

Industrial Inorganic Chemistry
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Lecture – 44
Silicon and its Compounds

Hello everybody.

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Potassium Permanganate

It is a **two step** melting and then **single step** liquid phase process:

$$2 \text{Mn}^{\text{IV}}\text{O}_2 + 6 \text{KOH} + 0.5 \text{O}_2 \longrightarrow 2 \text{K}_3\text{Mn}^{\text{V}}\text{O}_4 + 3\text{H}_2\text{O}$$
$$2 \text{K}_3\text{Mn}^{\text{V}}\text{O}_4 + 0.5 \text{O}_2 \longrightarrow 2 \text{K}_2\text{Mn}^{\text{VI}}\text{O}_4 + 2 \text{KOH}$$
$$\text{K}_2\text{Mn}^{\text{VI}}\text{O}_4 + \text{H}_2\text{O} \xrightarrow{-e^-} \text{KMn}^{\text{VII}}\text{O}_4 + 2 \text{KOH} + 0.5 \text{H}_2$$

Applications of Manganese Compounds:

- Mn(II) oxide: additives for fertilizer.
- Mn(II) sulfate: metallic Mn preparation.
- Mn(II) chloride: corrosion resistance Mg alloy.
- Mn_3O_4 and Mn_2O_3 : magnetic materials and semiconductors.
- KMnO_4 : oxidizing agent in organic synthesis.

The slide also features a portrait of Prof. Debashis Ray in the bottom right corner and logos for IIT Kharagpur and Swayam in the bottom left corner.

So, welcome back to this class where we are talking about this manganese and their applications. So, some a list of many compounds we have seen that starting from your MnO_2 potassium permanganate. So, if we take only these 3 - 4 compounds so we will be very much familiar with these things that how we can use it is you will have a huge demand in industrially.

So, MnO the manganese 2 oxide which can be additives for fertilizer these are not fertilizers, but sometimes to improve the quality of that particular fertilizer or some micronutrient; that means, some amount of manganese can be useful when we add say urea or when we add n p k type of fertilizers. So, these are some time additives or making the solid material; that means, urea or the solid material like that of your nitrogen potassium or phosphorus base compounds, some amount of manganese 2 oxide can be used.

Then simple manganese sulfate salt MnSO_4 , that MnSO_4 salt just now we have seen that if we go for electrolytic production of some compound; that means, the electrolytic reduction of manganese from its corresponding bivalent or the trivalent state we go for its electrochemical reduction.

So, electrolytic you can have sulfuric acid is the electrolytic medium. So, if you take manganese sulfate MnSO_4 along with H_2SO_4 . So, that is the corresponding medium where we can go for the electrolysis and your manganese sulfate can be reduced, your protons can also be reduced to hydrogen. So, for elemental or metallic manganese; that means, the manganese metal preparation we can use manganese sulfate very well.

Then MnCl_2 the manganese chloride which we mostly used very much from our teaching classes, the teaching laboratory, the research laboratory and some of their other laboratories, R and D laboratories, but industrially it is also important in some other area; that means, for metallurgical engineering that this manganese is a very simple one, if we go for something where the magnesium based alloy we have and if we can go for corrosion resistance magnesium based alloys some amount of manganese can be added to it for its production.

Then if you go for the corresponding Mn_3O_4 and Mn_2O_3 ; that means, two forms of these oxides they are very useful magnetic materials. So, making of these magnetic tapes also like that of your iron; that means, Fe_3O_4 or Fe_2O_3 those are also very much useful as the magnetic tapes and other useful magnetic application. So, they are very useful magnetic material and sometime they can also be use for semiconducting application and KMnO_4 is a very useful material for as oxidizing agent, the analytical reagent for analytical chemistry and for the different organic synthetic reactions as they very useful oxidizing agent.

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Silicon

Tetravalent metalloid and semiconductor

7th most abundant element in the universe by mass, but very rarely occurs as the pure element in the Earth's crust.

