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

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Lecture – 27
Structure of Non-crystalline Solids Glasses

So, good morning all of you.

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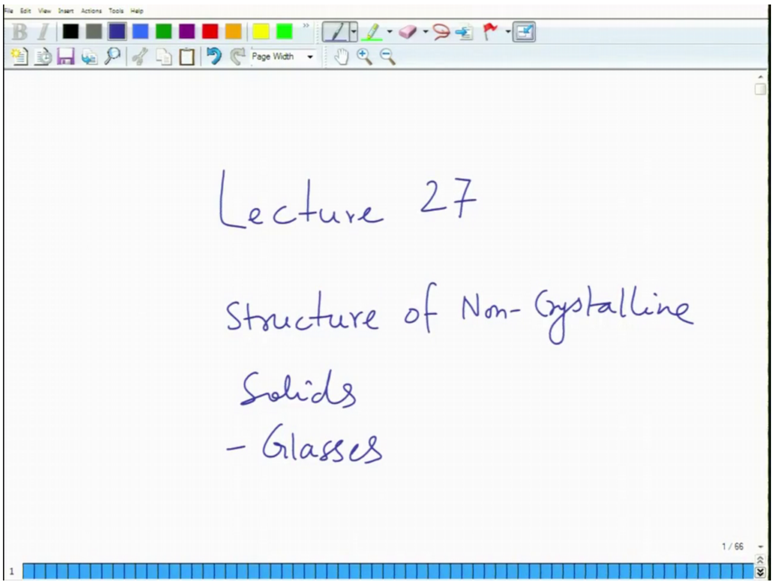

Lecture 27

Structure of Non-Crystalline
Solids
- Glasses

So, we will start a new lecture today, lecture number 27, in which we will discuss the structure of crystalline solids and we will begin with among this category of materials with glasses ok.

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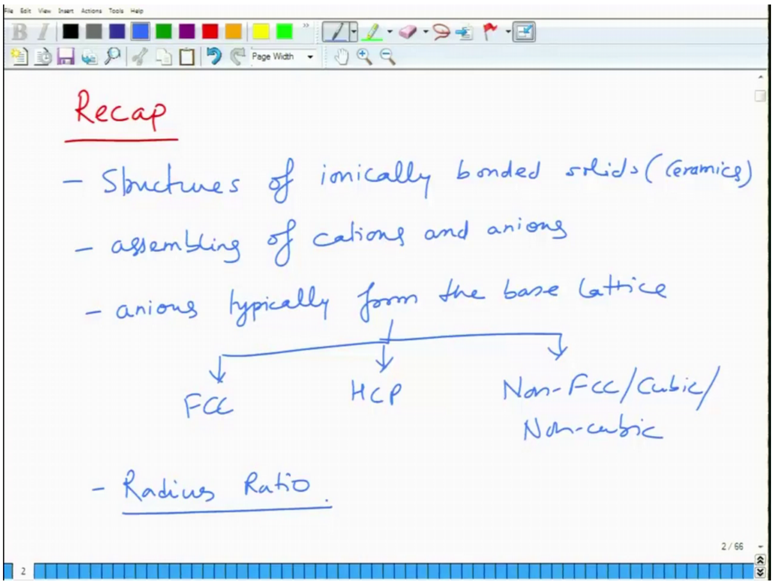

Recap

- Structures of ionically bonded solids (Ceramics)
- assembling of cations and anions
- anions typically form the base lattice

FCC

HCP

Non-FCC/Cubic/ Non-cubic

- Radius Ratio.

So, what we have, so, let me just give you a recap of previous two lectures. So, in the previous two lectures we discussed about the structure of structures of ionically bonded solids which are also basically ceramics and it most of them done many of them turn out to be oxides, but there are the materials like carbides, chlorides, halides and so on and so forth.

So, in this we saw that these structures are based on assembling of assembling of cations and anions and by the virtue of elimination of potential energy they tend to make crystal structures in which cations and anions are arranged in an ordered fashion. So, what happens is that since anions are bigger anions typically form the base lattice . So, they form the basis basic lattice in the material for example, it could be FCC based structure, it could be HCP based structure or it could be non-FCC, but cubic or it could be non-cubic as well .

