An Introduction to Materials: Nature and Properties (Part 1: Structure of Materials)

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Lecture – 28
Structure of Non-crystalline Solids Glasses (contd.)

So, we begin with a new lecture again. So, and this is again on a structure on non crystalline solids mainly glasses, we will continue from the previous lecture viewer.

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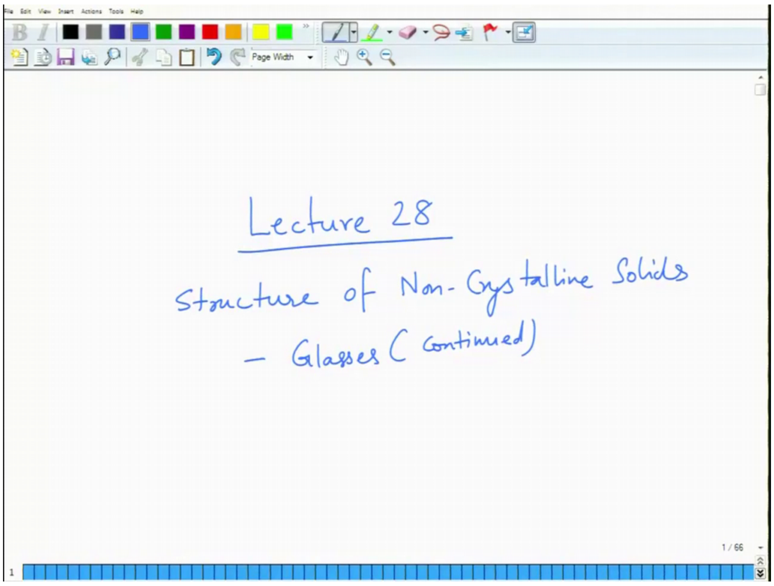

So, let me just give you a recap of what we discussed in the last lecture.

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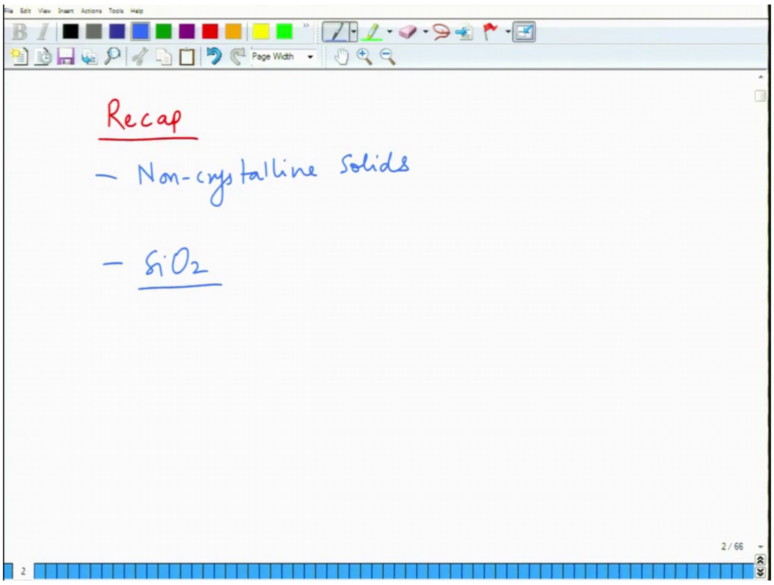

. We basically introduced the term called as non crystalline solids.

Basically these are the materials which do not have any long range periodicity, the periodicity of molecules in the form of any kind of periodicity. Let us say special periodicity, it exists over very short ranges, few nanometers and beyond that it breaks down. So, if you go to few tens of nanometers or hundreds. So, nanometers and microns and. So, on and. So, forth you do not see any periodicity in the crystal structure.

So, as a result they do not have long range periodicity. Another thing is that, they do not tend to have fixed bond lengths. They did not to have variable bond lengths which allows them to have multiple bond energies and as a result they have they tend to solidify over a range of temperatures and hence they have a broad and diffused melting behavior as against crystalline materials which show a very sharp melting transition at the melting point.

So, and by and large these materials are based on the basic building block is silica and it is by the arrangement of the silica-silica molecules within the structure which allows them to have a very specific structures. So, we looked at last time in the first structure that we looked at was crystalline silica in which in which the hexagonal array of silicon silicon tetrahedra forms a silica tetrahedra if you recall it was basically sio4 4 minus tetrahedra.

