**Main Group Chemistry**
**Prof. M. S. Balakrishna**
**Department of Chemistry**
**Indian Institute of Technology, Bombay**
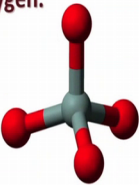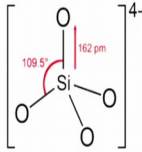
**Lecture – 36**
**Chemistry of Group 14 Elements**

Welcome to MSB lecture series on main group chemistry. In my previous lecture I was discussing about silicates and their transformation. Essentially when on kind of silicate undergoes transformation it involves breakage of one or more SiO Si linkages. So, let me discuss more on silicates in this lecture.

Silicate minerals are rock forming minerals and made up of silicate groups, they are in fact, the largest and most important class of rock forming minerals, whatever the minerals we have in the earth crust.
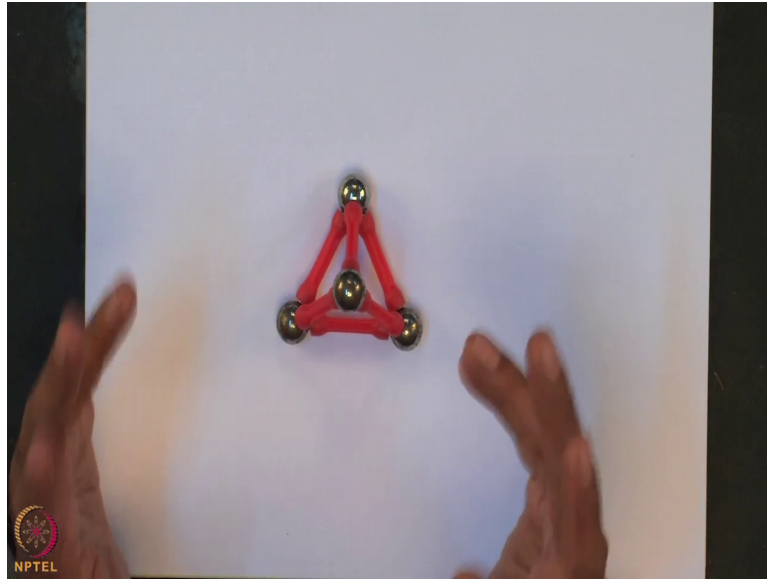
(Refer Slide Time: 00:54)



The silicate minerals accounts for 90 percent of them the basic unit of all silicates is essentially a tetrahedral ion something like this, something like this here these 4 corners of a tetrahedron are occupied by oxygen atoms at the centre silicon is there.

(Refer Slide Time: 01:14)



So, total charge will be SiO 4 4 minus; that means, O minus O minus O minus O minus here. These are the basic units of all silicates whether we have 1 dimensional, 2 dimensional or discrete silicates or 3 dimensional they consists of this kind of units. Essentially these silicates are classified based on the structure of their silicate groups which contain different ratios of silicon and oxygen having SiO Si linkages.

So, let us look into the classification of silicates now.

(Refer Slide Time: 02:03)



## Classification of Silicates

❑ The classification of silicates depends on how the tetrahedral units are arranged. Main classes of silicates are-

1) Orthosilicate or Nesosilicates or Island Silicates
2) Pyrosilicates or Sorosilicates or Double Island Silicates
3) Cyclosilicates or Ring Silicates
4) Inosilicates or Chain Silicates
   I. Single Chain Silicates
   II. Double Chain Silicates
5) Phyllosilicates (Sheet Silicates)
6) Tectosilicates (Framework Silicates)

We have several type of silicates orthosilicates or nesosilicates or island silicates where we have discrete groups. Pyrosilicates essentially involve having one SiO Si linkage something like this where we have Si is here one Si and one Si is here they are linked by one oxygen atom. So, this is essentially pyrosilicate.

(Refer Slide Time: 02:24)
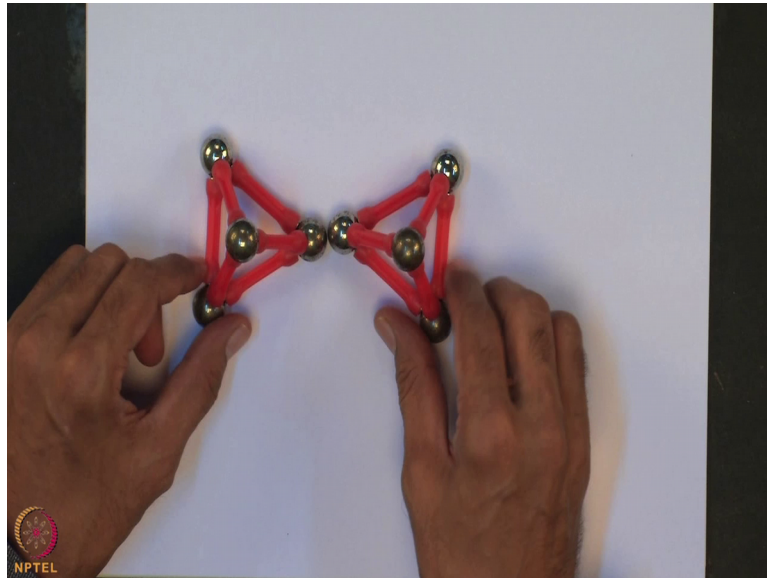


And then of course, we have cyclosilicates where 2 oxygen atoms are linked with the neighbouring once in cyclic fashion or in one dimension chain fashion. So, when its chain they are called inosilicates or chain silicates and again among chain silicates we have 2 type of silicates single chain silicates and double chain silicates and also we have sheet silicates where 3 oxygen atoms are shared with the neighbouring SiO 4 tetrahedra. Also we have tectosilicates or frame silicates in which all 4 oxygen atoms are sharing with the neighbouring ones to give a thread 3 dimensional network.

So, the corner oxygens are not shared with other in case of orthosilicates. They are discrete having this kind of independent units.
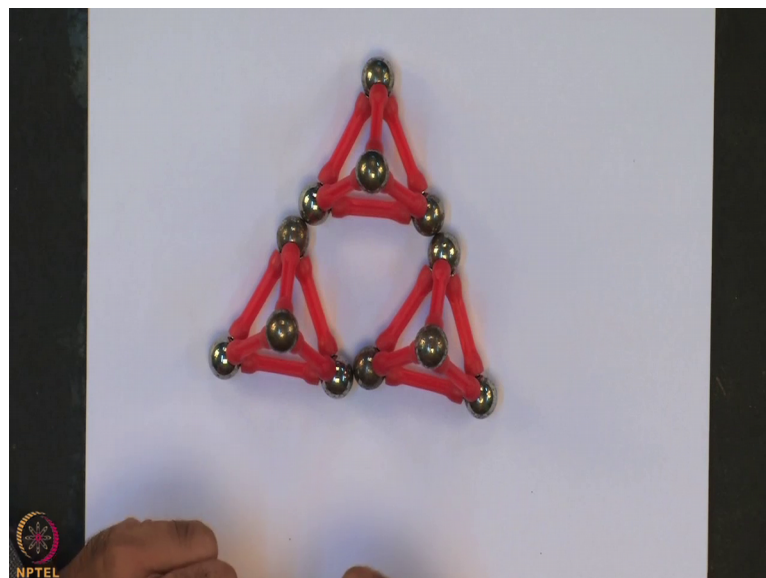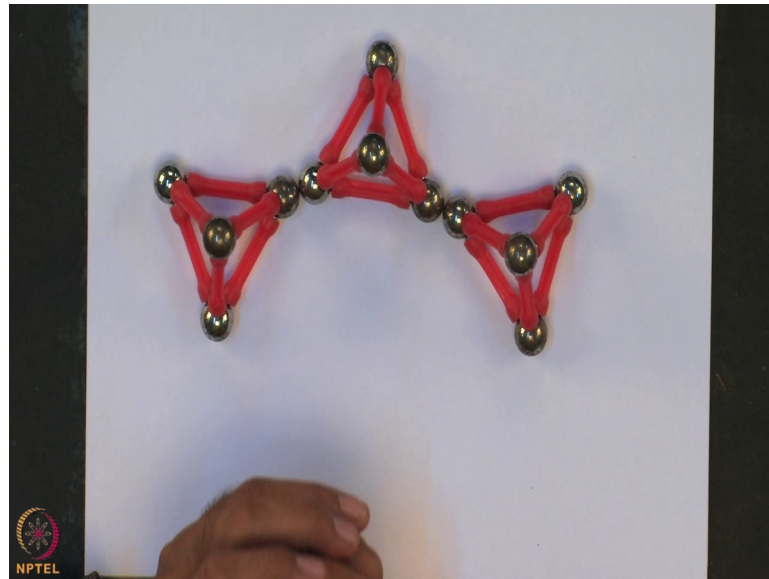
(Refer Slide Time: 03:15)



Each tetrahedron is isolated this group is often referred to as the island silicate group because it does not have any linkage with neighbouring groups the basic unit as I mentioned is again SiO 4 4 minus. In this group the oxygens are shared with octahedral groups that contain other cation such as magnesium, iron or calcium in the divalent states. Olivine is a good example that has composition of Mg Fe twice SiO 4 and you can see here this is a cyclic silicate, essentially something like this if you connect like this it leads to the formation of a cyclic silicate.