So, among these three categories where anions basically form a base lattice, but they packed themselves in face centered cubic lattice form or hexagonal close packed lattice form. Ah, the cations go and occupy the interstitial which are typically octahedral and tetrahedral, but they could be some other kind of interstitial cell which they occupied depending upon their radius ratio. So, we discussed that radius ratio determines by and large to which interstitials the cations will go and as a result you form various structures.

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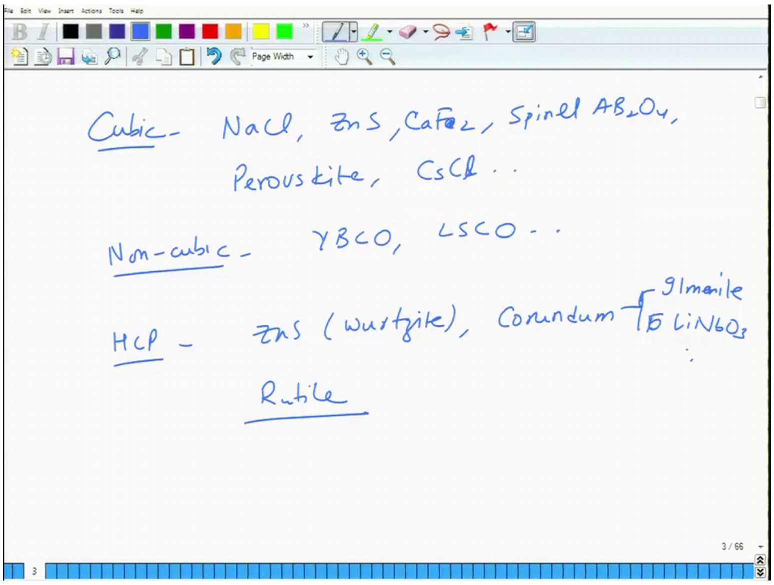

Cubic - NaCl, ZnS, CaF_2, Spinel AB_2O_4,
Perovskite, CsCl . .

Non-cubic - YBCO, LSCO . .

HCP - ZnS (wurtzite), Corundum – Ilmenite, $LiNbO_3$:

Rutile

So, we looked at variety of materials such as in cubic category, we looked at sodium chloride and zinc sulfide or zinc blende structures, calcium fluoride based structures and spinel structures which are basically AB 2 O 4 kind of structures, and then we looked at some other structures such as perovskite we looked at CsCl and so on and so forth. And, then we looked at some non cubic structures such as YBCO, LSCO these compounds make tetragonal orthorhombic unit cell and within this unit cell there are perovskite units or sodium chloride units.

And, then we finally, looked at HCP structures starting with the zinc sulfide based wurtzite structure and then we looked at corundum based structures and then derivative of corundum such as ilmanite Li lithium niobate and so on and so forth and then we looked at what is the what was the Rutile structure. So, these were the very common structures that you come across in ionic solids. Now, however, there are some oxides which are also which have a large fraction of covalent bonding and they tend to crystallize in a non crystalline form.

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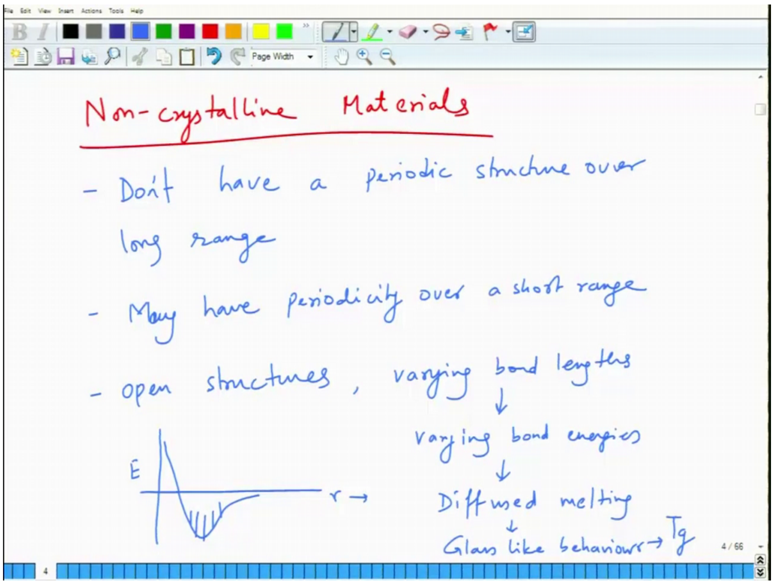