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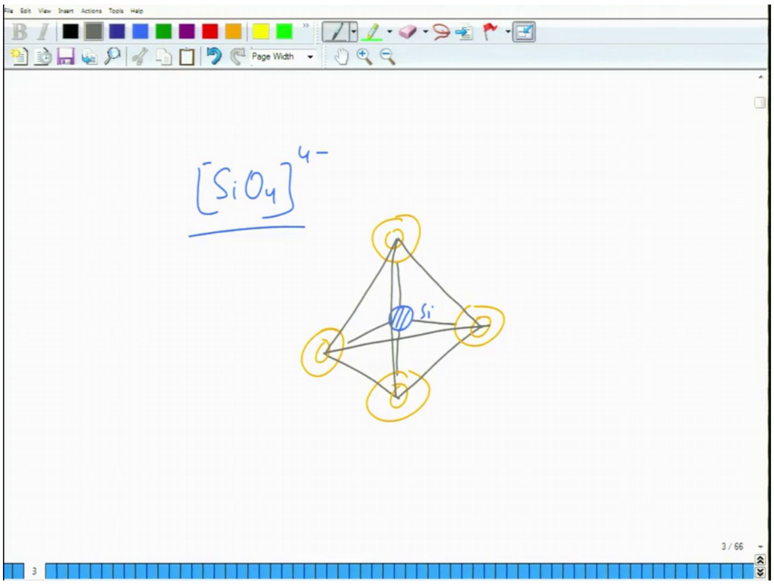

Because each silicon atom is coordinated by 4 of these oxygen atoms, if this is oxygen; this is silicon and then you have the bonds between these and this basically makes a tetrahedral. If you connect these atoms here, but this basically makes it a tetrahedra and at the center of tetrahedra is this silicon atom. Since it has this minus 4 charge on it, it has not really neutral as a result it needs to have either sharing of oxygen atoms to ensure that that is overall electrical neutrality.

So, one way to do that was to make a hexagonal network in which you have a corner sharing of atoms. So, the structure that we drew last time was you had a structure like that.

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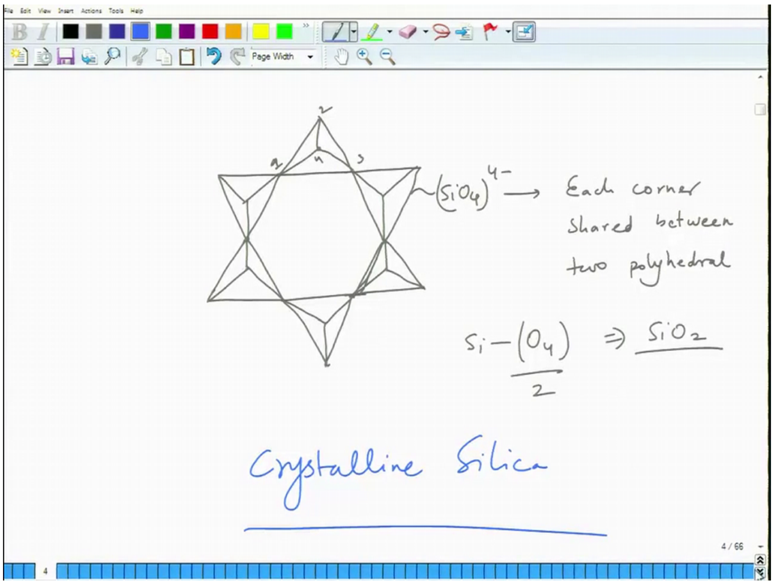

All right and so, these are all polyhedral arranged in such a fashion. So, they make a hexagonal network ok. So, it is odd.

Student: (Refer Time: 3:52).

Yeah.

Student: So, how does (Refer Time: 3:57).

So, you have, one shared here; another shared here; another shared here and one other one shared on top, all right. It is a 3 dimensional network it is sort of. So, what I am showing here is in 2D. So, each corner is shared between. So, each corner is shared by 2 polyhedral ok. So, what you will have is basically sio4. So, 4 divided by 2. So, basically you have these, these are sio4 units and then for each of them shared by shared between each corner shared between 2 polyhedral.

So, what we see here is in the plane, but shared out of plane as well. So, this is the top of this polyhedral for example, this is going to shade by the top one. So one here, 2 here, third here, fourth here, Si is at the center o4 divided by 2 it is going to be SiO2 right. So, this is the crystalline form which has this hexagonal array of polyhedral.

