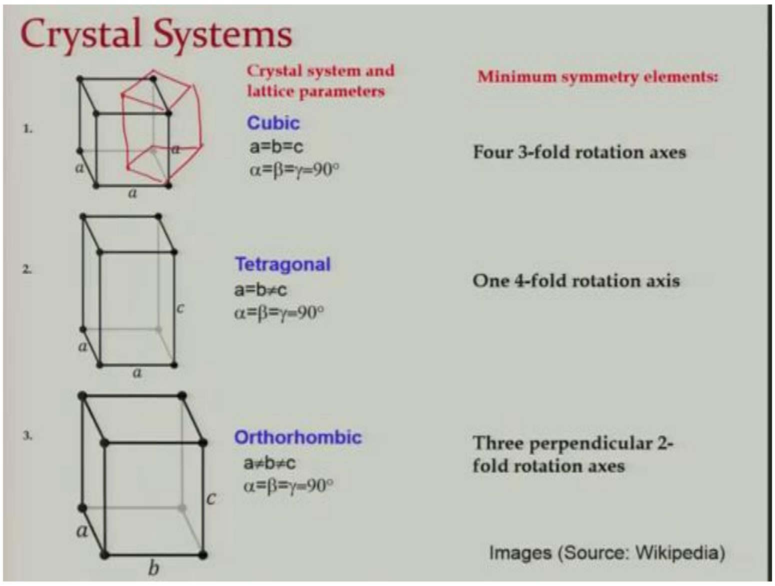

Crystal Systems

	Crystal system and lattice parameters	Minimum symmetry elements:
1.	**Cubic** a=b=c $\alpha=\beta=\gamma=90^\circ$	Four 3-fold rotation axes
2.	**Tetragonal** a=b≠c $\alpha=\beta=\gamma=90^\circ$	One 4-fold rotation axis
3.	**Orthorhombic** a≠b≠c $\alpha=\beta=\gamma=90^\circ$	Three perpendicular 2-fold rotation axes

Images (Source: Wikipedia)

So, just to briefly recap. You have seven crystals systems. Out of these seven crystal systems, first one is cubic which must have four 3-fold rotation axes. This is the minimum symmetry requirement and the lattice parameters are defined as a = b = c and alpha, beta, gamma are all equal to 90 degrees. If you distort this a little bit along c axis, then c lattice parameter goes different. So, a is still equal to b but both of them are not equal to c, but alpha, beta, gamma are again 90 degrees.

So, because of change in lattice shape, now, the symmetry requirement has changed. This structure is called tetragonal. It must have one 4-fold rotation axis which is along perpendicular to c-plane or perpendicular to 001-plane. Then, if you distort it further, when a is not equal to b is not equal to c, but again angles remain 90 degrees, then it becomes orthorhombic and it must have three perpendicular 2-fold rotation axes. So, three axes perpendicular to every face. So, these are all orthogonal systems.

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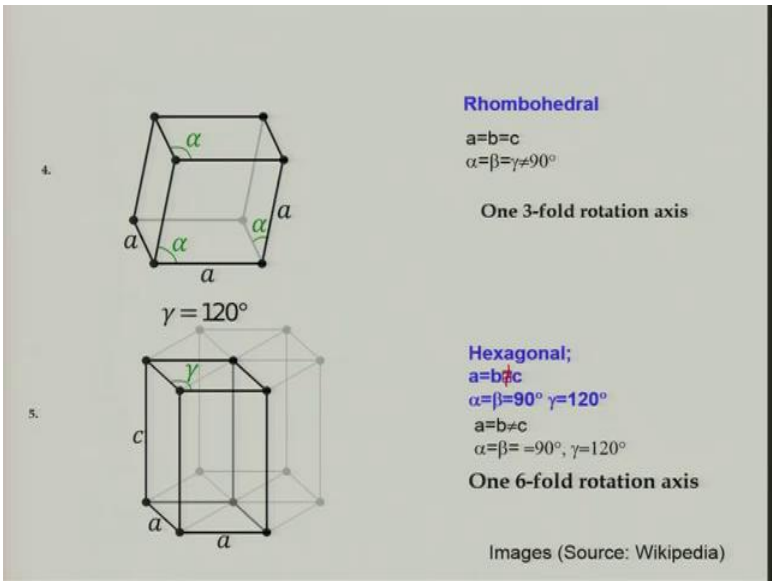

4.

Rhombohedral

a=b=c

α=β=γ≠90°

One 3-fold rotation axis

γ=120°

5.

Hexagonal;

a=b≠c

α=β=90° γ=120°

a=b≠c

α=β= =90°, γ=120°

One 6-fold rotation axis

Images (Source: Wikipedia)

Then, we have non-orthogonal systems where we have rhombohedral where a, b, and c are equal but α, β, γ are equal but not equal to 90° and the minimum symmetry that you require for this is one 3-fold rotation axis and 3-fold by default is along [111] axis. Then, we have this hexagonal system.

So, this should be not equal to c. In the hexagonal system, you're $a = b \neq c$ and $\alpha = \beta = 90°$ and $\gamma = 120°$. So, γ is the angle between a and b, whereas α and β are angle between b and c and a and c. This must have 6-fold rotation axis as you can see that if you rotate it by 90°, you will repeat the unit cell.