Non-crystalline Materials

- Don't have a periodic structure over long range
- May have periodicity over a short range
- open structures, varying bond lengths

↓

varying bond energies

↓

Diffused melting

↓

Glass like behaviour → Tg

So, in this lecture we will start with materials which are non crystalline materials which do not have do not have a periodic structure over long range. They may have periodicity over short range, short range; by short range we will mean maybe a few nanometers there is a very fuzzy definition about a short range, but typically of the order of a few nanometers. So, they may have periodicity over short ranges, but no periodicity over long distances when you for example, look at fewer tens and hundreds of nanometers and the periodicity breaks down.

So, they may have periodicity over short range, but they do not have periodicity over long range. Such structures are typically open structures and they have varying bond lengths. So, as a result since they have varying bond lengths; so, if you look at the energy minimum it goes something like this. So, you have right, so, this is potential energy, this is distance. If a material has varying bond lengths what it means is that it also, so, it also means that you will have a very varying bond energies and if you have varying bond energies it also means that you have a range of temperatures at which melting occurs. So, that is where they have very diffused melting phenomenon.

And, this is basically characterized by the materials having typically a glass like behavior glass, like behavior and as a result they have something called as T g which is called as glass transition temperature. So, I will not get into details of what the physics and the thermodynamics and kinetics of glass formation, but basically these materials do not crystallize themselves in a in a crystalline form, as a result they tend to form structures which are non periodic glassy structures.

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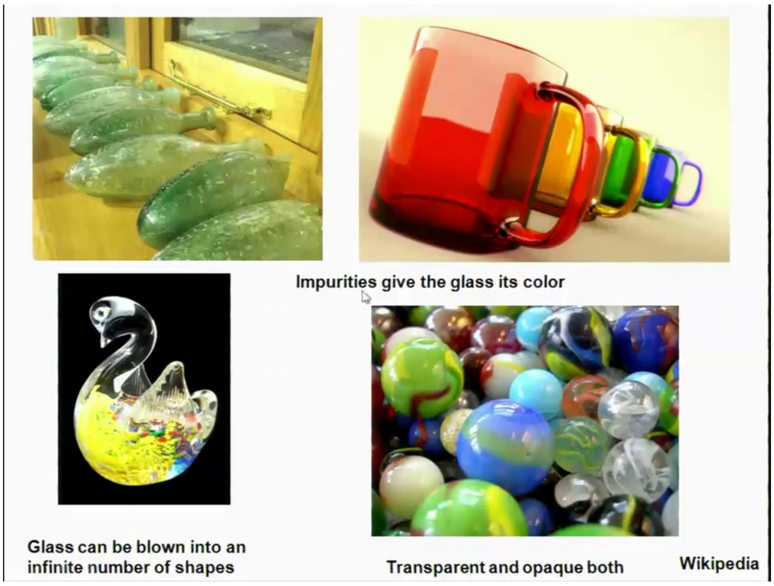

Impurities give the glass its color

Glass can be blown into an infinite number of shapes

Transparent and opaque both

Wikipedia

So, there are materials such as I will show you some slides on just look at for instance this slide. So, this for example, this is taken from Wikipedia.

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Moldavite, a natural glass formed by meteorite impact, from Besednice, Bohemia

Trinitite, a glass made by the Trinity nuclear weapon test.

Wikipedia

So, this is a natural glass which is formed by a meteorite impact. This is called as moldavite. So, you can see that it has at this slight greenish texture and sort of transparency in it is flakes. So, it has this naturally solidified structure which is basically a glassy structure. Then this is a tree this is another glass which is called as trinitite which is a glass made by the trinity nuclear weapon test. So, again it has undergone solidification solidification does not result in formation of a periodic structure.