Now, second another thing that you can have is, you can have amorphous silica. Now amorphous silica will have will be present in such a fashion. So, that you have these polyhedrals which are present more or less in a sort of random fashion, . This will have somewhere here, it will have another network. There is no fixed angle and there are no fixed numbers of neighbors. Now the problem here is the electrical neutrality again.

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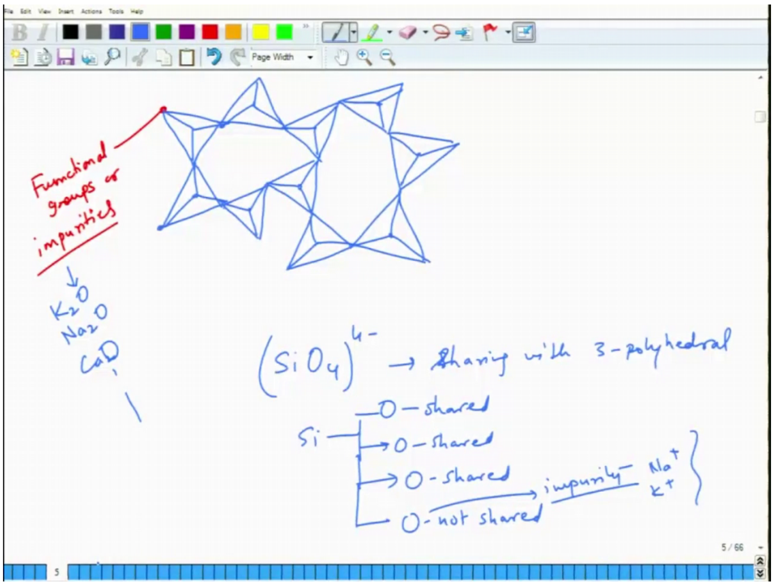

So, in order to have such kind of random network, this random network is possible only when the corners are shared by something else. So, that there is something electrically something which is electrically neutralizing it and this happens by addition of impurities. So, when you add for example, you can see that, in the previous structure you had the 4 corner shared by neighboring polyhedrals.

In this case, you do not see a neighboring polyhedral, right. You see that this may be this may have a sharing, but this will not have a sharing. So, what happens in this case is is you attach now, what we call as Functional groups or Impurity oxides. So, for instance, for instance, if you have a let us say sio4 4 minus instead of sharing with 4 polyhedrals, you are sharing only with sharing with let us say 3 polyhedrals right.

So, silicon is all right. This oxygen is shared; this oxygen is shared; this is shared, but this is not shared. So, which means that, in extra charge ok this extra charge is going to be compensated by let us say if you have an impurity with it ok. So, for example, you can have sodium plus; potassium plus some of these impurities will attach to that group and they will ensure that, they will take the extra electron that is there, because these are all electro positive elements. So, they will attach themselves to those groups forming structures which are electrically neutral.

So, this will make. So, things like K 2 O, Na 2 O, CAO, variety of elements can get into the structure of glass, modify the structure in such a fashion. So, that polyhedrals are not any longer shared by in such a fashion. So, that each oxygen is shared by 2 polyhedrals. They make a random network sort of thing. So, the a good image of this would be, I will show you in the in the power point.

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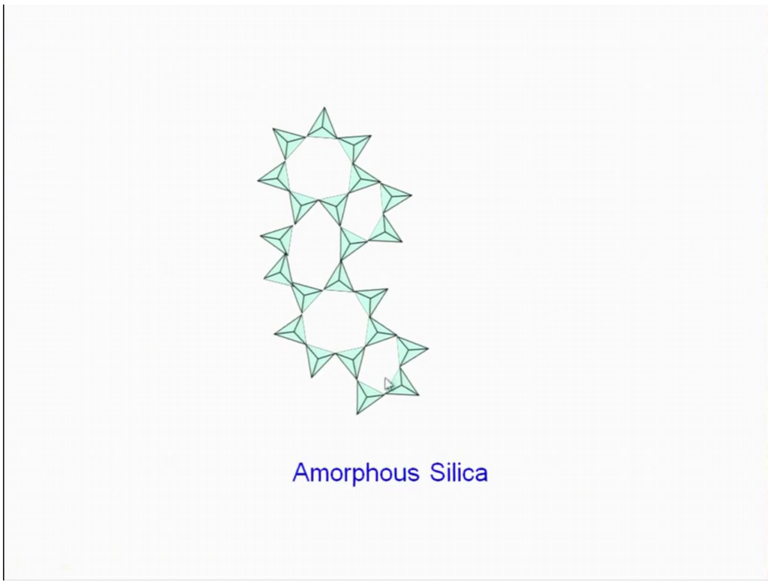