Available in three different commercial forms

olivine, $(\text{Mg,Fe})_2\text{SiO}_4$

Ferrosilicon: Si-contents from 8-13% (FeSi 10) up to 87-95% (FeSi 90)

Technical (metallurgical) Si

Ultrapure silicon (semiconductor silicon)

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Now, we after this 3 D metal ions we have taken the example only for chromium as well as manganese, we do not have that much time to cover all other 3 D metal ions, but we have considered some very basic form where we can use this for their production that we have seen for chromium. As well as we have seen for manganese because the manganese we are handling about from your hydroxide, we are utilizing from oxide, we are utilizing carbonate and some other higher oxidation state of the manganese up to manganese oxide.

Similarly, if we go for nickel, if we go for iron, if we go for cobalt, we will find that the basic strategy for getting the all other compounds or all other metal ions for their large scale production in industrially will be the same. Next we will move to some other element which is your silicon, silicon industrially is very important while we consume huge amount of silicon for the production of very precious elements. So, the tetravalent metalloid you can consider as the silicon in the tetravalent state up to say simple quartz silica or silicon dioxide, where silica is present as SiO_2 . So, the tetravalent metalloid and that can also be used as a semiconductor in its elemental form.

So, after 12th we have just now consider that the 12th most abundant element we come down because the silicon availabilities pretty high and it is the 7th most abundant element in the universe by mass. It is also heavier because you have the silicate rock materials geologists are also very very much interested to handle those silicate material

or the silica based compounds, but very rarely occurs as the pure element in the earth crust. So, we are not been able to get silica as elemental silica from the earth crust, but we will get the different form starting from fairs part to quartz to the glass material as silicon dioxide or the silicates or much more alumino complicated form of aluminosilicates.

So, this is one of the variety very beautiful variety if we just show you, how beautiful it is. So, is basically a very good crystalline form and which is nothing, but a silicate material and that silicate material is nothing but olivine and olivine is a silicate material composed of magnesium as well as iron, because the color quality everything will change by say if we consider that it is a iron silicate or ferro silicate.

Then the incorporation of magnesium in it will improve the quality; that means, it is texture color texture or it is corresponding stability; that means, your corresponding strength will also increase like that of the doping of some of the material we always know that if we get or if we dope chromium into Al_2O_3 which is corundum we know something dramatically changed due to that chromium incorporation.

Similarly, magnesium incorporation in silicate structure and if it is only r n silicate or in the entire silicate structure if we dope both of them; that means, both magnesium and iron we get a particular system which is your olivine. And this particular one is available in three different commercial forms; that means, whatever silicon we get and commercially if we are able to produce that particular silicon and basically we will consider as the three available forms; that means, the three commercially available form, one is your ferrosilicon like that of your olivine where iron is the integral part of your silicate structure.

But when you have the elemental form of these along with your silicon; that means, 8 to 13 percent of silicon content within the iron part; that means, we considered as FeSi 10. So, the average percentage of it is in the 10 within 10 so, it is go down to 8 or it is go up to 13. So, a value of 10 average 10 value of silicon in that particular material is known as ferrosilicon and we can have a large amount of this particular incorporation; that means, silicon incorporation can go up to in the range of 90 which we considered as the ferrosilicon 90.

Then some variety we consider as the technical silicon or the metallurgical grade silicon, where the metallurgical grade it is also true for any other elemental form also that the metallurgical grade material can be utilized for your isolation and corresponding production of the metallic or the sorry metalloid form or the elemental form of silicon from that particular grade.

Then a very high purity form is your ultrapure silicon form which we all the time make as a semiconductor silicon. Whether we go for making solar cell or the components of the computer, because the silicon industry we considered that the entire thing the computer industry or the silicon valley's we call sometime they are purely dependent on the amount of good quality silicon what we can consider for making the hardware, the software part little bit and all.

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Production 96–99% purity is made by reducing quartzite or sand with highly pure coke, in an **electric arc furnace**, with an excess of SiO_2 used to stop SiC from accumulating

$$\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO}$$
$$2\text{SiC} + \text{SiO}_2 \rightarrow 3\text{Si} + 2\text{CO}$$

Carbothermal reduction of silicon dioxide

Performed in the presence of scrap iron with low amounts of phosphorus and sulfur, producing ferrosilicon.

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The production is basically dependent on a range where 90 plus percent; that means, from 96 to 99 percent of purity can be obtained by reducing quartzite or sand. If we take a SiO_2 only and if you try to get silicon production of silicon from sand not that quartzite; quartzite can also give you the SiO_2 of different variety with highly pure coke; that means, your carbon reduction process again we will be utilize definitely at high temperature producing or converting that silicon to that particular one; that means, the corresponding reduction of that SiO_2 .