Similarly, and there are plenty of applications of these glasses. For example, when you add the impurities to these glasses these impurities tend to give it different colors. So, you can see that these different colors of glasses all of them a transparent, but they have different colors again you can see on the left you have different colors of you can see the greenish texture. You can see that quality of glasses that since glass is a glass melts at lower temperature it has it has a broad range of melting temperatures, as a result it can be blown into it can be casted and blown into various shapes.

So, this is for example, a complicated shape out of glass. It can be transparent as well as opaque depending upon how you make in what is inside it. So, glass is a very important and very fascinating material and its solidification phenomena of glass is something which is very which is not yet very well understood and the physics of that is still perplexing.

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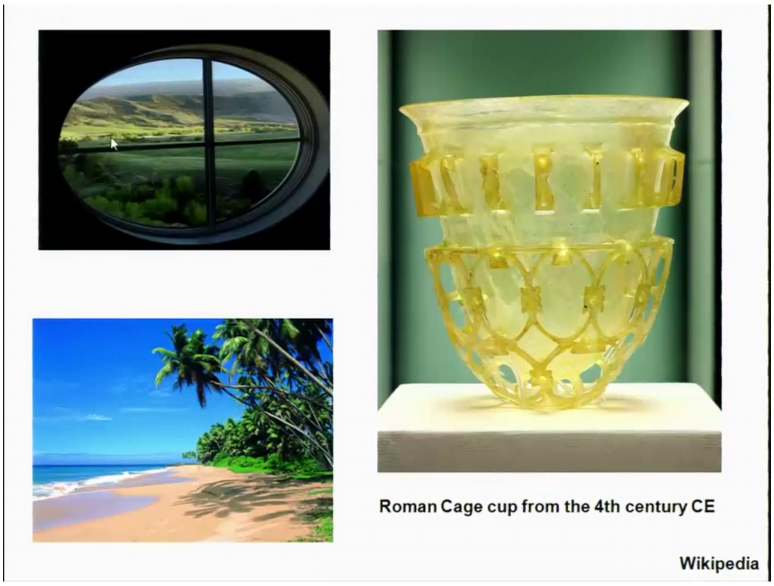

Roman Cage cup from the 4th century CE

Wikipedia

So, you can see that this is a transparent window glass this is a painting on which you have a glass cover, this is a cage roman cage cup which is from fourth century AD.

So, you can see that fourth century on as old as fourth century you had glasses. So, glass is something which has been existence since long time. Humans have been using it in a variety of applications. Ah, however, it is something which is not as well as understood as metals are in comparison to crystalline materials.

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Non crystalline Silica

- Typically used for fabricating windows, vessels etc
- Note that most use of this silica is in amorphous state
  - permits manufacturing of window glass
- Typically amorphous phase cryallizes upon solidification
  - It will solidify in liquid like structure
  - Impurities present in silica lowers the viscosity and make it softer
  - Glass transition temperature will be lowered

Variety of these glasses happen to be non crystalline silica. So, glasses are used in a variety of applications they are used for fabricating things like vessels and windows as we see on daily ware, potteries and so on and so forth. Most of the time, the basic component this glass happens to be silica; silica is basically SiO 2. So, Si O 2 happens to be the basic building block of these glasses and this amorphous phase basically which we which we have at room temperature it crystallizes upon solidification. It solidifies as if the liq, all of us know that liquid has a random structure. It is as if the liquid has frozen in the same structure at the upon solidification.

We add a lot of impurities to glass, for example, sodium oxide and all that to lower the viscosity and various like boron oxide, sodium oxide all these impurities are added potassium oxide these are all added to glass to make it to change or to modify it is viscosity and to make it softer or harder and these impurities also change the glass transition temperature; the temperature at which class will soft and not large glass will melt.

So, they have several you can tune the glasses very well.

