Advanced Ceramics for Strategic Applications
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Lecture - 4
Crystal Structure (Contd.)

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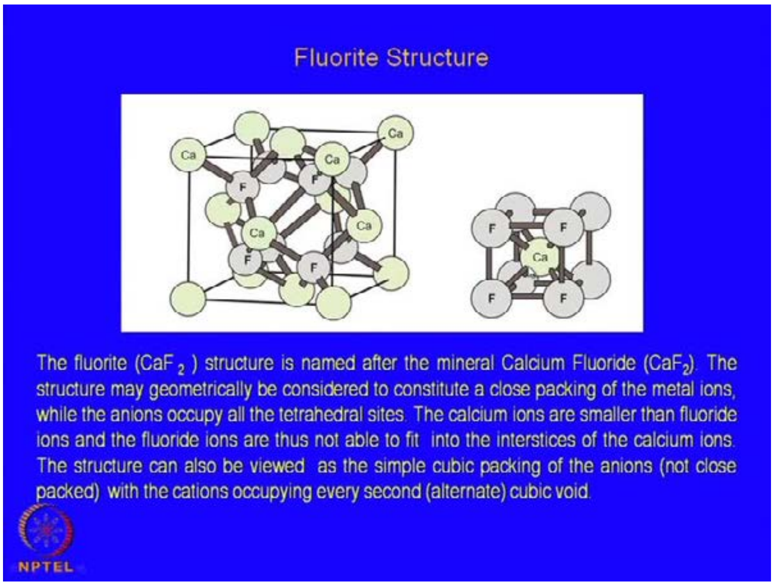

Fluorite Structure

The fluorite (CaF_2) structure is named after the mineral Calcium Fluoride (CaF_2). The structure may geometrically be considered to constitute a close packing of the metal ions, while the anions occupy all the tetrahedral sites. The calcium ions are smaller than fluoride ions and the fluoride ions are thus not able to fit into the interstices of the calcium ions. The structure can also be viewed as the simple cubic packing of the anions (not close packed) with the cations occupying every second (alternate) cubic void.

Let us continue our discussion on crystal structures. We already discussed the simple oxide structures and some alkali halide structures. Let us go to little bit of complex structures. To start with, will have a fluorite structure, what we call fluorite structure. Once again, just like sodium chloride structure, it is called the rock salt structure. Fluorite is also a mineralogical name of calcium fluoride, CaF 2. So, the fluorite structure can also be described more or less in the same fashion. Of course, unit cell is little complex, but one can discuss more or less following the same principle.

Here, fluorine is a cation, sorry the anion and calcium is the cation. Calcium has a smaller size compared to fluorine. If you look at this structure to start with, we have to see fluorine ions, being the larger ions, they found the skeleton and forms a cubic symmetry. So, it is once again a cubic symmetry just like sodium chloride structure, where the chlorine ion forms the skeleton of the cube. But unlike sodium chloride, sodium does not go to the octahedral side or the calcium does not go to the octahedral side. The size is slightly bigger than sodium and therefore, it does not go to the octahedral sites, but it goes to the body centered position. Here, it is the calcium ion. So, it is actually a body center position. Now, if you go to the body centre position or body centre structure, B C C structure, you will find the contribution of the fluorine ions to this particular unit cell is 1, one-eighth into 8 and that gives you 1 fluorine ion and the calcium being at the centre of the cube, it is not shared by any other neighboring unit cells, so its contribution to this particular unit cell is also 1.

So, if this particular unit cell is repeated in the volume, then the chlorine, sorry, fluorine is to calcium ratio should be 1 is to 1 in the compound. However, you have different molecular formula CaF 2, that means, there are double the number of fluorine ions compared to the calcium ions and that gives a different kind of situation, so that, in the cubic structure, when you try to repeat them, one after the other, then it can be described in the following manner. Calcium ions do not sit in all the cubes. In this particular example, we have seen the calcium ion is sitting at the centre of cube formed by the fluorine ion. Unfortunately, what will happen is, in the next neighboring side or next neighboring unit cell, the calcium ion will be missing. It will be vacant, so that each alternate cube has a calcium ion. So, the calcium ions are not in all the cubes. Only in the alternative cubes, weather you go in the x direction, y direction or z direction, right.

So, that is the structure and that has been seen or that has been demonstrated in the left figure here. So, this is not the unit cell. This is the part of the unit cell, whereas, this complicated looking structure is actually unit cell. So, calcium ions are not always at all the corners of the body centre positions of the cube, but it is only in the alternate cubes. So, it says here, the fluorite CaF 2 structure is named after the mineral calcium fluoride, CaF 2. The structure may geometrically be considered to constitute a close packing of the metal ions, while the anions occupy all the tetrahedral sites. This is a different description than what is been given here. Here it says, the calcium ion is larger and fluorine ion goes to the tetrahedral sites. The calcium ions are smaller than the fluoride ions and the fluoride ions are thus not able to fit into the interstitials of the calcium ions.

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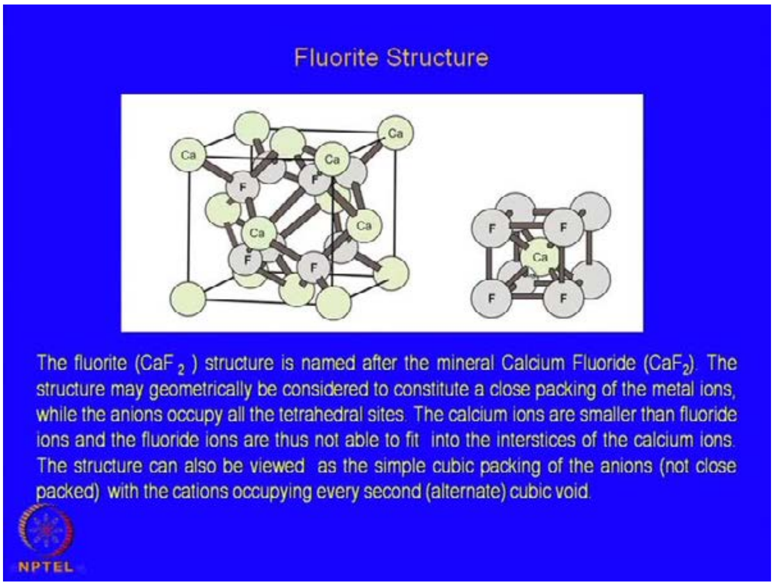

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The structure can also be viewed as the simple cubic packing of the anions and not closely packed within the cations, with the cations occupying every second or the alternate cubic void. That is what the description I gave just now. This is the second part of it, but the structure can also be viewed in a slightly different way because this is one exception situation where calcium ion is much bigger than the fluorine ions. So, normally anions are bigger than the cations and here, the cations are slightly bigger than the anions. As a result, anion goes to the interstitial site. That is one way of describing the structure. The same structure can be viewed in different ways. Anyway, so this is the particular way you can describe the arrangement of calcium and fluorine ions in a calcium fluoride structures. This is what we call a structure type.