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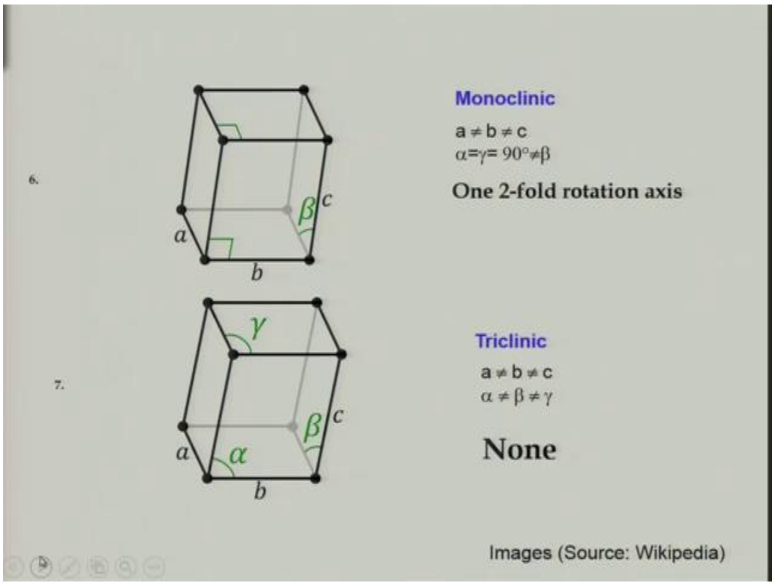

6.

Monoclinic

a ≠ b ≠ c

α=γ= 90°≠β

One 2-fold rotation axis

7.

Triclinic

a ≠ b ≠ c

α ≠ β ≠ γ

None

Images (Source: Wikipedia)

And then, the other two are monoclinic and triclinic. Monoclinic you have one 2-fold rotation axis minimum symmetry requirement, but a, b, c are all not equal. Two of the angles alpha and gamma are equal to 90 degrees but they not equal to beta which means beta is not 90 degrees. As a result, it has a 2-fold rotation axis. Then, we have triclinic where a is not equal to b is not equal to c and alpha is not equal to beta is not equal to gamma. It does not have any symmetry element.

It has just 1-fold symmetry which is considered as no rotational symmetry at all. So, this is the basis of defining various shapes into seven crystal systems and the basis is symmetry. So, for example, if you look at the cube. I will just give you this example, when you say cube must have four 3-fold rotation axes, so this has 3-fold rotation, four of them along body diagonals which is called as 111 axis in the Miller indices form. But if you put an atom, for example, here and here, then you lose the 3-fold rotations.

So, it does not remain a cube. Even though it looks like a cube it does not remain like a cube. So, instead, it converts into a tetragonal unit cell. You can make a smaller tetragonal unit cell like this and there will be one on the other side. So, this is how you will make a smaller tetragonal unit cell with 4-fold rotation. I am not going through details of this as I said you can look at the other course which is nature and properties of materials, structure of materials part one for details of crystallography and symmetry.

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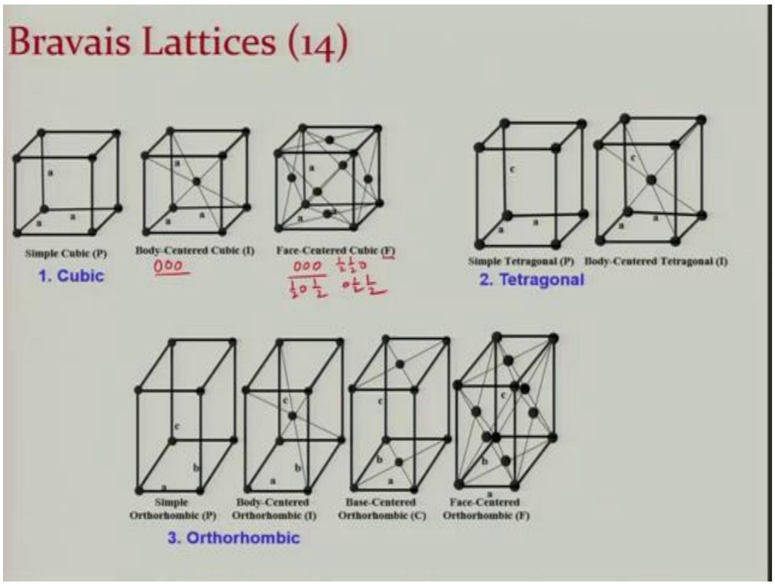

Bravais Lattices (14)

So, these crystal systems are further divided into, now that you know the concept of primitive and non-primitive lattice; primitive lattice is the one with one lattice point, non-primitive lattice is the one with more than one lattice points. You can define them into several primitive and non-primitive shapes and this is mainly because of symmetry considerations, because sometimes what happens is that non-primitive shapes they have higher symmetry as compared to primitive shapes.

So, the cubic can be divided into three categories. One is simple cubic where you have lattice points only at the corners, and if you put a lattice point at the center of the unit cell, then it becomes body-centered cubic. It is represented as I in the crystallography notation. So, motif for this would be 000 and I means there will be one lattice point at 000, another will be at half half half, by default it means.

Similarly, you can have another form which is face-centered cubic where lattice points are not only present at the corners, but also at the face centers of the unit cell, and this is represented as F and here again the motif is at 000. What it means is that automatically you have lattice points at half half 0, half 0 half, and 0 half half. So, that is automatic. Similarly, in tetragonal you have only two options. One is simple tetragonal and body-centered tetragonal.

Simple tetragonal you have again at the corners, body-centered tetragonal you have lattice points at the corners of the cell as well as at the center of the cell. You can see that there is no face-centered tetragonal here and it is an interesting exercise to work out why do not you have a face-centered tetragonal which we have discussed in more detail in the other course in structure of materials. Then, we have orthorhombic system. This can be classified into four Bravais lattices. So, one is simple orthorhombic with lattice points only at the corners.

Then, we have body-centered orthorhombic where lattice points are at corners as well as body center. Then we have base-centered orthorhombic or C-centered orthorhombic as we call it where one lattice point is present at two of the opposing faces, but four of the faces do not have any lattice points. Finally, we have face-centered orthorhombic as well which is presented as F. You can see that these are nine Bravais lattices. There are five more Bravais lattices based on other systems.