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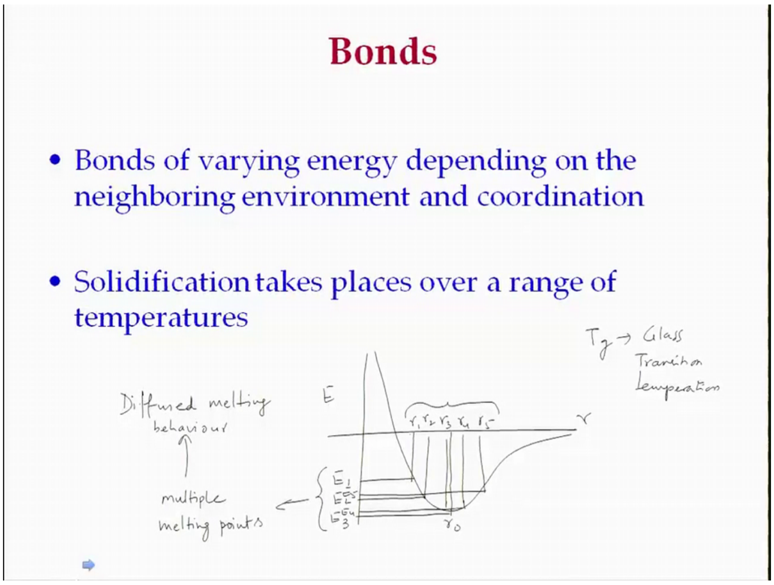

Bonds

- Bonds of varying energy depending on the neighboring environment and coordination
- Solidification takes places over a range of temperatures

As I said that that the essential issue in the glasses is that there are bonds of different lengths and this different length bonds as I told you in the previous slide, the different lengths of these bonds if you have for example, this is a potential energy plot ok. So, this is E versus r, if you have bonds of different lengths ok; so, let us say r 1, r 2, r 3, r 4, r 5. In case of crystalline material you have a minima at r naught, and that is what you have all over the place. In case of glasses what happens is that since you have these way this multitude of bond lengths which means you have an energy corresponding to r 1 is E 1, energy corresponding to r 2 is E 2, to this it is you E 3 to this again it is E 4 and this again is E 5.

So, you have this multitude of energies and these multitude of energies will mean you have multiple in some sense it is like having multiple melting points and that is why many a times glasses tend to have a diffused behavior and that is why the solidification takes place over a range of temperatures rather than at a single temperature and this is what makes glasses having a temperature called as glass transition temperature which is called as T g .

There are multi two- three temperatures which are in which typically are talked in the context of glasses; we will not get into that. There is a concept of free volume and so on and so forth. So, we will probably skip that, but I just wanted to emphasize that this is the reason that you have variety of bond lengths and there is variety of bond lengths force the material to have multiple solidify over a range of temperatures.

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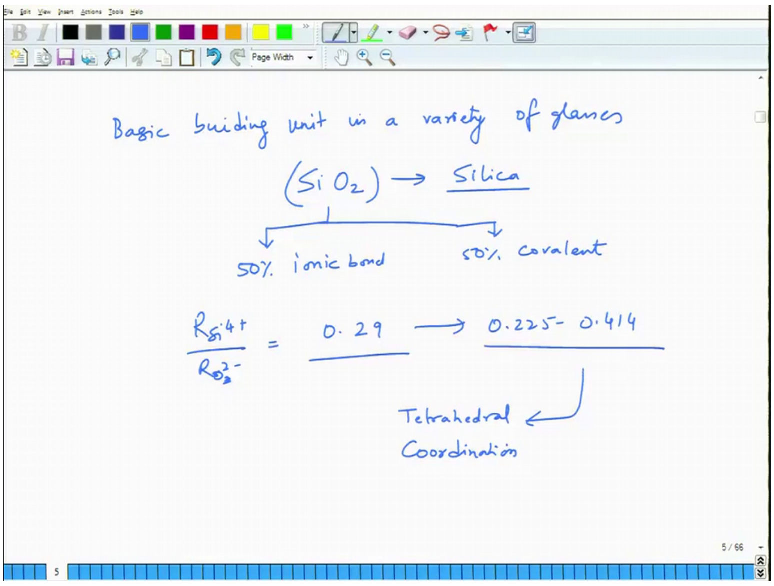

