Non - Metallic Materials
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Module – 03
Diffusion, phase transformation in non – metallic materials, glass and glass - ceramics
Lecture – 17
Glass - ceramics and specialty glasses

Welcome to my course Non-Metallic Materials and today we are in module 3 Diffusion, phase transformation in non-metallic materials, glass and glass-ceramics. And in lecture number 17, I will be covering glass ceramics and specialty glasses.

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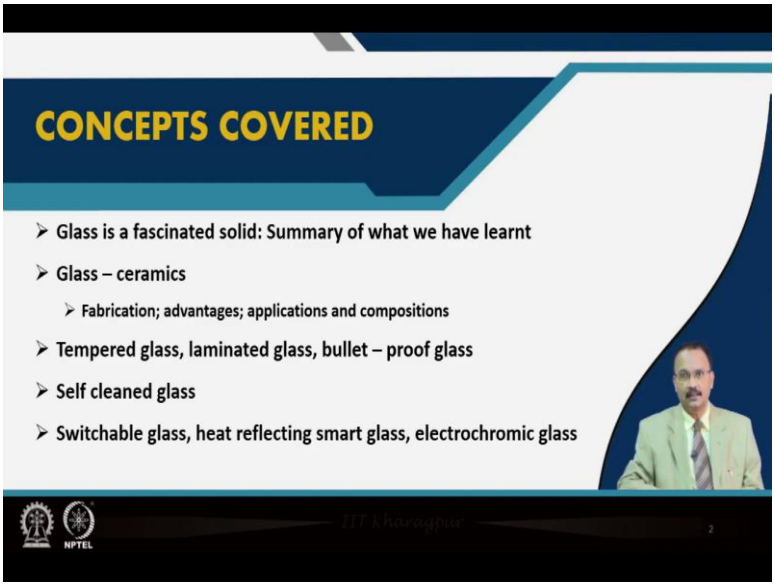

Now, as you can understand that I have already taken two classes on glass and we understood that glass is a fascinated solid. And first I will summarize that what exactly we have learnt. Because, when I solve mathematical expression it is assumed that simultaneously you will also try to derive it to have a better fill.

What is more important for you to understand that out of those mathematical expressions what are the physical things that you are learning and what exactly you will be able to use those expression to better understand the glass an amorphous material.

So, first I will summarize what exactly we have learnt. Then I will introduce the concept of glass ceramics and throughout the last two lectures mostly, I was talking about that, what is to be done so that the glass does not crystallize? And does not have crystal growth, but in glass ceramics we are we intent to make crystalline material.

So, glass and ceramic both are there in the same phase, the glassy material is converted to crystalline material. How they are fabricated, what are the advantages of this kind of compositions and what are the specific composition of industrial relevance? So, that I will cover and after that I will be talking about specialty glasses, how to make glass strengthened by different procedure? And laminated glass will come tempered laminated glass you know that we use in the wind screen of the car.

And also bullet proof glass, which is a bit advanced then we will be talking about self-cleaned glass. Because you know in the solar cell in solar panel you have the glass panes that cover the solar cell. And the one of the major problem is to clean those panes because that will retort the transmission of light to the solar module.

So, the concept of self-cleaned glass that will be covered and apart from that several interesting glasses like switchable glass, heat reflecting glass those are called as smart glass and electrochromic glass. The list may be length I mean quite a bit one can talk about specialty glass, but certain important thing I will be covering in this particular lecture.

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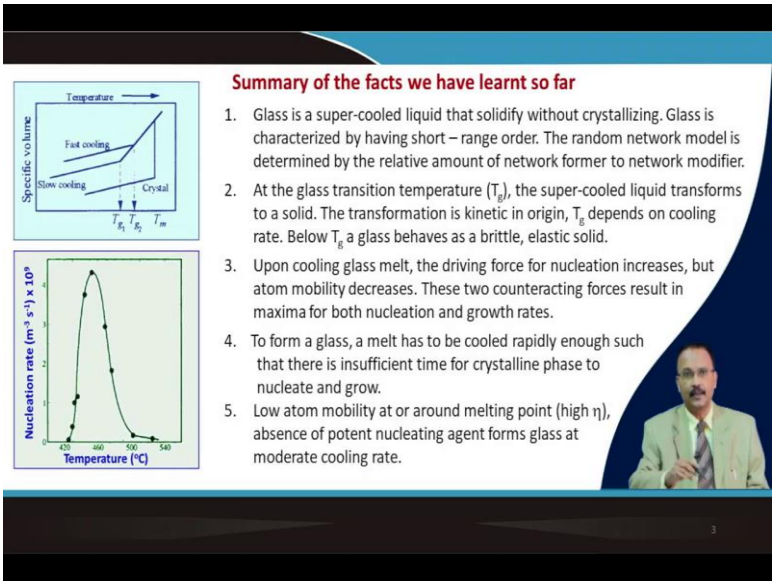

So, we have learnt that glass is a super cooled liquid and that basically solidifies without crystallization, unlike the metallic material once you start to cool the glass then the same slope will be maintained. And at one particular temperature we called it is a transition temperature then the slope changes.

And this is having the glass is having a short range order as compared to the long range order that we find in the crystalline material. And basically it can be explained in a random network model, which is controlled by the network former, which of the glass former and as well as addition to network modifier into the composition.