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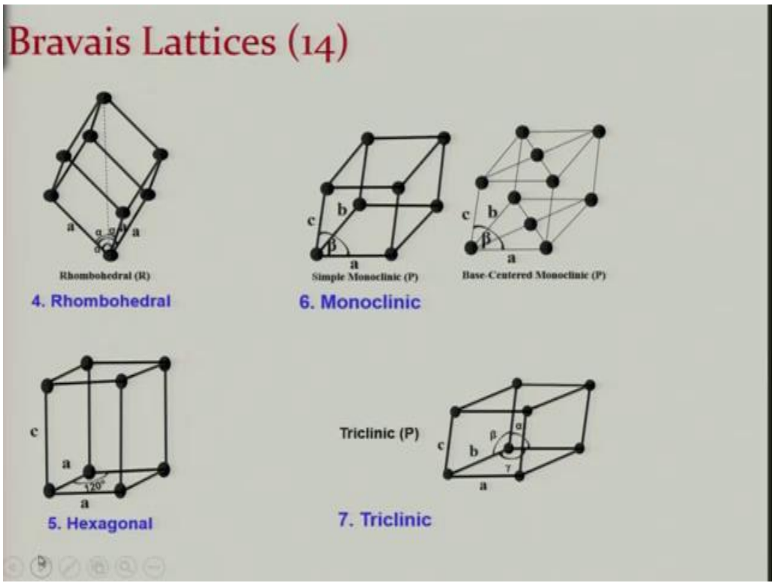

Bravais Lattices (14)

4. Rhombohedral

6. Monoclinic

5. Hexagonal

7. Triclinic

So, we have rhombohedral. There is no other Bravais lattice. It is only primitive rhombohedral that we have. Again, in hexagonal system also we only have primitive hexagonal. In monoclinic not only we have simple monoclinic which is primitive P, but we also have a base-centered monoclinic which has a lattice point at the center of two of the faces and this is basically a,b face or a,b plane.

And then we have triclinic. It does not have any other variant. It only has simple primitive triclinic as its variant. So, these are 14 Bravais lattices. You might ask questions why do not you have 15 or 16 or 17? But then, it remains an interesting exercise to work out why do not you have more than 14 Bravais lattices. Partially, the answers are given in books as well as in the other MOOC course on structure of materials.

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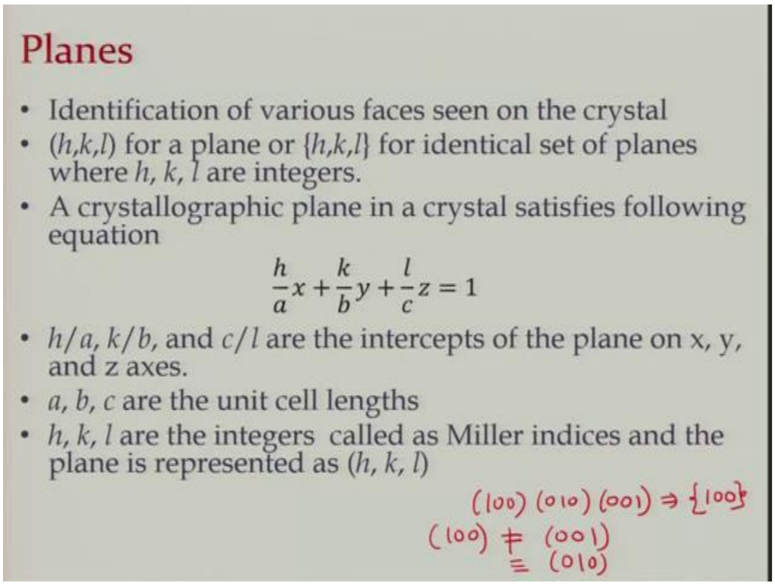

Planes

- 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)

$(100)\ (010)\ (001) \Rightarrow \{100\}$

$(100) \neq (001)$

$\equiv (010)$

So, this sort of brings us close to the essential crystallography that is needed to understand the structure of dielectric ceramics. The other thing that you need to know is the planes and directions. Planes means you need to have a mechanism to identify various faces on a crystal and they are generally depicted by these indices which are h,k,l for a given plane. And if you these round brackets, which means it is for a plane.

And if you have these curved brackets, it means they are for identical set of planes. Identical set means they are crystallographically identical planes and that depends upon the crystal system. For example, for a cube, (1 0 0) is equivalent to (0 1 0) is equivalent to (0 0 1) and you can write all of them for a cube (1 0 0), (0 1 0), (0 0 1), all of them can be written as (1 0 0) because they are identical. But for a tetragonal system (1 0 0) is not identical to (0 0 1) but is identical to (0 1 0). So, you cannot write (1 0 0) as (1 0 0) for all the three planes.

So, that is why there is a distinction. So, you cannot use it loosely, you have to use it very carefully. Crystallographically speaking, if you have a plane in a crystal that satisfies this equation where

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

and basically these h/a, k/b, l/c are the intercepts of the plane on x, y, and z axes, a, b, c are unit cell lengths, and h, k, and l are just integers.

