Advanced Ceramics for Strategic Applications

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Lecture - 5

Crystal Structure (Contd.)

We are going to continue our discussion on crystal structures of different ceramic compounds. Last time, we have started preliminary discussion on silicates, the silica bearing compounds. We will come back to that discussion a little later. However, before that, let me go back and discuss some of the features of the crystal structures, which I have not discussed so far.

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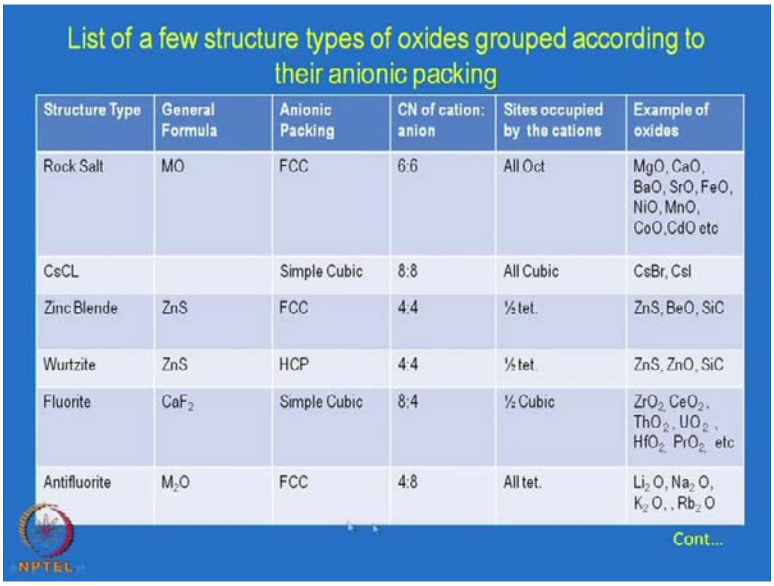

List of a few structure types of oxides grouped according to their anionic packing

Structure Type	General Formula	Anionic Packing	CN of cation: anion	Sites occupied by the cations	Example of oxides
Rock Salt	MO	FCC	6:6	All Oct	MgO, CaO, BaO, SrO, FeO, NiO, MnO, CoO,CdO etc
CsCL		Simple Cubic	8:8	All Cubic	CsBr, CsI
Zinc Blende	ZnS	FCC	4:4	½ tet.	ZnS, BeO, SiC
Wurtzite	ZnS	HCP	4:4	½ tet.	ZnS, ZnO, SiC
Fluorite	CaF_2	Simple Cubic	8:4	½ Cubic	ZrO_2, CeO_2, ThO_2, UO_2, HfO_2, PrO_2 etc
Antifluorite	M_2O	FCC	4:8	All tet.	Li_2O, Na_2O, K_2O, , Rb_2O

Cont...

The very first thing we want to discuss is a consolidated picture of what we have already discussed. That is, a list of different compounds, primarily oxides, some sulphides may be and their crystal structures. We can classify them according to the formula of compounds, their complexity of the structural features and then the coordination numbers and so on. Some are the structures we have already discussed. Rock salt structures we have discussed and its basic features, what we are presenting here is a consolidated picture of all the different oxides we come across and their structural features.

So, the simplest form are simplest structure type is actually rock salt. Its general formula is basically MO a divalent metal with oxygen. In case of rock salt structure or sodium chloride structure, as we have discussed earlier, if the basic anionic packing is closed packed structure of F C C, that is face centered cubic are cubic close packed structure. We discussed about the coordination number, either cation or the anion and what it is presented here, what is the coordination number, if the cation is of the coordination number of the anion. So, it happens so, that in rock salt structure, both cation and the anion have a six fold coordination.

We also mentioned earlier that there are a skeleton of oxygen ions and the interstitial positions are primarily occupied by the cations. So, there are octahedral sites as well as tetrahedral sites. For each oxygen atom, there are two tetrahedral sites in the structure and one octahedral site. This all octahedral, all octahedral means all the available octahedral sites are occupied by the cations in this particular structure. Examples of this kind of oxides, if the mention, this is magnesium oxide, calcium oxide, barium oxide, strontium oxide, iron oxide, nickel oxide, manganese oxide, cobalt oxide, cadmium oxide etcetera. So, all these oxides of the general formula m o, normally specializes or they have the rock salt structure.

Next, we also discussed this particular structure is cesium chloride structure and of course, there are not too many compounds or there are hardly any oxides, which has this cesium chloride structure, but for the sake of completion, this is a simple cubic. This is only one of the rare compounds having a simple cubic structure and formula of course is c s c l and in this case, the cation having eight fold coordination and also the anion, anion and cation both have this eight fold coordination, right. All the cubic sites are filled up. So, because both of them have the same coordination and it is a simple cubic structure, so it is a cubic coordination. So, all the cubic sites are basically filled up by either cesium or the bromine or in this case, another compound is cesium iodide. So, this is one simple crystal structure type. This we did not discuss earlier, but the structure type, there are many, some oxides do crystallize in this particular structure. This is a zinc sulphide. Zinc sulphide, in fact has two different polymorphs; one is called zinc blende and the other is called wurtzite. The basic difference, the main difference is here. The packing in one case or the symmetry in one case is face centered cubic.

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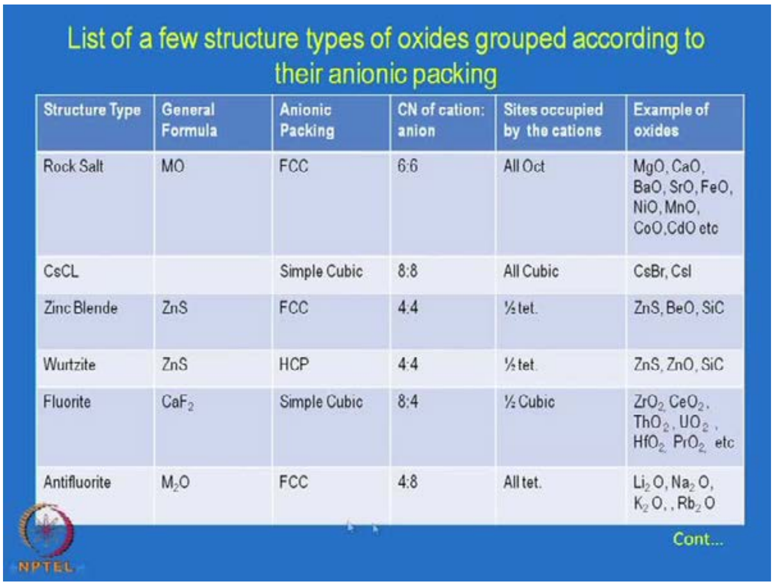

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CsCL		Simple Cubic	8:8	All Cubic	CsBr, CsI
Zinc Blende	ZnS	FCC	4:4	½ tet.	ZnS, BeO, SiC
Wurtzite	ZnS	HCP	4:4	½ tet.	ZnS, ZnO, SiC
Fluorite	CaF_2	Simple Cubic	8:4	½ Cubic	ZrO_2 CeO_2, ThO_2, UO_2 , HfO_2 PrO_2 etc
Antifluorite	M_2O	FCC	4:8	All tet.	Li_2O, Na_2O, K_2O, , Rb_2O

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It is also a close packed structure as also the H C P. Both H C P and F C C has a close packed structure, but one polymer has a face centered cubic structure and other has a hexagonal structure. Otherwise, they are all same. The anion and the cation, both have four fold coordination, and that means tetrahedral coordination. Both in the case zinc blende structure, the cubic structure as well as the hexagonal structure. In both the cases, half of the tetrahedral sites are occupied by the cation. Half of the tetrahedral sites are occupied by the cation, because the ratio you can see, the ratio of the cation and anion is same.