So, electric arc furnace, if we use and that electric arc furnace with an excess of SiO_2 is used to stop the silicon carbide formation which is being accumulated in the reaction mixture or the furnace mixture. So, the silica is available as sand which is SiO_2 we use its corresponding reduction with carbon coke or other charcoal or any other coal form also giving you Si plus twice of carbon monoxide. Then you get some of these amounts because you are going for the corresponding reduction with that of your carbon.

So, silicon carbide can also be formed and if we have the silicon carbide or directly from outside also that silicon carbide can be utilized also for the reduction of silicon dioxide giving you 3Si and 2CO . That means, side by side you produce silica as well as the carbon monoxide and the process since it is a high temperature process carbon is your reducing agent is known as your corresponding carbothermal reduction of silicon dioxide.

So, this carbothermal reduction of silicon dioxide will tell us that we can use this particular silicon dioxide for its reduction because the cardboard like your aluminium again it has more affinity for oxygen. So, it can take up that amount of oxygen which is attached to your silicon. So, is basically performed in the presence of scrap iron, with low amounts of phosphorus and sulfur which can produce the ferrosilicon, because the ferrosilicon can also have some impurities like your phosphorus or sulfur along with your iron. So, iron is being trapped and that iron basically can consume giving you the corresponding variety of material which is industrially very important and we get ferrosilicon formation.

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Aluminothermal reduction of SiO_2

$$3\text{SiO}_2 + 4\text{Al} \rightarrow 3\text{Si} + 2\text{Al}_2\text{O}_3$$

Greater purity is needed for semiconductor applications, and can be obtained from the reduction of **Tetrachlorosilane** or **Trichlorosilane**.

Former is made by chlorinating scrap silicon and the latter is a byproduct of silicone production.

These compounds are volatile and should be purified by repeated fractional distillation, followed by reduction to elemental Si with very pure Zn metal as the reducing agent.

Spongy pieces of Si thus produced are melted and then grown to cylindrical single crystals, before finally purified by zone refining.

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Then we use aluminium. So, aluminium as we have seen the elemental form of aluminium like coke or charcoal aluminium is also very useful high temperature reducing material; so it is aluminothermal like your carbothermal reduction aluminium is used also for your aluminothermal reaction of SiO_2 .

So, SiO_2 is a very simple reaction always you have to just maintain the stoichiometry and we all know then aluminium use it has more affinity for oxygen. Like that of your carbon the carbon has the affinity because if we can consider the corresponding oxidation. If we just basically sometimes see the different diagrams we know the Latimer diagram, then the Ellingham diagram for your oxide formation at high temperature.

So, here we simply logically considered that one carbon is used that carbon is taken up that oxygen forming carbon monoxide leaving behind your elemental form. Similarly the aluminum can also take out that oxygen which is attached to your silicon; that means, the oxides can be reduced any metallic form or the metalloid form of oxides can be reduced to its elemental form.

So, that is the most important or the strategic course of action only thing that you have to know that what particular temperature according to those two diagrams or any other information that this thermochemical data we should have in our hand. And that thermochemical data will tell you we will use that particular furnace and we will said that particular temperature for this particular reduction process, where at high

temperature; if aluminium can take up that oxygen of silicon dioxide forming alumina and your silicon and its elemental form back to you.

So, when we go for higher purity of this for making different types of semiconductors, different types of transistors and much more sophisticated material the chips and all these thing left in electronic industry and computer industry while you make the different computers. So, from the molecular level basically we will now go down to the molecular level and in the molecular level we have to choose some important silicon based compound, such that we can check the purity of that compound because is very difficult to check the purity of silicate material.

If you consider that silicate material can be your ore or mineral or the source of silicon, similarly silicon dioxide the quartz variety can also be your source of the material, but to check their purity, their stability in the solid state also do not allow us to go for a take the strategy for getting the semiconductor quality silicon. And also we will be utilizing very small amount not a huge amount of silicon will be utilizing for this purpose.