(Refer Slide Time: 04:06)

On the other hand it can be something like this. It can it can continue like this.

(Refer Slide Time: 04:16)



And one will be that side. So, if you have something like this, this will be a chain silicate as you can see in deposide and in the cyclic one it is we have 1 2 3 4 5 6 are there. So, that is essentially another 3 I had to put here.

(Refer Slide Time: 04:36)
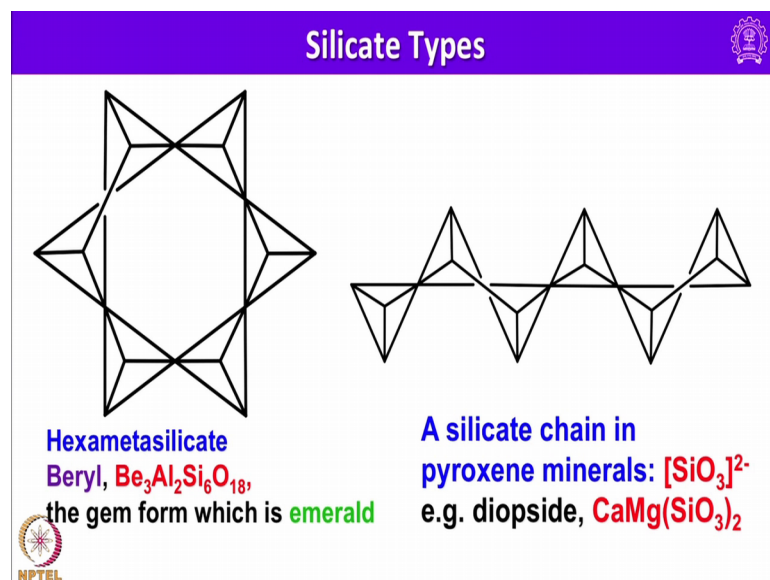


This is an example for beryl the berrylium ore as well as this, this is referred to as emerald this essentially a gem.

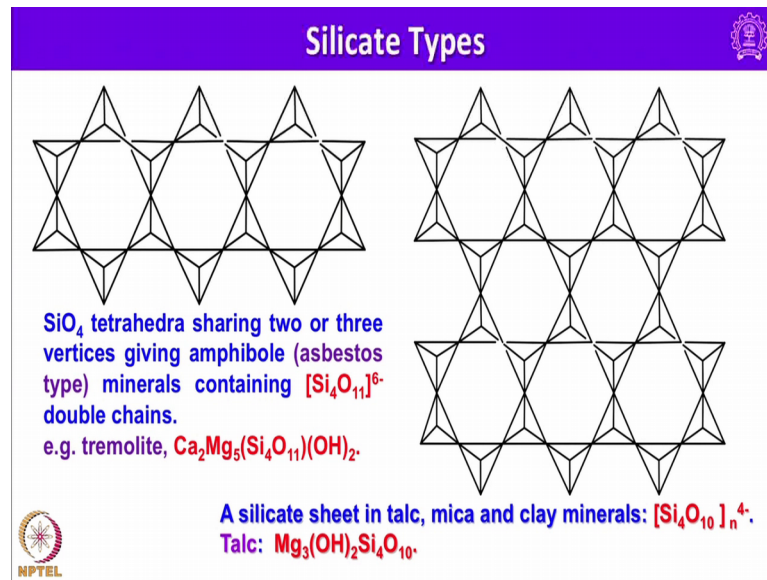And then as I said if they share 2 stands then we will be having chain silicates of this type here cyclic silicates of this type and this is an example for asbestos and here you can see here.

(Refer Slide Time: 04:58)



And of course, in case of asbestos what we have is we have some of the silicon atoms replaced by calcium as well as magnesium and the composition of tremolite is given here, and in case of silicate sheet this is how it looks like 3 oxygen atoms essentially 3 oxygen atoms are here 1 2 3. These oxygen atoms are shared essentially here something like this.

(Refer Slide Time: 05:31)
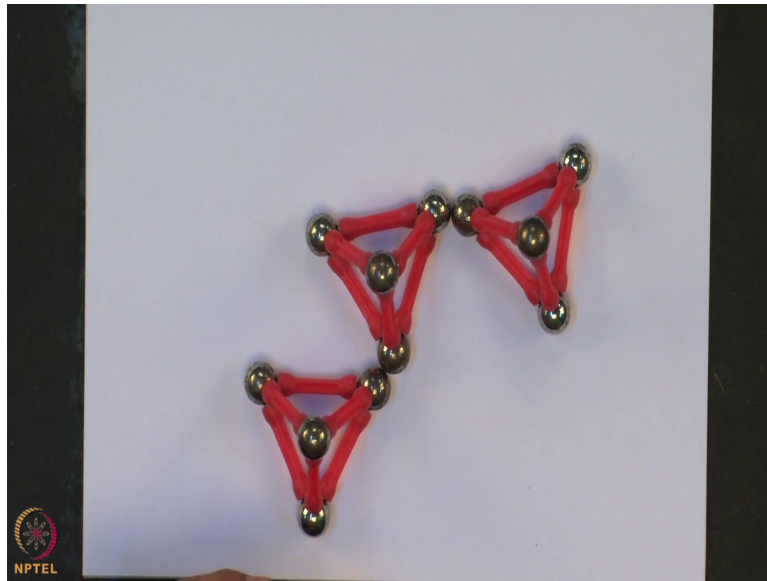


So, that leads to the formation of a sheet silicate. Example is talc, mica and several clay minerals and of course, talc composition is this one here Mg 3 OH twice Si 4 O 10 is the composition of monomeric unit.