So, this would be sort of the image that you would like to see. So, this is amorphous silica, but in this case again, electrical neutrality has to be maintained and the electrical neutrality is going to be made by is going to be satisfied by presence of, some sort of neutralizing factor which could be a impurity, basically to neutralize the charge. So, there are a variety of a forms of silica, let me now show you, how it happens.

So, if you have this. So, let us say silica structural units can be presented in different ways ok.

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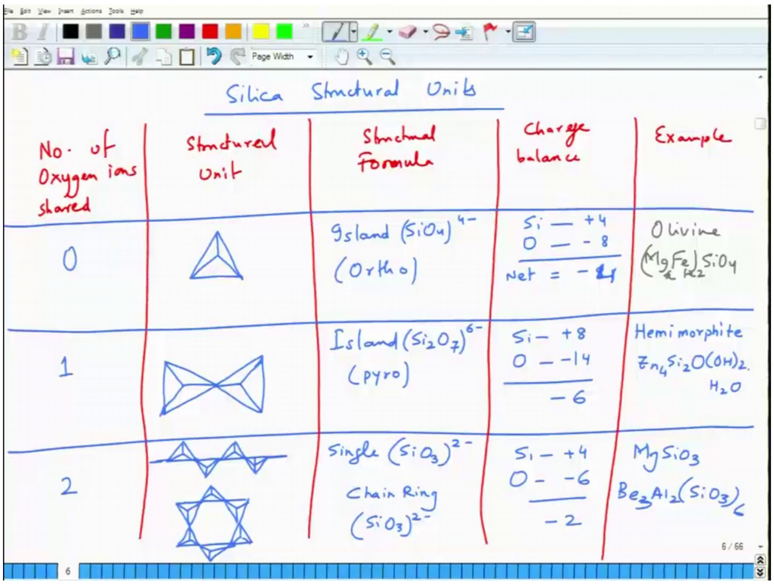

So, let us say, the criteria is, how many numbers of Oxygen Oxygen ions which are shared ok, that is the first column. Structural unit then we will second is the structural unit and then we write what is the Structural Formula.

Then we write, what is the charge balance, then look finally, let us look at the example. So, you see from the previous slide that key thing is how do these unpaired electrons or imbalance charge imbalance gets accommodated. Because it has to be electrically neutral that is the bottom line. So, how does it get to do that? How does it do that?

So, the first thing is, let us say number of oxygen shared is 0. So, in this case the structural unit will be one tetrahedral, just one tetrahedra. So, we are going to if there is no sharing, which means it is going to remain it a try; it will form. So, this is basically island kinds of structure. Island sort of sio4 kind of structure and here you can see the charge balances, silicon is going to give you plus 4 oxygen is going to give you minus 8.

So, the total charge you are going to be left with is minus 4, sorry yeah. This structure, where there is no sharing of polyhedrals is followed by materials such as, these are called as olivine structured materials basically mg mg iron twice sio4. You can see that, there is attachment of these magnesium and iron atoms which fulfills a charge neutrality condition ok.

So, these are cations which are look in to look in to pair themselves with a silicate polyhedra. So that, the extra charge that is minus 4 is going is taken care by magnesium iron. So, it could be 1 Magnesium 1 iron Fe2 plus basically it could be 2 Magnesium's it could be 2 ions. So, it could be MgSi, Mg2SiO4, it could be a Fe2SiO4 or it could be 1Mg, 1FeSiO4 and if both of them are in plus 2 charge state, then you can have any fraction of them ok, it could be Mg x Fe one minus x if both of them are plus 2.

So, they will make it charge neutral by attaching itself to the corner of the polyhedral. So, this is a essentially a olivine structure, a sheet like structure. The second structure in this category would be , when the number of shared oxygen atom is equal to 1 and in this case, you have first polyhedral like that; second polyhedra like that ; like this, all right.

