Material Science
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Lecture No 9
Structure of Solid Materials

So in the last class we looked at the geometry of void spaces which we call interstitial, interstitial void spaces or interstices in the close packed structures one was tetrahedral void another was octahedral void we saw the geometry, the sizes of the small spheres which can probably sit in their metallic crystals having had a look at that we talked of the solid solutions, interstitial solid solution and substitutions solid solutions talked about the Hume-Rothery rules and then we also told you that solid solution can also be random or ordered solid solutions. Now continuing with stacking of spheres of different sizes we go over to the ionic crystals where again the bond is non-directional in nature but the 2 ions are of different sizes.

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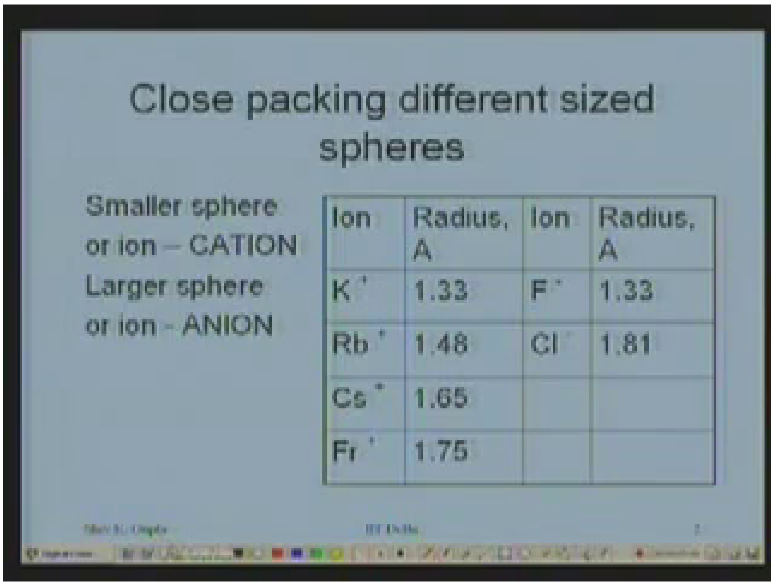

Close packing different sized spheres

Smaller sphere or ion – CATION
Larger sphere or ion - ANION

Ion	Radius, A	Ion	Radius, A
K^+	1.33	F^-	1.33
Rb^+	1.48	Cl^-	1.81
Cs^+	1.65		
Fr^+	1.75		

So continuing with the assumption that ions are the hard spheres we can talk about them as cations and anions but in my discussion what is a cation what is an anions that is what has to be very clear to you it is not necessary what you studied in chemistry one is going to be a smaller ion other is going to be a bigger ion, the one which is a smaller ion I call it cation the one which is a bigger ion I call it anion. This by and large satisfies the definition you had in chemistry that positively charged ions are cations and negatively charged ions are anions. I have some exceptions here to my definition and comparison to the chemistry these are some of the elements from the group 1 potassium, rubidium, cesium and francium their ionic ADI are 1.33, 1.48, 1.65, 1.75 respectively and I have taken 2 of them group 7 fluorine and chlorine 1.33 Angstrom 1.81 Angstrom bromine iodine will be still bigger than that.

So you can see that fluorine which is the smallest here is equal into potassium in size but smaller than these elements, these 3 ions. So if there is a compound rubidium and fluorine my definition would be this is cation this is anion, this is a small ion this is a bigger ion right but even if I go to chlorine and chlorine is bigger than all of them and these will be all cations and chlorine will be the anion, so these 2 - 3 examples which are the exceptions otherwise my definition is not going to clash with chemistry definition. Why I am talking about the smaller ion and the bigger ion shall become clear to you when I start talking about geometry.

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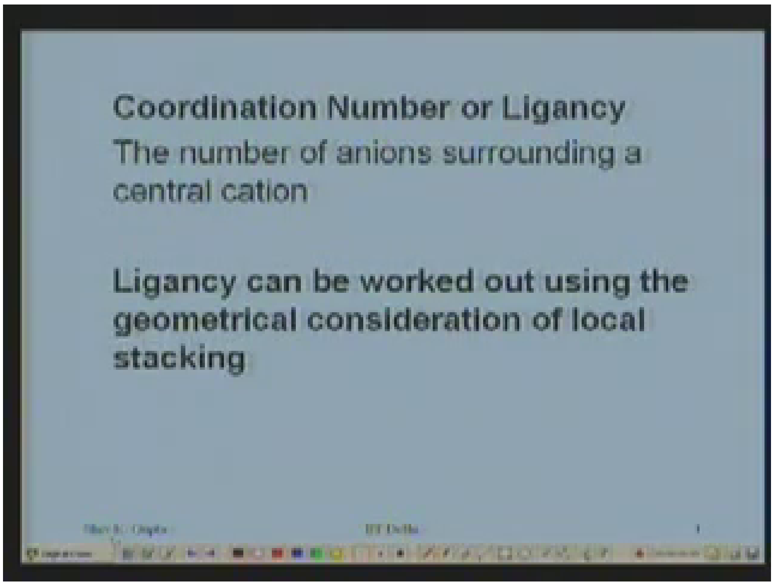

Coordination Number or Ligancy

The number of anions surrounding a central cation

Ligancy can be worked out using the geometrical consideration of local stacking

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Then we define the coordination number or the ligancy as the number of bigger spheres surrounding a small sphere in the centre in other words number of anions surrounding a central cation that is the going to be a coordination number or the ligancy. Well we shall work this out when we look at the geometry by working out the numbers of these bigger spheres surrounding the smaller spheres in the centre. By looking at the geometry we shall work this out we shall talk about these numbers but before we go over to that we have to talk about certain rules of stacking spheres which are of different sizes because they are also electrically charged one is positively charged other is negatively charged.

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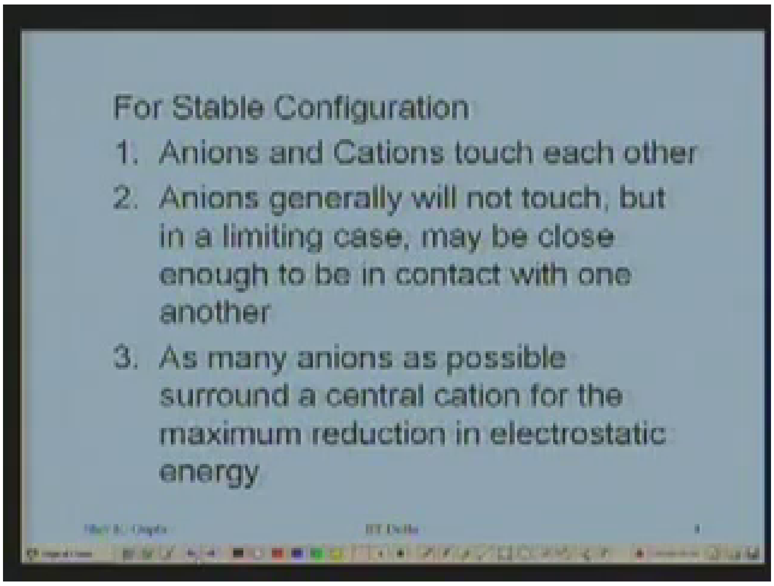