When SiO 4 tetrahedra shares 3 vertices with adjacent tetrahedra sheet silicate results with the formula Si 4 O 10, Si 4 O 10 4 minus and n.
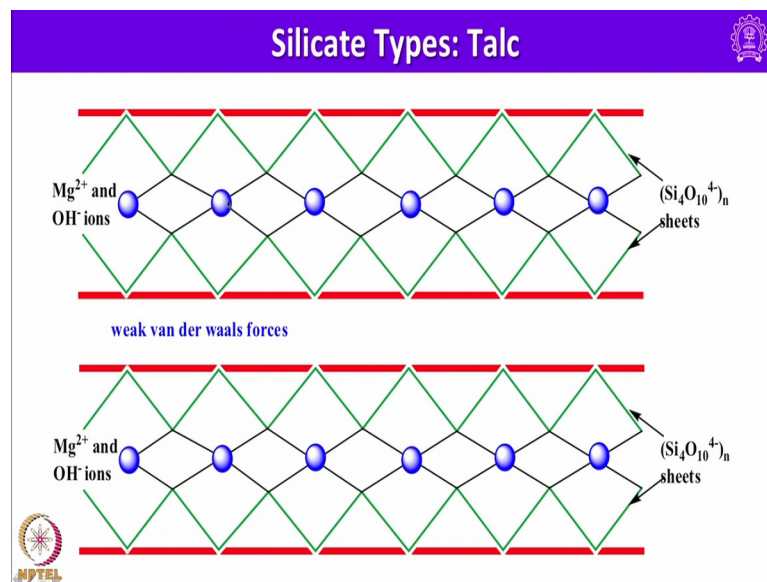
(Refer Slide Time: 06:17)
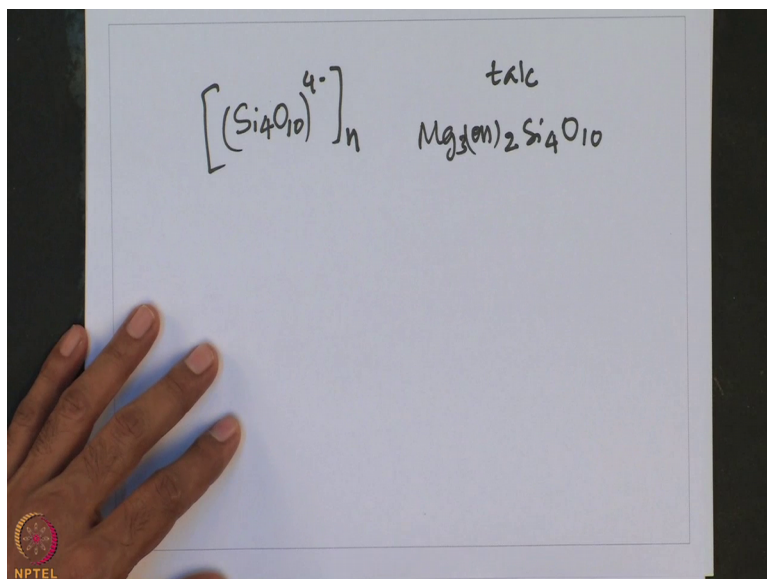


So, this is typically for a sheet silicate composition of monomeric unit. The bonding within the silicate sheet is very strong, but between them is weak. So, the compounds

having this kind of can be cleaved into thin sheets and these thin sheets are held by weak forces as a result they slide over other. In talc for example, we have Mg 3 OH twice Si 4 O 10 this is talc.

Here cations only reside between the alternate silicate layers, sandwiched between the 2 Si 4 O 10 4 minus sheets with magnesium and OH ions. These silicate metal silicate sandwiches then stack together. The bonding between the sandwiches is weak van der waals forces. So, talc is very soft you can see here. So, this is how in one two silicate layers are sandwiched with magnesium 2 plus and OH minus ions and such sandwiched silicates are held together by weak van der waals forces.

(Refer Slide Time: 07:29)



So, these forces are so weak they slide over that is the reason we see it is very smooth the talc whatever we use is an example for this silicate.

(Refer Slide Time: 07:54)
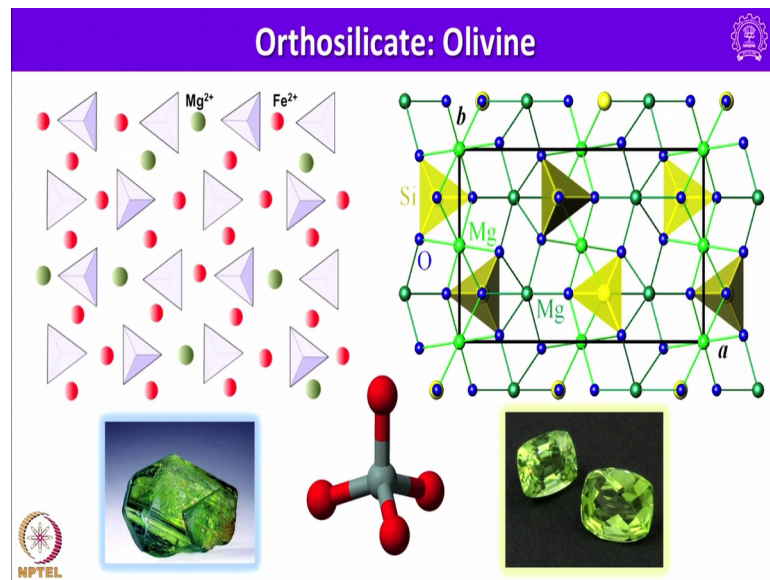


Orthosilicate you can see how it is SiO 4 4 minutes tetrahedral spread out without having any O Si linkages.
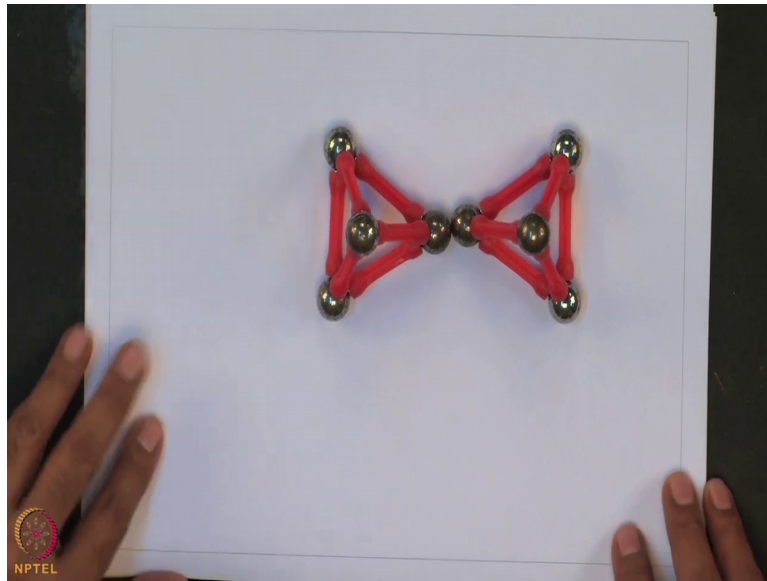
(Refer Slide Time: 08:04)



And pyrosilicates if one of the corner oxygen is shared, this is an example for pyrosilicate here. So, this is an example for pyrosilicate of course, pyrophosphate is also there. So, we have only one O SiO Si linkage.

(Refer Slide Time: 08:20)



And in this case the basic structure unit is if you can count now 1 2 3 4 5 6 and 7 so that means, $Si_2O_7$ 6 minus will be its composition. A good example of a pyrosilicate is the mineral hemimorphite having the composition it shown here in this slide. This is essentially $Zn_4Si_2O_7$ OH and $H_2O$, some pyrosilicates are a combination of single and double island silicates as you can see in epidote with this compositions shown here.
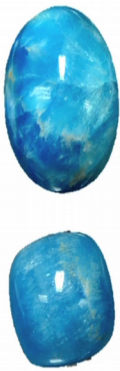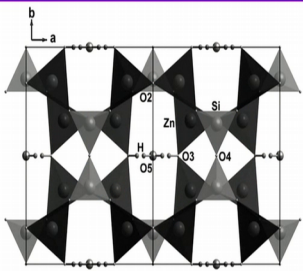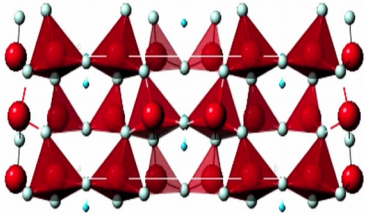
(Refer Slide Time: 09:01)
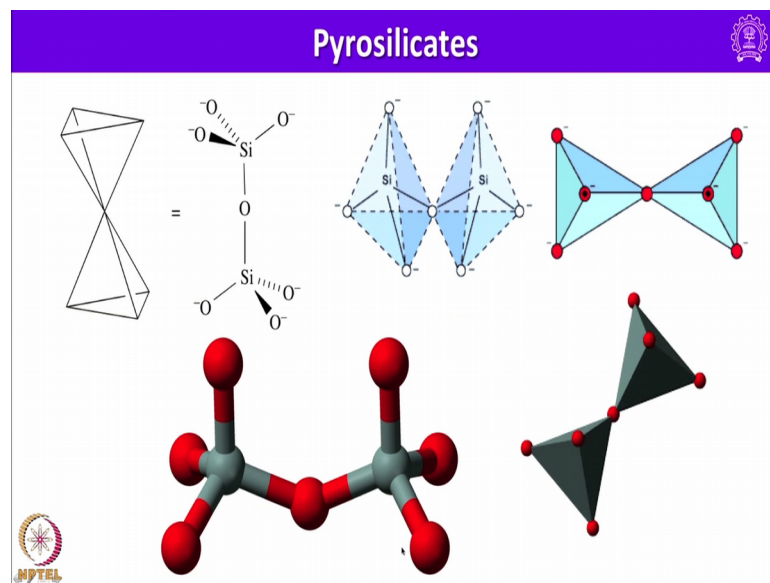
And of course, this how the pyrosilicate looks like having one SiO Si linkage of course, O is tetrahedral here you can see here this are all the examples for pyrosilicates you can see here.