The tetrahedral sites in a close packed structure are actually double the number of oxygen or anions. So, only half is filled up and the examples are zinc sulphide. This is also zinc sulphide. One form of zinc sulphide is called wurtzite and another form is zinc blende. Beryllium oxide crystallizes in zinc blende structure. Silicon carbide, silicon carbide is one of the carbides commonly used in ceramics, the traditional structural ceramics. Again, just like zinc sulphide, it has two different polymorphs. Silicon carbide has the cubic structure as well as the F C C structure, the hexagonal structure. Zinc oxide has a hexagonal structure. So, this is another group of oxides, quite important oxides having either zinc blende or wurtzite structure.

Fluorite, we have discussed earlier. Calcium fluorite, the structure type is calcium fluorite and the mineralogical name or calcium fluorite is actually fluorite. It is a simple cubic structure and to some extent, similar to cesium chloride. However, the coordination numbers are slightly different for the cation. It is eight fold and for the anion, it is only four fold. So, this is different compared to the cesium chloride structure. Half of the cubic sites, that means, the eight fold coordination sites are been filled in the fluorite structures. So, in that, all the cubes or body centered of the cube is not filled up. Only the alternate sites, alternate cubes are filled up with the cations and therefore, you have a large number of oxides. All of them are of m o 2 type oxides, m o 2, z r o 2, c e o 2, thorium dioxide, uranium dioxide, hafnium dioxides and a host of, this is praseodymium and then you have host of rare earth oxides. Many of these rare earth oxides do have this fluorite structures and they have certain important properties, which we will discuss later.

Then, in addition to fluorite, we have another structure type is called anti fluorite. If you look at the chemical formula, these compounds, one is c a f 2, whereas the other is m 2 o. So, these are, you can see these are monovalent of metals, like lithium or alkali metals like mostly, lithium oxide, sodium oxide, potassium oxide, rubidium oxide. So, all these do have a so called anti fluorite structures and this is not simple cubic.

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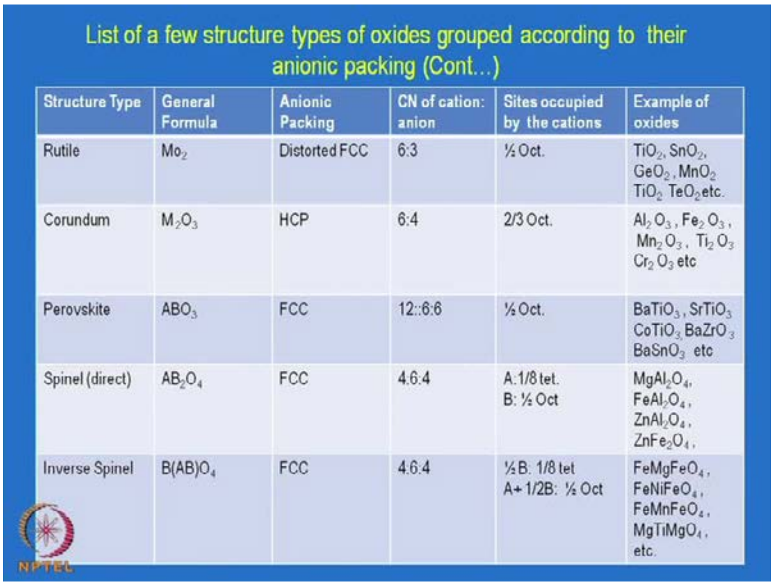

List of a few structure types of oxides grouped according to their anionic packing (Cont...)

Structure Type	General Formula	Anionic Packing	CN of cation: anion	Sites occupied by the cations	Example of oxides
Rutile	Mo_2	Distorted FCC	6:3	½ Oct.	TiO_2, SnO_2, GeO_2 , MnO_2 TiO_2 TeO_2etc.
Corundum	M_2O_3	HCP	6:4	2/3 Oct.	Al_2O_3 , Fe_2O_3 , Mn_2O_3 , Ti_2O_3 Cr_2O_3 etc
Perovskite	ABO_3	FCC	12::6:6	½ Oct.	$BaTiO_3$, $SrTiO_3$ $CoTiO_3$ $BaZrO_3$ $BaSnO_3$ etc
Spinel (direct)	AB_2O_4	FCC	4:6:4	A:1/8 tet. B: ½ Oct	$MgAl_2O_4$, $FeAl_2O_4$, $ZnAl_2O_4$, $ZnFe_2O_4$,
Inverse Spinel	$B(AB)O_4$	FCC	4:6:4	½B: 1/8 tet A+ 1/2B: ½ Oct	$FeMgFeO_4$, $FeNiFeO_4$, $FeMnFeO_4$, $MgTiMgO_4$, etc.

This is F C C close packed cubic and this is different. This is just the reverse. Reverse of this. Here, the cation has fourfold coordination, whereas the anion has eight fold coordination and all tetrahedral sites are filled up, which is quite obvious in the fluorite, because of the particular formula, only half of the cubic sites are cubic interstitial sites are occupied, whereas here, all the tetrahedral sites are occupied. because the ratio is m 2 o. So, there is a double number of oxygen. The metal cations is double the number of anions. So, all the tetrahedral sites are actually filled up.

To continue with this list, we have a rutile structure. This is the formula m o 2. We have discussed earlier and the type of compounds which crystallizes in this particular structure is t i o 2, s n o 2, g e o 2, germanium dioxides, manganese dioxide, t i o 2 again. I think there is a mistake. We have repeated. It should be tellurium. This is tellurium dioxide. So, these are distorted F C C structure. It is not a completely or exactly F C C or it is not a cubic. In fact, we will see, the symmetry is towards tetragonal, not F C C. But, for our purpose, at this point of time, it is F C C and coordination number of the cation is 6 and that of anion is 3. Half the octahedral sites are occupied in this case.

Corundum we have also discussed. The chemical formula of the structure type is m 2 o 3, askew oxides and this is H C P. The symmetry is hexagonal and cation having coordination number of 6, whereas the anion has a coordination number of 4. Only two-third of the octahedral sites, two-third of the octahedral sites is occupied by the cation, because of the formula here. It is 3 is to 2. So, we have only two-third and rest one-third is vacant. The oxides, which actually crystallizes or have this particular structure is a l 2 o 3, f e 2 o 3, m n 2 o 3, t i 2 o 3, c r 2 o 3 and so on.