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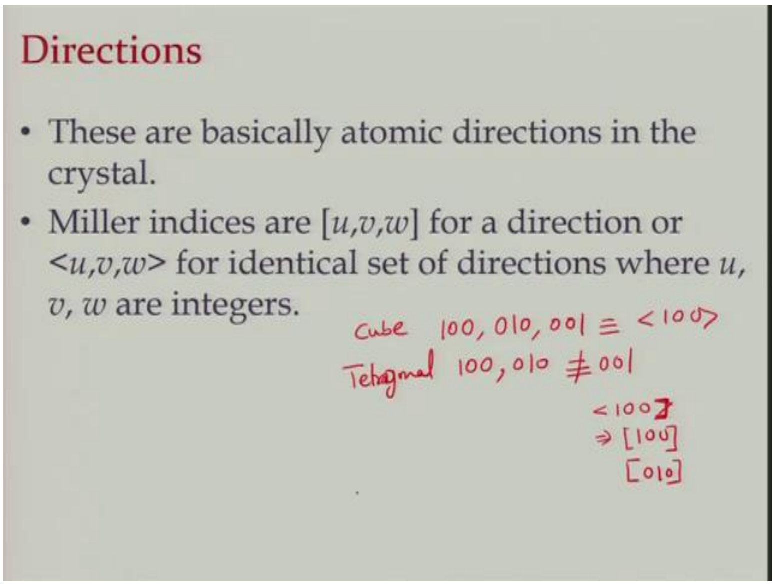

Directions

- 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.

Cube 100, 010, 001 ≡ <100>

Tetragonal 100, 010 ≢ 001

<100>

⇒ [100]

[010]

We will just look at one or two examples of how to determine or draw a plane. Directions are essentially vectors, they are atomic directions, and they are written as u, v, w for a direction.

Again, in the triangular brackets, if it is u, v, w in the triangular brackets and identical set of directions. So, again, as I said, for a cube, [1 0 0] direction, [0 1 0] directions, [0 0 1] are all identical for a cube and you can write them as <1 0 0>. But for a tetragonal system [1 0 0] and [0 1 0] are identical but they are not identical to [0 0 1] and hence [1 0 0] you write it as like this <1 0 0]. So, this will imply 1 0 0 and 0 1 0 only, okay?

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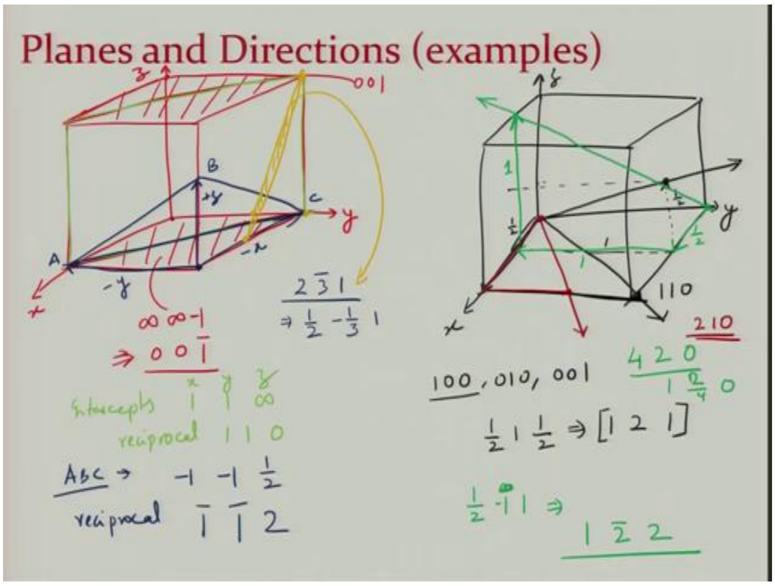
Planes and Directions (examples)

Now, how to draw the planes and directions, I will just give you a brief example. So, let us say you make a parallelopiped, let us say this is our x-axis, this is our y-axis, this is the convention to draw x,y,z. Let us say, I want to determine this plane, the one which is there. This plane, as you can see, if you look at the intercept on x,y,z axes, for this the intercept on x is parallel to x-axis which means intercept for x is infinity, parallel to y-axis which means intercept on y is infinity.

For z, this is equivalent to this plane, so basically, you can say that intercept is equal to 1. You can keep your origin here. Here, the choice is given to shift the origin. So, you can shift the origin in a unit cell. Since you cannot determine the intercept by keeping the origin here, you shift the origin here. So, you keep the origin there. This has the intercept of minus 1 along the z direction.

So, if you now invert this, take the reciprocal of this, this becomes 0, this becomes 0, and this becomes -1. So, this is $(00\bar{1})$ plane. If you take this plane, this will be (001) plane. Now, what about the plane which is here in the middle. So, if I change the color, let us say, if I take this particular plane, this particular plane has indices of, so it is parallel to z-axis but it has intercept of 1 on x-axis, 1 on y-axis.

So, intercepts are 1, 1, and infinity, right? It is parallel to z-axis. So, this is x, this is y, this is z. Now you take the reciprocal, it comes (110). I can take a little bit more difficult example. Let us say, I take an example of different colour. So I choose a plane which is like this, okay? So, this is a A, B, C. So, in this case, you can see, now it has intercept along z-axis in this direction, okay, so you cannot choose this as the origin because you cannot count the intercept.

So, essentially, what you do is that, to count the intercept, you shift your origin to this point. Now, if I see the intercepts, I have one intercept along x-axis, one intercept along y-axis, and one intercept along z-axis. But along the x-axis I have in the negative direction. So, this is in minus x, this is in minus y because I am traveling along minus x in this direction, traveling along minus y, and I am traveling along this point to plus z.

So, for A, B, C the intercepts are -1, -1 and 1/2. And if I take the reciprocal, then this becomes, so minus is written as bar, bar 1 and 1. So, this is$(\bar{1}\bar{1}2)$. That is how you draw the planes and that is how you determine the indices of a plane as well. So, if I ask you to draw a plane, let us say(231) how will you draw (231)? Let us say$(2\bar{3}1)$, tough example, so what basically you do is that you first draw the reciprocal, ½, -1/3 and 1.