So, at the glass transition temperature if you remember, the super cooled liquid transforms to a solid otherwise it is a viscous mass here and then it transform into a solid. And this kinetics this is a kinetically controlled process therefore, with the rate of cooling you see this transition temperature changes.

So, in fast cooling you have a higher transition temperature whereas, if you cool it sufficiently slow then you can have a lower specific volume and the glass transition temperature is reduced down to lower temperature. Now, the driving force is the amount of this super cooling. So, the driving force of nucleation of course, it will increase, but at the same time at the melting point it has a very high viscosity. So, atomic mobility is not that high.

So, therefore, when you talk about the nucleation as well as the growth of this tiny crystallite, then you will see that it goes through a maxima and we have derived the equation for the nucleation and. So, you need a rapid cooling. So, there is an insufficient time that is there for the crystalline phase to nucleate and subsequently to grow.

And also low atomic mobility at around the melting point because of the high viscosity. So, absence of any potent nucleates for heterogeneous nucleation to take place that you will have to retard in order to get a good glass composition.

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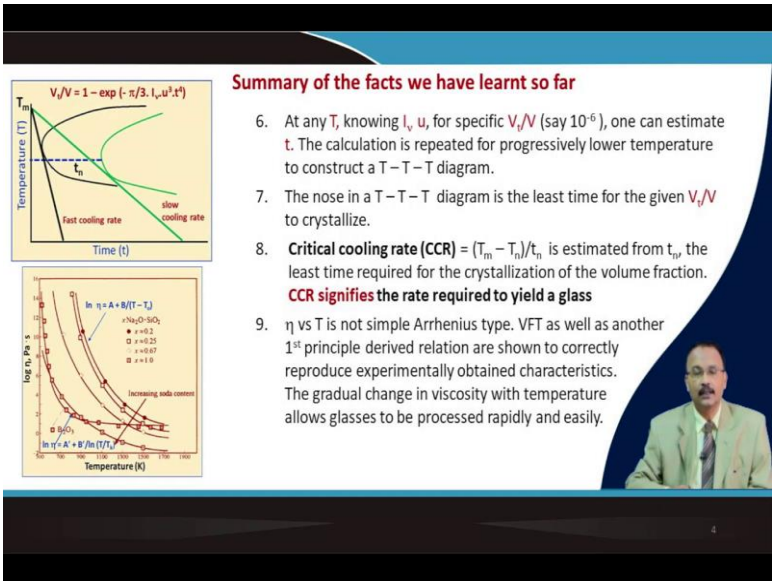

Now, this part is very important that at any temperature, if you estimate the nucleation rate and the growth rate for a specific volume fraction. So, we are taking a very small volume fraction about 10 to the power minus 6 inside the glassy matrix. So, if you assume that and you take this expression which I derived in the last class.

So, volume what I what is being crystallized and you know the nucleation rate you know the growth rate. So, you can calculate that what is the time that will be required. So, this T one can estimate and progressively you can go to lower temperature you keep on lowering the temperature. And finally, you calculate for the same volume fraction what is the time required for it to get crystallized? So, you get this kind of curve and there is a nose of this curve which identify a very specific time required.

So, that is the least time that is required for a given volume fraction of a crystalline phase to get crystallized. So, I defined a critical cooling rate, which you can estimate you know the melting point here and you know this particular temperature here at this nose and you know this time. So, this is the critical cooling rate you can estimate for example, for this kind of curve and also for this kind of curve.

So, in one case you can see it is a very rapid cooling is required and here relatively slow cooling is required. So, this critical cooling rate once you can estimate then that signifies the rate required to yield a glass. So, what you will want that you want that this should be as slow as possible. So, that you can get enough time for crystallization it is not very rapid crystallization.

So, if you have a very slanty kind of slope here at the nose temperature, then this is a good material as far as the glass is concerned. This is not a very good material for a glass is concerned because you will have to maintain this kind of heating rate. And also within no time within a very small amount of time it will get crystallized. So, this concept was built in the last class through deriving several equations deriving I deriving u and I tried to convey that, but this is the reason of the significance of the critical cooling rate.

Also we talked about that this viscosity dependence of the glass as a function of temperature it does not follow a normal Arrhenius kind of relation. And rather it follows a Vogel Fulcher Tammann type of relation. And you remember that we derived one equation based on the first principle, which is very identical to VFT slightly different, but eventually we talked about that this gradual change of viscosity.

And this is very important for any glass composition you need to know a particular viscosity no matter at what temperature you achieve it and that will decide your melting, that will decide your working that will decide your strength point annealing point everything will be dependent on that particular viscosity.

So, here we showed that irrespective of the glass composition. In fact, both this equation they are equally valid and one can fit with this this parameters you can adjust and you can fit this. So, the relation of the viscosity and temperature that was also described. So, this is in a nutshell what we learnt about the basic of the glass material.