(Refer Slide Time: 09:18)



And pyrosilicates of course, 2 such units are bridged by some of the other cationic species zinc here you can see this is an example and this also a precious stone hemimorphite this blue in colour.

(Refer Slide Time: 09:40)

Let us look into Cyclosilicates if the 2 oxygen atoms of a tetrahedron are arranged in a cyclic fashion something like this. So, this leads to the formation of cyclone silicate.

(Refer Slide Time: 09:53)
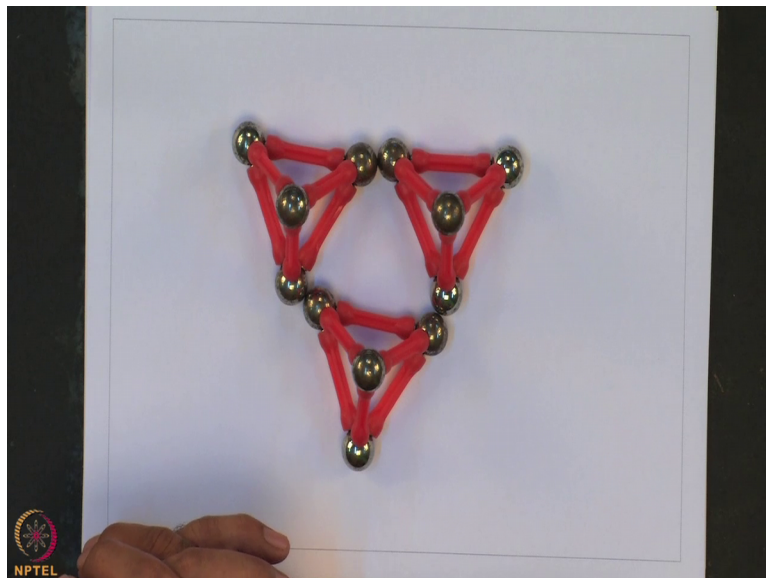


Of course, here you can have 3 6 membered or even 8 membered or even 11 membered you can have. A 6 membered ring forming the structural group of Si 6 O 8 12 minus, 3 membered rings have Si 3 O 9 you can see here 1 2 3 if you can just see here; 3 plus 6 3 plus 1 2 3 plus 2. 2 2 6 it will be 9, so Si 3 O 9 6 minus here or 4 membered rings can also be there. So, something like this, you can also have a 4 membered ring then you will have SiO 4 O 12 8 minus and so on and so forth you can have similarly a 5 membered ring also.
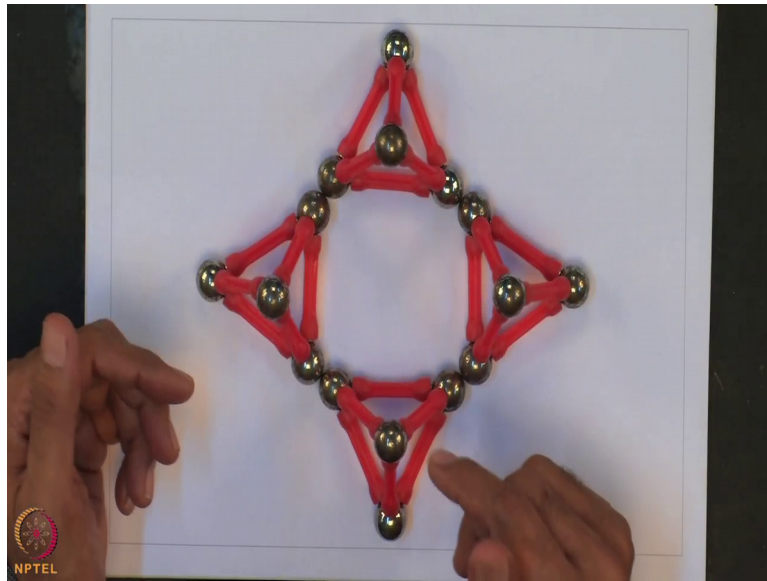
In this cases the composition of basic structural unit is SiO 3 n that I have shown here 2 n minus a very good example for the cyclosilicate is the mineral beryl again Be 3 Al 2 SiO 6 O 18 beryl. Beryl is also a source of berkelium, that also I showed you how to extract berelium from beryl when discussing the chemistry of group 2 elements. So, yes this is the trimer, this is a tetramer and this is hexameric structure of cyclosilicates.
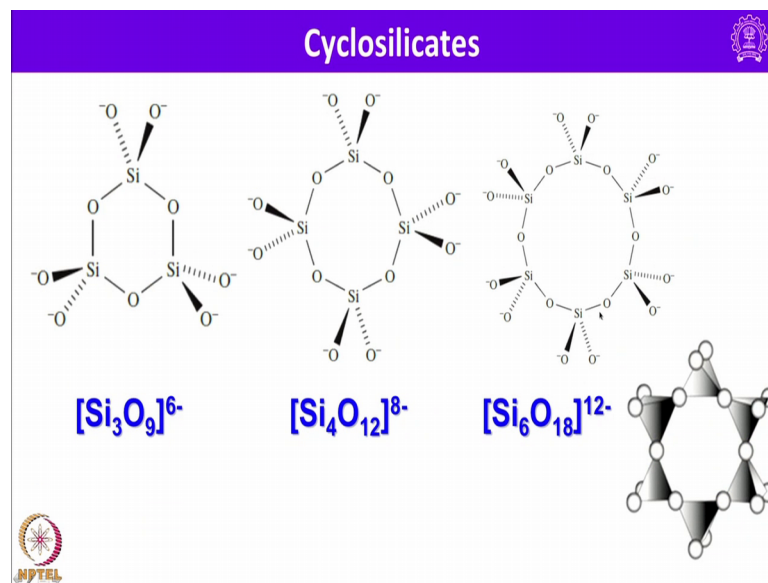
Of course, here you can see the beryl this how it looks like.

(Refer Slide Time: 11:19)
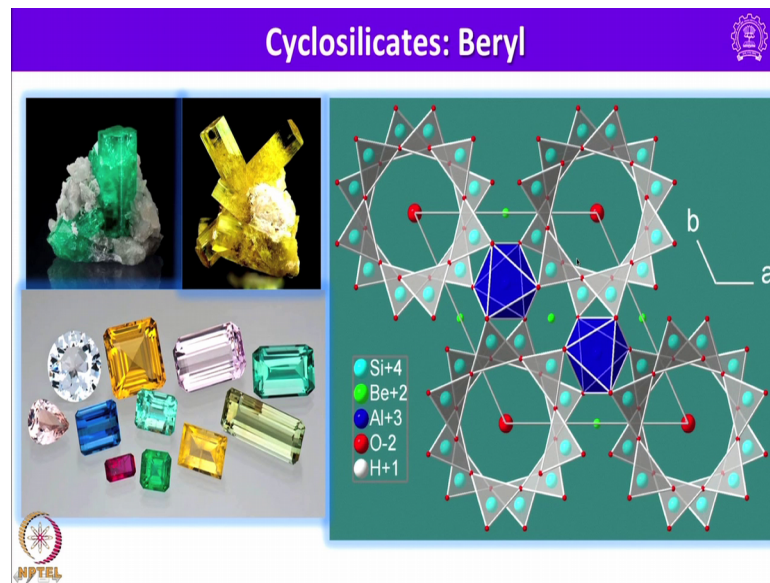


And when we change this cations we can see a different colour comes into picture this are all used in jewellery.