There are many compounds, several compounds, which actually crystallizes in this particular structure. One of the very important characteristics of this kind of a structure is that, since calcium ion is sitting on alternate sites and alternate sites are vacant, so there is a channel kind of and through the structure, there is lot of void spaces and that is void is not distributed and is a long a particular direction. This void space is quite important for ionic mobility. Sometimes, these voids are beneficial for the moment of the ions, where if you heat the material at higher temperature, then atoms can move through this voids. We will see later on how the atomic moment takes place and what is the role of crystal structure or imperfections. Crystals are not always perfect. There will always be some imperfections and that is the rule of the game. Imperfections are much more common than having a perfect crystal structure. It is almost important impossible to get perfect crystal and imperfections are always there. We will discuss a part of it at a later class.

So, in addition to that, the structural features are also important for the movement of the cations or movement of the anions in this particular case. So, we will discuss that when we discuss the property. So, that property is actually derived from this particular typical structure. Now, as I said, this is a structure type, fluoride structure type and some of the important oxides which crystallizes in this particular fashion or in this particular arrangement are zirconium dioxide, particularly the cubic form, cerium dioxide and ph o 2. We will all find that the cationic to anionic ratio is always 1 is to 2, in all these oxides as in c a f 2. So, all this particular structure and they have also some common characteristics, common property characteristics, we will discuss them later and find that these oxides, because of the structural similarity, they have certain similarity in electrical properties in particular.

Now, we have mentioned here zirconia cubic, because many of these oxides do have different polymers. That means, at different temperatures, I mentioned in earlier class that iron has different polymers. At low temperature, it has B C C structure and at higher temperature, above 900 degrees, it has F C C structure. Similarly, zirconium also have different structures. Zirconia have different arrangements of atoms at different temperatures. At room temperature, it has a monoclinic crystal structure. So, the CaF 2 structure is not (( )). Although the chemical composition is same but the structure is different. We will discuss that at a later stage, how the polymorphic changes takes place in zirconium and that is the reason we have mentioned that zirconium in the cubic form. Particularly in cubic form and that is a very high temperature stable form, above 20 and 25 (( )) degree centigrade, zirconium has a cubic polymer and that has been the fluoride structure.

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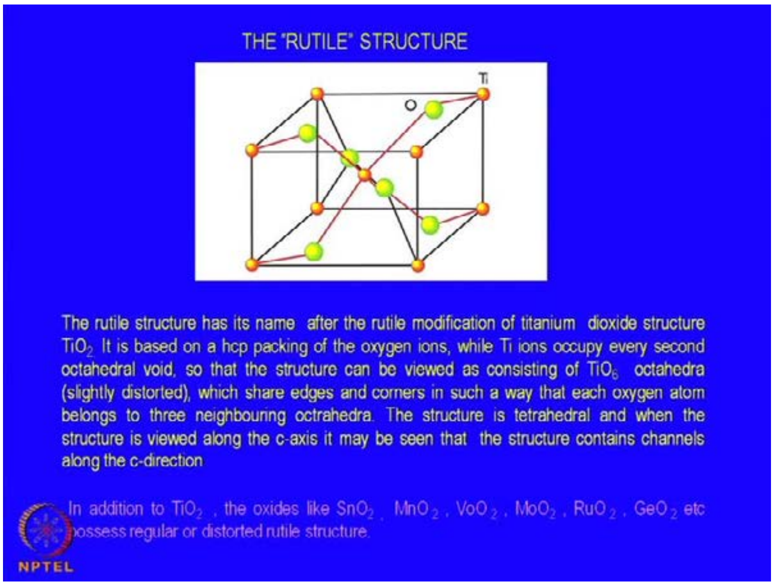

THE "RUTILE" STRUCTURE

The rutile structure has its name after the rutile modification of titanium dioxide structure TiO_2. It is based on a hcp packing of the oxygen ions, while Ti ions occupy every second octahedral void, so that the structure can be viewed as consisting of TiO_6 octahedra (slightly distorted), which share edges and corners in such a way that each oxygen atom belongs to three neighbouring octrahedra. The structure is tetrahedral and when the structure is viewed along the c-axis it may be seen that the structure contains channels along the c-direction

In addition to TiO_2, the oxides like SnO_2, MnO_2, VoO_2, MoO_2, RuO_2, GeO_2 etc possess regular or distorted rutile structure.

Now, that is not so in case of CeO 2 or ThO 2 thorium oxide. CeO 2 throughout is a fluoride structure and same is the case with thorium dioxide. Next, we come to another structure once again in the similar molecular formula. This was c a f 2, but this is TiO 2 and one of the polymers of TiO 2 is called as is called rutile structure. This is of course is not a cubic structure. Incidentally, it is not a cubic structure. So far we have discussed only cubic structures, but this is a deviation from the cubic structure. Rutile structure has its name from the rutile modification or particular structure type of titanium dioxide, TiO 2.

It is based on a hexagonal close packed structure. It is not a close packed structure although, but it has certain similarity with the hexagonal symmetry. In fact, the symmetry is basically a tetragonal symmetry. While titanium ions occupy every second octahedral void, here again we come back to an oxide and so the titanium ions or the metal ions or the cations are much smaller than the oxygen ions. So, they go to the; and the radius is such that it occupies octahedral sites rather than tetrahedral sites. So, titanium goes to the octahedral site. So, the structure can be viewed as consisting of t i o 6 octahedral. So, there are 6 oxygen surrounding a titanium ion. So, that is a preferred coordination number for titanium, particularly titanium core plus and then that octahedral is slightly distorted. It is again not a very regular octahedral. It is not a symmetric octahedral. It is distorted, which share edges and corners in such a way that each oxygen atom belongs to 3 neighboring octahedral. We have seen earlier, in case of a cube, the corner atoms, corner oxygen or corner atoms share 8 unit cells, and here, they are belonging to cell 3 neighboring octahedral. The structure is tetrahedral and when the structure is viewed along c axis, it may be seen that the structure contains channel along the c axis. Once again it has channel, this channel in the particular direction means, that basically we have an isotropic property. That means, in different directions, they will have different properties because they have not symmetric completely. So, it has certain non isotropic property along the c direction, but this is the symmetry, basically tetragonal. So, these are titanium ions at the corners and oxygen actually surrounds or titanium ion is surrounded by 6 oxygen.