For Stable Configuration

1. Anions and Cations touch each other
2. Anions generally will not touch, but in a limiting case, may be close enough to be in contact with one another
3. As many anions as possible surround a central cation for the maximum reduction in electrostatic energy

My rules are maintaining the stability in the configuration and we are talking about the local coordination, local arrangement and where I have to satisfy the electrostatic attraction, so I define anions and cations touch each that is the definition of an ionic bond and our assumption that ions are hard spheres, when 2 hard spheres positively charged negatively charged attract each other in touch each other with the form a bond, the bond length is the radius of the anion plus the radius of the cation, centre to centre distance that is why we say anions touch cations and cations touch anions because that is how the ionic bond is formed, so in other words a bigger ion touches a smaller ion and a smaller ion in turn touches the bigger ion.

Anion generally will not touch will show you the geometry because anions are also charged even if it is negatively charged these charge density of the surface would be smaller because it is a bigger one as compared to the charge density on the cation it is a smaller one therefore the repulsion between them may not be a strong authority will be impulsion because they are same charges, so they usually will not touch, however there could be limiting situation while talking about the geometry in which anions can be made to just come as close as their diameters means they just start touching each other that is just a limiting case that is not the general situation and thirdly as many anions the bigger anions will surround the central smaller ion, the cation as possible but the space can provide the geometry can provide for, so that the electrostatic energy is minimised is a maximum possible reduction there, so these are the rules on which my stacking of spheres of different sizes is going to be based on, so that when we start looking at the short-range arrangement 1st and then go over to the long range arrangement.

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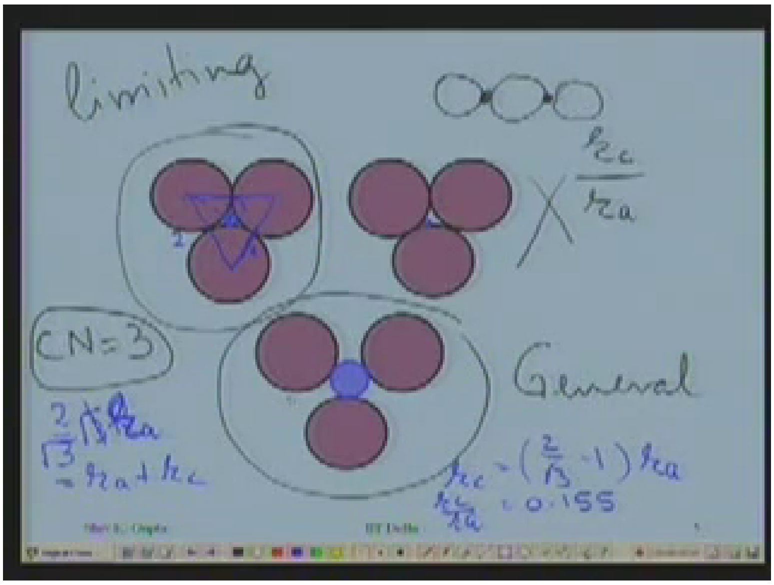

Here I show you a certain coordination there are central sphere the blue one surrounded by the bigger spheres the anions 3 of them, anion is touching cation, cation is touching anion, cation is touching this anion and they are all touching all 3 of them but anions are not touching anions there is a gap between them the separation between… This is what I mean by anion touch cations and cations touch anions and anions in general do not touch each other. The central cation would like to surround itself with as many bigger anions as possible, how many it can…that is what we are going to look at? Now in this case we also said that what is a limiting situation when anion just begin to touch that is the limiting situation when anion touch anions and anions are also touching cation, cation is touching anion and cation is touching this anion but anion also touching each other.

This is the limiting situation or this is the limiting case, right that is what I talked about as the limiting case and this is going to be my general case that is now mostly will find the stacking of spheres of different sizes which are charged spheres anions and cations general but this is a situation not acceptable let us see what is the situation? Anions are touching anions, the central cation is so small that the hole what is formed is rattling in that hole either at the most can it can be close to 2 of them like I have shown here or it is slightly displaced it will be close to only one, so in this local arrangement cation is touching anion only one or twice but it is not touching all the 3 and anions are also touching anions which is not generally the situation, so this is not an acceptable case or coordination 3, for coordination 3 this is the most general situation and that is the limiting situation right.

In this situation it is either touching one or at the most 2 anions, so this would be as good as if I have an anion, a cation and anion touching like this and again maybe another cation another anion, so every cation has only 2 anions around it, it does not have 3 so this does not go for the coordination 3 it goes for coordination 2 only this situation, so this is what about the coordination number 3 same is a situation for coordination number 4, 2, 6, 8, 12 whatever we have those are the situations which will be similar in nature this is what I mean by when I said what are the rules in which we are going to decide this? Now from this it is very clear if I define the radius of the cation as rc and define the radius of anion as ra then this is a certain value which can be worked out for the limiting case if it is greater than that this is possible, if it is less than that is the situation this coordination is not possible, so limiting case when I work out shall give me the radius ratio of the cation to anion which is the smallest value of that coordination right for this triangle can you work it out?

It is an equilateral triangle. This perpendicular drawn from this onto the side of the triangle passes through the center of gravity and two third of this distance is this radius anion plus the radius of cation, if this is 2 this is one in this right-angle triangle that side is under root 3, so I get and that distance 2 by 3 is 2 by 3 of under root 3 of R which is the radius sorry radius of anion let us put it like this, right. 2 by 3 under root 3 of the radius of the anion that is this distance and this is equal to radius of the anion plus the radius of the cation and under root 3 will make it 2 by under root 3 here, so if I get the radius of cation from here it will be 2 divided by under root 3 minus 1 of radius of the anion. You can simplify this it will be 0.155, so if the radius ratio is smaller than 0.155 this is the situation coordination is 2, if it is 0.155 it is the limiting situation or coordination 3 if it is greater than 0.155 is the coordination 3. This is the meaning of those 3 conditions which I have placed in understanding the geometry, is it clear? Yes please.

Student: If you go with more number of coordination is it always planar coordination or (()) (17:09)

Prof: I am coming to that I have not finished my talk. I am going to next and because after all my crystals are three-dimensional in nature they are not planes like this alright we will come to that is as local arrangement we have to make the three-dimensional arrangement we will come to that.