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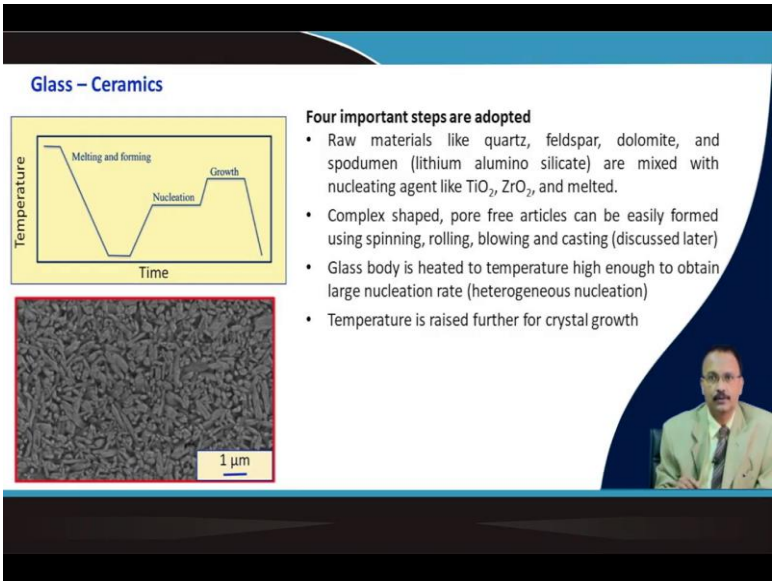

Now, as far as the glass ceramic is concerned it is very interesting because now you are talking about formation of glass. And there are certain composition I mentioned lithium aluminum silicate, that leads to very close to homogenous kind of nucleation and those composition is used for making glass ceramics.

So, basically there are four steps first the raw material like your glass former feldspar is agent which reduces the temperature, dolomite is a glass modifier, spodumen they are used. And along with that in the melt we are using a nucleating agent titanium oxide and zirconium oxide, which is having very high melting point say they do not actually melt and they remain as a crystalline phase.

And then you reduce the temperature and you come to the forming temperature and any complex shape you can make out of this glass because this is the beauty of glass you can cast it, you can blow it, you can draw it. So, this processing I will be describing in part of a later class.

And then you start to heat treat this glass because you have already a nucleating agent you can control the heating rate. And first it nucleates small crystallites grow and which does not go back into the matrix and then you follow another heating rate to grow this crystal.

So, this process once you soak at this particular temperature, then you cool it down you will find that the glass form a very homogenous crystallize crystalline material and most of it is crystalline little bit glassy part is there. So, this micrograph we have shown that the glassy part has been edged. So, they are not the porous region so, you form a glass ceramic.

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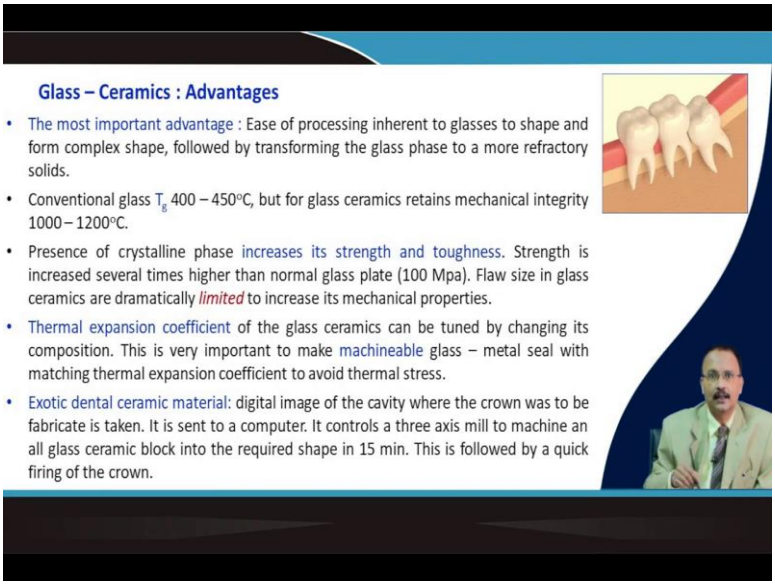

So, glass ceramic is very interesting material and as you can understand ease of processing is there. So, you can process any complex shape like the tooth also nowadays is been the crown after the RCT, root canal treatment you have the cap and this is a glass ceramic cap nowadays used any complex shape you can make. Conventional glass they have T g about 400 to 450 degree Celsius. For glass ceramics the mechanical integrity is there at relatively higher temperature you can go up to 1000 1200 degree Celsius.

And the presence of the crystalline phase it increases its strength and roughness for example, a normal glass you have the tensile strength about 100 mega pascal, which is many fold increased in case of glass ceramics because you have limited defects in it we will be talking about that in our next class.

Thermal expansion coefficient also you can tune by tuning the composition And this is very good thing because a glass metal cell you can make out of this you can machine it because it has a crystalline part mostly it is crystalline. So, it is machineable you can control the thermal expansion coefficient.

So, it is very good for glass metal seal for the vacuum chambers. And as I mentioned that dental ceramics one can make. So, you have a piece of glass ceramic and then you can mill it with a robotic hand any complex shape and then once you get the required shape then quick firing you do for nucleation and the growth and this kind of complicated shape is ready for you to use.