Although, this is a different description, one has to remember that, according to our convenience, we describe the structures sometimes the cations at the corners or the anions at the corners. We have seen earlier that, most of the cases, the cations or the anions we put in the corner position. But here, the cations or the titanium is put in the corner position. Rest of the description is not that important. But, except that it has a tetragonal symmetry and titanium has a octahedral coordination. So, most of the time, it is not a symmetric only which is important, particularly for complex oxide, you find that symmetry is not always very important. More importantly, you need to know what is the coordination number, coordination number of the cations involved or what is the coordination number of the oxygen. That means, how many cations are surrounding oxygen ion and how many oxygen is surrounding a cation. So, this is the way we normally describe the structure of so many oxides. There are quite a few oxides, which crystallize, which has this TiO 2. Once again, this is a structure type and it is a rutile structure.

So, if you have to say that, what is the structure of m n o 2, one can very easily say it is a rutile structure. That describes everything. You do not have to go to the description of the, symmetric description of the, position of the ion, position of the cations and anions, you do not have to do it because they have identical. So, s n o 2 just like TiO 2, the rutile structure. m n o 2, v o o 2, molybdenum trioxide, ruthenium oxide, germanium dioxide, all of them have this particular structure. Their lattice parameters may be different of course. Their exact distances between the cation and anion or two cations may be different, but basic symmetry remains same. So, that is how one can always describe the structures of an oxide or other compounds as well.

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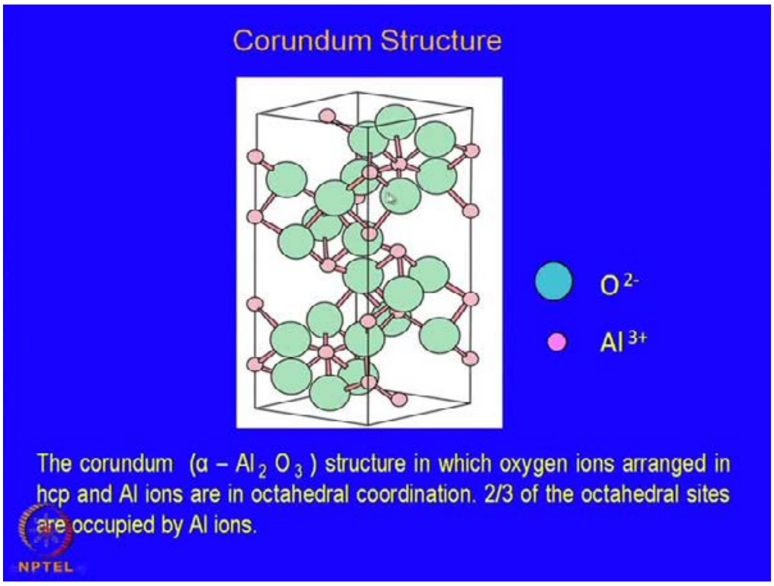

Corundum Structure

The corundum ($\alpha - Al_2O_3$) structure in which oxygen ions arranged in hcp and Al ions are in octahedral coordination. 2/3 of the octahedral sites are occupied by Al ions.

We go to another type of structure, which is very important structure incidentally and it is very important compound as such, aluminum oxide and mineralogical name of one form of aluminum oxide, and that is called the alpha aluminum oxide. That has a alpha beta gamma, gamma aluminum oxide is also there having a different crystal structure. It is more of a cubic structure and in this case, alpha aluminum oxide, which is the most common variety of aluminum oxide and mineralogical name for that, is corundum. So, this is the structure of corundum, in which oxygen ions are arranged, even again h c p. So, symmetry must be also known and then the coordination number of the cation and anion should also be known. That is how actually we describe the structures.

So, it is a corundum structure, in which oxygen ions are arranged in h c p and aluminum ions are in the octahedral coordination once again. Now, in h c p structure, we have seen earlier whether it is h c p or a close packed structure or F C C structure, face centered cubic structure; both of them are close packed structure. There are as many number of octahedral sites as there are oxygen sites. So, if oxygen creates a h c p structure, so the number of oxygen in a unit cell will give the same as that of the number of octahedral sites. We have seen earlier, the number of octahedral site and the number of anions is same in F C C structure. Same is the case with the h c p structure, because both of them are close packed structure. They are identical structure, except as we discussed earlier that, there is a change in stacking. One is a A B C stacking and another one is A B A B stacking, but otherwise they are identical.

So, the number of octahedral sites available to us will be the same as the number of oxygen ions in a molecule. So, the compound has a molecular formula, which is Al 2 O 3. That means, number of cations to the number of anions is 2 is to 3. If you have same number of octahedral sites as that of oxygen or the basic, which forms the basic skeleton, then the molecular ratio should have been a l o. But it is not. The molecular formula is Al 2 O 3 and therefore, the number of aluminum ions occupying the octahedral sites is actually two-third, because the ratio is two-third. So, two-third of the available octahedral sides is actually occupied by the aluminum ions, whereas one-third is remaining vacant. So, that is another very important feature of corundum structure.

It is basically a hexagonal close packed structure, where aluminum ion goes to two-third of the available octahedral sites and all the tetrahedral sites, because any close packed structure will have two types of interstitial sites, octahedral sites as well as tetrahedral sites and aluminum goes to the tetrahedral site. So, that satisfies the conditions of the radius ratio of the octahedral sites. So, it does not go to the tetrahedral sites. So, all the tetrahedral sites remain vacant, whereas, only two-third of the octahedral sites is occupied by the aluminum ions.

So, that is how one can describe the corundum structure. Otherwise, although it looks quite complex, there are bonds between the cation and anion have been soon as in any other structure, but basically, for example, here you can see this is the aluminum ion and it is surrounded by 4 oxygen ions in the octahedral form. So, all the aluminum ions, which are shown here, are actually surrounded by 6 oxygen ions. Now, this is also surrounded by 6 oxygen ions, but some of them belong to this unit cell and others should belong to the neighboring unit cell. So, the aluminum ions, which is sitting on the edge, are actually surrounded by some oxygen ion of this particular unit cell and few others from the neighboring unit cell, but all of them will have octahedral coordination. Whatever available octahedral interstitials are there, only two-third will be filled up. So, that is how one can describe Al 2 O 3.