And you have to look at the minus digit. Minus digit means you have minus digit in the y-axis, which means you have to shift origin with respect to y. So, what you do is that, let us use a different colour here, may be yellow is not the best one, but orange one, yeah, so instead of keeping the origin here I shift origin here because I can travel to minus y direction now. So, I have an intercept along x which is half in this direction, I have intercept along -1/3 along y, and I have intercept long z which is equal to 1.

I just connect these three points together. So, this plane is basically $(2\bar{3}1)$. That is you draw the planes. How do you draw the directions? Let us just look at a brief example of directions. I am giving a brief overview because this is going to come handy as we see later on, especially non-centrosymmetric crystals. So, if I have to draw direction [100] what it means is that if I take this as the origin, I travel one step along x, 0 along y, 0 along z, so that is basically direction parallel to x-axis is [100].

Similarly, [010] is parallel to y-axis, [001] is parallel to z-axis. Now, what is this direction by the same logic? One step in x, one step in y, so this becomes [110]. What about this direction from here to here? So, to reach that point, now I need to do a bit of, I can see that it has an intercept, so I need to draw various possible options, okay? So, I can travel to this point half along. So, this is half, then I go 1 along y, and then I go half along z. So, how much I have traveled for this, half along x, 1 along y, and then half along z.

Now, in this case, you do not take the reciprocal, you multiply it the by an appropriate integer so that all of them become smallest possible integers. So, this will become [121] direction. Again, you can choose the origin for negative ones. So, let us say if you have a vector which is like, I do not know, if you start from this point, let us say you come to that point, okay? So, your starting point is this point, end point is that.

So, how do you go to reach that point, you travel half distance in x like this, you travel 1 distance in y, along negative y, so you come this way half, this way 1, and then you go this way 1. So, what is it? We went positive in x, we went negative in y minus 1, let us say, and we went positive in z. So, this direction will become $[1\bar{2}2]$ all right? This is what the direction will be.

So, now let us say if you want to draw, let us say [420] direction. How will you draw [420] direction. 4 means 4 distances, 4 unit lengths along x, 2 unit lengths along y, and 0 unit length on z. Since you cannot go out of the unit cell, you divide it by 4, so this becomes 1, 2 by 4, 0. We will change the colour, these are all positives so you do not have to change the origin.

So, if you keep the origin here, so you go 1 along x, half along y, and 0 along z, which means this is the vector that I have. So, basically, [420] is nothing but [210], all right? So, this is how you draw the direction. You can look at the course structure of materials for details about it.

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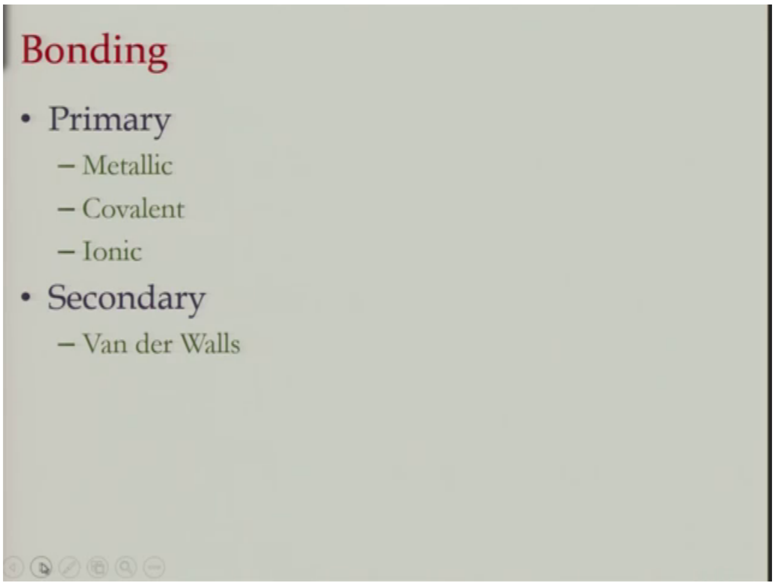

Bonding

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

So, now, having completed some essentials of crystallography for dielectrics ceramic, what you need to understand is the type of bonding they have. From basics of chemistry we know that there are three types of primary bonding that exists; one is metallic, second is covalent, third is ionic. There are secondary bonds as well which are weaker and which are basically Van der Walls type of bonds that primarily exists in solids.

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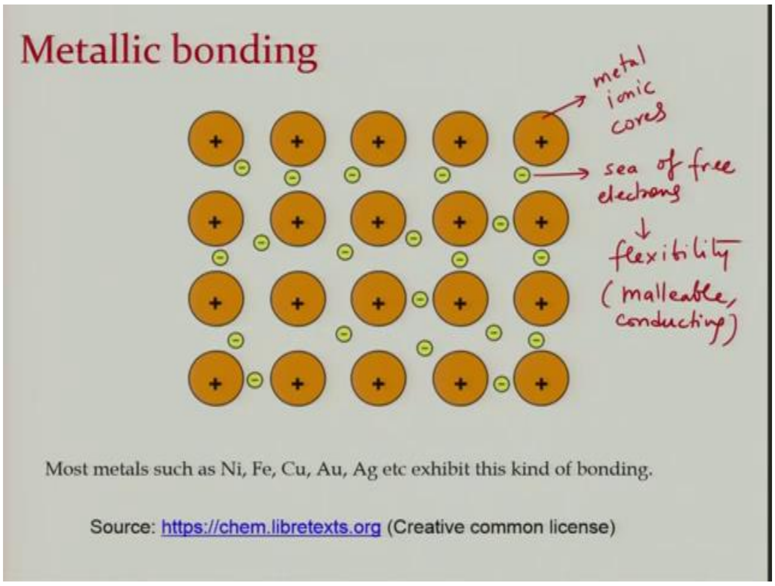

Metallic bonding

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

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So, if you look at metallic bonding, metallic bonding is nothing but, you know, you have metallic core with a sea of electrons around them and metals such as, you know, nickel, iron, copper, gold, silver, etc., they all show this kind of bonding behavior. So, basically, there is a sea of electrons. The sea of electron provides malleability to metals. So, basically, these are all sea of free electrons, right?