So, in this case it makes basically again. So, in this the first structure was ortho structure and the second case it is again an island kind of structure because it does not make a structure which is continuous in 3D because you do not have complete sharing. So, here it makes Si2O7 6 minus. So, basically, silicon will be plus 8, oxygen will give you minus 14 and net will be minus 6 Si2O7 molecule . This is called a spiral form of it and these materials are basically, for example, Hemimorphite .

Hemimorphite , whose structure is Zn 4SiO2, OH twice dot H2O; this is for example, an example this is a case of a one fold one one sharing sharing of one oxygen atoms in the polyhedral not very common; but there is example. Third one is called as 2 sharing of this, but this is in this case what you have is a single layer of Si O3 these are 2 minus.

So, basically what you will form here is a chain or. So, you will have this kind of structure. So, you can see that you have 2 neighbors only; it has just a chain like structure no 3d structure. So, just shared along these 2 sides so, this is SiO3 single layer, you can have this kind of structure in which it will make a hexagonal sheet, just a single sheet structure just a single sheet and this is basically called as chain ring molecule which is SiO3, 2 minus again only twofold sharing ok.

So, in both these cases, the net charge is equal to , you can see that Silicon is plus 4, Oxygen is minus 6, net is minus 2 and this is followed by compounds such as MgSiO3 Be3Al2 SiO3 6 . So, these compounds follow this kind of structure. Other examples that we include how many columns we need to draw 1, 2, 3, 4, 5.

Student: (Refer Time: 17:03).

They are not, they cannot be crystalline, some I mean.

Student: (Refer time: 17:09).

You have a pattern, but how does this pattern repeat it into the 3d? You have only one, for example, there is no corner sharing here ok. In this case although there is no corner sharing. There is only one corner sharing, in this case it is only 2 corner sharing. So, they are all semi crystalline structures.

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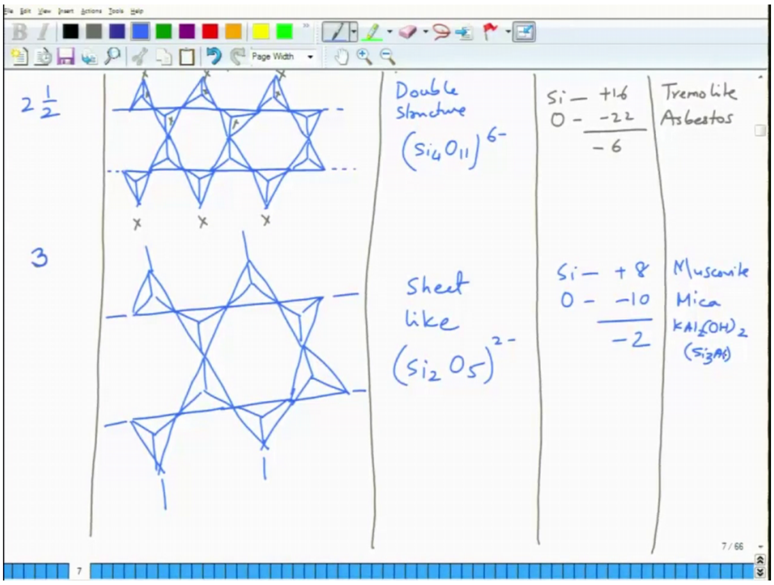

Now, let us look at this. So, now, let us look at, what is the next one is, next one is interesting we call it 2 and a half sharing.

So, what happened in 2 and a half sharing is essentially, you have this kind of a layer. Let me just move this something like that ok. We will have a just let me draw one more polyhedral. So, it has a 3 of them are sharing. So, you have one guy shared here, another guy shared here and this guy is shared here. So, this is called as a we call it just for the sake of calling it, it is called as 2 and a half sharing of polyhedra or oxygen. This is called as double structure which is based on Si4O11 6 minus.

So, the charge balance in this case would be, you can see that Silicon will be 16; Oxygen will be minus 22; this will be minus six. So, for example, minerals such as tremolite , asbestos they follow this kind of sequence of these are these are basically 2 dimensional sheets. There is no 3 dimensional pairing in this case. It is just a 2 dimensional sheet like structure.

And then we have the, in this case the pairing was only in this direction. There was no pairing here. So, no pairing here; no pairing here; effectively it works out to be 2 and half because some of them are paired in 2, some of them are paired in 3, effectively it works out in 2 and a half. So, the threefold shearing is in this fashion as we. So, if you continue this the same structure that is present up.