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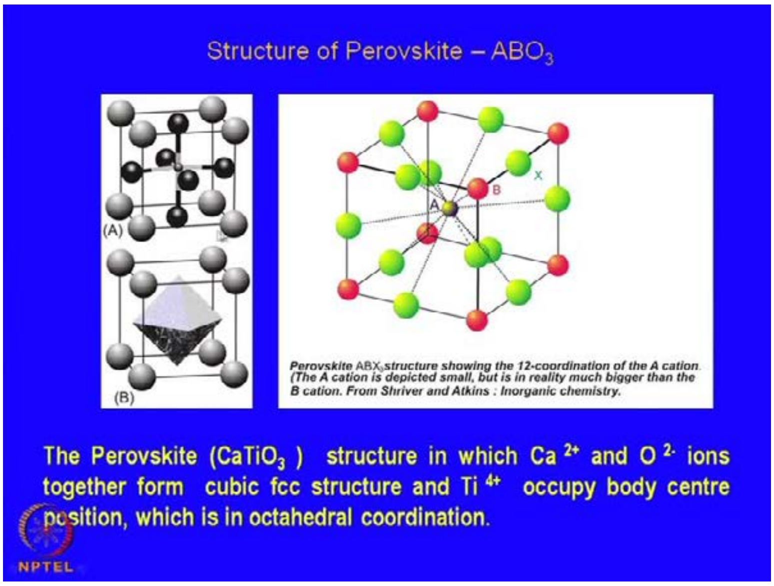

Structure of Perovskite – ABO_3

Perovskite ABX_3 structure showing the 12-coordination of the A cation. (The A cation is depicted small, but is in reality much bigger than the B cation. From Shriver and Atkins : Inorganic chemistry.

The Perovskite ($CaTiO_3$) structure in which Ca^{2+} and O^{2-} ions together form cubic fcc structure and Ti^{4+} occupy body centre position, which is in octahedral coordination.

There are quite a few oxides, which have this structure. So far we have been discussing only simple oxides, where only there are one type of cation present, either barium strontium or aluminum. So, there are simple oxides or we what we call the simple oxides. Now, we go to another group of oxides, which are normally referred to as complex oxides. That means, oxygen of course is the only cation in all these oxides, but sorry, oxygen is the only anion present, but the cation will be more than one. So, this is one such compound is called a b o 3. That is the general formula of the compound, where a is basically a divalent ion, a is divalent and b is tetravalent like this and the perovskite, it is called the perovskite type, just like fluoride is calcium fluoride and rock salt is sodium chloride, calcium titanate has a mineralogical name called perovskite.

It is very important group of compound, very important group of mixed oxides, which have many many different applications and many different properties. Later on we will see. So, we must understand what is this and how would we describe the atomic arrangement in this kind of compound. So, calcium titanate, where a is the calcium and the general formula of these groups of titanites, there are titanites, tanets and so on. So, one of them is alkali metal oxides. Calcium is divalent and it can be replaced by barium, it can be replaced by strontium and so on, magnesium, and other one is titanium 4 plus. So, 2 plus plus, 4 four plus and then it is 2 minus.

So, what is the description? Description is, well, relatively simple. Once again it is a cubic symmetry. First of all it is a cubic symmetric and not hexagonal symmetry. It is a cubic symmetry and calcium and oxygen, we have seen earlier, the size of the calcium is fairly large and that is the reason, with fluorine, it is more than fluorine, so the calcium is very close to that of oxygen. Therefore, when you are talking about a cubic symmetry, both calcium and oxygen together forms the cubic symmetry or a close packed structure.

If you look at this particular part of the diagram, you see these are calcium, the dark ones are calcium and lighter ones are oxygen. So, these are oxygen or it can be reverse also. In this case, I think this is oxygen. The dark ones are oxygen and these are calcium. The lighter ones are actually calcium. It is not written. So, this is your titanium. Titanium sits at the center of the cube, body center of the cube, here and these are oxygen. The oxygen around the face center. Center of the face of the cube and corners are occupied by the calcium. So, calcium goes to the corner and oxygen goes to the face center and titanium goes to the body center, center of the cube and that is how titanium is six fold coordination. Titanium has six fold coordination and calcium is at the center.

Now, that is why in the bottom, we can see this is the six fold octahedral. It is bi pyramid kind of structure. This is a square pyramid, the basis square. So, we have 4 oxygen ions; one in the top and one in the bottom. That is how it forms the octahedral. That is a typical structure of octahedral or regular octahedral. It can be distorted also in some cases. So, that is the description of calcium titanate and this has been represented in this manner, in a slightly different manner, but the same structure is there. So, more or less it is the same thing. Occupy, the description is also given. Titanium 4 plus occupy the body center position, which is an octahedral coordination.

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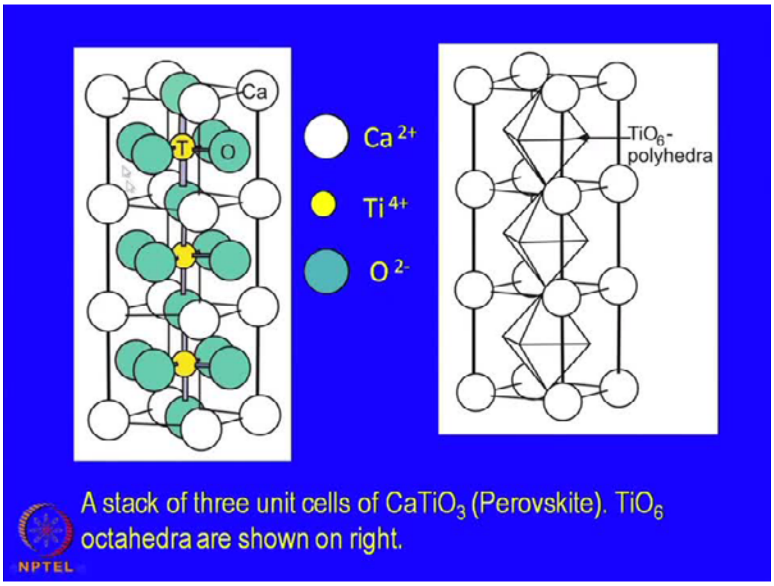

A stack of three unit cells of $CaTiO_3$ (Perovskite). TiO_6 octahedra are shown on right.

There are few more diagrams. Here, instead of, earlier we have seen two layers. Here is a three layer. So, this is one unit cell and this is another unit cell and this is a t unit cell. So, this is repeated here. We can see the octahedral and this is another octahedral and then octahedrons of T i 6 minus octahedral or there is a polyhedral. So, these are oxygen ions at the body center. The corners are calcium and titanium is a much smaller ion, much smaller than both oxygen and calcium. So, they go to octahedral side.

Once again, all the octahedral sides are not occupied. There are as many as 4 octahedral sides in this structure, but only 1 of them is occupied. The rest remain vacant and all the tetrahedral sides are also vacant. So, that is another way of looking at it. So, there are a lot of voids present in this structure. Although oxygen and calcium are in close packed position, but rest of them are really voids.