You can say free electrons, and these are metal ionic cores. And this provides basically flexibility. So, that is why metals are malleable, conducting thermally as well as electronically. So, this is metallic bonding, I am not going to get into details. You can look at any chemistry book. For example, you can go to this website chem.libretexts.org, there is fantastic discussion on bonding of materials.

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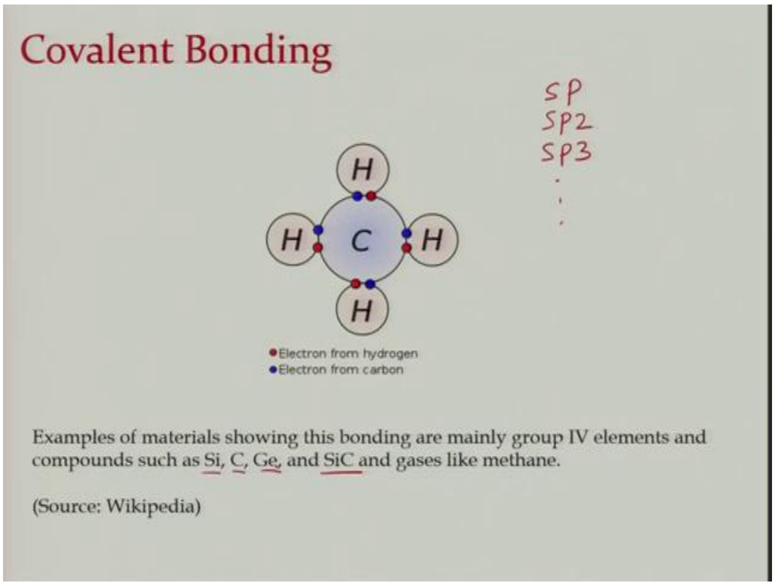

Covalent Bonding

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

(Source: Wikipedia)

The second type of bonding that we encounter is covalent bonding and this is basically based on sharing of electrons. So, for example, you can look at this CH4 molecule. So, carbon has four atoms in the outer shell to complete its electronic configuration. To come to low energy configuration it needs four more electrons. So, when you pair it with four hydrogen atoms, hydrogen is also able to complete its configuration, carbon is also able to complete its configuration, and based on sharing this is called as covalent bond.

There is a theory of covenant bonding that I am not going to go into details, but basically covenant bonding is based on valence bond theory as well as hybridization of orbitals. So, in solids such as diamond and graphite and in methane, etc., there is a strong orbital hybridization. This orbital hybridization is necessary because the angles which are observed in these molecules cannot otherwise be explained.

So, you can have sp hybridization, you can have sp^2 hybridization, you can have sp^3 hybridization and so on and so forth. These hybridizations give rise to certain molecules shapes which can be determined using a variety of techniques. So, materials generally belonging to group 4 elements as well as compounds which are between silicon, carbon, germanium, silicon carbide.

So, you can you can take silicon carbide, for example, similarly, zinc sulfide, etc., all of them show this kind of bonding. And then silicon, carbon, germanium they are predominantly covalently bonded materials, and you have gases like methane etc., which are also covalently bonded.

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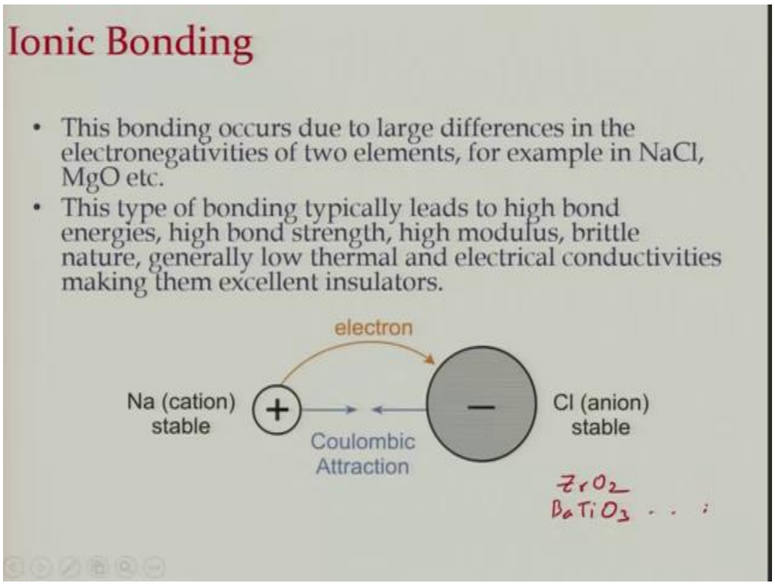

Ionic Bonding

- 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.

ZrO_2
$BaTiO_3$ . . . ;

Then, we have ionic bonding. All of us know that ionic bonding is because of differences in the electronegativities of two ions. So, for example, if you have sodium chloride, the best example that we learned from our childhood, is that sodium is electropositive element, chlorine is electronegative element.

Sodium has a tendency to give away the electrons and chlorine has a tendency to take the electron, and because of this tendency and because of necessity to complete the electronic orbital configuration to put them into lowest energy configuration they form what we call as an ionic bond and this ionic bond is very strong bond because of this coulombic attraction between the two elements.

Electron is donated by sodium to chlorine and electron is gobbled up by chlorine to complete its electronic configuration. As a result, generally ionic bond has high bond energy. It is a very stable bond and high bond strength. It has high modulus and generally the materials with ionic bonding also are very brittle because one energy is very high and they are generally poor electrical and thermal conductors and that is why they are use for applications where you require them to be insulating.