So, for example, you have this, this, this, this. So, basically it is allowed to be paired in , it is allowed to be paired in this direction, this direction, this direction and in this direction, but not in the vertical direction ok. So, this would be, you have to draw these lines right, otherwise you would miss out on the top bone.

Similarly, here, all right. So, in this case that the y direction bearing was missing and this was missing. There was no missing; there was no top bond right. Here, only the top bond is missing. The xy pairings are there and this structure is called as basically a sheet like structure, sheet like structure. It has Si2O5 and this will be 2 minus. So, Si will be you can see here, plus 8, oxygen will be minus 10 net will be minus 2 le , you can say muscovite or mica .

You might have heard of mica. This basically compound as KAl2OH twice by 3 Al O 10. So, complicated form a sheet like structure, and then the final one was the 4 pairing.

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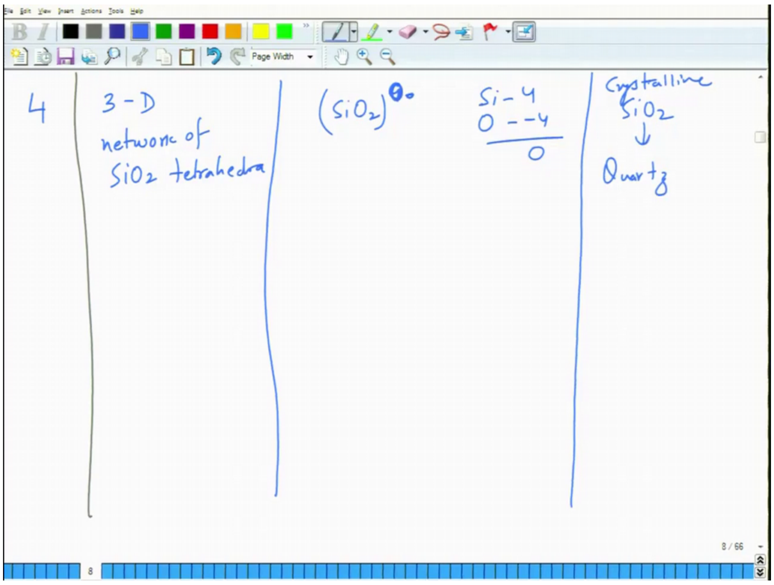

As we saw in the first slide, you have 3D network of SiO2 tetrahedra and this is basically SiO2 4 minus Si basically SiO2 0 ok. So, you have here Si will have 4 oxygen will have minus 4, net will be 0.

So, this is basically crystalline silica which is called as Quartz. So, these are various forms of placate solids that may occur depending upon how the oxygen is shared between the tetrahedra. So, there is there is a whole variety of these materials.

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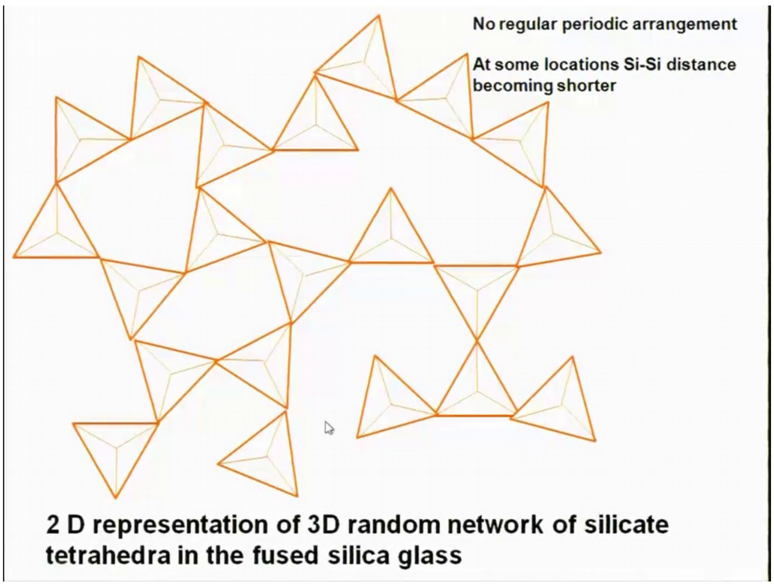

So, this is for example.

So, this is for example a to a representation of 3D random network of silica tetrahedra in fused silica, a few silica is amorphous.

So, these are all, you can see that you have 6 polyhedra, but they are all at random angles; various sports possible co-ordinations. So, at some places the silicon-silicon distance is longer, at some places the silicon-silicon distance is shorter. So, it does not have regular periodic arrangement.