Next the complex oxides. We have discussed both of them in the last class. The general formula of a b o 3 and we have a cubic structure, cubic close packed or face centered cubic, in other words. They have three different elements here. One anion and two cations. So, the coordination number here is 12 6 and 6. So, one of the cations has a twelve fold coordination, whereas the other has six fold coordination and they anion has a six fold coordination. Half the octahedral sites are actually occupied in this particular system.

In fact, this is a very important group of oxides having many different functional properties. We will discuss them later, particularly electrical properties. Many of them have very interesting electrical properties. We can modify even the electrical properties and most of them are known for their high dielectric content material. Barium titanate, strontium titanate, cobalt titanate, barium zirconate and barium stagnate, different kinds of basically titanates, zarconetes and stagnates, most of them have this perovskite structure. We have two varieties of spinel structure. The general formula is a b 2 o 4. Again, it is a cubic symmetry; cubic close packed and the ratio of, the cation and anion coordination numbers, not the ratio. They are actually the coordination number of different ions. Cation is 4 and another cation is 6 and anion is 4.

So, we have two different cations occupying two different sites, because we have tetrahedral sites and octahedral sites. In perovskite, there is none of the tetrahedral sites or occupied, whereas in spinal, both the tetrahedral and octahedral sites are occupied. One-eighth of the available of the tetrahedral sites are occupied by A atoms and half of the available octahedral sites are occupied by B atoms. So, that is what you call the direct spinel structure and the examples are, magnesium aluminate, iron aluminate, zinc aluminate and zinc ferrite. These are spinel structures with this kind of distribution a and b, distributed between tetrahedral and octahedral sites.

Last variety in this series is inverse spinel and the chemical formula or general formula is b a b o 4. Here it was a b 2 o 4. Incidentally, a is a divalent and b is trivalent. Here, a is divalent and b is tetravalent. B here is a trivalent and 2 of the cations have been distributed between octahedral and tetrahedral and a has gone inside the octahedral site. So, what has happened is, b has come out from the octahedral to the tetrahedral. b was here in the spinel structure, normal spinel structure or direct or it is mostly called normal spinel. Not direct spinel. In the normal spinel structure, it is actually b atoms are in the octahedral sites, whereas in the inverse spinel, b atom is actually distributed between octahedral and tetrahedral. So, half of b atom is occupying one-eighth of the tetrahedral site. In half of the octahedral available sites, a atoms are there plus half of b.

So, there is redistribution of the a and b ions between the tetrahedral and octahedral sites. The example are iron, magnesium ferrite, iron nickel ferrite and then iron; in fact, it is not iron, it is manganese ferrite, it is nickel ferrite and magnesium ferrite and then of course, and there is another titanate is also there. So, magnesium, magnesium, magnesium is on this side and also in this side and titanium, it forms a titanate. So, these are the different kind of oxides available to us and most of them are used for different advanced applications.

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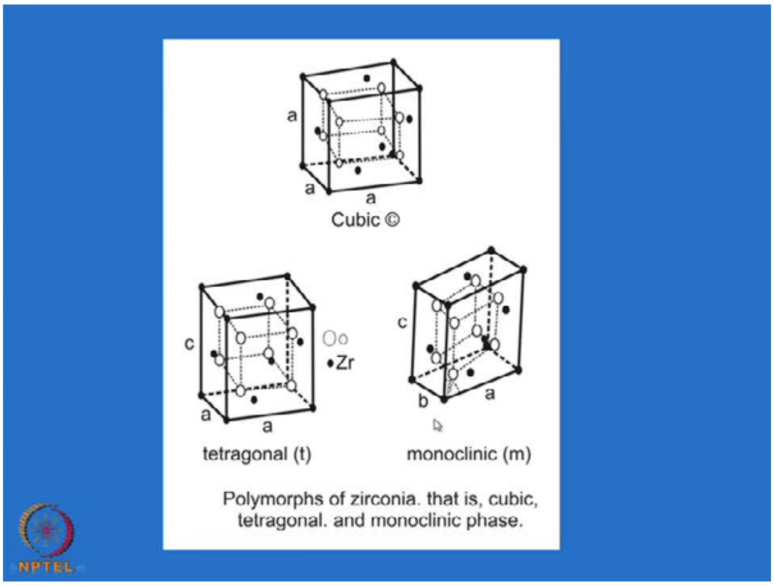

Polymorphs of zirconia. that is, cubic, tetragonal. and monoclinic phase.

One of the major oxides is zirconium dioxides, z r o 2. It has many different important properties, which we will be discussing later. So, it may be worthwhile to know little bit about the structure of this particular oxide and trying to give little bit emphasis on the zirconia structure. Zirconia, z r o 2, we have seen that, just before this slide, it was indicated that zirconia have a cubic fluorite structure. But, all zirconia do not have the cubic fluorite structure. We have a cubic modification. So, this is the distribution of atoms as for as the cubic fluoride structure is concerned. So, this is stable at a very high temperature. About above 2200 degree centigrade, whereas, room temperature, zirconia has a monoclinic structure.

So, there is a not so symmetric structure. It is a distorted structure. We discussed about this different symmetric in a few minutes. So, zirconia has three different polymorphs. One is monoclinic and is tetragonal and then the other one is cubic. This is the low temperature modifications and room temperature is about 1100 degree centigrade. From 1100 degrees to about 2200 degree centigrade, this particular structure is stable. That is tetragonal and then above 2200, it becomes cubic. So, higher is the temperature, the symmetry becomes more regular or it becomes, the structure becomes more symmetric. That is the normal tendency in any polymorphic transformations.

So, these are the polymorph transformation. Polymorphic, polymorphs of zirconia, that is the cubic tetragonal and monoclinic in the descending order of the temperature. We will discuss those things at a later stage, because zirconia is one compound, which has very important properties, both from the point of view of electrical properties as well as from the mechanical properties. So, mechanical properties which is the tough ceramics, one can toughen zirconia, what we called the transformation toughing. So, these polymorphs can be designed properly. The micro structure can be designed in such a way that the material becomes quite tough. It is not so brittle. If you feel I am very fast, research paper has come out on zirconia. As far as toughing is concerned, at that time, people talked about ceramics steel. So, it was equivalent to steel, applications of steel or metallic materials can be replaced by zirconia. So, on the other hand, zirconia also has very interesting electrical properties. It is one of the very few oxides having oxygen ion conductivity. A very high level of oxygen ion conductivity and that is again useful from industrial point of view, extensively used industrially for many different purposes. We will see that at later stage. So, zirconia is a very important member of structural ceramics, sorry, the advanced ceramics materials.