Basic buiding unit in a variety of glasses

$(SiO_2) \rightarrow$ Silica

50% ionic bond

50% covalent

$$\frac{R_{Si^{4+}}}{R_{O_2^{2-}}} = 0.29 \longrightarrow 0.225 - 0.414$$

Tetrahedral Coordination

So, let me now get back to notes. So, basically the basic building block in a glass is in a variety of glasses not all of them, but in an in most variety of classes is SiO 2 which is called as silica and by and large the structure of silica is such that that silica has nearly 50 percent ionic bond and 50 percent of covalent bond. So, it has this character that it must have this kind of behavior.

Now, if you measure that if you take the radius ratio of silicon 4 plus 2 oxygen 2 minus, the radius ratio works out to be nearly 0.29 and this 0.29 you can see falls between 0.225 to 0.414. As a result, it must have a tetrahedral it is preferred to have a tetrahedral coordination.

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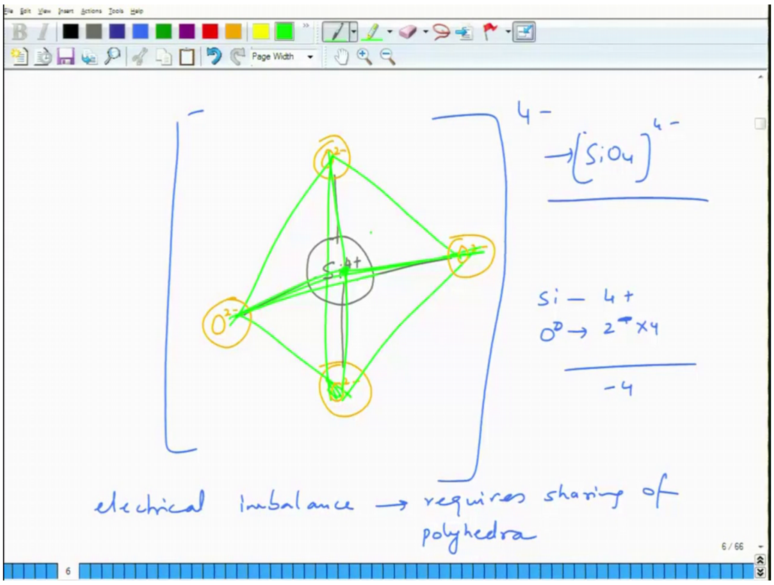

$\rightarrow [SiO_4]^{4-}$

$Si - 4+$
$O^{2-} \rightarrow 2^- \times 4$
-4

electrical imbalance → requires sharing of polyhedra

So, basically what you are going to have is you are going to have this atom of silicon which is 4 plus and this is surrounded by we are going to have one oxygen here another oxygen here oxygen here and the oxygen here. So, this is O 2 minus O 2 minus 2 minus and O 2 minus . Now, if you look at the sum of charges silicon has 4 plus and oxygen has 2 minus and 2 minus into 4, right. So, this the tetrahedra itself will have a charge which is minus of 4. So, if you now make this as a unit this unit will have 4 minus charge which means this needs to so, tetrahedra cannot survive on it is own it has to connect with other tetrahedra or something else to detorize the charge. So, that it becomes charge neutral thing the way it happens is that, so, basically you can say it is electronic it is electrically unbalanced, all right. So, I can say that. So, this is minus charge requires it there is a electrical imbalance and this requires sharing of polyhedra .

Now, how does this sharing off which means oxygen, whatever oxygen is there it has to be shared between the polyhedra. So, how does this work and this is the tetrahedra where you know. So, you can say that this tetrahedra you can characterize at SiO4, 4 minus tetrahedra. So, basically if you look at the structure the structure would be, so, if I just make a tetrahedra all right, there is a tetrahedral you will have and in between that tetrahedra you will have sorry this would be like this and then you will have one here.

So, in between of this tetrahedra you will have. So, this will make a bond here, bond here, bond here, bond here at the center you will have a silicon ion.