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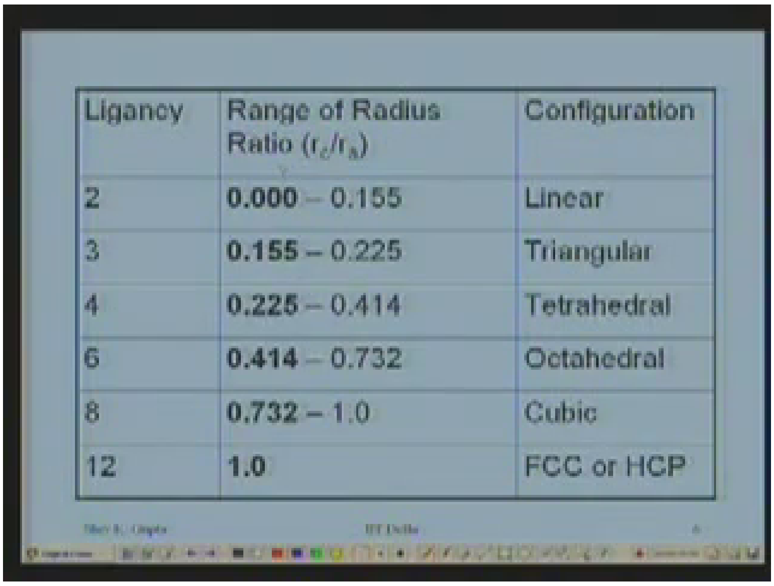

Ligancy	Range of Radius Ratio (r_c/r_a)	Configuration
2	0.000 – 0.155	Linear
3	0.155 – 0.225	Triangular
4	0.225 – 0.414	Tetrahedral
6	0.414 – 0.732	Octahedral
8	0.732 – 1.0	Cubic
12	1.0	FCC or HCP

Right in here now I place these limiting situations for coordination 2 it will be 0 anion would touch anion means the size of the cation is 0 as compared to the size of anion there is no such situation, so limiting cases is only as I said just the limiting case general case would be rc by ra greater than 0 but less than 0.155 I shall get the ligancy 2 which means the coordination is linear just now which I showed in the picture. Then coordination 3 also I showed you starting from the limiting case of 0.155 goes up to 0.225 that is what I want to talk about the triangular configuration which is a plane. Now configuration with ligancy 4 that means central cation is surrounded by the 4 anions this geometry we have seen in the last class. If I make a tetrahedral void in FCC or HCP the whatever sphere I put in there is going to get bonded to the 4 neighbouring anions and those 4 are touching themselves therefore that becomes a ligancy 4 an configuration becomes tetrahedral and what did we find the sizes sphere that we can fit in it tetrahedral void?

Student: 0.225…

Prof: 0.225 of the parent atom, now the parent atom in our case is anion, so the radius ratio cation to anion ratio would become 0.225 that is a limiting situation here and gives me the tetrahedral coordination. Now this will go on expanding the cation size and anion will go separate out right this will go on till it is possible or the 5th anion to come around it from somewhere some direction but when we are able to put the 5th we are also able to put the 6th simultaneously and that situation also we saw in the last class when we make an octahedral hole in a closed pack structure that means the anions are just touching and we have a hole in the middle where we can put a small sphere which is the cation and that sizes 0.414, so radius ratio becomes 0.414 I have 6 neighbours to the central sphere small sphere, these 6 are the anions and configuration is octahedral.

This is where my friend sometimes confuse because here the word comes octah, octahedral means the configuration is forming 8 faces which are equilateral triangles that does not mean there are 8 neighbours to the central cation. Number of neighbours the number of anions surround the central cation is 6 right, so do not get confuse with that and 0.414 is the limiting situation these 2 you have body seen in the last class. Now we shall see the next one when I keep on now separating the anions because my size of the cation is increasing it will go on till it is possible to bring 8 of them close to 8 not the 7.

When 8 comes this also is very simple understand you have seen the simple cubic structure it just touch each other and the body centre will be the place where the central cation can sit, if it sits there it will be touching all the 8 corners right, so that is the situation in that if you find the body diagonal is 1.732 under root 3, so radius ratio you will find out to be 0.732 is what it is. I am not working it out in the class you do it yourself it is 0.732 days when the central sphere touches the 8 anions in the corner of a cube and we call it cubic coordination. Now it keep on increasing the size of the cation again, anions will go separate out but this situation will go on till it is possible to bring in 12 neighbours when the size of all the ions is the same or all the spheres is the same as what we have body seen in the metallic crystals FCC or HCP. Now if the cation size becomes bigger than that…

Student: (())(22:30)

Prof: My definition will change anion would become cation, cation would become anion and it will fall somewhere here right. Why I define is smaller (())(22:40) cation it should become clear to you now, so if it becomes bigger it will have to fall in back somewhere there, is it right? Okay.

Having had a look at the short-range arrangement I have to develop an ionic crystal must be the three-dimensional crystal and to get 3rd three-dimensional crystal I have to make this local arrangement same everywhere have to repeat this in such a way that I get the three-dimensional crystal however electrical neutrality has to be maintained because no ionic crystal is electrically charged take sodium chloride is not charge you do not touch it you do not get any shock because it is electrically neutral, right but when I make the radius ratio for sodium chloride it will be talking about is about 0.53 if I am not wrong around there from your list what will you say or suggest?

Student: Octahedral coordination.

Prof: Octahedral coordination means there is a sodium ion in the middle and 6 chlorine iron around it. Each chlorine iron has one negative charge minus 6 sodium ion is plus one, so net charge on this local group is minus 5. If I repeat this minus 5 charge it will be ultimately charged material, so I have to ensure that this is not electrically charged it has to be electrically neutral 2nd thing is the bond between a sodium ion, chlorine iron or a cation and anion is non-directional in nature though I must start them as closely as possible, okay.

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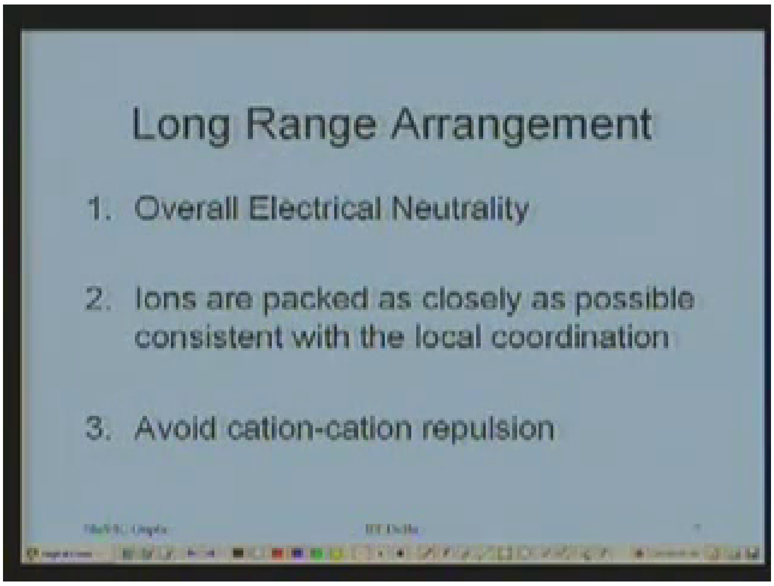

Long Range Arrangement

1. Overall Electrical Neutrality
2. Ions are packed as closely as possible consistent with the local coordination
3. Avoid cation-cation repulsion

Then I am talking of these spheres which are charged spheres, if suppose I have 2 spheres one is smaller one is bigger and both of the same charge, that charge density on this spherical surface of the smaller sphere would be more and charge density on the bigger sphere be less, so repulsion between cation cation would be very large because the charge density on the surface is very high as a result I must avoid cation cation repulsion and this becomes very dominant when the charge on the cation is or than 3 have to be very careful we will see some of those structures.

