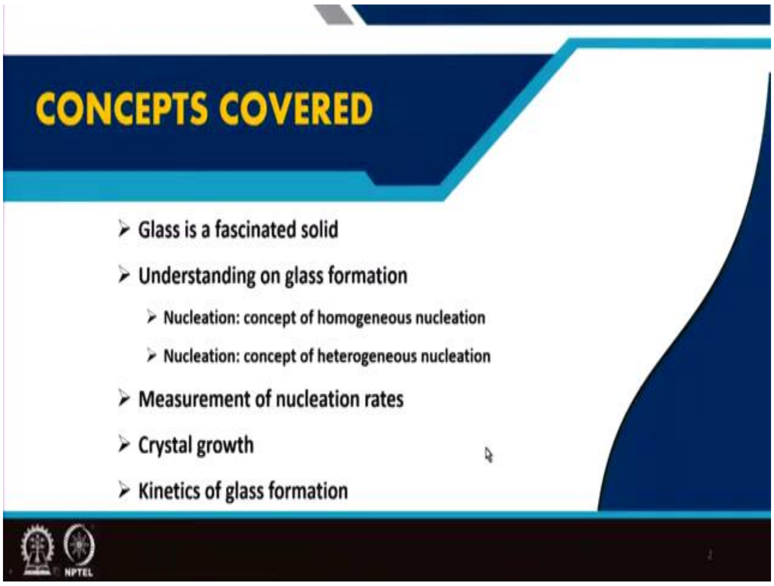
Non - Metallic Materials
Prof. Subhasish Basu Majumder
Department of Materials Science Centre
Indian Institute of Technology, Kharagpur

Module – 03
Diffusion, phase transformation in non – metallic materials, glass and glass - ceramics
Lecture – 15
Introduction to glass and amorphous solids

Welcome to my course Non-Metallic Materials and we are in module number 3 Diffusion phase transformation in non-metallic materials and glass and glass-ceramics, that is the name of the module and today it is lecture number 15, where I will be Introducing glass and amorphous solid materials. So, mostly the concept of the glass will be introduced.

(Refer Slide Time: 00:57)



CONCEPTS COVERED

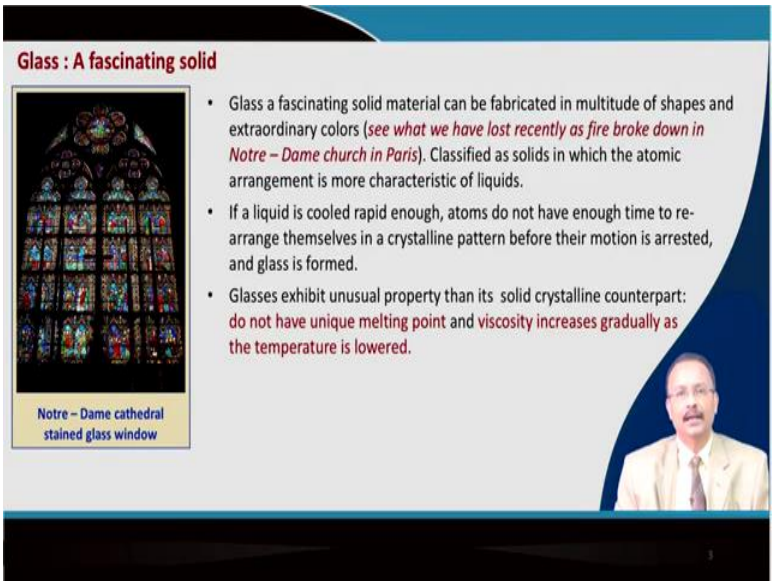
- Glass is a fascinated solid
- Understanding on glass formation
  - Nucleation: concept of homogeneous nucleation
  - Nucleation: concept of heterogeneous nucleation
- Measurement of nucleation rates
- Crystal growth
- Kinetics of glass formation

Now, if you go through this concepts: then first you will understand that the glass is a very fascinated solid and this has several exotic applications and the formation of the glass that is very different from that of a solid crystalline material.