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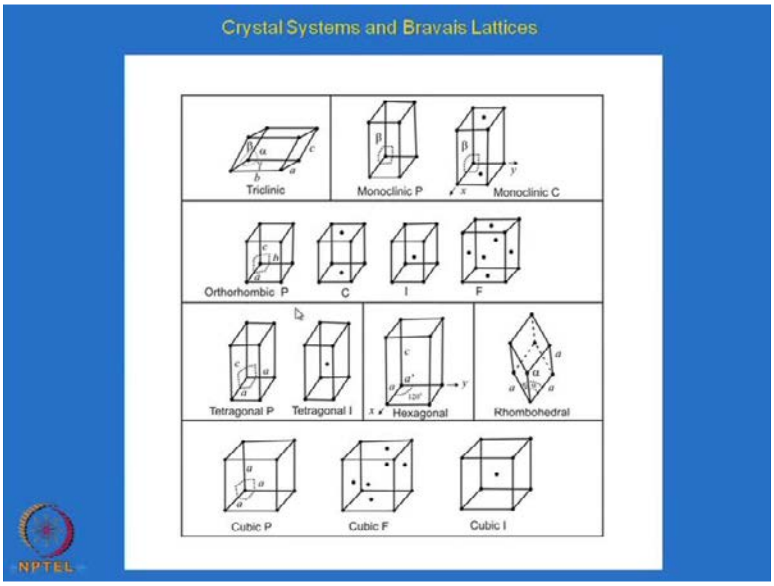
Crystal Systems and Bravais Lattices

Well, coming back again, we have discussed, while the structure, many a times we were talking about the symmetry, symmetry in the distribution or in the atomic arrangement of the different materials. Let us try to look at it very briefly, what are the different crystal systems available. Sometimes, you talk about hexagonal crystal structures; sometimes cubic crystal structures and we have also discussed about monoclinic, for example zirconia.

So, there are different kinds of symmetric elements and it may not be possible to discussing everything here. However, very briefly, let me tell you there are 7 crystal systems. There are 7 crystal systems depending on what is the relationship between the 6 parameters, what we call the lattice parameters. 6 parameters in the sense, we have three dimensional picture and a three access system, a b c or x y z axis and along the x y z, we have unit vectors called a b c. So, then you have different ways of expressing this volume. The symmetry may be different in different structures. So, alpha beta gamma are the angles and it will be c c a and a b. So, these are the axis you can see. This is a axis, this is b axis and this is c axis. So, alpha is the angle between a and c, beta is the angle between a and b, beta is the angle between b and c and alpha is the angle between the a and b. So, these are a b c axis and alpha, beta, gamma, are the angles between them. So, if that be so, you can imagine various different relationships between them and this is what we called triclinic system.

The list I will give you in a minute, what is the relationship between a b c and alpha beta gamma. So, you have triclinic system; you have monoclinic system and then again monoclinic as two different forms. One is called the primitive form and other is called base center form. Well, in all these cases, the corners are occupied by the atoms or ions. All the corners are occupied by the atoms or ions and in addition, in some of the cases, we have extra ions or extra atoms, like in this case, it is what we call base center. Only there are two faces. Two faces of these two sides. Opposites are occupied by the two atoms or ions.

So, in this case, orthorhombic, these are all orthorhombic. Four varieties of orthorhombic are available. One is the simple or the primitive cell, then we have a base center and then we have a body center here and then the fourth one is face centers. So, in addition to the corner positions, the face center positions are also occupied by the atoms. So, depending on the atomic arrangement, one can imagine these kinds of unit cells and definition of the unit cell is, these unit cells once repeated in all the three different directions completely fills up the volume and the vectors are repeated in all the three different directions. Here again, we have a tetragonal symmetry and we have only body centered. Not the others. In case of tetragonal, only body center. In case of monoclinic, only base center.

Hexagonal, of course it is a primitive cell. There is no other body center, face center or base center. So, it is only one variety of hexagonal cell and we will discuss and will just point out what is the relationship and how hexagonal system is different from cubic or other systems. We have a rhombohedral here. There is no again. Only primitive cell is there. There is no base center, face center or body center. In case of cubic, three varieties are there. So, it is the primitive. There is no atom inside or either in the body center or face center, whereas, this is a face center cubic structure. We have discussed this. All the face center cubic and hexagonal we have discussed extensively and there is a body center. Body center also we have discussed earlier. So, in all, there are 14 kind of systems, what we call crystal systems. Sometimes, it is called Bravais Lattices. So, any kind of structures can be described by one of these 14 systems. So, any structure, any atomic arrangement, what you can think of, are actually, really, in reality whatever exists, they can be described by these 14 bravais lattices.

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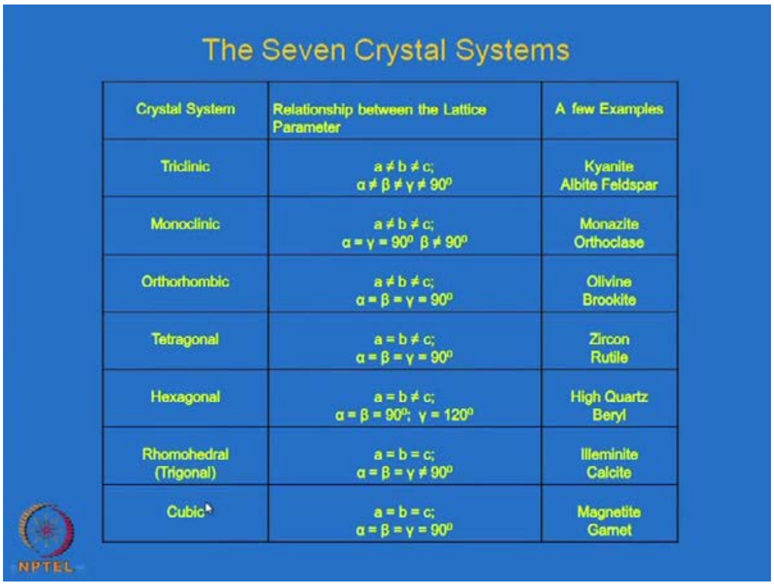

The Seven Crystal Systems

Crystal System	Relationship between the Lattice Parameter	A few Examples
Triclinic	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90^0$	Kyanite Albite Feldspar
Monoclinic	$a \neq b \neq c$; $\alpha = \gamma = 90^0$ $\beta \neq 90^0$	Monazite Orthoclase
Orthorhombic	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90^0$	Olivine Brookite
Tetragonal	$a = b \neq c$; $\alpha = \beta = \gamma = 90^0$	Zircon Rutile
Hexagonal	$a = b \neq c$; $\alpha = \beta = 90^0$; $\gamma = 120^0$	High Quartz Beryl
Rhomohedral (Trigonal)	$a = b = c$; $\alpha = \beta = \gamma \neq 90^0$	Illeminite Calcite
Cubic	$a = b = c$; $\alpha = \beta = \gamma = 90^0$	Magnetite Garnet

Their relationship is given in the next slide, how this a b c and alpha, beta, gamma are related. In the triclinic system, a, b and c, none are equal. So, the unit vectors are different. So, they are completely different and then alpha not equal to beta not equal to gamma and none of them are 90 degrees. So, it is not an orthogonal system metal at all. So, the angle between any of the two axis is really not 90 degrees different from that and that is how a triclinic system is described. It is a very least amount of symmetry is available there in this kind of a system and some of the compounds we will be discussing about the formulae of these compounds later on, but these are some ceramic systems like kyanite, basically aluminum silicate, then albite and feldspar. Feldspar we have mentioned earlier. It is one of the major components or raw material and is used white wares or white clay products.