(Refer Slide Time: 11:36)



And sheet silicates are quite important when we consider mineral such as micas and other things. So, here basically what happens? 1 or more silicon atoms are replaced by aluminium atom. When you replace 1 silicon with aluminium atom in order to balance the charge one extra cat ion needs to be added in these cases what happens essentially potassium or magnesium comes into picture. So, these minerals are essentially called as

micas. So, when you replace 1 silicon there is a deficiency of 1 cation. So, in that case basically what happens? 1 element such as sodium potassium can be added or one can also add magnesium for 2 silicon atoms. So, that way that is taken care the charge that charge balance is taken care.

In micas additional cations K plus (Refer Time: 12:34) or lithium in the lithium ore lipidolite lie between, so these cations will lie between the silicate sheets and thus they are bonded more strongly by ionic interactions compared to the weak van der waals forces we come across in talc the cleavage of mica is still into thin sheets. So, other important mineral which have the sheet silicate structure are essentially a variety of clay minerals. Quartz is one of the most known and having several thermally stable crystalline form of silica having SiO 2 composition.

The most important forms of silica include alpha quartz, beta quartz, tredymide, cristobalite, (Refer Time: 13:21) and stishowide and also we have network silicate minerals if an SiO 4, if a SiO 4 tetrahedra shares all 4 of its vertices; that means, here if I consider here, if all this 4 vertices are shared by neighbouring SiO 4 tetrahedra. So, then that results in network silicate minerals. If 3 times network, here essential a negative charge is readily introduced with the framework by replacement of some silicon atoms by aluminium atom. So, in these cases if you replace one or more silicon atoms naturally what happens a negative charge is introduced. So, to compensate that one basically what happens some counter cations will be added. So, commercially important class of network of alumina silicate is essentially known as zeolite. A large in the both synthetic and natural zeolites are known one of the basic building blocks for several zeolites is the soda light cage. I will show you what is sodalite cage is, this is how the sodalite cage looks like.

(Refer Slide Time: 14:33)



**3D- Silicates**

(a)
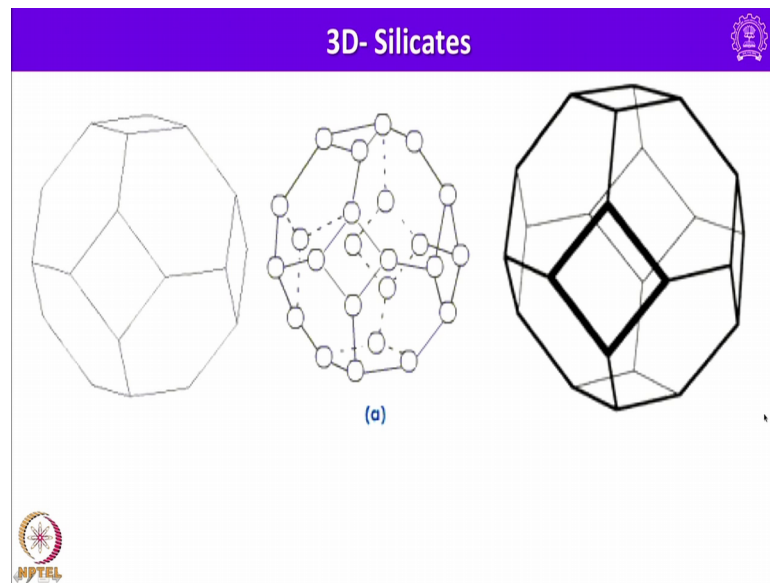
In this one you can notice we have O 2 1 2 3 4 5 6 4 membered rings are there and 8 6 membered rings are there so that means, essentially each sodalite consists of 6 4 membered rings and 8 6 membered rings. Several synthetic coordination polymers and metal organic frameworks having this kind of structures are known.

(Refer Slide Time: 14:56)



**Sheet Silicates**

The structure of zeolite A, composed of interconnected sodalite cages.
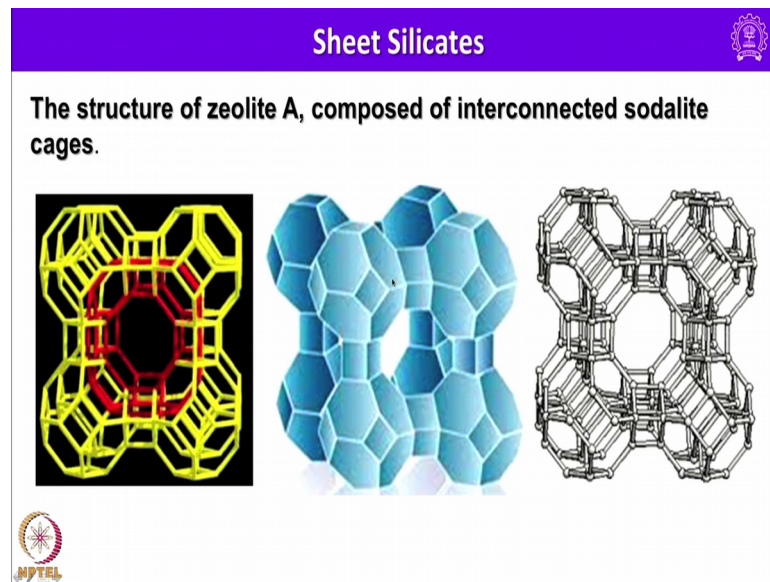
For example, you can see here 4 such units are linked in this fashion and here. So, in this one we have essentially 8 such units interlinked together.

Of course, this is another example that was made in our laboratory.

(Refer Slide Time: 15:08)
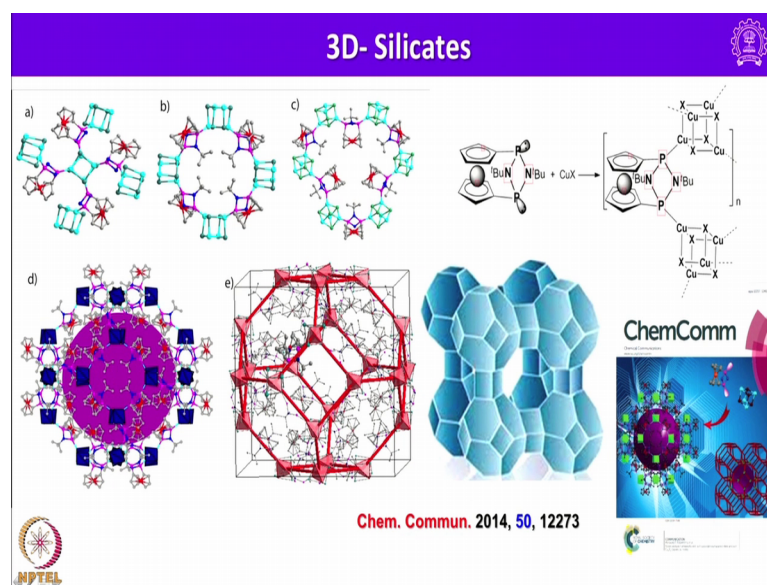


Working on copper one with bisphosphene, and you can see here the monomeric unit in this reaction of cyclo diphosphasane with copper iodide result in the formation of this cubanes Cu 4 x 4 cubanes and this cubanes are shown here and these bisphosphenes are shown here. It also consists of you know 1 2 3 4 5 6, 6 4 membered rings and 8 6 membered rings this is very similar to the monomeric unit we come across in case of sodalite and this is a rare and only the example of soft copper one and phosphorous 3 ligands leading to the formation of this kind of soda light network.

(Refer Slide Time: 15:57)

Let us look into the chain silicates if 2 of the oxygens are shared in a way to make long silicon single chains of linked SiO 4 tetrahedra we get the single chain silicates or inosilicates and again here the basic structural unit can be seen here Si 2 O 6 4 minus or SiO 3 2 minus. This group is the basis for the pyroxene group of minerals having this composition I have shown here, having counter cation such as magnesium iron in this one or calcium and magnesium along with iron in case of this chain silicate and of course, this how the chain silicate looks like.