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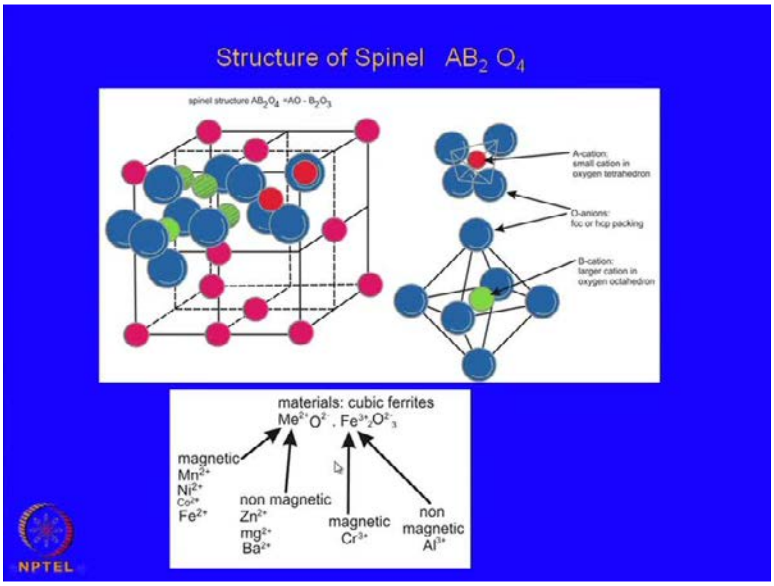

Structure of Spinel $AB_2\,O_4$

materials: cubic ferrites

$Me^{2+}O^{2-} \cdot Fe^{3+}{}_2O^{2-}{}_3$

magnetic Mn^{2+} Ni^{2+} Co^{2+} Fe^{2+}

non magnetic Zn^{2+} mg^{2+} Ba^{2+}

magnetic Cr^{3+}

non magnetic Al^{3+}

Another very important structure is called Spinal structure. A formula just like a b o 3, here the compound is slightly different; it is AB 2 0 4. So, it is again a compound of two different oxides. One is a o and another is B 2 O 3. So, together forms AB 2 0 4. So, a is a bivalent metal, b is a trivalent metal and then oxygen. So, there are large numbers of compounds in this spinal structure also. In fact, perovskite and spinal, there are huge number of compounds available in this particular structure.

Now, the description is like this. These are A cations, red ones. Here is A cations, small cations in oxygen tetrahedral. So, once again it is a cubic structure, in which both tetrahedral sides and octahedral sides are available and both of them are occupied. May not be fully, but at least we to a certain extent. So, we have two different metals. One is A and another is B and to be specific, A can be magnesium and B can be aluminum. So, it has become a magnesium oxide and Al 2 O 3, m g o Al 2 O 3 or m g a l 2 o 4. This particular compound, just like calcium chloride has a mineralogical name, which is called fluorite and sodium chloride has a mineralogical name like rock salt. Here, magnesium aluminate has the mineralogical name spinel. That is the reason this structure type is called spinel.

I forgot to mention that perovskite is the mineralogical name of calcium titanite. That is the reason calcium titanite has a structure type and that is known as perovskite, whereas magnesium aluminate, the mineralogical name is spinel and that is the reason this particular crystal structure is called spinel structure. There may be many compounds having this particular structure. So, once again coming back to the description here, both octahedral and tetrahedral sides are occupied partly. Not fully, partly occupied and A site or A cation, in this case the magnesium, magnesium goes to the tetrahedral side. So, magnesium ions has a fourfold coordination, whereas aluminum, we have seen earlier in case of Al 2 O 3 or corundum structure, that aluminum has a six fold coordination. So, aluminum prefers to go to the six fold coordination all the time in any compound, except some. There are exceptions of course, but normally aluminum goes to the octahedral side and magnesium goes to the tetrahedral side, which also indicates that the cationic size or the ionic radii of magnesium is much smaller and that of aluminum is larger. So, that is what is also mentioned here that, smaller cation goes to be tetrahedral side and larger cation goes to the octahedral side.

Now, here in this structure looks little complex, but actually there are eight units of the cube. If you look at it carefully, you can find out there are eight units of the cube. In the structure, in the spinel structure, there are again two kind of varieties or two types of spinel structure are available. Not one type. This is one type, we have said that all the A ions goes to the tetrahedral side and all the B ions goes to the octahedral side. This is what is called the normal spinel. m g a l 2 o 4 is actually having a normal spinel structure. That is also called normal spinel.

There is another variety of spinel structure which is called inverse spinel structure, in which there is re distribution of the cation, the two types of cat ions which is present, A and B cations. So, B, particularly the B cations, which are larger cations, normally goes to the octahedral sides. In inverse spinel structure, the situation is slightly different. In the inverse spinel structure, half of B goes to the tetrahedral side and half remains here. So, in a inverse spinel structure, actually all the A cations remains in the tetrahedral side, but part of B also goes to the tetrahedral side and that is because some of the cations, in some of the situations, some of the cations actually have a border line situation, as far as the radios ratio is concerned. Radius ratio is such that they can go to the octahedral as well as the tetrahedral side and therefore, those structures are different from the normal spinel structure.

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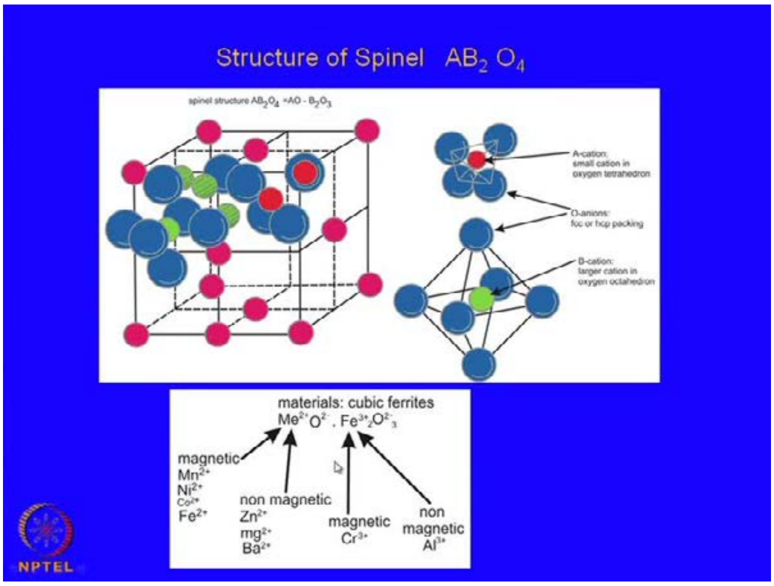

Structure of Spinel $AB_2\ O_4$

Although the basic consideration is same, but if you would go to the details of the structure, there will be some difference and that is very important and that particular distribution of some this cations give rise to many interesting properties, particularly, when you talk about magnetic properties. In fact, it is this redistribution or the inverse spinel structure, which is important for magnetic properties. We will find when B cation is iron and iron can have two different (( )) states. So, one is 2 plus and 3 plus and iron of course, in this case, it will be 3 plus and Fe 2 O 3. So, whenever Fe 2 O 3 is there, then that spinel structure will have a inverse spinel structure.