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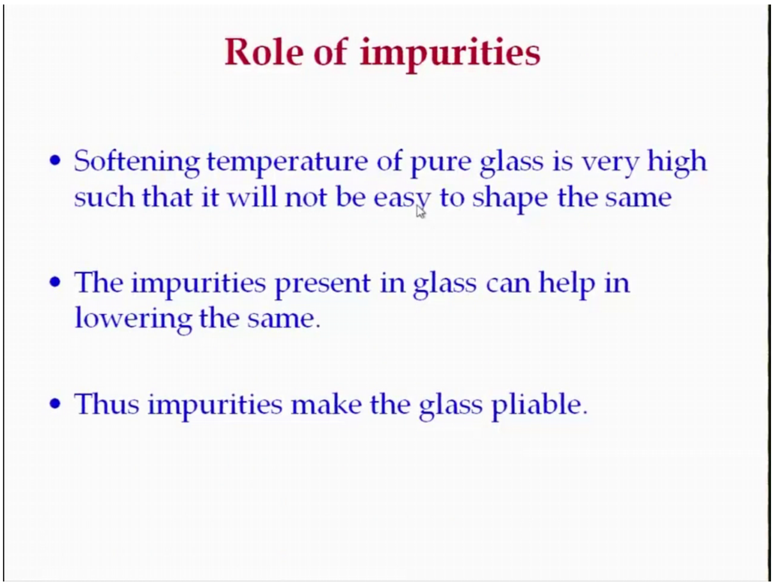

Basically, this kind of thing is achieved by adding impurities. And these are impurities basically ah, lower the softening temperature of glass which otherwise is very high. And if softening temperature is very high, you cannot mold the glass into a shape which you require very easily and that is why one adds these impurities like sodium oxide, potassium oxide to the glasses. So, that one is able to achieve the required level of softness to the glass to be able to mold up in various shapes.

So, ah; so perhaps we can wind up this lecture here very quickly.

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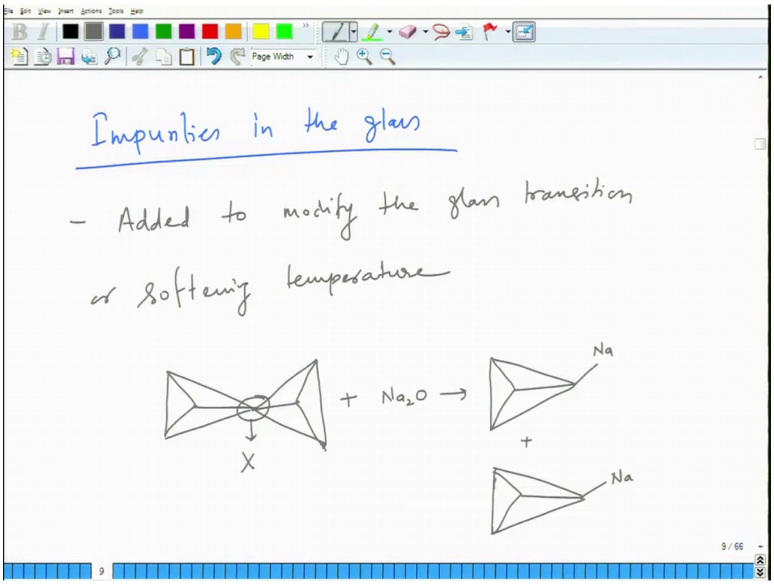

So, basically what you do is that, you have Impurities in the glass and these are basically added to modify the, or softening, softening temperature. So for example, if you have a structure like this ok; this is how tetrahedra are shared in certain structure ok.

Now, this is shared at the corner. If you add sodium to it for example, what it might look like is you may have a tetrahedra like this which is attached with one sodium here and you can have another tetrahedra which can remain attached with itself; we do not the sodium atom here ok. So, they will become loose tetrahedras by breaking of this point between, this is the bond which gets broken by addition of for example, sodium.

So, this is you can say sodium is a glass modifier or it is a network modifier. So, this is how it is going to change the viscosity of glass for example. Same purpose is achieved by adding various other elements which we look at in the next class. So, basically in this class we have looked at variety of glasses, the structures of glasses and the way oxygen is shared between various polyhedrus to, to develop into various structures in glasses ok.

Thank you.