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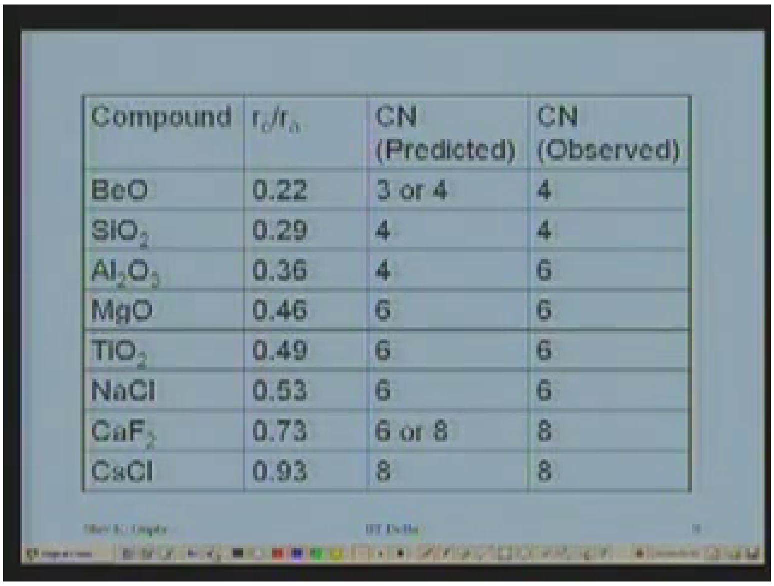

Compound	r_c/r_a	CN (Predicted)	CN (Observed)
BeO	0.22	3 or 4	4
SiO_2	0.29	4	4
Al_2O_3	0.36	4	6
MgO	0.46	6	6
TiO_2	0.49	6	6
NaCl	0.53	6	6
CaF_2	0.73	6 or 8	8
CsCl	0.93	8	8

Now this is what we observed as far as local stacking is concerned in some of the well-known ionic crystals beryllium oxide radius ratio we observed this 0.22 you predict from your table 3 or 4 because 0.225 is just for the 4 so just around there knocking what we observed is 4. Silica 0.29 you expect 4 you observe 4 it is also a covalent bond spends most of the time means 50 percent of the time as covalent 50 percent time ionic and satisfies the conditions of both Sp 3 bonding as well as the radius ratio it satisfies both of them. Al 2 O 3 radius ratio is 0.36 you expect 4 but you observe 6 plus a charge on the aluminium is plus 3.

Magnesium oxide 0.46 you expect 6 you observe 6, TiO 2 0.49 it you expect 6 observe 6, sodium chloride 0.53 expect 6 observe 6 so on and so forth calcium fluoride 0.73 which is very close to the limiting case 0.732 is expect 6 or 8 but you get 8, caesium chloride 0.93 expect 8 observe 8, so that is about the geometry the except 1 or 2 exceptions in this case only Al 2 O 3 is the only exception really speaking we observe whatever we have talked about.

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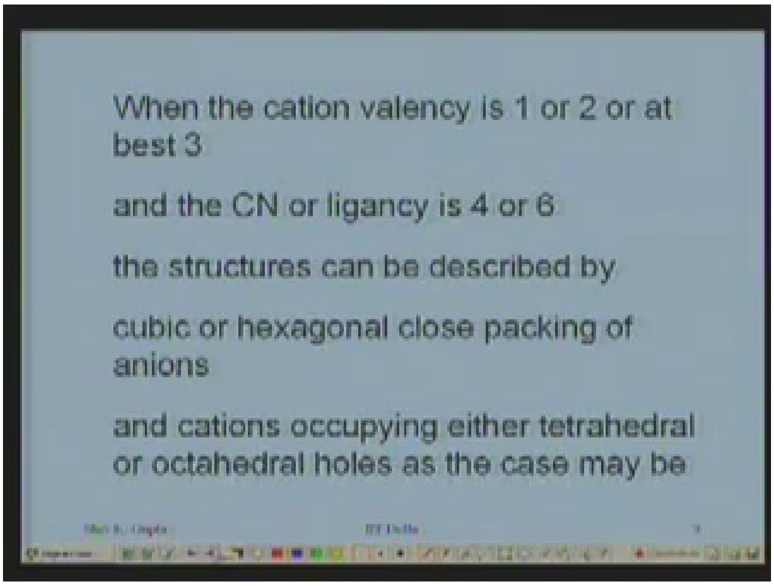

When the cation valency is 1 or 2 or at best 3

and the CN or ligancy is 4 or 6

the structures can be described by

cubic or hexagonal close packing of anions

and cations occupying either tetrahedral or octahedral holes as the case may be

Now to make the long-range arrangement where I have to ensure electrical neutrality, close packing then whenever valency of the cation is 1 or 2 usually but at sometimes like aluminium I talked about the 3 is also possible we can do that. Coordination number or leniency is 4 or 6 I am specifically talking about 4 or 6 okay. The structures can be described in a very simple manner by the cubic close packing we talked about and the hexagonal close packing we talked about this we have been talking about last 2 classes, so it can be defined on that and then whatever the tetrahedral voids and octahedral voids are formed those are occupied by the cations depending upon what is the legacy is whether it is a tetrahedral coordination or it is say an octahedral coordination.

Only one thing I have to be very clear about this case that FCC closed packed structures when we talked about all these spheres were touching and central sphere was touching the neighbouring 12 ones, now when I make the FCC packing of anions I have already stated in the beginning of the class anions generally do not touch anions when that happens as if you made an FCC packing with spheres of radius let us say r and then reduce replace those locations with spheres of radius 0.5 r or 0.6 r so there is a space between them now.

This is what I mean by FCC packing of anions or closed pack…cubic closed packing of anions, anions are not touching anions similarly the hexagonal, so the closed pack plane when you look at their spheres are not touching but the locations are similar to what we find in the close packed structures I had that is what I mean by this when I talk about the consideration of the structure is as a cubic closed packing or hexagonal close packing and the cations going into the tetrahedral voids or the octahedral voids depending upon what the ligancy is and majority of your ionic crystal will be covered in this.