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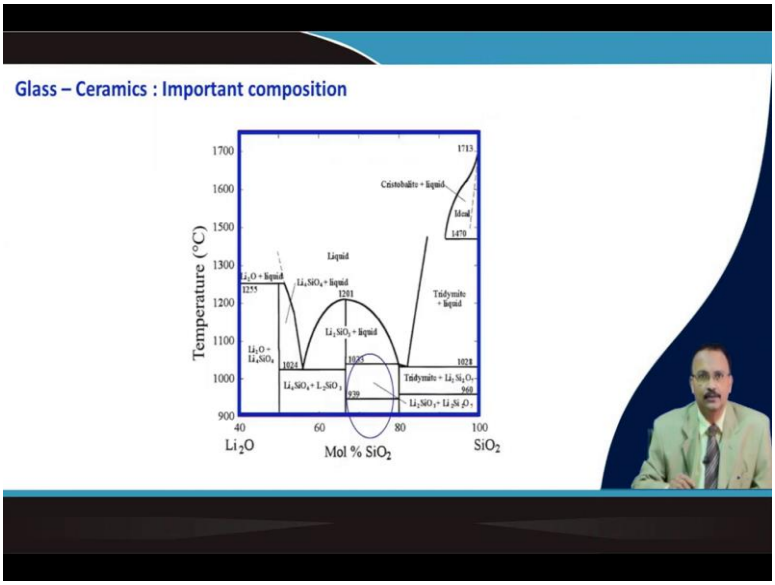

So, it is indeed advantage advantageous to have this glass ceramic composition and lithium oxide, silicon oxide that is one of the most important commercial compositions. And this kind of composition actually it is used for your glass ceramics.

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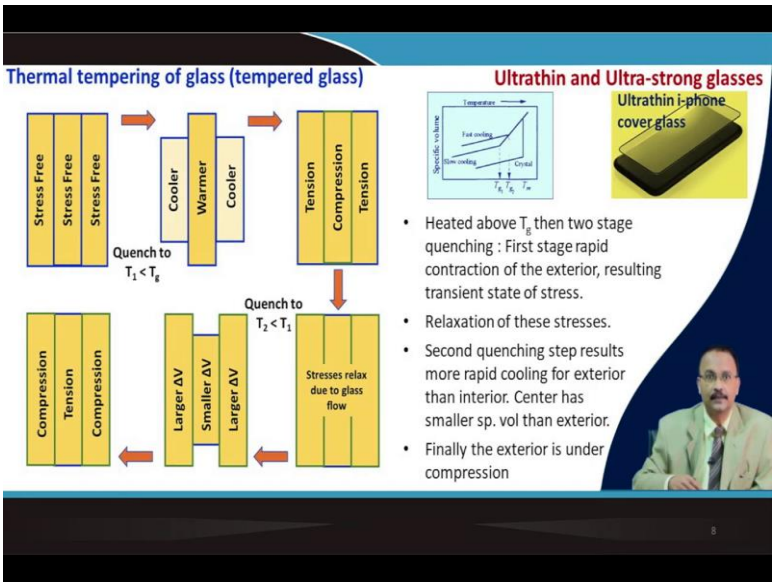

Now, glass is a brittle material. So, you need to strengthen it. So, there are two mechanism to make this strengthened glass. And this tempered glass you know that is used they call it a gorilla glass on your mobile just to avoid scratch etcetera of its original screen you use this kind of tempered glass. It is done by two quenching process initially the glass is heated beyond its transition temperature then after the first quenching the, and it is thermally non conducting material.

So, this will be cooled fast. So, it will be under compression. So, this phase which is still viscous the inner part of it that will be under tension. So, this phase will be under tension and this one will be relatively under compression. Then you wait for some time so that the stress is relaxed.

And then you do the second quenching and in case of second quenching you cool it very fast and the middle portion will be relatively low rate of cooling it will experience you know that when your cooling rate is relatively slow, then the specific volume is reduced. So, this part will have smaller volume as compared to this one.

So, as a result this surface will be under compression and this compressive stress you will have to overcome before the glass fails. So, that is one advantage that you are having for this kind of tempered glass composition.

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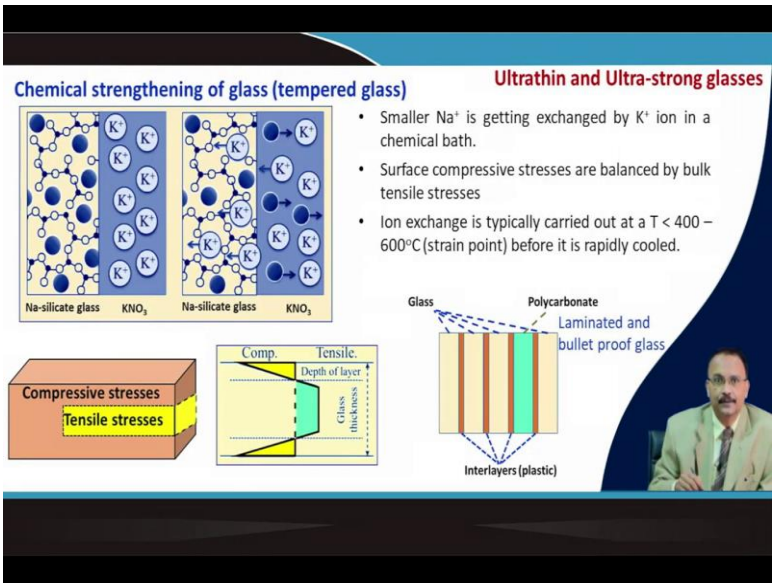

The same thing is also you can do when you dip this glass in a bath, which is having larger ions like potassium ion, which is larger in size as compared to sodium ion, which is there in your glass composition. So, there is a base exchange and it induce a compressive stress because they are having larger size as compared to sodium ion.