So, then we come to the second system. It is called monoclinic. The diagram or the axis, relationship of the axis is given in the previous slide. Here it is, a not equal to b not equal to c. Once again, the unit cell vector in three different directions is not equal. They are all different. Alpha and gamma are equal to 90 degrees, whereas, beta is not 90 degrees. So, that is the relationship between the axis as well as the angles in the monoclinic system. Two of the most important examples are what we call monazite. Monazite actually is a mineral, which contains thorium, thorium phosphate and orthoclase silicate. So, these have a monoclinic structure.

Orthorhombic relationship is like this, a not equal to b not equal to c, whereas, all the angles 90 degrees. So, all the angles are 90 degrees, but the axis unit vectors or lattice parameters are different. Olivine and brookite, they are again two different silicate minerals, which have this kind of a structure. Of course, these are only few examples. There are many, many different compounds, which may have orthorhombic structure or any of these structures or symmetry structure. Tetragonal, a equal to b not equal to c, but in this case, again alpha equal to beta equal to gamma equal to 90 degrees. All the angles are 90 degrees. Only one axis is different. a and b is equal, but c axis is not same as a b.

So, the two components, which has this kind of a structure is zircon. Zircon is basically a zirconium silicate structure, z r o 2, s i o 2 and rutile, we have already discussed. So, rutile has basically a tetragonal structure, tetragonal symmetry. Hexagonal, hexagonal has a equal to b not equal to c. Similar to tetragonal, but only difference here compared to any other, we can see alpha equal to beta equal to 90 degrees but gamma is 120 degrees. So, it is a slightly different geometry than any of the other one. So, hexagonal has this kind of a relationship between their axis. Sometimes, hexagonal is also described in a slightly different way. Instead of a b c, sometimes it is also described their as a 1, a 2, a 3 and c. Anyway, we are not going to discuss the details of that, so high quart, one form of silica, high quartz and beryllium. Once again silicate minerals do have a hexagonal structure and many elements like copper, do have hexagonal symmetry. So, many of the metals do have a zinc copper, zinc, sorry, I am making a mistake, not copper. Copper is a F C C. Zinc actually has a hexagonal structure. Copper is a F C C structure.

Rhomohedron or sometimes is also referred to as trigonal. It is called a b c. Here, a equal to b equal to c and then alpha equal to beta equal to gamma and none of them are 90 degrees. So, illuminate, it is another mineral. It is actually iron titanate and that is illuminate and calcite is calcium carbonite. So, rhomohedral is the structure, which is available in this kind of compounds. Cubic is of course the simplest to describe and the most symmetric material I think, where a equal to b equal to c and alpha equal to beta equal to gamma equal to 90 degrees. So, there are many, many oxides. Only two of them is given here, magnetite and garnet. Garnet, again a general formulae, and there are many varieties of garnets.

So, that is seven crystal systems and they apply to any, whenever we are discussing the crystal structure, they will follow, they will one kind of systems will be fitted into that structure.

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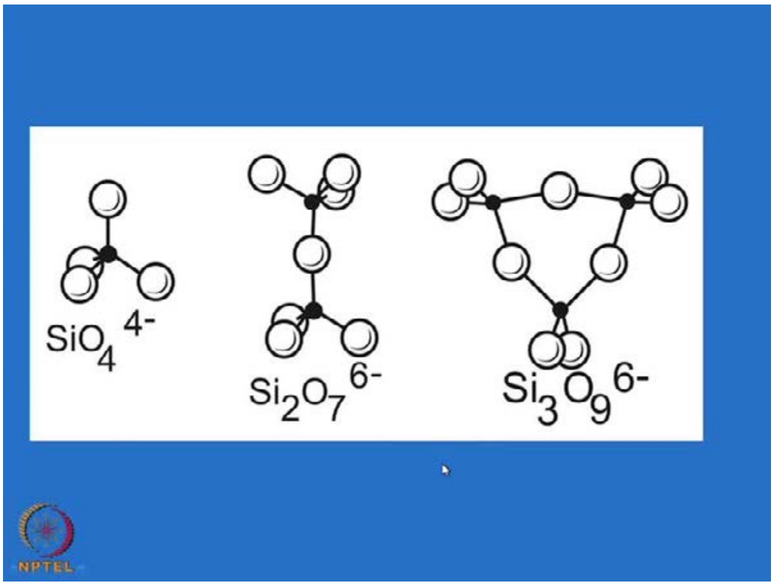

Well, I now come back once again for the discussion on the silicate structure. It is one of the most exciting and interesting subject as far as the structural features are concerned. This I discussed last time. Basic unit of any silicate structure or silica is s i o 4. That means, a silicon is coordinated tetrahedrally by oxygen ions. This is a unit which actually repeats itself in many different ways. So, it has a unsatisfied bond of 4 or charge of 4, so s i o 4 with 4 minus. So, this is the basic unit of any silicate structure and even silica glass. Then they can be combined in different ways. So, 2 silicon can share one oxygen and the other oxygen's can be available for binding to other cations. So, silicon is being shared or a oxygen is shared between two silicon ions.

So, then this becomes one unit and the formula will be s i 2 o 7 6 minus. So, it has 6 negative charges, which can be satisfied by combination with other cations other than silica. It may be aluminum, it may be magnesium, or it may be calcium. So, some of these things will come and join and satisfy the unsatisfied bonds here. It can form a ring of this nature. Two silicon ions once again sharing a oxygen and out of the 4 oxygen, 2 are actually shared. Here, none of the oxygen's are shared between the silicon ions, whereas here, one oxygen is being shared by 2 silicon ions. In this structure, 2 of the 4 oxygen ions of each tetrahedron is being shared by silicon.

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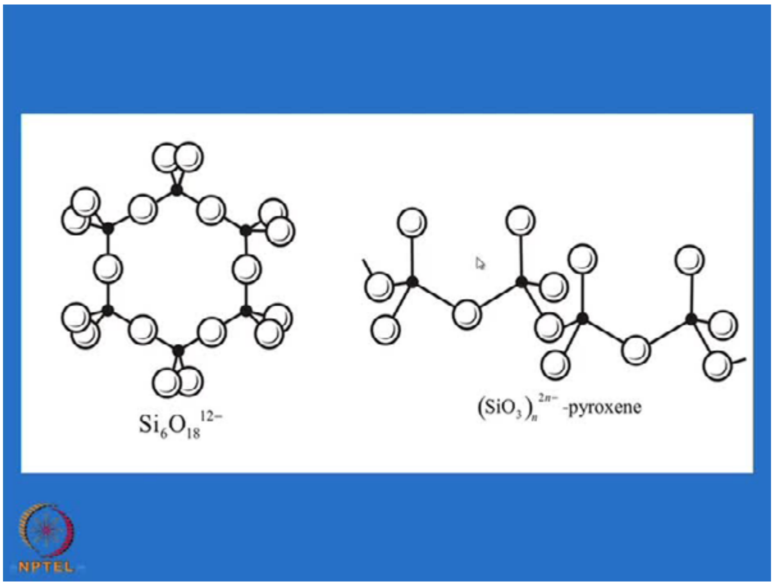

So, there is a ring formation, what we call a 3 member ring formation and the overall charge, unsatisfied charge is 6 minus. So, S i 3 O 9 6 minus. Then we have a slightly bigger ring. Here, is a 6 member ring. Instead of a 3 member ring, we can have a 6 member ring and this can be a repeating unit for the other cations to join in and form the total structure. So here, once again 2 of the oxygen ions are shared by silicon ions and the overall group formula is S i 6 O 12 with 12 negative charges. So, more number of cations can join in and form a much bigger molecule.