And this is what basically your dielectric ceramics are based on. Most of the dielectric ceramics that we see they are predominantly ionically bonded materials. So, materials like zirconium oxide, barium titanate, all of these dielectric ceramics they are primarily ionically bonded materials.

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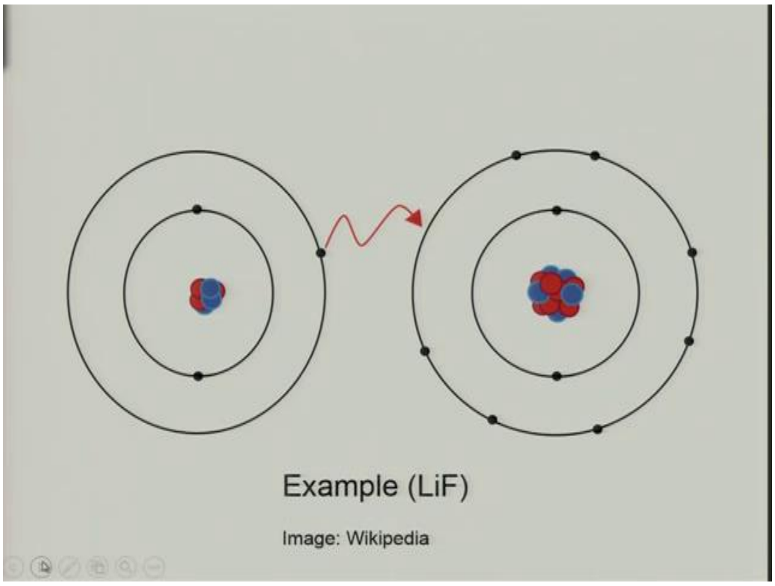

Example (LiF)

Image: Wikipedia

So, another example is lithium fluoride. So, lithium as an atom it has three electrons, fluorine has nine electrons, so fluorine requires one electron to complete its configuration. Lithium needs to give away one electron, and as a result, they form a very strong ionic bond. So, another example. So, most of the oxides that we will see as dielectric ceramics will follow this ionic bonding.

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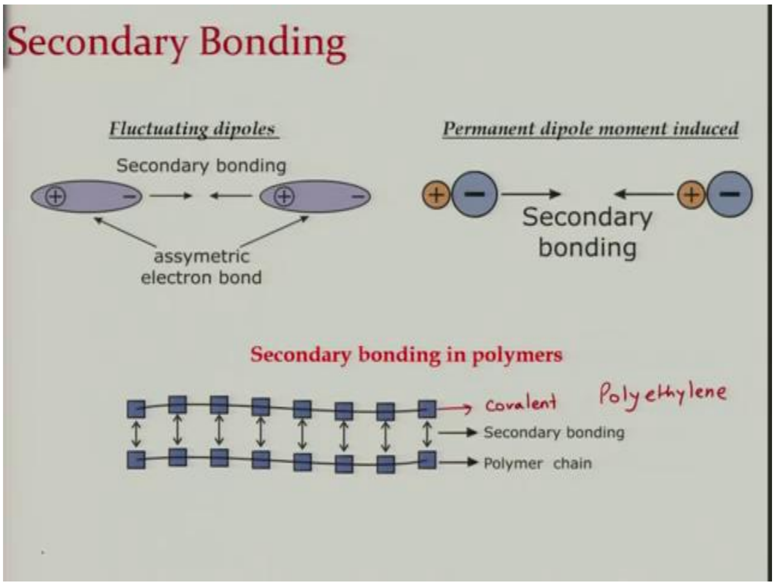

And then, of course, we have secondary bonding which can be because of fluctuating dipole, which can also be because of permanent dipole moments and so on and so forth. So, basically, wherever you have this little bit of shifts in the electrons positive or negative charges that gives rise to formation of these secondary bonds. For example, in polymers you have chains which are covalently bonded.

So, along the chain you may have covalent bonding. So, you can say polyethylene, right? But attraction between the chains are secondary bonding. Similarly, in graphite the carbon atoms between the graphite layers are also covalently bonded, but between the carbon layers you have secondary Van der Walls kind of bonding. This is generally a weak bonding. The energy scales are much lower.

In the case of ionic and covalent bonding the energy scales may be as high as few hundred kilojoules per mole, whereas in the case of secondary bonding it may be just a few, may be about 0.1 to 1 or 10 kilojoules per mole, very weak bond.

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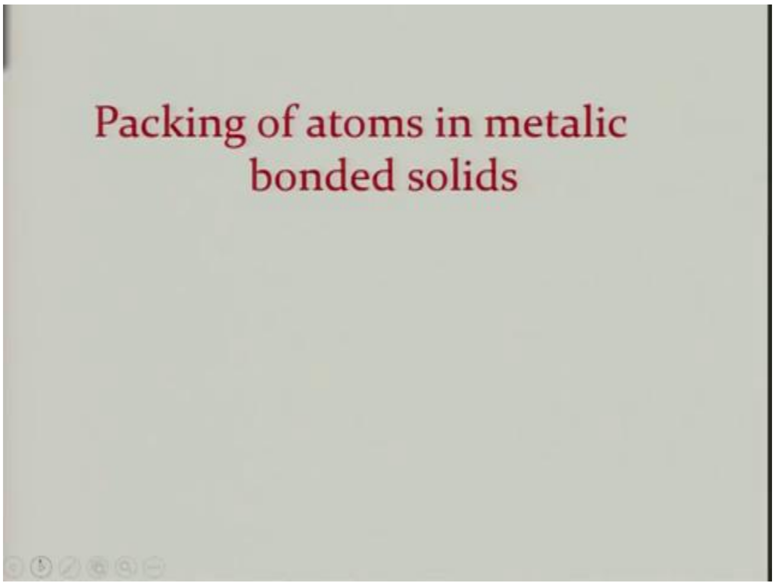

Packing of atoms in metalic bonded solids

Before we go to ceramic structures, we need to understand how atoms are packed in materials.