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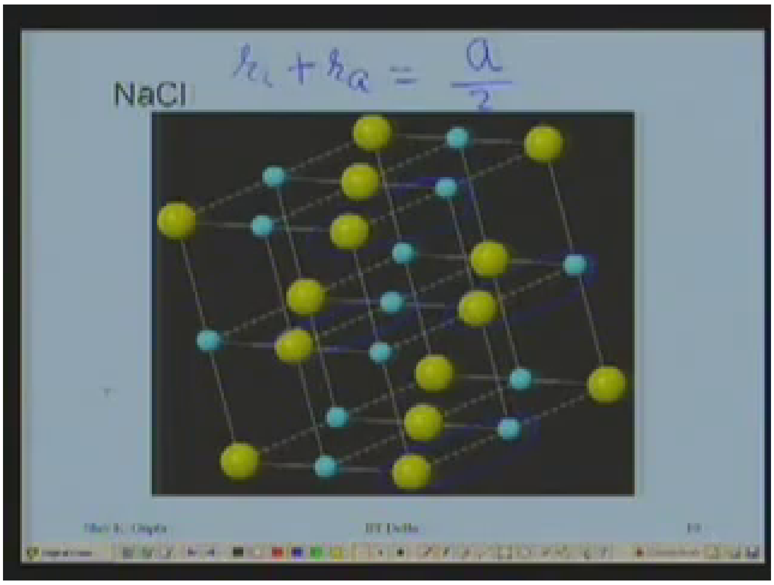

NaCl

$r_c + r_a = \frac{a}{2}$

Here is sodium chloride, these yellow spheres are the anions which in this case are chlorine ions, the blue ones are the cations the sodium ions, coordination we have already seen is 6, octahedral coordination. In an FCC closed pack structure where are the octahedral hole located?

Student: Body centre and the edge centre.

Prof: Body centre and the edge centre, very good and see whether you are your cations are, the cations this one is in the body centre these 4 on the edge centres, this is on the edge center 4 again these 4 on the edge centres. There are 12 edges and 12 on the edge centres one of the body centre and we have even chlorine ions and the 8 corners and the 6 faces enter 4 here and 2 there, this is FCC of sodium ions this is what I mean by FCC of sodium ions or FCC of chlorine ions because I can also start from here and make the FCC of sodium ions. FCC of chlorine ions are the anions (())(31:27) is this that anions are not touching and where the holes form between them are going to be same regular octahedral holes and regular tetrahedral holes because placement is the same as that in a closed packed structure, so this octahedral hole is occupied by the cation and this is the…Now this itself becomes a long-range arrangement, why this itself becomes a long-range arrangement? This is the unit cell which can repeat and is electrically neutral. Somebody had asked me how is it electrically neutral?

Student: Number of sodium ions…

Prof: Number of sodium ions and number of chlorine ions in this FCC is equal 4 and 4. From the FCC location I get 4 from the edge centres I get 3 sodium ions and body centre gives me one, so I have 4 cations and have 4 anions this is absolutely neutral there is no electrically charged on it and this can repeat, right. So this is how we can define…

Student: although anions are not looking (())(32:44) cation and anion…

Prof: They have to touch I have not shown it here they are not…I have not shown them touching because I want to show you inside, I want to show you inside and the edges and the back therefore I did not make it touching, if I make them touching it will probably see the top, front but you not be able to see inside, this inside thing is what I wanted to show that is why I made it open right but this means what I am trying to say is radius of the chlorine ion plus the radius of the sodium iron become half the lattice parameter of the unit cell right so in here what you observed is radius of the cation plus radius of the anion is equal to lattice parameter a divided by 2 right and if you are talking this as a crystal which is FCC space lattice motif also you can define his here, this is the motif, chlorine ion and the sodium ion and this motif is placed at every lattice point, on this lattice point, on this that is point right want to see on this lattice point, it is same everywhere it is same it is not different, so that is how you can define the space lattice and the base is for sodium chloride structure.

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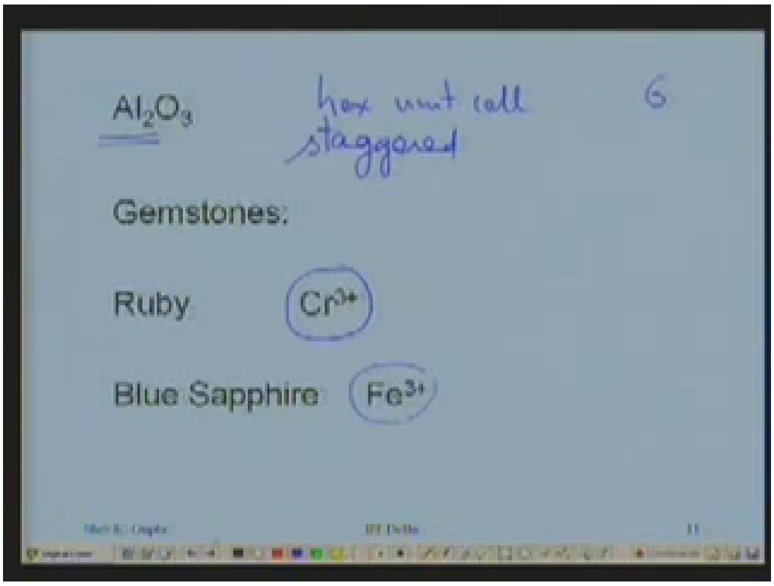

Al_2O_3 hex unit cell staggered 6

Gemstones:

Ruby Cr^{3+}

Blue Sapphire Fe^{3+}

Next we have talked about a Al 2 O 3 where we said that we observe 6 the coordination is that of 4 radius ratio, it forms hexagonal close packing of oxygen ions. If I look at the hexagonal unit cell and form a closed packing of oxygen ions, how many oxygen ions do I have in hexagonal unit cell. I shall have since I am making closed packing it should be 6 oxygen and how many octahedral holes will I have?

Student: Equal.

Student: 6.

Prof: 6 but how many cations to I have? 4 for 3 oxygen I have 2, so therefore for 6 I shall have 4, so out of the 6 octahedral holes I have to use 4, I got use of all 6 and these are staggered in the crystalline form of Al 2 O 3. This is the next are material as after diamond for where we cannot use diamond being diamond being a very expensive we use Al 2 O 3 or grinding, polishing and other things and there are certain gemstones they are also placed on this Al 2 O 3 structure only but they are not pure Al 2 O 3. Then I add 3 to 5 percent of chromium ions that means I am substituting 3 to 5 percent of aluminium ions by chromium ions trivalent chromium ions replace the trivalent aluminium ions I get Ruby which is Redstone very one of the expensive stones, well this is also a very hard material we use them in making jewelled earrings.

Now of course we have all electronic watches, we used to have mechanical watches where you write 17 jewels, 21 jewels those are the bearings in which the gears are rotating and there are different gears of different ratios, so that the 2nd needle moves the minute needle moves and hour minutes moves all those things are there, these bearings are used for that kind of thing. Blue sapphire, when we place 3 to 5 percent by iron ions, the aluminium is substituted by iron ions I get blue sapphire which is also an expensive or semiprecious stone.

Student: Sir again this was substitutions solid solution.

Prof: It is a substitutions solid solution.

Student: Then again interstitial is possible there are 2 octahedral voids left unoccupied.