(Refer Slide Time: 16:40)
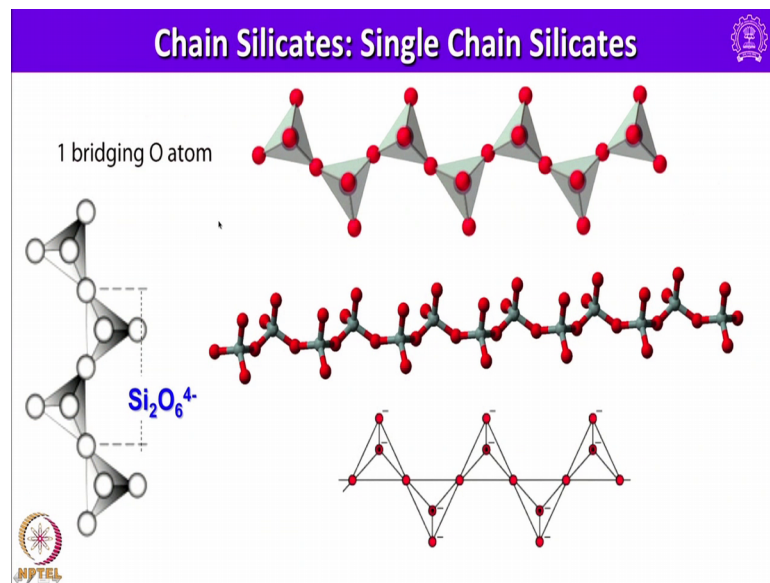


(Refer Slide Time: 16:46)
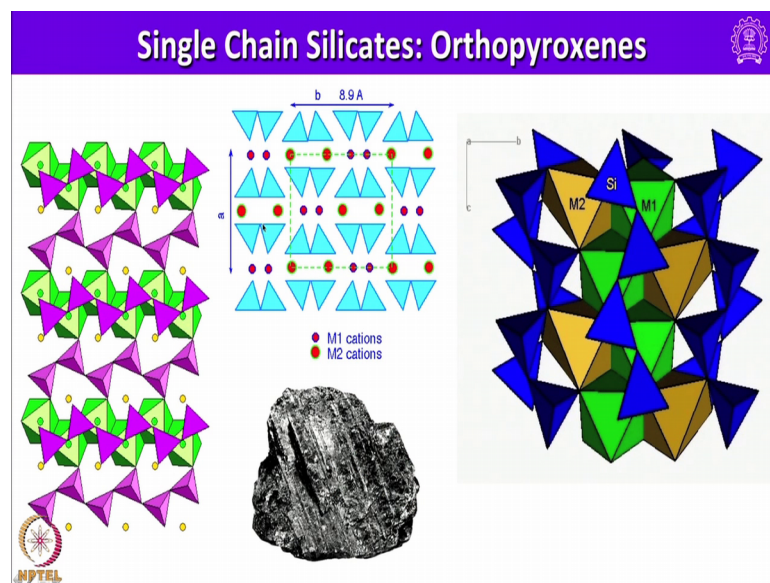
And of course, one can also come across single chain silicates as we see in case of orthopyroxenes. You can see here this is how the clay looks like, the mineral looks like and the interlinking can be seen from this picture here.

(Refer Slide Time: 17:04)



So, if 2 such chains are linked together. So, that each tetrahedral group shares 3 oxygen atoms we can have double chains. The basic structural group being having a composition of SiO 4 O 11 6 minus or Si 4 O 11 6 n and this is the repeating unit amphibole group of minerals have this double chain silicate structure for example, one can look into this one where we have calcium magnesium and iron along with silicon in this one. This is how it looks like when 2 strands are joined together in between we have a cyclic unit coming into the picture you can see here.

(Refer Slide Time: 18:03)
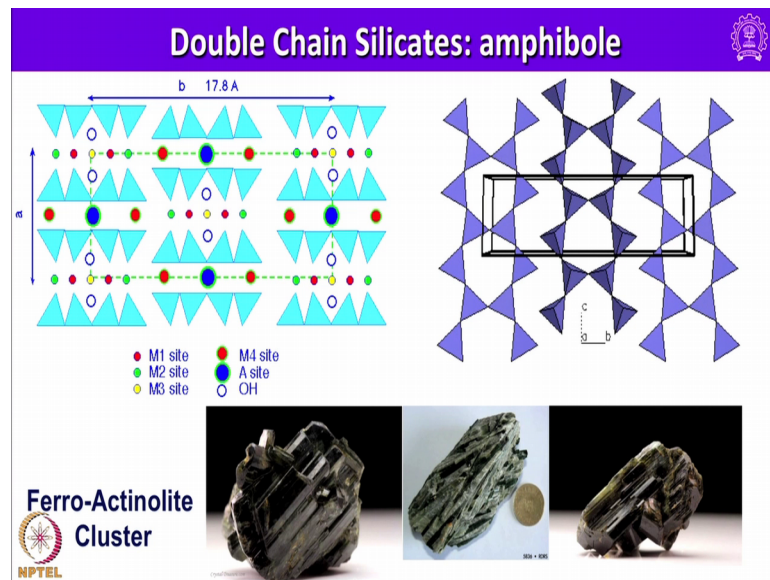


So, this again example for double chain silicates amphibole.

(Refer Slide Time: 08:05)
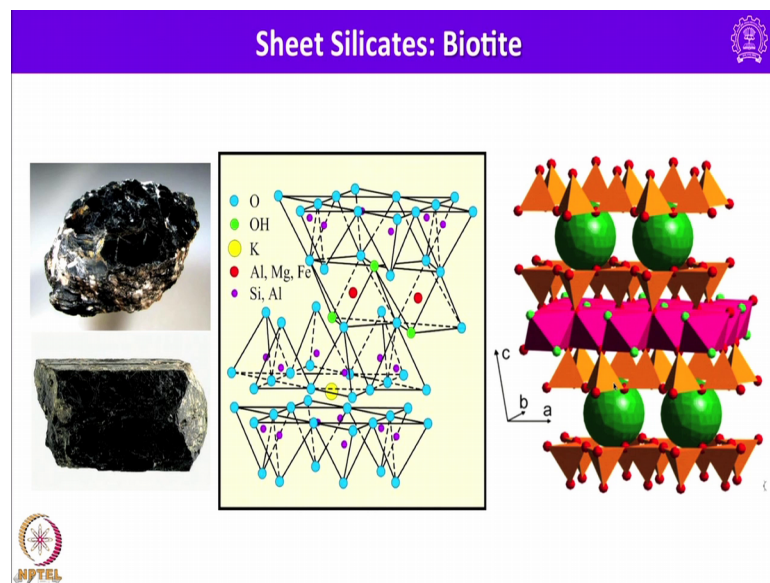


And this how these units are interlinked together to give a sheet and this how one can see how this cations will come and occupy between the sheets getting sandwiched. So, when we talk about framework silicates again as I mentioned all the oxygens are shared with another SiO tetrahedron the basic structural group is essentially SiO 2; that means, composition of this one is SiO 2.

(Refer Slide Time: 18:32)



## Framework Silicates

❑ If all the oxygens are shared with another $SiO_4$ tetrahedron, then a framework structure develops.

❑ The basic structural group then becomes $SiO_2$.

❑ Minerals such as quartz, cristobalite, and tridymite are based on this structure.

❑ If some of the $Si^{4+}$ ions are replaced by $Al^{3+}$ then this produces a charge imbalance and allows for other ions to be found coordinated in different arrangements within the framework structure.

❑ Thus, the feldspar and feldspathoid minerals are also based on the tectosilicate framework.

Mineral such as quartz cristobalite and tridymite are based on this structure and this is how they look like the arrangement of these can be seen here. For example, quarts is an ideal example for network silicate.

Let us look into the silicones now silicones are essentially a group of organosilicon polymers the complete hydrolysis of Si Cl 4 use SiO 2 which has a stable 3 dimensional structure that is we call it as silicates. But instead what we can have is we can have 2 organic groups and keep to chlorides and then if we hydrolyze then we can generate SiO Si linkages through the elimination or condensation reaction. So, that leads to the formation of silicones. You can see here how it is done.