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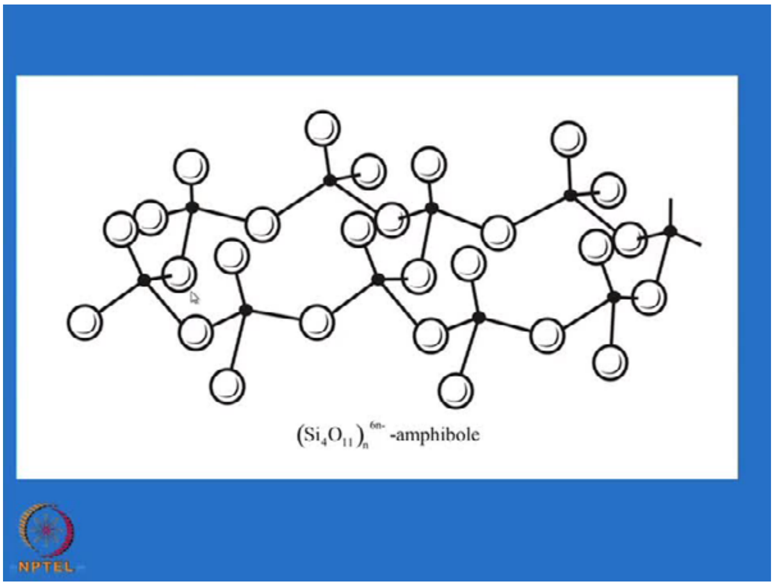

$(Si_4O_{11})_n^{6n-}$ -amphibole

Instead of a forming a ring, still 2 of the oxygen ions can be shared by silicon in this forming a chain. So, it is called pyroxene structure and here again, two of the four oxygen ions are being shared by silicon and rest will be connected or joined to or bonded to other cations. This is another structure. Again, the basic unit is silicon oxygen tetrahedron and you can see, it is what we call a double chain. This is one chain and this is another chain and then there is a kind of cross linkage. Here, this oxygen is shared by silicon of one chain with the silicon of other chain. As a result, in this 4 oxygen of this particular tetrahedral, all the 3 are shared. This is shared, this is shared and also this is shared between two neighboring silicon ions.

So, in this particular tetrahedron, all the 3 are shared, whereas next one only 2 are shared because there is no cross linking. So, cross linking is been done at certain intervals. Not all of them or cross linked between the chains. So, both kind of, 2 bridging oxygen’s and 3 bridging oxygen’s are available for the different tetrahedrons. So, effectively 2.5 out of 4 is actually shared and this particular structure is called amphiboles. The unit formula is about depending on what is the number of tetrahedron in a chain, you will get a value of (( )). So, it is variable. So, there will be different kind of structures or minerals having different kinds of formula.

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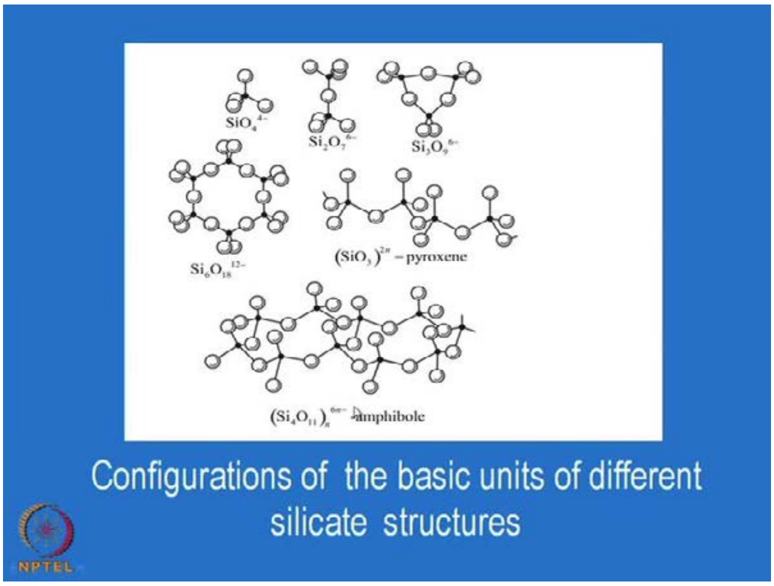

Configurations of the basic units of different silicate structures

These are all summarized here. We have started with this and then we have 2 silicon and oxygen tetrahedral are shared. It has a three member ring, six member ring, single chain and double chain. So, the same thing has been summarized in this case.

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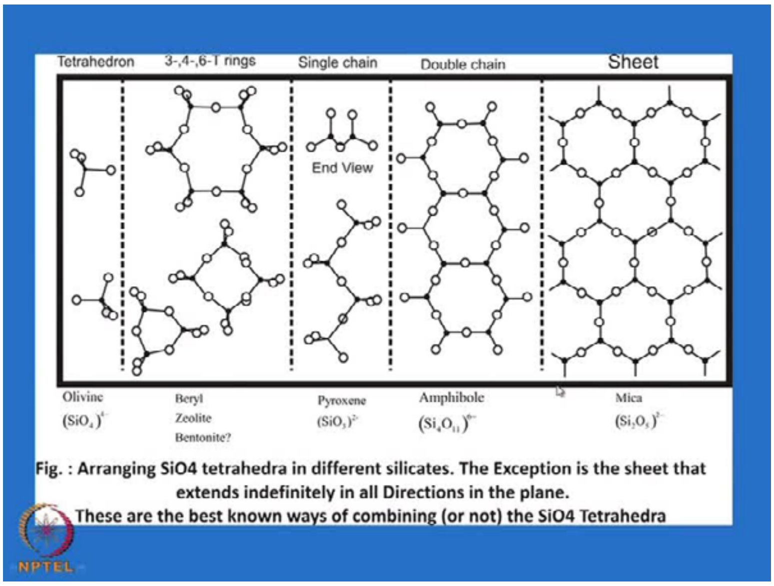

Fig. : Arranging SiO4 tetrahedra in different silicates. The Exception is the sheet that extends indefinitely in all Directions in the plane.

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

This is also another summary. Of course, an additional structure is also there. The only additional information is these are called olivines in mineralogical name. Here, these are all beryl. This kind of structure is available in beryl, one kind of mineral, silicate mineral. Then pyroxene and amphibole have been discussed. The only new thing here is mica.