Prof: Well what you are saying it can there will be an interstitial solid solution in an ionic crystal that would be charged ion, the charges will be problem these charges if it is there then charge has to be adjusted somewhere else, so some of the iron has to be missing from it sight we shall talk about those kind of structures just wait a week later we will talk about that right these are called imperfections in the crystals, we will talk about those imperfections. Right now we are talking about perfect crystal, Idol crystal okay.

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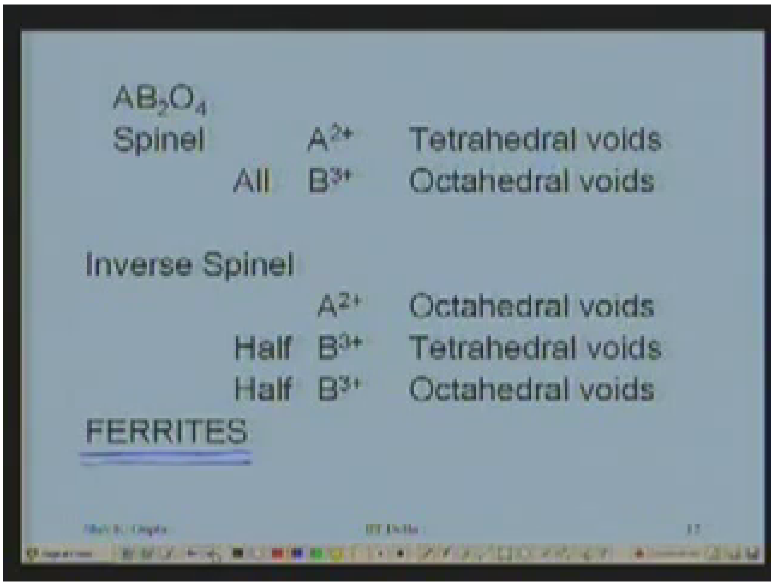

AB_2O_4

Spinel		A^{2+}	Tetrahedral voids
	All	B^{3+}	Octahedral voids
Inverse Spinel			
		A^{2+}	Octahedral voids
	Half	B^{3+}	Tetrahedral voids
	Half	B^{3+}	Octahedral voids

FERRITES

Then the another ironic crystal of interest was AB 2 O 4 kind of where oxygen is there and A is a bivalent cation and B is a trivalent cation there are spinals in which case all the bivalent A ions go in the tetrahedral voids and all the trivalent B ions go into the octahedral voids and oxygen forms cubic closed packing, okay. It forms a cubic closed packing that means FCC, in FCC I have 4 oxygen from the FCC unit cell there are going to be 4 octahedral holes but I am using only 2 of them. There are going to be 8 tetrahedral holes but I am using only one of them, so repeating unit actually becomes bigger it becomes 8 times size of the unit cell which has only 4 oxygen and more important than spinel is the inverse spinel structures these are magnetic materials which are called ferrites, manganese ferrites or you talk about zinc ferrites or you talk about chromium ferrites so on and so forth.

Here you bivalent ions is what like zinc or chromium but trivalent ions are iron, this is called inverse because the place of trivalent ion here is taken by the bivalent ions and place of bivalent ions is taken by the trivalent ions like this bivalent ions go into the octahedral voids. Here it was a trivalent iron going with the octahedral voids and trivalent ions half of them only go into the tetrahedral voids because you notice here one tetrahedral void and 2 octahedral voids are occupied in 1 FCC unit cell these are 2 out of 4 this is 1out of 8, so number remain same even here only one 8th of the tetrahedral voids are occupied and one half of the octahedral voids are occupied 1 by this other one by that.

So 2 of them are occupied 2 octahedral holes are occupied and one tetrahedral void is occupied. In here who octahedral voids are occupied because trivalent ions are 2 in number as one tetrahedral void is occupied, so that remains the same inverse because what was in tetrahedral void has gone into the octahedral void now? These are the ferrites and we will talk about them when we come to the magnetic materials we will talk about these structures there.

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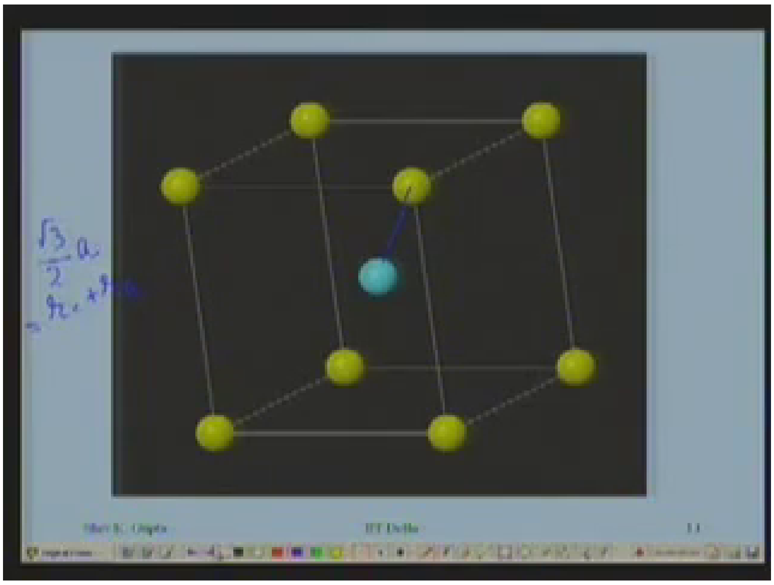

Right after these 4 or 6 coordination we come to this coordination number 8 and in here I gave an example of caesium chloride radius ratio is 0.93 this is a caesium body centre location and chlorine ions are the body corners of the cube. This is the short-range arrangement and this itself is electrically neutral if I make it a repeating unit because these chlorine ions will be shared by 8 unit sales each there is only one within this volume and one caesium ion is within the volume, so caesium chloride becomes electrically neutral. Isolated, yes it is charged but when I repeat it the reputation this being the common one this being the common one that is get electrically neutral alright, so that is the arrangement of coordination number 8. In here from body centre to the body corner distances under root 3 by 2 of A and this is equals to radius of cations plus the radius of anion right, so that is the arrangement which we have looked at in these structures.