(Refer Slide Time: 19:34)
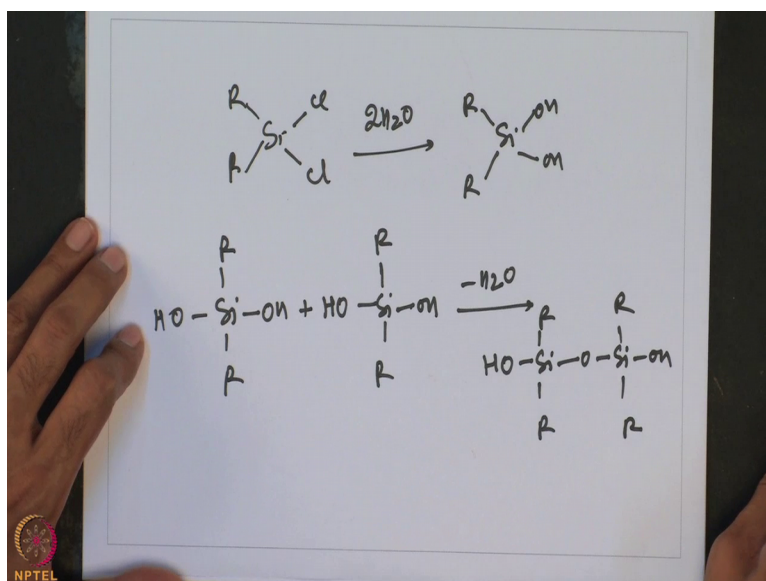


For example, let us take dichloro silane this when it is treated with water it initially it forms hydroxy groups. So, this one now this reacts with another one, so it continues. So, here again another molecule can come and it condense and it eliminate a molecule of water and to give you one dimensional chain. So, this is how silicones are made essentially.

So, this organo silicons of general composition $R_2SiO_n$ are the most important synthetic polymers with a purely inorganic backbone. They are essentially synthesized by hydrolysis of dialkyl silicon dichloride that is $Me_2SiCl_2$ or $et_2SiCl_2$ etc.
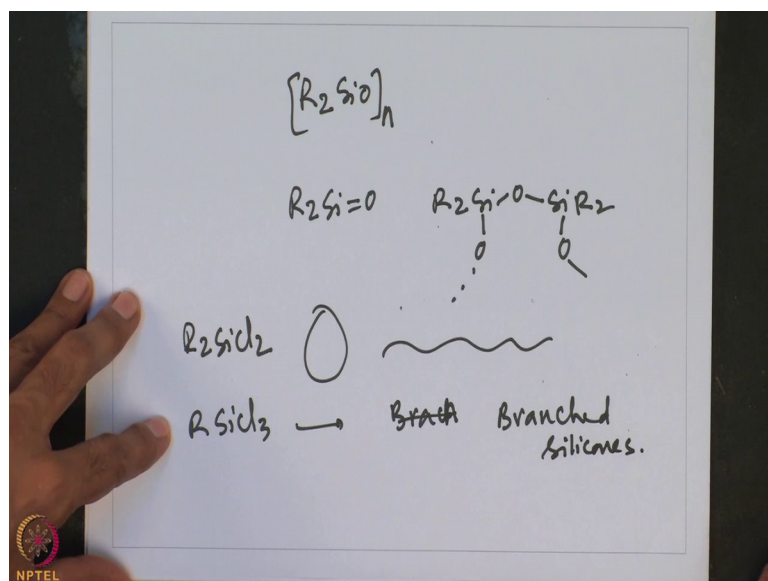
The monomer unit Me 2 SiO if you consider is a highly reactive species in contrast to the carbon analogue silicons have the polymeric structure because Si bond is very highly unstable as a result what happens it leads to the formation of single bond through having this kind of linkages it goes like this, it continues.

So, depending on the condition we are employing cyclic silicones can be formed or it can be chain type silicon polymer also can be formed. So, and of course, one can also think of branched silicons here provided we use in between or Si Cl 2. Simplify if we use R 2 Si Cl 2 basically what happens it can give a cyclic or it can give a linear one and if you incorporate in between R Si Cl 3 one can think of a branched chain branched silicon also we can see. So that means, essentially we need to have a starting compound such as R 2 Si Cl 2 for this kind of polymerization. So, the general method of preparation of such dichloro species in commercial level involves the treatment of Si with 2 Me Cl. So, this is passed over copper heated to 300 degree centigrade to form Me 2 Si Cl 2.

(Refer Slide Time: 23:01)
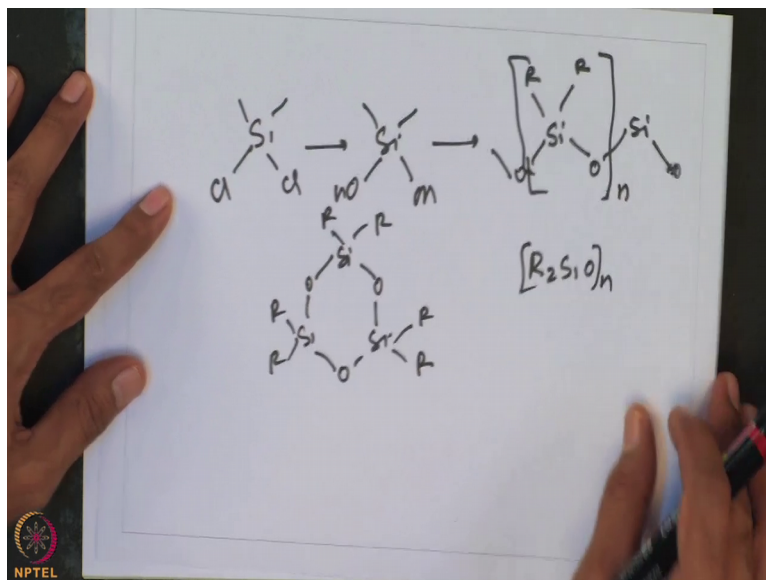


So, the commercial production of starting compound for various polymerization involves the reaction of silicon with methyl chloride over heated copper at 300 degree centigrade. You can see here, so this should be converted into through hydrolysis first and like this and then this one again if you perform condensation you can generate something like this it goes like this. So, here we have R group. So, you can consider, this one this essentially gives R 2 SiO. So, this is how n comes into picture here this is the monomeric unit. And here of course, this can also go like this or if it condenses in a different fashion one can also think of a cyclic one. This is an R group here. So, either we can have cyclic silicates we can have or we can have linear silicon polymers of this type.

So, hydrolysis of course, it can give a trimeric or tetrameric and here the whatever the ratio n I should here, this n depends on the ratio of whatever we are using sometime what we can do is we can terminate this one by taking an appropriate combination of R 2 Si Cl 2 and R 3 Si Cl.
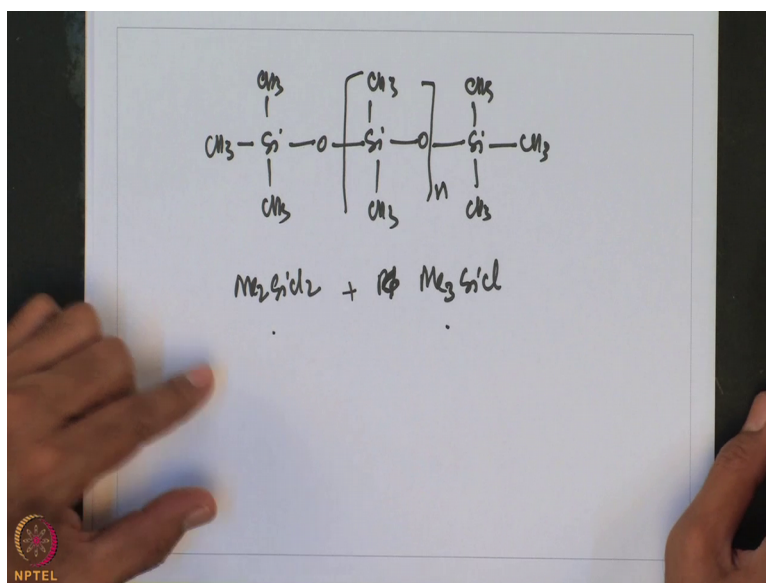
For example let us consider this one here. So, here, while performing this reaction at some point of time. So, for this one what we need is Me 2 Si Cl 2 hydrolysis and then condensation at some point of time for this one if you add R Me 3 SiCl we can terminate it; that means, the chain length whatever is there if I consider this one this n the number of the n depends on the ratio of this one as well as this one and that way one can also perform and grow a polymer of desired chain length. So, silicons are robust materials resistant to high temperatures and hydrolysis and also find a range of applications including lubricants, sealants, hydraulic oils, cosmetics, car and furniture polishes, medical implants and also in contact lenses. So, with these let us proceed to the chemistry of oxides of other group 14 elements.