So, at least the surface both the surface of the glass they are under compression and this is just a view graph how this compressive stress actually reduced. And then there is a neutral plane and then this is under tension and this two surface is under compression.

So, it is giving the same kind of effect as we introduced in the last slide by thermal tempering. And once you get this kind of tempered glass you can put inside a polymer film to make it laminated so this glass in between there are polymer film. And this you put it in your wind screen and also in the side window of the car.

So, if something happens to the glass window particularly were in front of the driver if something happens, then the glass due to its compressive stress there it will not be shattered. So, it will form small granule kind of thing and this polymer film will basically it will get adhered there, so it will not be lethal.

And another variety is the bullet proof glass there are many multi layered of this kind of thing followed by a poly carbonate shield here and this bullet proof glass is used particularly in in many places.

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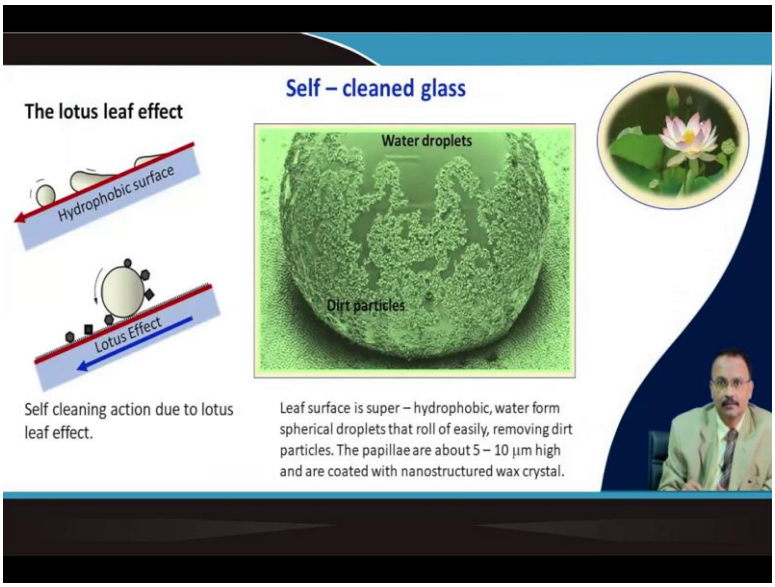

Now, we will talk about the cleaning of the glass and usually this process is imitated from the lotus, you know the lotus is very pure it does not adhere any kind of dirt. So, the idea is that to make the water hydrophobic on the surface. And this hydrophobicity is due to a very small nano crystalline kind of structure and which is coated with wax.

And that basically reduces this contact angle sorry it contact angle is more, but the surface contact that is reduced to form a bid. And then the dirt actually is rolls of when

the bid of water goes off, then it takes out all the dirt. So, that is the concept that is taken from this lotus leaf.

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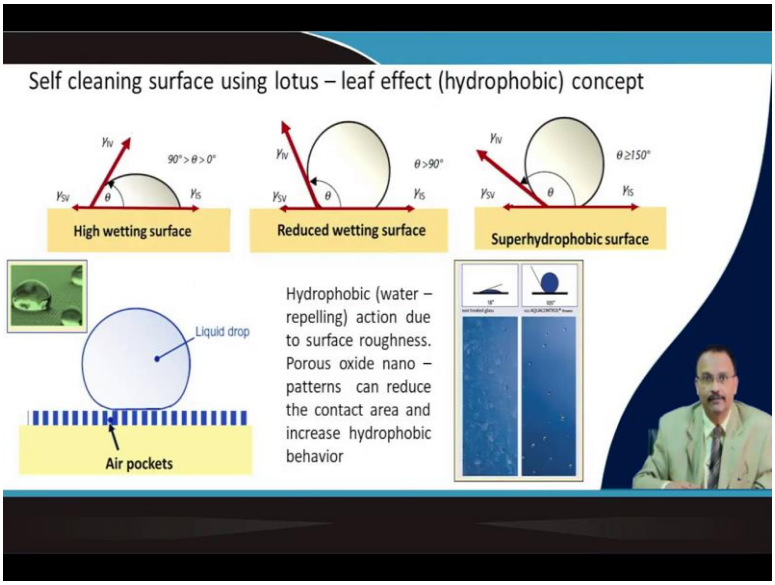

And. In fact, this is known as lotus leaf effect. So, idea is to play with the different types of surface energy to control the theta the weighting angle. So, it should be super hydrophobic in nature this angle is very large. And you have a small nano crystalline coating of various oxide materials and that control these three surface energy term. So, that you get basically cos theta value is less as close sorry cos theta value is high. So, that it is hydrophobic in nature the theta is quite high as you can see.

And this actually is used in the inner surface, I mean inside the room where this kind of dirt is no longer there. So, it is a normal shower curtain kind of thing application, where the water wets the surface, but here the water is not wetting the surface. In fact, all the dirt's are ruled off because of the super hydrophobicity of the coating and which is imitated from the lotus leaf effect.