One example is, for example here you can see the manganese, nickel, cobalt and iron. Manganese 2 plus, nickel 2 plus, cobalt 2 plus and iron can have both 2 plus as well as 3 plus. So, that way iron can be present both and tetrahedral side and in the octahedral side, whereas these are normal spinel. When zinc is there, that is a normal spinel structure. Zinc, these also 2 plus and these are also 2 plus. So, it is actually A cation, A is 2 plus. So, when zinc is, A is zinc or magnesium or barium, they go to the tetrahedral side, whereas these ones, these ones also go to the tetrahedral side, but part of the trivalent ion also comes to the tetrahedral side. That is why this a move, m e o, sorry, m e 2 plus oxygen, that is a o and B 2 O 3, in B 2 O 3, b is 3 plus. When these things, one of the compound is f e, and that is called ferrite.

So, the ferrites has another, they are not, from the point of view of the crystal structure, they are point of view from their properties. So ferrite, Fe 2 O 3, when B 2 O 3 is a Fe 2 O 3, then that compound, that spinel compound is called ferrites and ferrites normally has inverse spinel structure. Part of f e 3 plus remains at the octahedral side and half of it goes to the tetrahedral side and that is how it creates a magnetic property. It is very important for many different applications. So, the ferrites do have a inverse spinel structure, but aluminates, that means, when the b cation is aluminum, it has a normal spinel structure. Chromium can also have both structures, both inverse spinel as well as normal spinel. So, depending on which particular cation you are getting involved in, in the compound, the structure will change. So, that is what is the description of the spinel structure. Both perovskites and spinel are very important structures as far as the oxides are concerned. We will see later on that many of the properties do depend on this particular structure type or the description, where exactly the cations are present.

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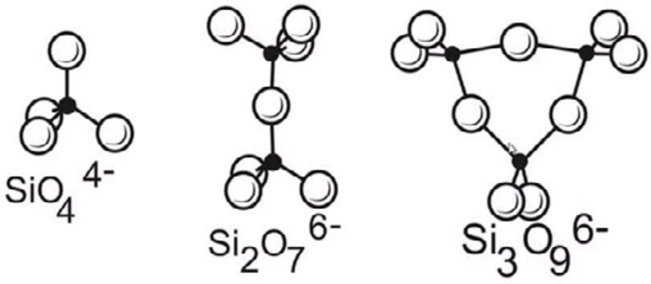

While having discussed all the different kinds of, some of the oxides, let us look at one of the very important oxides, which is very common for ceramic materials, that is silicon SiO 2. Silica just like alumina, aluminum oxide is very important constituent of ceramic group of materials. So, let us try to look at, what is the silica compound, silica SiO 2 and what are the different compounds based on silica. In fact, there are large varieties of silicates because silica, pure silica is also available. So, that is an important constituent of glass, glass making. In addition of course, it gets combined with many other cations and many other oxides and forms many different kinds of silicates. These silicates are very important raw materials for ceramics, particularly traditional ceramic materials. As we have discussed earlier, the traditional ceramics, most of the traditional ceramics raw materials are naturally occurring and they are some form of silicates. Silica is the one of the major constituents. In addition to silica of course, there are many other cations. Sometimes, we require complex structures and in addition to other cations, there may be some hydroxyl ions. So, in fact, many of the silicates do have a hydroxyl ion present there and that determines some of the very important surface property of silicates.

In fact, one of the properties of silicate is the plasticity and because when it is mixed with water, it forms a kind of suspension and that suspension, depending on the amount of the water, you can have a good and stable suspension or you can have a plastic mass. You can deform those materials. The presence of water actually makes a material more plastic. Not in the complete dried form, but with the presence of water. So, silicate structures are very very important for the traditional ceramic raw materials. So, let us try to look at some of the structures available to us.

The basic consideration of silicate structure is what we call the SiO 4 tetrahedron. Silicon in the presence of oxygen forms a tetrahedral coordination. Fourfold coordination is a very important tetrahedral as far as the oxide structures are concerned. So, the basic building block in most of the silicates, almost all silicates is this tetrahedron. Silicon is at the center of the tetrahedron and is coordinated by a regular tetrahedron consisting of 4 oxygen ions. Silicon cation size is much smaller compared to oxygen and it forms a kind of molecule, right. A kind of molecule like this or some kind of a complex ion. So, if you have SiO 4, Si is 4 plus and it is a tetravalent cation and oxygen is 2 minus. So, you have actually net positive charge of 4 minus. So, all silicon oxygen tetrahedron has a 4 minus negative charge, some kind of a complex ion. So, if this 4 negative charge has to be combined with other groups and that way, it can have many complex structures.

Now, when two of such units are joined together by a common oxygen, this particular oxygen is common to this tetrahedron and also the other tetrahedron. So, this is common oxygen between two neighboring tetrahedrons, right. This is what we call bridging oxygen. It bridges between this tetrahedron and the other tetrahedron. So, it is also a very common phenomenon in any silicate structure that there are presence of bridging oxygen and non bridging oxygen. We will come to that later on. But, mostly when oxygen is common or oxygen bond is satisfied, one bond, one negative charge is with this silicon and another negative charge is satisfied with this silicon. Then it is bridging oxygen. There is no extra negative charge sitting on this, whereas these are non bridging oxygen. These are non bridging oxygen because some other cations can join can or combine with this oxygen. So, the total, the overall complex or the overall ion is Si 2 O 7 6 minus. This is SiO 4 4 minus; this is Si 2 O 7 6 minus and then you can also have another kind of a structure, again a unit, a structural unit like this. So, this will also have unsatisfied bonds at the outer surface or outside this ring, whereas, this has only one bridging oxygen, whereas in the form of a ring, it can have three different bridging oxygen's. This is isolated silicon oxygen tetrahedron and this is, two of them have combined together and here, three of them have combined. This is one silicon; this is another silicon; another silicon and forming a ring and this oxygen of course still unsatisfy discharges and therefore, it has a net negative charge Si 3 O 9.