This is sheet structure. These are single tetrahedron, 3 4 6 rings, tetrahedron rings. 3 rings, 4 rings and 4 rings will be not be discussed here. 4 ring is also possible. 6 rings we have discussed. So, there are different kinds of rings. Then we have single chain. This is one view of that and this is other view. Then you have double chain. That also we have discussed. What we have not discussed so far is this kind of a structure. So, this chain extends indefinitely in, particularly in x and y directions. So, it is horizontally extending in the form of a sheet. So, sheet structure, this is what we call the sheet structure of silicate. So, we have many different forms of silicates. We have olivines, we have beryl type of structures, pyroxenes, amphiboles and mica. Mica is suddenly a very useful product or useful mineral and the structure is what we call a sheet structure.

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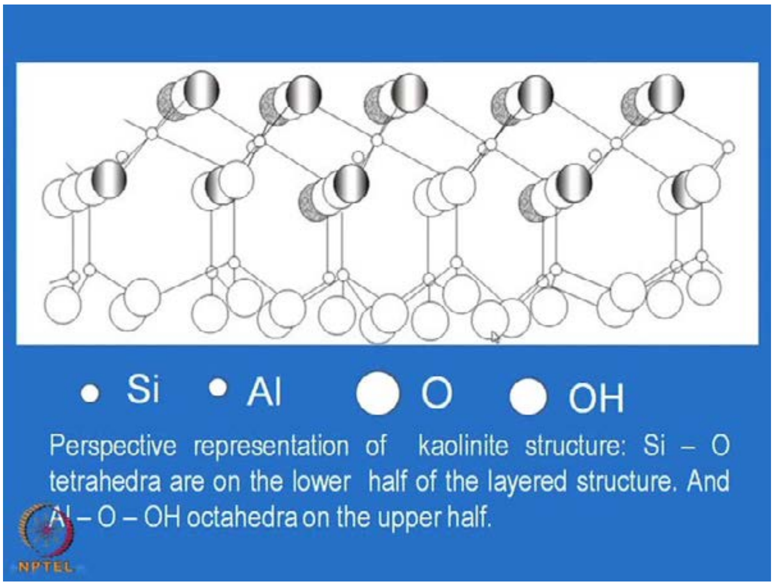

Perspective representation of kaolinite structure: Si – O tetrahedra are on the lower half of the layered structure. And Al – O – OH octahedra on the upper half.

Here, only 2 of the chains are joined together, whereas in the sheet structure, a large number of chains are getting joined together to form a complete horizontal structure of silicon oxygen sheet. So, that is another very interesting property of silica and there are many varieties of sheet structures. I will give some of them and most important sheet structure silicate is kaolinite or sometimes the compound is called kaolinite and the mineral is called kaolin. So, that is once again a naturally occurring mineral and is very very useful and one of the major components of traditional ceramics. Most of the white clay actually contains kaolin and when it is mixed with some iron oxide and other things, it becomes red.

But otherwise, it is a very white clay and less is the amount of iron oxide and white is the clay. So, this has a very important structure and has been studied in quite detail. The basic description is like this. It is a sheet structure, so you have a sheet here. It is along the vertical direction. This is not the horizontal thing. Earlier, we have seen a kind of planer configuration. This is you are seeing from the top. So, this looks like this.

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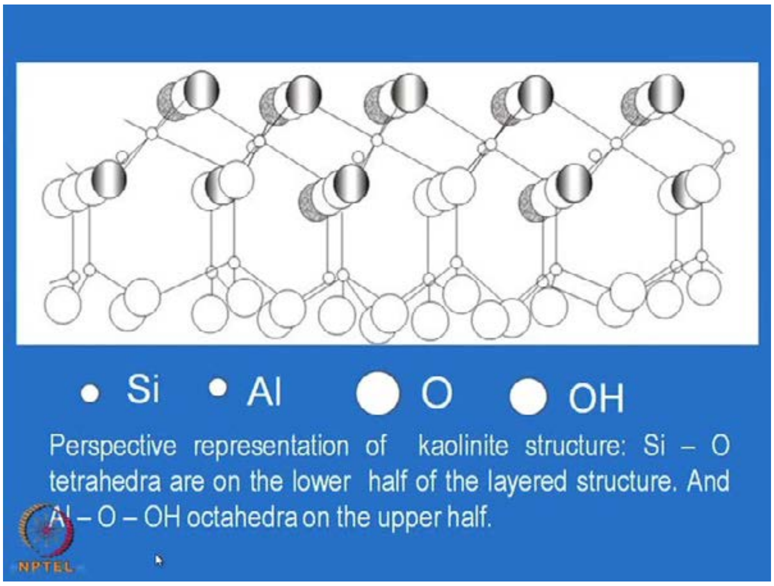

Perspective representation of kaolinite structure: Si – O tetrahedra are on the lower half of the layered structure. And Al – O – OH octahedra on the upper half.

But, if you are looking from the side, it will look like this. So, it is a kind of civil engineering terminology, elevation. So, this is the sheet. These are silicon. There are three oxygen on the side and one oxygen on this side. So, one oxygen is protruding out here in this and so there is, one of the oxygen is on this layer, whereas 3 oxygen's are on this layer and in between, you have smaller ions, the silicon ions. So, these are silicon ions. So, this is total is the silicon oxygen layer or silicon oxygen sheet. On top of that, vertically above, you have another layer and in this case, the kaolinite formula, the chemical formula is actually hydrogen alumina silicate.

So, it has silica, S i O 2, A l 2 O 3 and some hydroxyl ions. So, it is actually a kind of interpenetrating layer between (( )) and S i O 2. So, there are, this layer actually is a layer of aluminum, aluminum hydroxide layer. So, these ions, although they have not been differentiated between this silicon and this aluminum, these are all aluminum ions. These are all aluminum ions and this layer is actually aluminum hydroxide layer. So, these are hydroxyl ions and this white ones are oxygen ions. So, in this particular layer, there is both oxygen and hydroxyl and another distinctive feature of this structure is, aluminum is having an octahedral coordination, whereas silicon has a tetrahedral coordination. So, aluminum has a octahedral coordination, but not all the anions are oxygen. Only a part of it is oxygen and partly hydroxyl. So both hydroxyl and oxygen together form the octahedral and in between, at the center of the octahedral, aluminum ions sits. So, you have a interpenetrating or a joint. Two layers are joined together and one is the tetrahedral layer of silicon oxygen and another is a octahedral layer of aluminum, oxygen and hydroxyl. So, this is the composition or this is the structure. That is how you can describe the structure of kaolinite. So, it is a layer structure.