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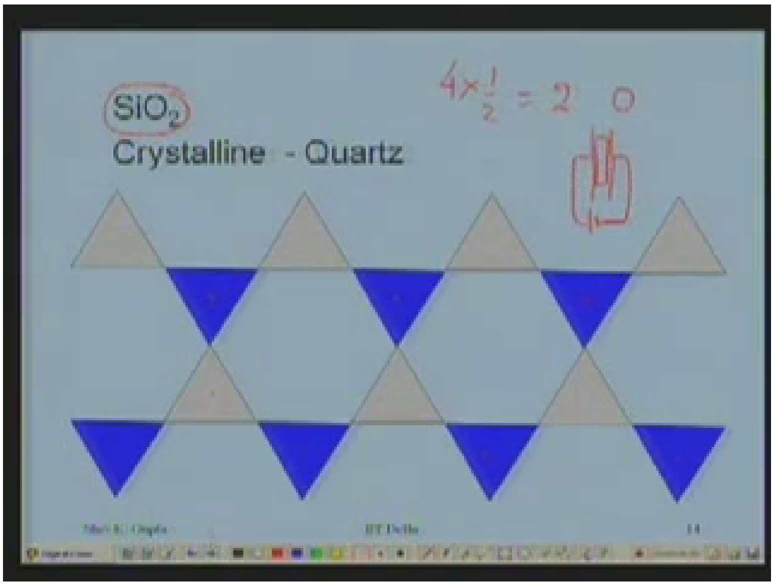

SiO_2

Crystalline - Quartz

$4\times\frac{1}{2} = 2$ O

Now we shall talk about the crystalline arrangement where I have tetrahedral coordination, silica SIO 2. Charge of the silicon is plus 4 I have to maintain a greater distance between 2 silicon ions because there is very strong repulsion between them and also I have to maintain the SIO 2 composition as well as the neutrality. So in here these are the tetrahedral let us consider the blue ones are the upright tetrahedral with apex being here on top… while these one grey ones are the inverted ones so that when I joined and upright tetrahedron, upright means considering this as a plane it is upright, okay and inverted going behind this plane, the apex is going behind the plane.

What we are doing as we are making the distance between the center and that center of the tetrahedral hole longest possible distance at any other position they will try to come closer, so that is the silicon which is the center of the tetrahedron and corners of the tetrahedron are all oxygen my formula is satisfied and I get a sheet like this, I can make a similar sheet like that and put one over the other, so here it was upright I will put here the inverted one of the 2nd sheet, so corner to corner sharing takes place that corner to corner sharing will be here, it will be here, it will be here, here, here, here. When I go behind continue put this in the corner to corner sharing will take place with this one upright of that will (())(45:34) with this, this, this, that, this, this and that.

So like the three-dimensional structure can be built up. Coordination silicon being at this body centre the tetrahedron, the 4 corners of tetrahedron gave me only 4 coordination, each corner is common between 2 tetrahedral, oxygen is half here and half there and 4 oxygen corners, 4 half of this makes it 2, so 4 corners oxygen, each corner giving half makes it 2 oxygen and within the tetrahedron only one silicon is there, so SIO 2 formula is satisfied, is it clear? See this is I said 50 percent covalent 50 percent ionic, ionic structure local arrangement is there we can see tetrahedral arrangement but it is so spacious arrangement this is lot of space here where you can put lot of tetrahedral inside in the space which is all vacant space because if I bring in something there will be silicon silicon coming closer and there will be strong repulsion between silicon and silicon and this is the hexagonal crystal of quartz.

Quartz is used for various applications by engineers one is that it has very low coefficient of thermal expansion that is where we use it when we do not want any expansion taking place in some locations secondly it is a piezoelectric material. Piezoelectric means when I apply a mechanical force piezoel pressure electrical field or the a field is generated in a crystal means ions displace themselves in such a way there is dipole form and once the dipole is formed is an electric field generated that is the use for this piezoelectric crystal which is exploited in forming the load cells, it is exploited in lighters where you want discharge to take place and that is the kind of application we put the… Otherwise being a very hard material again it is used in jewel bearings it is also used because of the piezoelectric behaviour as an natural oscillator which gives us the time on the watches, quartz watches are using this as an oscillator.

The application of an oscillator and we understood like this suppose this is a crystal between these 2 plates which are charged when the charge is applied or this voltage is applied the crystal shrinks in size, so contact is broken and once the contact is broken then there is no field applied to the crystal it comes back to its original shape, once it comes to its original shape it touches the 2 plates again, moment it touches it shrinks in size so that is how it is becomes behaving like an oscillator and that gives us very accurate timings because frequency is natural frequency is well-established that is what we are using in watches.

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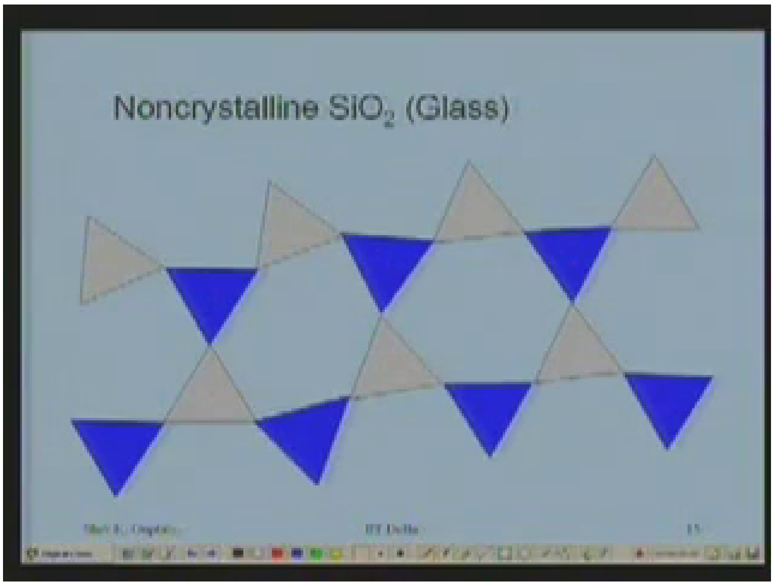

Noncrystalline SiO_2 (Glass)

But the more use of this SIO 2 for engineers is in the form of a non-crystalline state glasses, all classes, window planes, windscreen, et cetera they are made of non-crystalline silica, it may have impurities in it but we will see that in non-crystalline state it is not periodically repeating arrangement, these array is not a regular hexagonal sometimes it may have 7 around this or it may have 5, so it is not a regular periodic arrangement and silicon silicon distance is becoming shorter some places and that is what is usually known by the impurities when they are present, so that is known crystalline element and by enlarge and you melt silica and from the melting point I to solidify it is very difficult for it to crystallise, it has to be a solidifying in a non-crystalline state, liquid like structure solidifies and what the impurities do that we shall see next.