So, better you go for some important silicon based inorganic compound, one of them is tetrachlorosilane; that means, like your carbon tetrachloride it is silicon tetrachloride which is SiCl_4 . And another one is also the other variety; that means, you are trichlorosilane variety so, the first one the tetra one and the second one the tri one how we make them. So, we have the scrap silicon or the silicon produced from other source; that means, your aluminothermal process if we use and that aluminothermal process can be utilized for making some low grade or medium grade silicon and that silicon along with this; that means, it can high purity or sometimes the scrap silicon, but you know that scrap silicon.

Industrially when some material with throw away by product we call it is not utilized for some other purpose or making some other compound we call them as the scrap material, it can be your iron scrap material, it can be your chromium scrap material, it can be your manganese scarp material. So, silicon can also be available from some other process which can be considered as the scarp silicon form and that scrap silicon can be utilized for the production of tetrachlorosilane and trichloro variety is nothing, but your byproduct of silicone production.

And silicone not silicon now be careful about the spelling and the name and why it is like your silicone, what is silicone it is nothing, but your carbon based compound corresponding analogue is acetone. So, acetone analogue of silicon is known as silicon that we will see is basically a polymeric form not like your acetone; that means, your corresponding $\text{SiH}_3\text{SiS}_3\text{SiO}$ all these sort of thing is not there, but is a silicone polymer or silicone rubber and these two compounds are volatile and should be purified by repeated fractional distillation.

So, if you have volatility, volatility also sometimes not so good for handling a particular material because the material will evaporate, you have lose of material, but sometimes it is also useful. If we can go for the corresponding distillation process and all these distillation processes you know that the distillation processes are improving the corresponding material; that means, it is improving the purity of the material and this fractional distillation we can have, so you have the different fractionating columns we know industrially that fractionating columns are available, in the petrochemical industry also we go for fractionating column and this is a small unit out of that of that type for fractional distillation and we can go for low temperature fractional distillation because the material is volatile; that means, low boiling point.

Followed by reduction; that means, you have silicon tetrachloride or SiCl_3H that mans trichlorosilane we reduce them and if we go for it the elemental silicon form with very pure zinc metal so, zinc reduction now not aluminium reduction. So, carefully look at the material what we are utilizing for the reduction. So, for SiO_2 we are utilizing carbone or for a reduction of SiO_2 we are also using aluminium at a high temperature, but once we go to a very volatile very thermally unstable and is very quickly can be decomposed material is your silicon tetrachloride.

So, tetra and trichloride can be utilized for use of zinc as the reducing agent. So, zinc metal reduction can give us the corresponding material as spongy pieces of silicon. And that sponge pieces of silicon are then grown to cylindrical single crystals is very important term is single crystals they are not polycrystals. So, one variety of crystal one form of the crystal the crystal system we know whether it is a monoclinic of one one type or triclinic one type or orthorhombic one type.

So, monoclinic p 21 by c that sort of thing we sometime level it as is that single crystals. So, only one variety of crystals which are single in nature can be available from this material like that of your crystallization of the elemental silicon what we get through zinc reduction. And then we are still not happy that we will be getting a very high purity of silicon.

So, to get very high purity of silicon suppose 99.99 we consider sometimes we can go up to 99.999, you see the 10 times improvement of the purity the cost maybe 20 times or 30 times effective, but in the long run if your material is costlier one, but in the long run if your performance of that material is higher, we should also go for not we will happy with 99 we will go for 99.9 or we can go still further beyond that to 99.99 or 99.999 purity and it is the process very well known process for zone refining.

So, basically it is a long rod of silicon can be produced for that particular purpose; that means, one particular one and continuously the whole rod is getting melted and that mean crystallize melted and crystallize. So, when if we seat heating from one side to the other and if we heat it your silicon material silicon rod itself material is basically going to a molten condition or semi molten condition as we move the heating over an or the heating part the other part which is getting form; that means, crystallization part is taking place and more and more impurities will be coming out from that particular part which is re crystallize basically.

So, zone refining process is nothing, but a type of re crystallization in the solid state where the solid form which is form from the left say we are moving the corresponding heater from left to right. And that particular form and more and more new amount of that particular silicon is forming, your purity is increasing purity is changing from the starting material which is utilized as your silicon rod as the material which we use before your zone refining process.