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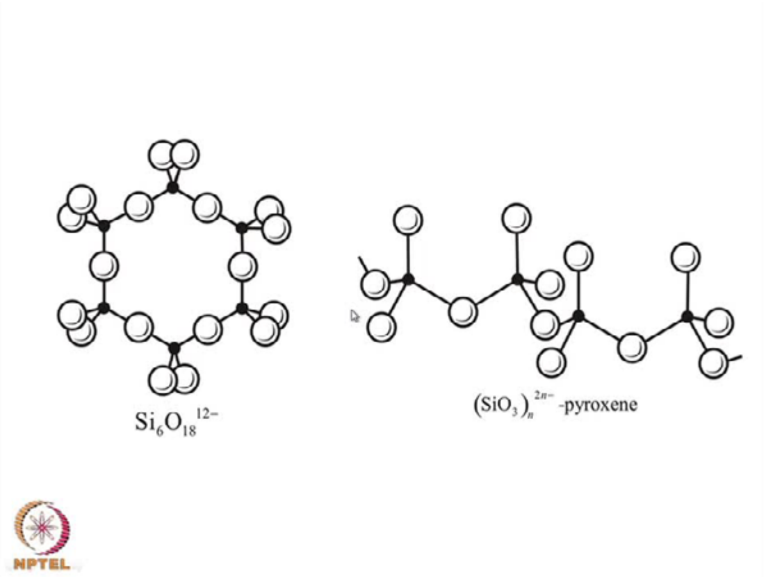

So, there is 1 silicon, 2 silicon and 3 silicon. So, these are the groups, the repeating groups one can have in different silicon structures. It can also have much larger rings like six of them forming an hexagon kind of ring, a kind of benzene ring. So, this is silicon, 6 of the tetrahedron had joined together and 6 of the oxygen have satisfied or have been shared between two neighboring silicon ions and therefore, there are 6 bridging oxygen's forming a hexagonal ring and the net negative charge is 12 minus, Si 6 O 18 12 minus. You can also have this kind of a chain. You can form a chain. Earlier, we have seen two of them can be joined and you can have Si 2 O 7 6 minus. You have seen that. So, only one bridging oxygen. But, this can be extended further. Instead of 2, you can have 3, 4 and go on, it can go on endlessly just like a polymer chain. So, it is a kind of an inorganic polymer chain.

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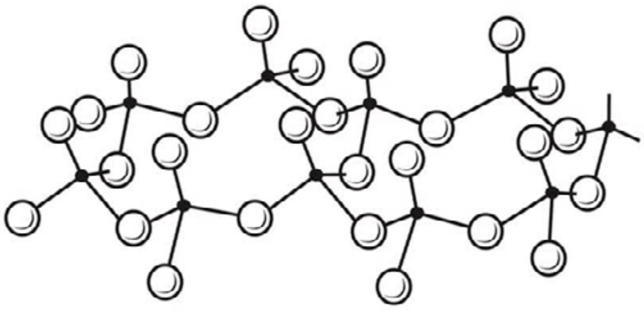

$(Si_4O_{11})_n^{6n-}$ -amphibole

So, you can have SiO 3. Depending on the number of such units, you can have n and the total charge, negative charge will be 2 n minus. This particular kind of structure is known as pyroxene structures or pyroxene silicates. It is also possible. As I have said, there are very complex situations as far as the silicon oxygen network is concern. It is some kind of a network. As there is a polymerization with monomers, so these are the units or monomers are getting together and forming a chain.

Now, you have seen a single chain. Here, there is a double chain. That means, one chain is this one, one pyroxene chain here and another pyroxene chain is also more or less parallel, but there are not isolated. They are not isolated. They are connected between these two chains, as if there is a, what you call a cross linking. Cross linking of polymerize. So, this is one polymeric chain and this is another polymeric chain and there is a cross linkage through a common oxygen ion. So, this silicon ion and this silicon ion sharing one particular oxygen, and then this silicon ion and this silicon ion is sharing another oxygen and once again, there is a sharing of oxygen and here you get.

You must notice that all the silicones are not sharing between the two chains. For example, this silicon and this silicon is not sharing, but this one is sharing. So, it is normally or the structural requirement of the, requirements is that, alternate silicon ions are actually sharing oxygen between them and therefore, a bonding is talking place between the two parallel chains. That kind of structures or this silicates are called amphiboles. This is the unit Si 4 O 11, it is n 6 n minus. That a simple calculation. So, amphibole is another variety of silicates. So, depending on the silicon oxygen arrangement, how the tetrahedral is shared between the neighbors, you have different kind of structures, different kind of properties and appear under different applications.

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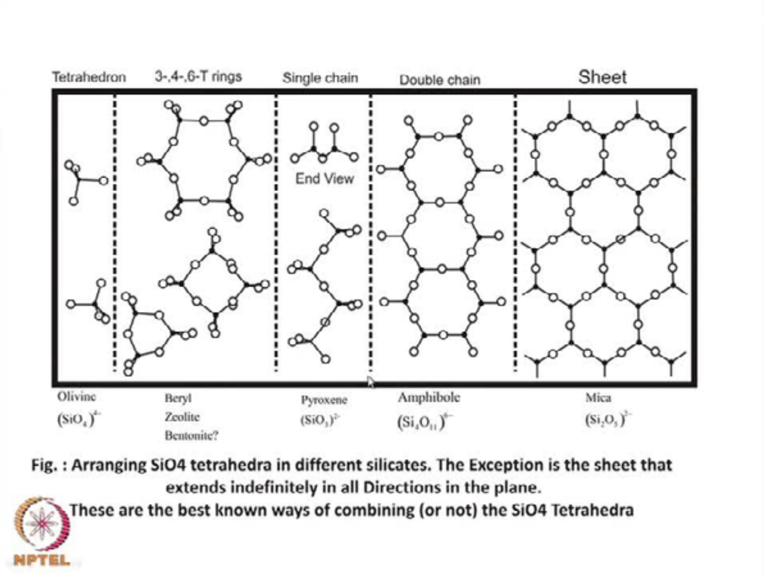

Fig. : Arranging SiO4 tetrahedra in different silicates. The Exception is the sheet that extends indefinitely in all Directions in the plane.

These are the best known ways of combining (or not) the SiO4 Tetrahedra

This is, in summary we have seen, you can see, there are, if it is isolated silicon oxygen tetrahedral, these are called olivine structure. This is called beryl structures. There can be rings. I have given you two examples of three member ring, six member ring, but it can be a four member ring also. There are different compounds present, beryl zeolite and bentonite. We will not be discussing too much about these things because they basically fall in the traditional ceramics arena and this course is on advanced ceramics. So, will be discussing mostly on the advanced ceramics compounds, but silicates being one of the major constituent of ceramics, particularly traditional ceramics, just have a idea what are they.