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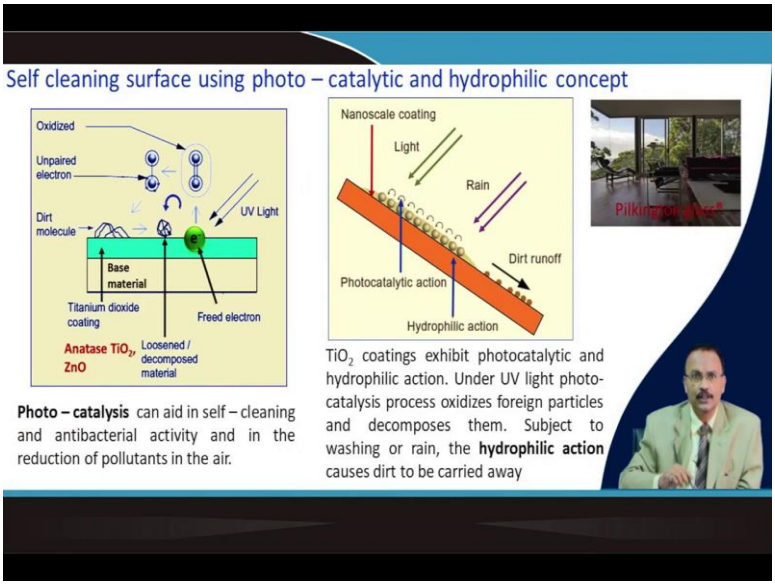

Another thing which you can do which is, a super hydrophilic kind of coating usually Anatase titanium oxide or zinc oxide it is coated with the surface. So, titanium oxide is having another advantage that it is photocatalytic in nature. So, when UV radiation falls on top of it then electron and whole pair is generated. And basically this electron helps to oxidize the dirt particle. So, that has been shown here.

So, the dirt particle initially was here and the free electron that is generated which acts eventually as a oxidizing agent oxygen is can be absorbed on the surface and then it reacts with the dirt molecule and that loosen the dirt molecule at the surface and it is super hydrophilic.

So, when rain drop falls on top of it completely wets the surface and once it wets the surface and this addition is very poor the dirt actually rules out. So, Pilkington is the company, which actually made this kind of glass composition which is based on both super catalytic as well as super hydrophilic kind of characteristics.

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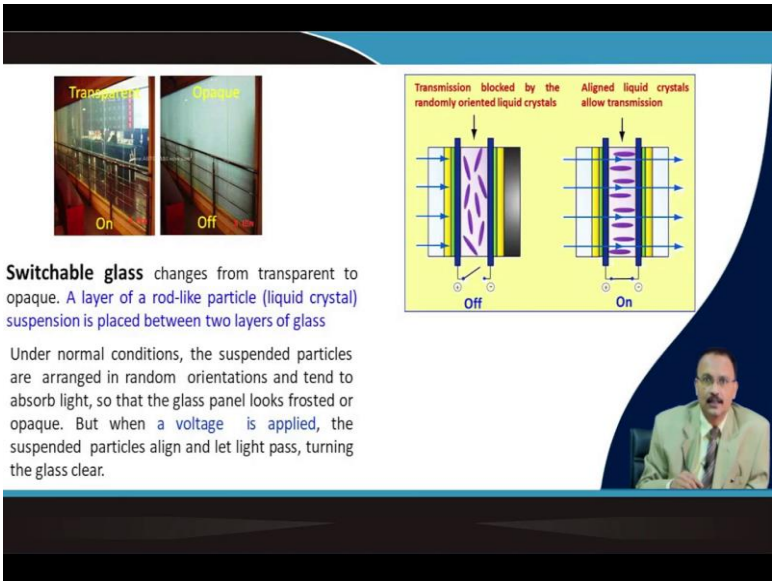

So, this is important. Another specialty glass that you can consider we call it is a switchable glass. So, initially the glass as you can see light does not transmit. So, between two glass panes shown here you have a conducting layer. So, that you can apply voltage across this and in between these two you have a liquid crystal and the phase of this liquid crystal crystals, they are randomly oriented.

So, it will not under normal condition it will not allow light to pass. So, it is completely opaque. So, there are many uses here in Australia one of the lift which takes you to 26 storied building. So, it is completely dark when you step in and when once the voltage is applied then this liquid crystal molecules they are aligned along with the lines of force of this electric field and then it allows light to transmit. So, suddenly it is all transparent.

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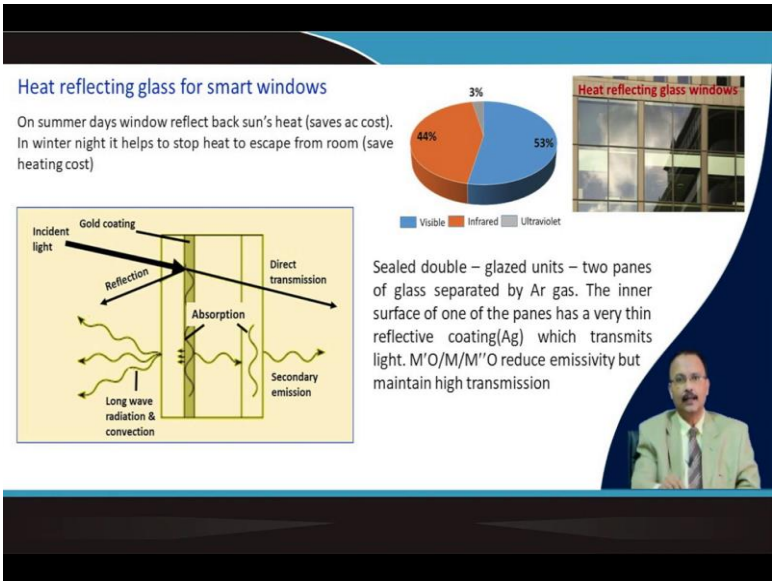

So, this is one thing which is very interesting as a switchable glass. Another smart glass composition is what we called is a heat reflecting glass and this is a part of a smart window you know the out of the solar radiation only 3 percent you are having which is UV. Then most of it is your visible light this yellow part and rest of it its thermal it is heat.