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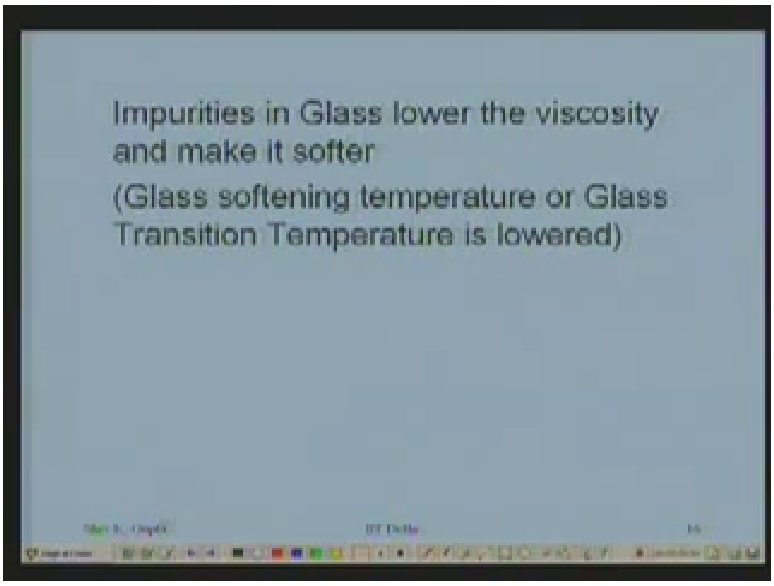
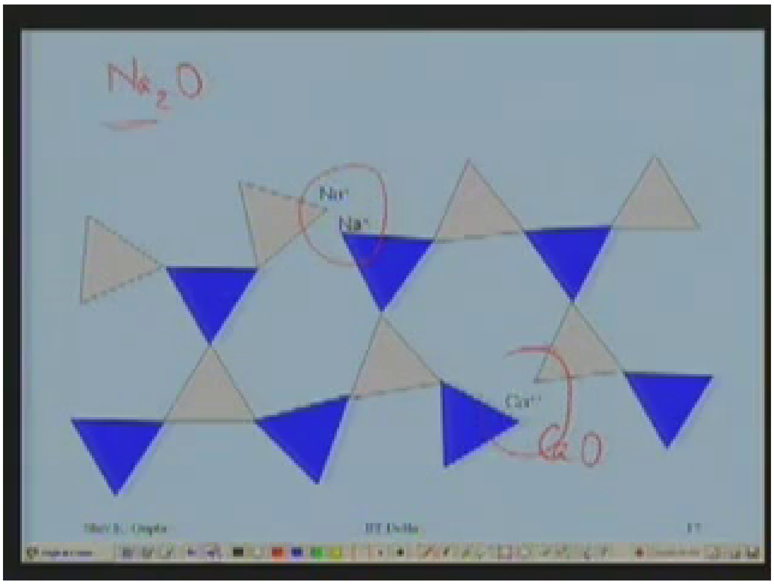


Impurities in Glass lower the viscosity and make it softer

(Glass softening temperature or Glass Transition Temperature is lowered)



Impurities which are present in glass the lower the viscosity and make it softer. Glass softening temperature or the glass transition temperature of the glasses lower because it is viscosity is lowering by the addition of impurities. We have seen crystalline and the non-crystalline form but there is tetrahedral network, one tetrahedral is joined to another tetrahedral they are all primary covalent bonds. Only when these primary covalent bonds are broken somewhere I can try to lower the viscosity and that is what the impurities are doing maybe you will be able to see that in this picture. Let us say I have added the impurity like soda Na 2 0 is the soda.

Oxygen contributed by the soda goes on one corner of the silica tetrahedral, it sits only one corner silica tetrahedral, so one extra oxygen is coming you see and therefore it breaks that oxygen corner which was shared now there is one oxygen extra, so they are all separated and that becomes electrically charged, this also becomes electrically charged, the 2 sodium ions which you are adding their goes and sit close to them to neutralise that because there is an attraction between negative charge and positive charge, so sodium ions sits there as I similarly the line when it is added calcium oxide it breaks the tetrahedral bond at the corner of the tetrahedron one extra oxygen comes there and this calcium sits in between the 2 for a because of the electrostatic attraction as a result I am creating electrostatic attraction like this but intern I am breaking the tetrahedral network which continues infinitely in 3 dimensions at many places as a result of the networks are becoming smaller and smaller.

Smaller smaller networks of tetrahedral sitting there one can translate with respect to other more easily rather than if I have the whole thing as one single network that is how the viscosity is coming down or the temperature at which it is possible to make the translation between 1 network with the other network becomes lower because there is a breaking of bond. More the impurities I add more such corners will be created lower will be the viscosity. Less the impurities I add less corners like this would be there, so higher will be the viscosity that is what we see in these glasses which we are using.

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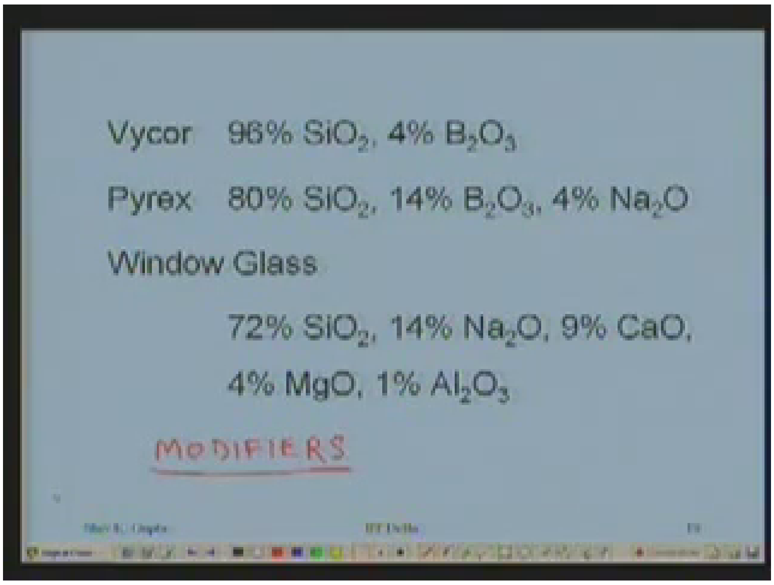

Vycor 96% SiO_2, 4% B_2O_3

Pyrex 80% SiO_2, 14% B_2O_3, 4% Na_2O

Window Glass

72% SiO_2, 14% Na_2O, 9% CaO,

4% MgO, 1% Al_2O_3

MODIFIERS

We use Vycor, Vycor is more or less silica with small quantity of like 4 percent impurity which is Borax, boron peroxide and 4 percent main it breaks only few places the corners, the viscosity is not still very low, softening temperature for such a glass is about 1100 degrees centigrade, quartz around 1800 degrees centigrade to fuses but this is just about 1100 degree centigrade so it can fuse but when I add more impurities to the tune of 20 percent where 4 percent is soda and 14 percent is Borax I get Pyrex which is the…you must have heard of the pyrexware in the market they are available and you must have heard about the hard glass test tubes yeah they are made of Pyrex and it contain about the 80 percent silica.

The fusing temperature of… they will fuse about 550 degrees centigrade you see how it come down 1800, 1100 come down to 550 then you have window glasses, window planes or soft glass test-tubes okay where lot of impurities in it 14 percent soda, 9 percent lime, 4 percent magnesia, 1 percent alumina and this window glass (())(55:36) which we use you can about 120 degrees centigrade you can fuse it right, so that is what the more the impurities added more corners of broken, more corners of broken means there are smaller large number of smaller tetrahedral networks and the smaller smaller networks can move more easily than one huge break at work alright that is how the viscosity is down in these materials. These addition of impurities is also called modifiers in the glass what we have added are the modifiers, they modify the viscosity, right so we shall close today and discuss the similar structures in the next class.