(Refer Slide Time: 26:50)



**Oxides of Ge, Sn and Pb**

❑ The dioxides of Ge, Sn and Pb are nonvolatile solids.

❑ Germanium dioxide closely resembles $SiO_2$, and exists in both quartz and rutile forms.

❑ It dissolves in concentrated HCl forming $[GeCl_6]_2$ and in alkalis to give germanates.

❑ Relatively few open-framework germanates are known, although this is a developing area.

❑ Although Si and Ge are both group 14 elements, the structural building-blocks in silicates are more restricted than those in germanates.

Dioxides of germanium tin and lead are essentially non volatile solids. Germanium dioxide closely resembles $SiO_2$ and exists in both quartz as well as rutile forms. It dissolves in concentrated hydrochloric acid forming $GeCl_6$ 2 and in alkalis to give germinates. Relatively few open work framework germinates are known although this is a developing area in recent years. Although silicon and germanium are both group 14 elements, the structural building blocks in silicates are more restricted than those in germinates.

So, larger size of germanium compared to silicon allows it to reside in $GeO_4$ tetrahedral or sometime $GeO_4$ square based pyramidal or trigonal bipyramidal structure and of course, $GeO_6$ is also possible; that means, having octahedral geometry in environment. Germanium monoxide is prepared by dehydration of the yellow hydride obtained by reaction of germanium dichloride with aqueous ammonia or by heating germanium hydroxide which was obtained from essentially hydrolysis of germanium dichloride with water. The monoxide $GeO_2$ is amphoteric, but it is not well characterized as $GeO_2$ and it disproportionate at high temperature; that means, the monoxide is essentially $GeO$, $GeO$ is amphoteric in nature, but it is not as well characterized as $GeO_2$ and disproportionate at high temperature. For example, I will show you.
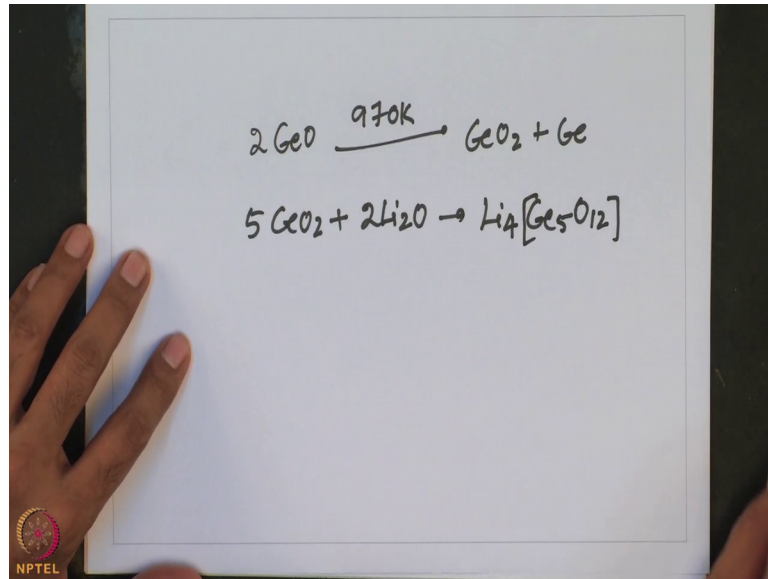
So, it gives GeO 2 plus germanium and the preparation of Ge 5 involves the treatment of GeO 2 with lithium oxide. So, this how one can make some of these germanium oxide.

Germanium oxide such as this one having network structure can be seen here. This composition is here you can see. The other oxides of tin and lead adopt rutile type structure. For example, SnO 2 if you consider, if you consider SnO 2 and PbO 2 the structures of these are very similar to rutile that is called TiO 2 having octahedral geometry surrounding the central atom.
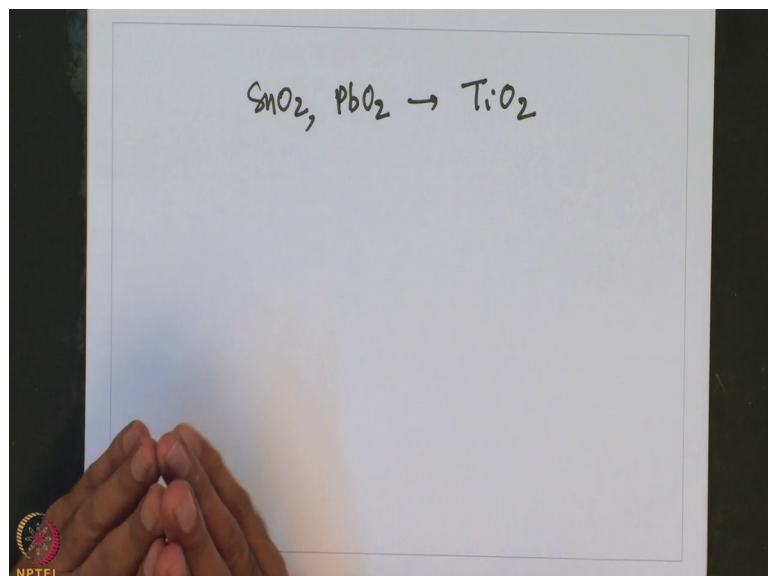
SnO 2 occurs naturally as caseterite, but can easily be prepared by oxidation of tin the formation of lead oxide requires the oxygen of powerful oxidizing agents such as alkaline hypochlorite on Pb 2 plus compounds, on heating PbO 2 it decomposes to PbO via a series of other oxides. Let me give how the lead oxide with lead in plus for state decomposes eventually give lead oxide with lead in plus 2 state before I conclude this talk.

(Refer Slide Time: 30:26)
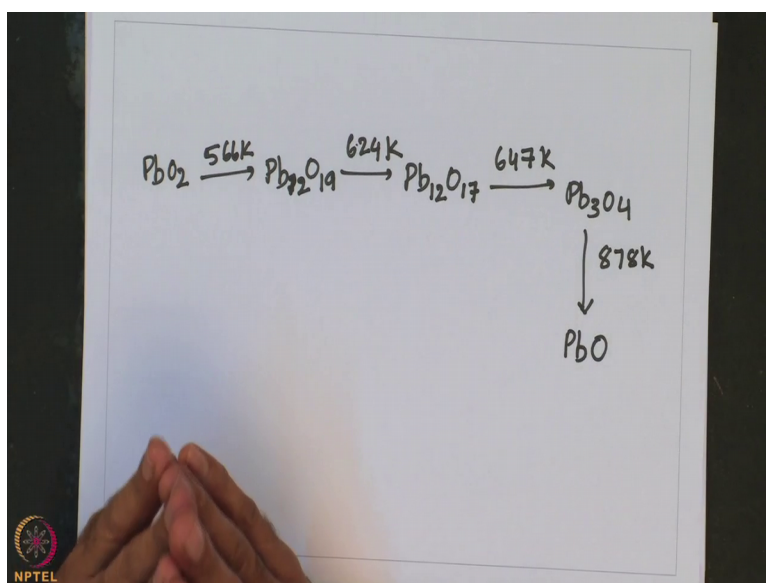


So, this on heating to 647 Kelvin gives Pb 3 O 4 which eventually gives PbO on heating to 878 Kelvin. So, this is how you can see of course, PbO 2 is oxidising in nature to get reduced to Pb 2 plus compound such as PbO.

So, let me discuss the remaining part of a group 14 heavier element oxides in my next lecture, until then have a pleasant reading of in organic chemistry.

Thank you very much.