These are single chains, pyroxene. We have discussed already and amphiboles, the double chain. This is one chain and this is another chain and forming a kind of hexagonal in between. Then there is the next variety is called sheet silica because there is a, it is a two chain, but if this extends in the other directions also, a large number of chain forming basically a sheet structure, a horizontal sheet structure. They are all in the form of a large number of chains or as a large number of units have put together in two different directions, x and y direction and not in the z direction. In z direction, the bonding will be different. We will see that electron, how the z direction also gets bonded together. Normally these bonds, the z direction bonds are much weaker than the x y direction bonds. So, this is what we call the sheet silicate structure. Mica is one of the examples of this. So, arranging a side of four tetrahedron in different silicates, the exception is in the sheet, that it extends indefinitely in all directions in the plane.

So, these are the best known ways of combining or not combining the SiO 4 tetrahedral. So, this is the different arrangements of SiO 4 tetrahedral, which is the basic unit of the building block of all this silicate structures and that building block is combined with the next building block in different patterns and different forms and that is how you will get different kind of silicates.

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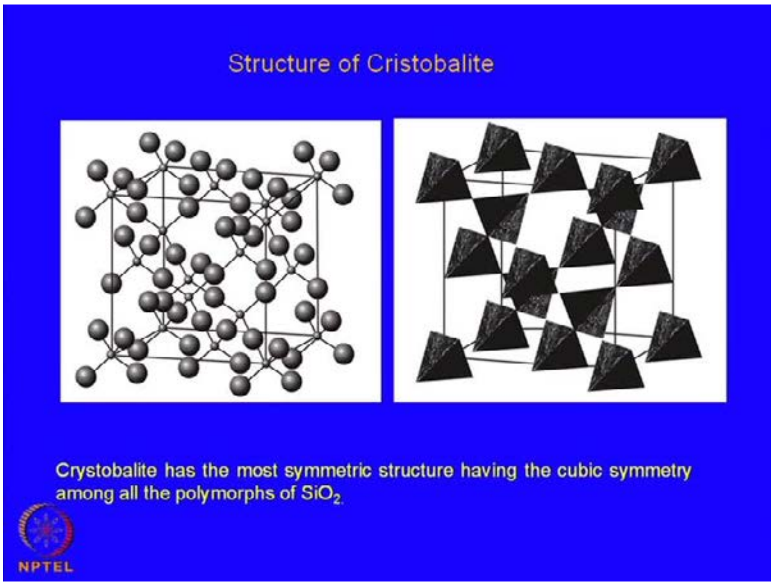

Structure of Cristobalite

Crystobalite has the most symmetric structure having the cubic symmetry among all the polymorphs of SiO_2.

Well, I think, besides of course silicates, we have not discussed much about the pure silica. Silica, as it is on its own, also it is a very important ceramic raw material and it does not combine with others.

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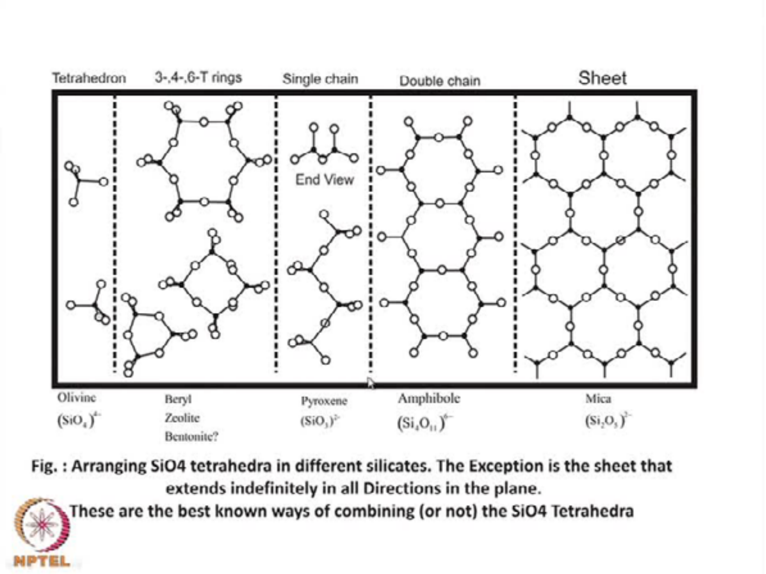

Fig. : Arranging SiO4 tetrahedra in different silicates. The Exception is the sheet that extends indefinitely in all Directions in the plane.

These are the best known ways of combining (or not) the SiO4 Tetrahedra

It is called silica and is basically a network structure, where all the oxygen ions we have seen in all earlier structures, which is, all oxygen’s are not combining with silica. Some of the oxygen is combining with silica and the rest un field or un satisfied bonds has to be satisfied the other cations, which has been not discussed here. But, in silica, pure silica structure, all the oxygen will be a kind of bridging oxygen. That means, only bond between silicon and oxygen and that satisfy the complete charge compensation or charge neutrality, right. S, there is no other cation is needed for combining with oxygen and therefore, in any silicate structure, it is actually what we call a frame work structure or a network structure.

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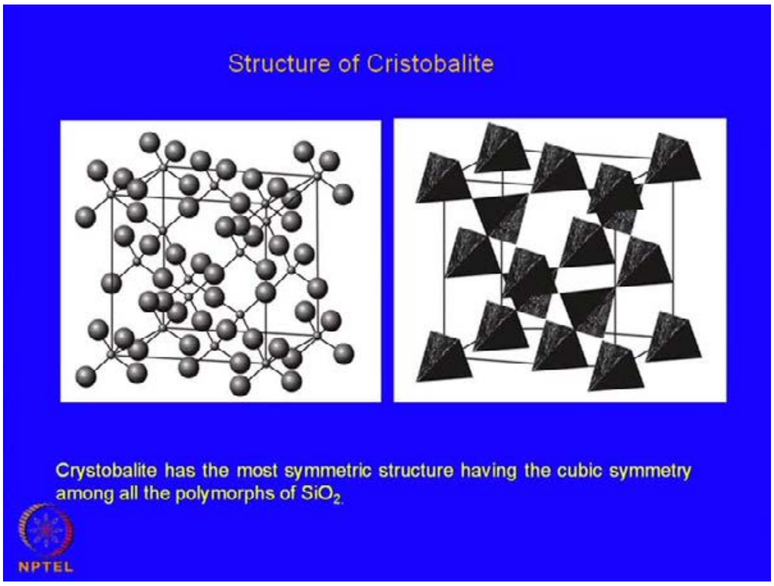

Structure of Cristobalite

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Therefore, only oxygen and silicon satisfy all the bonds of silicon as well as oxygen. Therefore, you have a repeating unit of this kind of tetrahedrons. These are tetrahedrons. They are arranged. So, these are actually, these molecules, silicon oxygen molecules, will form or arranged in a particular geometric pattern and that actually gives you the complete silicate structure, SiO 2. Now, there are different polymorphic forms of silica. We will discuss that may be in the next class and let us finish it here for the time being.

Thank you so much.