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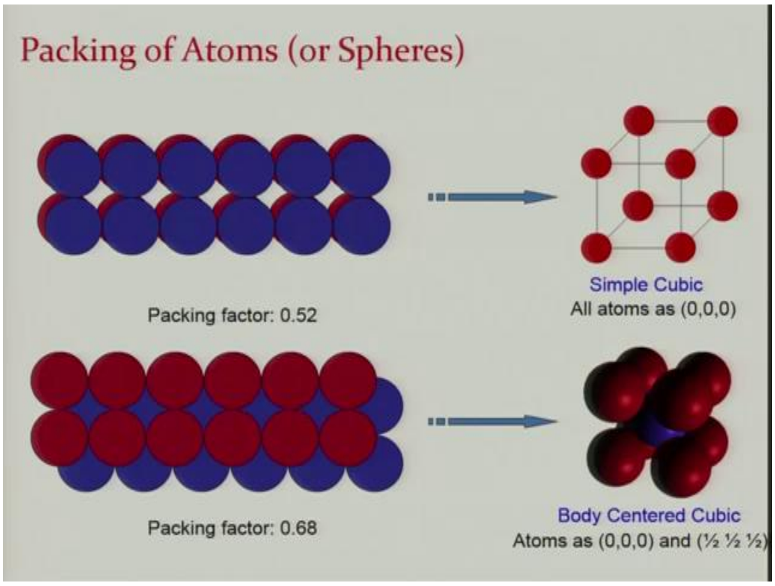

Packing of Atoms (or Spheres)

So, in materials, if you consider atoms as spheres, you can put the spheres in this fashion. All of them can be arranged in this fashion. Next layer can go directly on top of it and this will make what we generally call as a simple cubic structure. You can see that this is not the closest possible method in which you can put the atoms together.

However, there are certain structures in which atoms are packed in this fashion and this is basically simple cubic structure and the formation of these structures is dependent upon the minimization of energy. So, whichever configuration gives you minimum energy based on electrostatistics will be the final structure. You can have another configuration. In this case, all the atoms are located at positions such as (0,0,0). So, this is a simple cubic structure.

There is a possibility that first layer will be the one in the red color, second layer can go in the positions which are middle of the first layer, and the next layer can go directly on top of the first layer. This makes a structure which is called us body-centered cubic structure, okay, and this is again not the most densely packed the structure, but one of the structures which is found in many materials.

And in this case, the atoms are placed at (0,0,0) and (1/2,1/2,1/2). If you do it a little better, so if you calculate the packing factor which you can do easily, the packing factor of simple cubic structure is 52% or 0.52. In the case of body-centered cubic if you take all identical atoms of course the packing factor will be 0.68.

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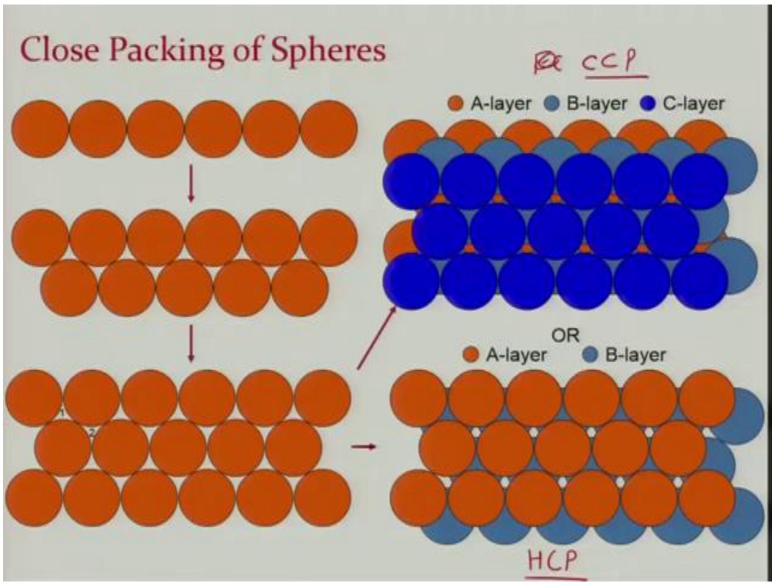

Close Packing of Spheres

You can also have closed-packed structures which is what many materials are based on, so you have one row of items, you put the next one. The next one does not need to go right below it, but the next one can shift itself in such a manner so that it touches the maximum number of neighbors. So, you can keep putting these layers together. Now, you form this layer which is more closely packed as compared to the other two configurations that we just saw. Now, the next layer how does it go?

The atom in the next layer can sit on top of 1 or sit on top of 2 which has vacant places. So, let us say it goes on top of 1 and that is how we keep making the structure. So, the bottom layer is called as A layer, the next layer is called B layer, and if you keep following this AB, AB kind of stacking, you will make hexagonal close-packed structures. So, this will lead to HCP, hexagonal close-packed structures.

And if you do ABC which means first the one type of vacant space is covered, then the second type of vacant space is covered, and you keep going in ABC, ABC kind of fashion. This gives rise to what we call as CCP, cubic close-packed structures, okay. So, these are the three ways, generally, the atoms are stacked in solids, especially in metals. And these are the structures also followed by many ceramic structures as we will see in the next lecture. So, we will stop here. We will look at the structural details of ceramic materials in the next lecture. Thank you.