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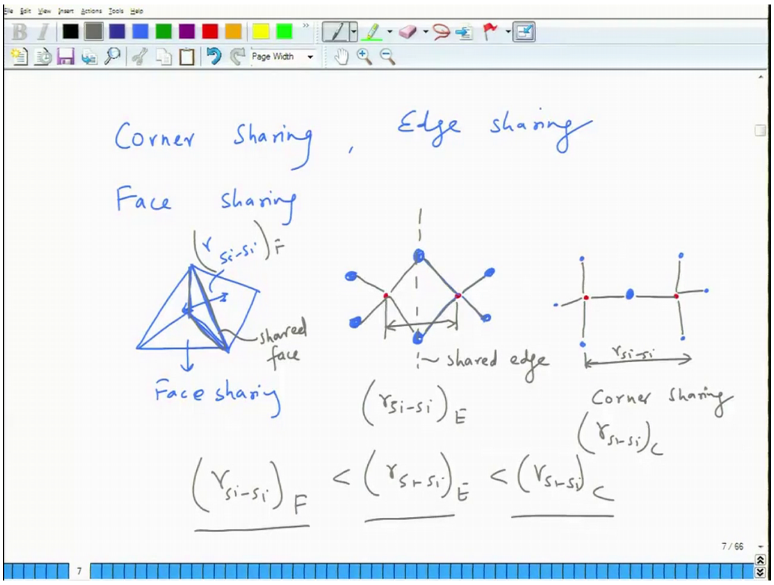

Corner Sharing, Edge sharing

Face sharing

$$(r_{Si-Si})_F < (r_{Si-Si})_E < (r_{Si-Si})_C$$

Now, the way tetrahedras can share polyhedra can share is it can happen by corner sharing it can happen by face sharing. In fact, after corner sharing it would be edge sharing because what will govern the edge sharing corner sharing of face sharing the depending upon the way it shares the distance between the cations will change.

So, for example, if you look at the face sharing tetrahedra you have a tetrahedra let us say like this all right and if you make another tetrahedra sit on top of this this is going to be the face which is shared. So, this one silicon atom is sitting here another silicon atom I am going to sit somewhere here. So, this is the distance between the silicon atom Si-Si distance, this is face sharing . So, if I draw it like this it is how is it going to turn out to be will be something like that. So, you have a tetrahedra coming from the side sharing the face.

So, this is going to be r Si-Si as compared to what you will have when you have. So, for example, edge sharing. So, if you have edge sharing this is your silicon atom let us say this is your silicon atom, these are your oxygen atoms ok. So, two are going to be present ah, one is going to present somewhere here one is going to present somewhere here. So, you are going to have tetrahedra like that and this another tetrahedra is going to be present somewhere like that only.

So, this is another silicon atom and other two oxygen atoms are going to be somewhere here and here this is for example, the tetrahedra all right ok, this is the edge sharing. So, this is the shared thing and in this case this is the shared face. This is a shared face, this is the shared edge. So, you can see that this again there is a distance between these two atoms. So, r silicon-silicon this is let us say face this is let us say edge and then third configuration that is going to be possible is you have silicon atom, silicon atom you are going to have one oxygen atom which is common to both of them and other other atoms are going to be present at certain. So, it is not very accurate, but I one bone. So, this distance is now again our silicon-silicon and this this is again oxygen this is your corner sharing ok.

So, this is going to give you again r silicon-silicon C. So, as you can see that r silicon-silicon, in case of face sharing is smaller going to be smaller than , so, cationic. So, now, this has repercussions in terms of cationic repulsion. You can see that in case of face shared polyhedral, there is going to be stronger cationic repulsion as as in as opposed to in the case of corner and edge sharing.