So, in the summer time you would like that the light should come in inside the window inside the room and air condition is on right. So, the heat should not come in. So, in summer in order to save the cost of a sea you need light to come in your room, but heat should not be allowed to come in.

So, that the cooling cost is increased now think of a winter time. In winter time the outside of your room is extremely cold particularly in the cold region in the cold countries not that much in India, but certain part of India of course, this is quite cold in the in the night.

And your fire place is on. So, you do not want that heat to go out or lower temperature cannot reduce the temperature of your room. So, you need a smart window in that case normal window will not work. So, in the smart widow as you can see it is a pane of glass and the lower surface is coated with a thin metallic coating.

So, usually gold is used, but nowadays silver is the material or several other metallic material is being coated and the coating is so thin that basically it will not bother the transmission of light. So, transmission on light will not get effected by this kind of

coating, but what happens that when in the hot time when the light is incident most of heat passes right and the other surface of this window pane is a plane glass pane.

So, it will just pass through and in between these two glass pane you have a gaseous medium and usually argon filled gaseous medium. So, this will allow suddenly the light to pass ok, but the heat transmission by convection or by other means that is grossly reduced. So, here what will happen that the heat wave will get reflected from this pane of metals and they will get out and you get light, but your air-condition will not be pressurized. So, you can save electricity bill.

And the reverse thing happens during the night time and during winter so, the heat inside the room that cannot go out. So, your room gets hotter. So, in that way this is a smart window. So, nowadays the thing is that you have this gold is very expensive.

So, Pilkington that company they are prepared a silver metal foil and two oxide coating in both the sides and this actually have very good transmission of light with very small light, I mean heat will be getting reflected from outside the surface either out in the ambient or inside the room as I explained.

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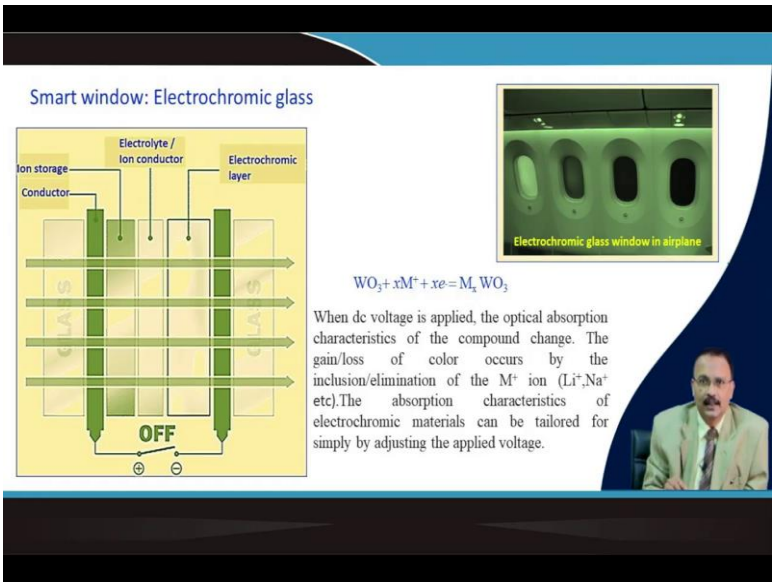

So, that is already in the market finally, you have another type of smart window where we call it is a electrochromic window and one of the carrier that is dreamliner if I remember correctly, they have this kind of window there is no shutter normal aircraft

they have the shutter to shut off this windows. But here you see a small button is there which apply a voltage across this window and by pressing this you can darken it you can make it transparent you can make it totally dark. So, you can control it.

So, this is why it is a smart window the technology is quite straight forward you have two glass pane and inside the glass pane first you have a metallic conductor then a source of positive ion then a conductor the that is a electrolyte kind of thing which lets the ions to pass, but not the electron to pass. And then you have tungsten oxide film coated on another metallic substrate and you have glass.

So, as you can understand this you can replace with transparent conducting coating. So, when you apply a field particularly when it is in off condition then what will happen that this tungsten oxide this tungsten oxide is in pure state, but when you switch it on then this is negative.

So, the mobile cation like lithium and sodium that will pass through this electrolyte and they will go to the tungsten oxide to form this phase. Now, once this phase forms then it is an on condition and when the phase is not there or you reverse the voltage then all this thing will go out.

So, the transparency will be there when there is no lithium or no sodium in it, but when it is when it is full of sodium or lithium this inclusion then this absorption characteristics will change or rather transmission characteristics will change. So, it will make it more darken.

So, the absorption characteristics of the electrochromic material can be tailored for simply adjusting the applied voltage you change the voltage and amount of lithium or amount of hydrogen or amount of sodium that is going inside the other material that will control the transmission of the light. So, this in that way it is a smart window in date.