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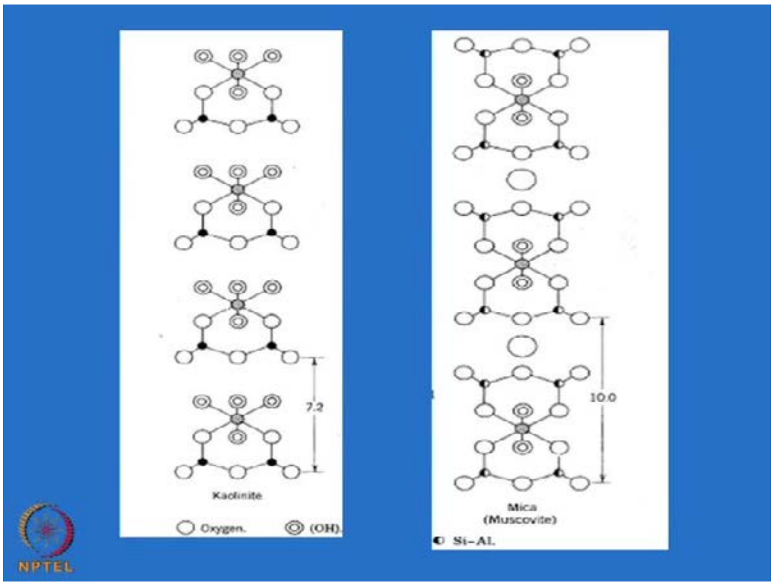

A double layer of kind of thing; a silicon oxygen layer and aluminum hydroxide layer, two of them are joined together very strongly and there is ionic bonding. So, these layers are quite strongly bonded and totally it is a sheet type like structure. So, this is the description of kaolinite structure and mostly they will be available in flaky form.

Next, we come to some few more sheet structure. I just, I will not discuss in greater details, but I will give you some idea, how this kaolinite structure is different from other sheets structures. This we have discussed. This is your silicon oxygen, this layer and here is the silicon. This is aluminum and you can see there are 6, totally 6. So, this is octahedron here. This is tetrahedron. So, this is the aluminum hydroxyl layer and here is silicon oxygen layer. Now, this forms the unit cell. Then in the vertical direction, this repeats. This repeats itself. So, this, this, this and this, are exactly identical. So, these layers are kind of stacked one over the other and forms a total volume or fills up the total volume. So, this is the basic description of kaolinite structure and this is our unit cell, from the lower end of this unit to the upper end of the next unit. That is your, what we call the unit cell dimension in the c direction. This is the c direction and the seat is in the x and y direction or a and b directions.

So, the layer is about 7.2 angstroms and this layer and this layer are bounded together by van der walls bond. There is no other chemical bond, except van der walls bond and so, this bonds are very, very weak bonds. This is very strong bond, because they have a ionic bonding between these different ions. So, this is difficult to separate. However, this van der walls bond is very weak bond. So, this layer can be separated out quite easily from the other one. But, they do have some bond. So, there are weak, very weak bond in the c direction, but they are very strongly bond in x y direction.

So, these are the different layers, atomic molecular layers of the kaolinite and that is how it is formed. Compared to that, if you go to mica, it is also sheet silicate structure, but in the structure of mica is quite different. Not quite different, it is slightly different in fact. If you look at this geometry and this geometry, you will find this top portion here is the exact mirror image of the bottom portion. This portion and this position are exact mirror image of each other. So, whereas up to this, is actually kaolinite structure. It is very close to the kaolinite structure. So, as if 2 silicon oxygen, 2 kaolin structures are inverted together and bonded together. So, this is actually a more symmetric structure. In the sense, this side also you have silicon oxygen and on the top side also you have a silicon oxygen and in between, you have aluminum oxygen hydroxyl.

So, 1 aluminum hydroxide layer is basically sandwiched between two silicon oxygen tetrahedral layers. So, they are all seeds in the x y z direction. This is extending x and y directions, but in the vertical direction, c directions, this is called the c directions, they are actually repeating itself in an inverted manner. So, unlike kaolinite, it is one layer of silicon oxygen and over that, a aluminum hydroxide layer. Whereas, in mica structure, what we call the double silicate, double silicate structure, we have one silicon oxygen and then aluminum hydroxide is sandwiched between another silicon oxygen layer. So, two silicon oxygen layers sandwiching the aluminum hydroxide layer, that forms the unit cell. So, you have a much longer or a much longer unit cell. Here about 10 angstroms and then that repeats. Here, this unit repeats itself, where in case of mica, this total unit repeats itself. So, there are three layers. However, there are some unsatisfied bonds.

For that, in between, you have some larger ions. Here is, they are joined together by only hydroxyl ions, sorry, van der waals bond and so they are very weak bonds. Here of course, it is not exactly van der waals bonds, but in between, we have some positive ions. These are alkali ions and they are replaceable ions. Between the layers, they are replaceable ions. These ions are normally alkali ions, like potassium or sodium. Mostly potassium or sodium and depending on whether it is a potassium ion or sodium ion, you have two different compounds or mica. In case of muscovite mica, its potassium and sodium mica is also available. So, these are the difference between two layers or two different kinds of sheet silicate structures. One is a kaolinite structure and other is a mica structure. There are many varieties of silicates and there is huge number of silicates available and most of them are naturally occurring and one can of course synthesize to some extent. But, they are difficult to synthesize. So, most of them are actually naturally occurring silicate structures.

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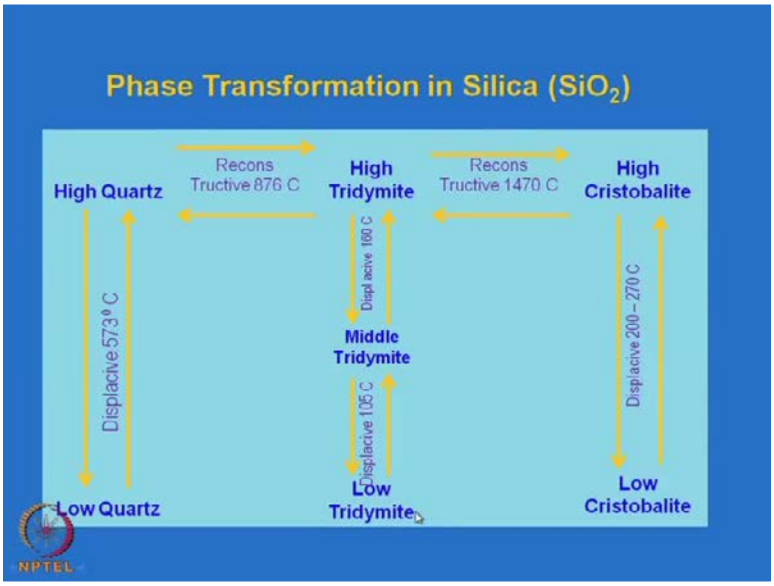
Phase Transformation in Silica (SiO_2)

High Quartz

Recons Tructive 876 C

High Tridymite

Recons Tructive 1470 C

High Cristobalite

Displacive 573° C

Displ acive 160 C

Middle Tridymite

Displacive 105 C

Displacive 200 – 270 C

Low Quartz

Low Tridymite

Low Cristobalite

Well, we have discussed just now about the silicate structures, where silica or silicon is getting combined, silicon tetrahedron, silicon oxygen tetrahedron is getting combined with many other cations, but silica as such is also very important ceramic raw materials, S i O 2, where it is all silicon oxygen tetrahedron only. So, this structure is sometimes called, mostly called framework structure. So, in all the three different directions, there are only silicon oxygen tetrahedron and they of course, have some crystalline formation, so that, we have very definite crystal structures, very definite geometric. So, these things we will discuss in the next class, because time is up and.

Thank you so much.