So, it is a very useful process for improving that since ultimately the whole range of that impurities are moving from one part to the other and the concentration of the impurities are getting accumulated on the right hand side and left hand side the purity is increasing. So, once it is reaching over there we do not rely on that further moment we basically reach there and we cut that particular part basically. Because the all the impurities whatever present in the entire rod has been accumulated in this particular small part and

that small part is now cut and allow it to utilize further for more and more amount of silicon making.

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Chemistry and compounds

Crystalline bulk silicon is inert, but reactive at high temperatures.

At high temperatures, silicon reacts with alkyl halides, catalyzed by copper to directly synthesize organosilicon chlorides as precursors to silicone polymers.

Upon melting, silicon becomes extremely reactive, alloying with most metals to form **silicides**, and reducing most metal oxides.

Silicides Their formula cannot be explained through simple appeals to valence

M_6Si , M_5Si , M_4Si , $M_{15}Si_4$, M_3Si , M_5Si_2 , M_2Si , M_5Si_3 , M_3Si_2 , MSi , M_2Si_3 , MSi_2 , MSi_3 , and MSi_6

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Then its chemistry little bit of chemistry we will consider quickly and the compounds. So, crystalline this particular silicon bulk silicon is inert, but reactivate only at high temperature, though way we are considering it is corresponding (Refer Time: 23:29) at high temperature. Similarly the silicon elemental form is also is only reactive at high temperature and high temperature it can react with alkyl halides, catalyzed by copper to directly synthesize organosilicon chlorides as precursors for silicon polymers.

So, we will be able to bring organic part; that means the carbon part. So, methyl part 2 silicon and it can be silicon chloride. So, if you have silicon trichloride or tetrachloride and trichloride we have seen that trichlorosilane is $SiCl_3H$ and instead of H we all know that H can be substituted by alkyl group also. If it is r we can have $r SiCl_3$ that can be your some starting material for making your silicone polymers and upon melting also that silicon becomes extremely reactive; that means, in the molten state it is high temperature reaction it is giving.

So, it is molten state it is reacting. So, different types of metals we use for alloying purpose to form silicides and reducing most metal oxides. So, if we directly use some metal oxide with that silicon so that can be considered as the corresponding silicide formation like your carbide formation. We know how we make calcium carbide, little bit

we have seen also earlier for your boride formation. That means, the anionic form which is there in the solid state is carbide C^{2-} similarly the boride B^{3-} and then also the corresponding silicide.

So, this particular silicide formation is there and the different silicides we can have. So, how we can have the corresponding magnesium silicide say so, magnesium will be there and silicide will be there at the in the silicon will be in the anionic form, like carbon as carbide, boron as boride, silicon as silicide. And if we consider the different formulas of these silicides and the formula the stoichiometric ratio of the metallic part say magnesium and the silicon part will not tell us that you have a very simple formula out of that.

So, therefore, we can write or we can say that their formula cannot be explained through simple appeals of valence. That means, we know the valence for silicon, we know the valence for the corresponding metallic state or the metal ion or the magnesium if you consider. So, the different types of formula we can have, we see range of compounds can be available. So, these are a pretty complicated material, silicon on the right hand side; that means, these are anionic part like oxide, nitride, carbide, boride, phosphide already I said so like this.

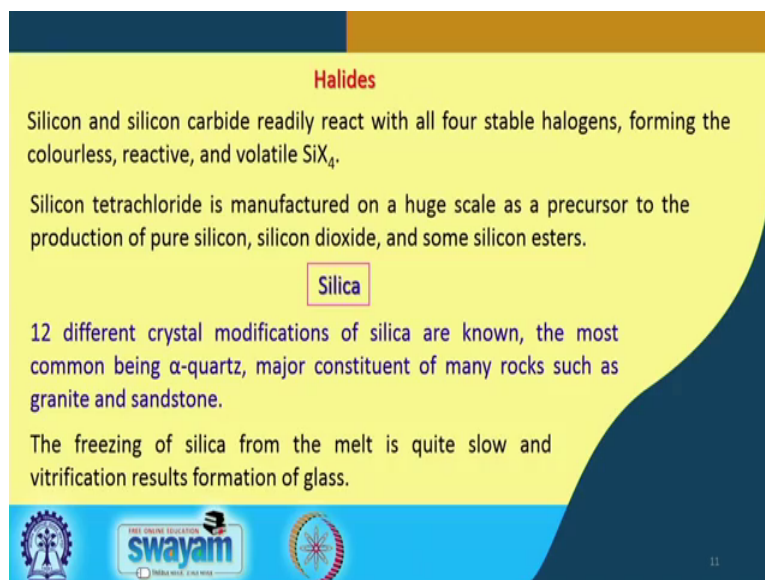
So, the first one if we consider which is Mg_6Si so, it is very difficult to think of the corresponding valence satisfaction. So, you see that the corresponding species so; that means, the silicon species what is there starting from 1 silicon to 6 metallic part to up to your MSi_6 . So, it is a silicon silicon cluster type of arrangement which you also considered as the poly silicide type of thing and we have the metallic form also there.