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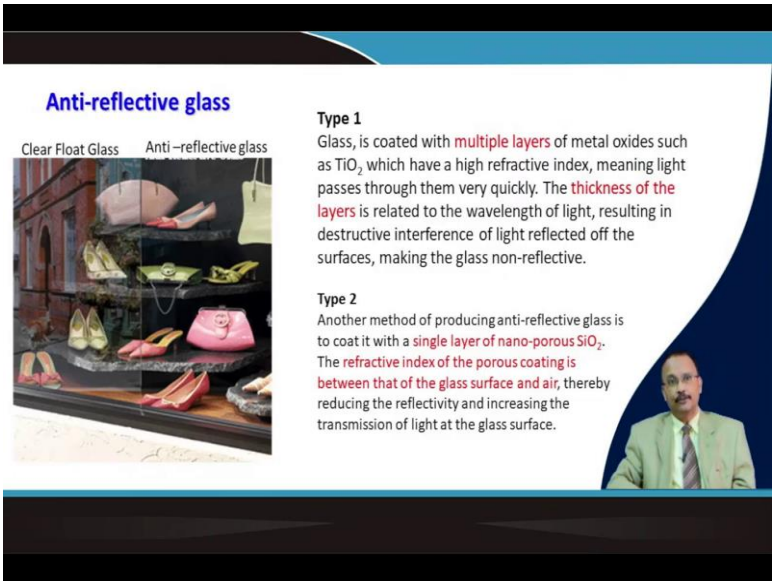

Finally we talk about anti reflective glass where you do not have this kind of reflection. So, that in the showcase you can see all the merchandise and this is basically done by multi-layer coating which controls the refractive index and there by the speed of the light.

So, sometimes the multi component ceramic oxides are coated on top of the glass, sometimes it is porous silicon oxide that is coated on top of the glass to have this kind of anti-reflection kind of behavior. It is also useful for driving nowadays and in the spec also this kind of coating is used.

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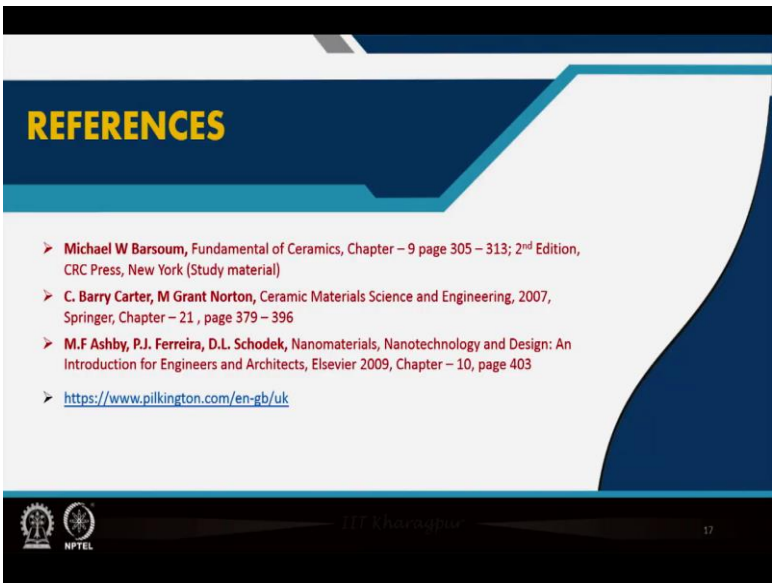

So, these are the reference material that one that is marked red that you can see that you can read it as a part of the study material.

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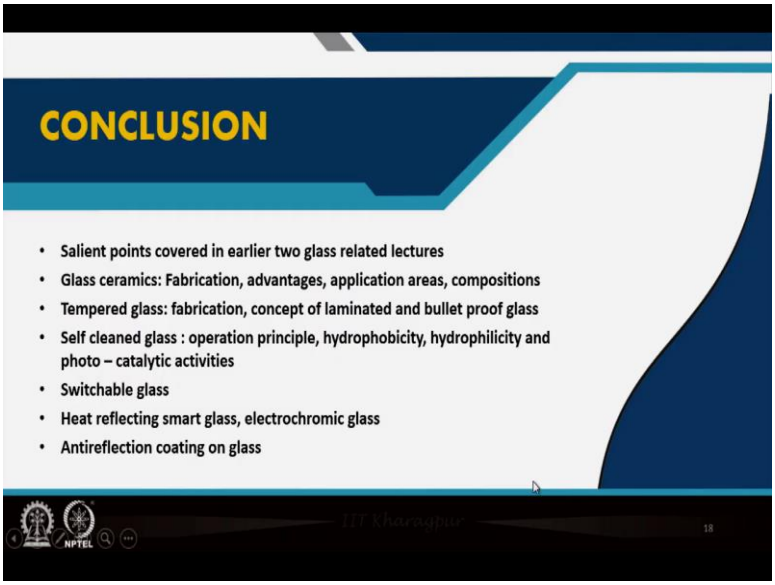

And also I have taken something from the web as well. So, the address is given. So, salient point of the first two lectures that I have covered then we talked about glass ceramics we talked about tempered glass fabrication composition then we talked about self-cleaned glass, we talked about switchable glass, we talked about smart glass electrochromic window and finally, anti-reflection coating on glass.

Thank you so much for your attention.