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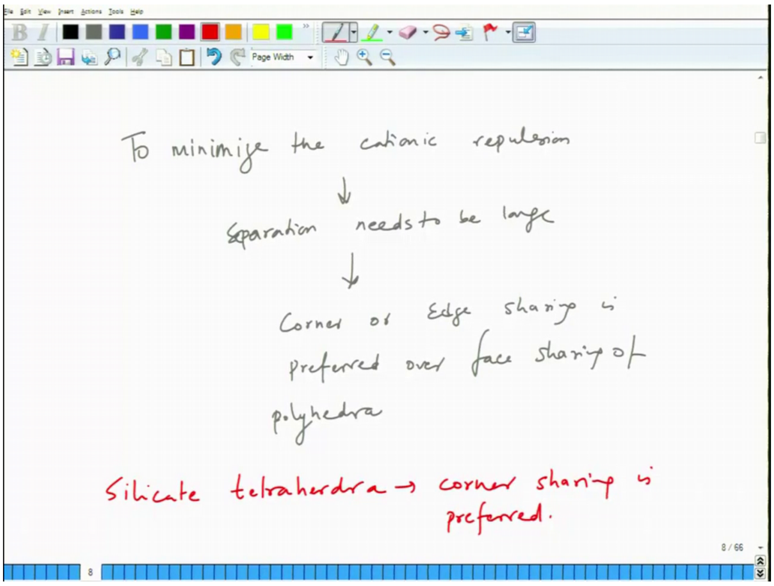

To minimize the cationic repulsion

↓

Separation needs to be large

↓

Corner or Edge sharing is preferred over face sharing of polyhedra

Silicate tetrahedra → corner sharing is preferred.

So, by and large, to minimize the cationic repulsion so separation needs to be large. As a result, corner or edge sharing is preferred over face sharing of polyhedra. So, as it happens in case of SiO 4, the silica tetrahedra corner sharing is preferred ok, but is not guaranteed that it is going to happen all right.

So, what you have here is, so, let us first look at the; however, silica does make a saline structure. So, let us first look at the crystalline silica structure and then we look at the other forms of silica structures.

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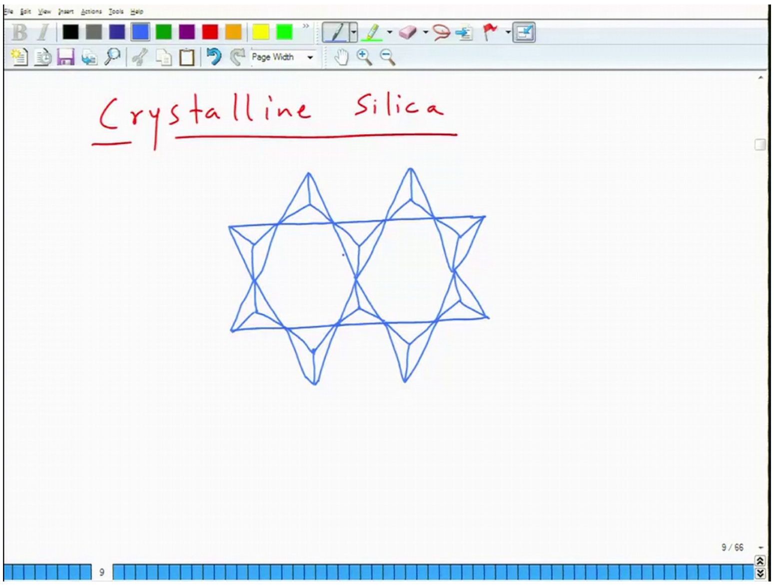

Crystalline Silica

So, the first thing is if you cool it slowly enough and if you achieve right conditions it will make a a structure which is so, what you have here is silicon tetrahedral like that . So, let us say this is the tetrahedron top view ok, the second tetrahedron is attached to it in such a fashion this is the second tetrahedron. In the third tetrahedron is a present in such a fashion and the fourth one again ok. And, this one is going to be shared with a guy right here and then I am going to have one here and this one will be or the other way round ok, like this. So, basically this is how it is going to continue and if you continue. This in the 3D, you will form a silicate network ok.

So, this is the form of this these are the hexagonal sheets of silica molecules arranged in a crystalline form there's a periodic pattern of hexagonal layers that deform. So, this is the first structure crystalline form they make. If you break these, the corners here or here or here or here to change the bonds and if you manage to manage this to happen in a more in a random fashion then what you will make will be amorphous form of silica. So, we will break here. Ah, we look at the remaining forms of crystalline solids in the next lecture.