So, the metallic form is also reducing so, at one end we have a $6Si$ and on the other end we have MSi_6 . So, all of them will be your silicides so, large number of compounds of this type is available and which are very much useful for our thinking or process making upon all these thing. So, if we consider this M_2Si because the silicide Si if we present if we consider that is like that of your not simple carbide, carbide that corresponding carbide we know the calcium carbide is CaC_2 only.

So, C_2 is species is C_2 , but some other carbides we can have the corresponding formula C only. Similarly M_2Si if you consider as the magnesium silicide it is Mg_2Si . So,

silicon is the corresponding Si 4 minus and magnesium is 2 plus 2 is 4 so, it is nicely balanced.

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Halides

Silicon and silicon carbide readily react with all four stable halogens, forming the colourless, reactive, and volatile SiX_4 .

Silicon tetrachloride is manufactured on a huge scale as a precursor to the production of pure silicon, silicon dioxide, and some silicon esters.

Silica

12 different crystal modifications of silica are known, the most common being α -quartz, major constituent of many rocks such as granite and sandstone.

The freezing of silica from the melt is quite slow and vitrification results formation of glass.

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So, you have to consider all these formula and all these compounds like this and also quickly we will see the how we can have the corresponding silicon halides. Silicon and silicon carbides basically we can take these 2 together and this silicon as well as silicon carbide can react with all 4 stable form of halogen starting from your fluoride, chloride, bromide and iodide, forming volatile silicon tetra halide thing SiX_4 , but all of them are colorless, reactive and volatile.

So, that is very important, but problem is that if they are colorless and the volatilities also varying to some extent only and is also reactive is very difficult to think of or very difficult to handle if you have the mixed halides or if we have a separately if we have the silicon tetrachloride or silicon tetra bromide in your hand. So, we will see only some processes or the methods where we can think of that the silicon tetrachlorides, how we can manufacture it. It is basically a production of pure silicon so that is why not that the corresponding silane thing is also silicon things are also we can have for the production of only Si pure silicon, elemental silicon, silicon dioxide and some silicon esters.

Then possibly tomorrow we will just consider little bit of the next class we will consider how we get the pure quality or the higher quality or the higher variety of silica because we can have silica SiO_2 . We know your glass is silica, your quartz is also silica there are

basically now see the number is very high is 12 different crystal modifications of silica are known. That means, it is a very loose term if you only consider silica that way we are seeing that manganese dioxides similarly is SiO_2 .

In case of manganese dioxide we are seeing that the different solid state varieties we are considering about alpha, beta, gamma, epsilon and all. Similarly silica is also can be leveled as 12 different crystal varieties, the most common being now again we are putting like that of your alpha, beta, gamma things alpha quartz form. So, quartz form is there and that quartz form not only that only quartz form it is alpha quartz form you can have therefore, then beta quartz form also is a major constituent of many rock samples.

So, naturally occurring rock samples which we can have which we get geologist get these compounds for us. These are basically the different huge structures of granite and the sandstones basically we utilize for making temples and all these things. So, sandstone and the granite varieties are basically a variety which we can consider for your material available as your alpha quartz.

So, it is the major constituent of many rocks and the up to your sandstone and silica handling silica SiO_2 like that of your silicon we will see also that the freezing of silica from the melt is quite low and vitrification results formation of the glass material. So, what is your quartz? We will see quickly very quickly we will see also in our next 2 classes may be that how we get that particular quartz and how we get the glass form ok.

Thank you very much.