So, in solid crystalline material basically the nucleation concept is involved and followed by growth. So, both nucleation and growth is important and this you do not want for a glass do not want glass to be crystalline except for some speciality glass, which I will be taken in this part of this module.

There we will see that the crystalline glass is also important they have certain applications which are quite good. So, that thing we will cover and then we will show that, how to measure the nucleation rate? Or, how to retard the nucleation rate rather, how to retard the crystal growth? And, what is so special about the kinetics of glass formation?

(Refer Slide Time: 02:07)



Glass : A fascinating solid

- Glass a fascinating solid material can be fabricated in multitude of shapes and extraordinary colors (*see what we have lost recently as fire broke down in Notre – Dame church in Paris*). Classified as solids in which the atomic arrangement is more characteristic of liquids.
- If a liquid is cooled rapid enough, atoms do not have enough time to re-arrange themselves in a crystalline pattern before their motion is arrested, and glass is formed.
- Glasses exhibit unusual property than its solid crystalline counterpart: do not have unique melting point and viscosity increases gradually as the temperature is lowered.

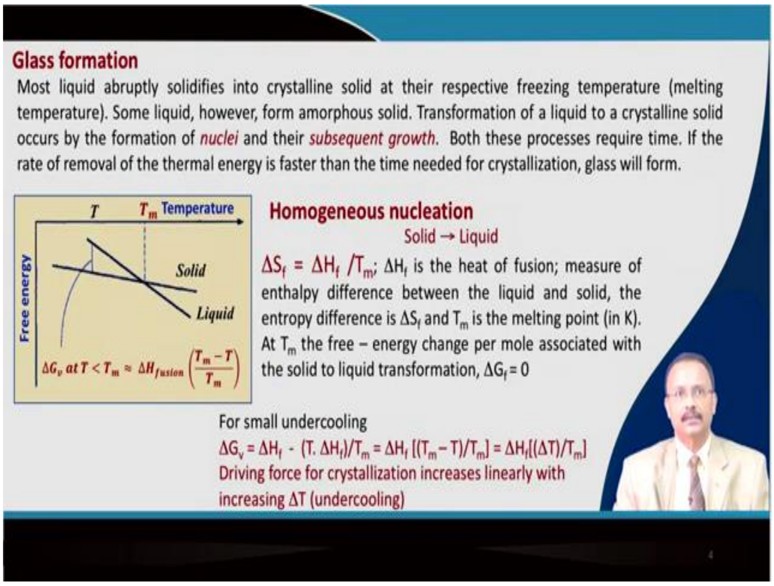
Notre – Dame cathedral stained glass window

So, this will be covered in this course and let us start with this fantastic Notre-Dame church, where stained glass people have used and this has been burned you know that we have lost many of this exotic thing. So, that is really not a good thing and that happened with human kind. So, in general if a liquid is sufficiently fast cooled then they do not have time so that the atom, respective atom sits to the lattice position to form a crystalline structure.

So, then the motion atomic motion is arrested wherever they are. So, the liquid like behaviour that is retained in the solid and it forms a glass. So in principle anything you can make in the form of a glass if you can control the cooling rate. So, in case of metal also it is possible, you can cool it at a very fantastic rate, very, very high rate we call it’s a splat cooling to get metallic ribbon which is in glassy form.

So, it exhibits the glass exhibit some unusual property and first of all unlike the crystalline material they do not have a specific melting points, they have always a range of melting point and viscosity that gradually increases at the temperature is lowered. So, when you lower the temperature the degree of under cooling then the viscosity rise of the glass system.

(Refer Slide Time: 03:39)



Glass formation

Most liquid abruptly solidifies into crystalline solid at their respective freezing temperature (melting temperature). Some liquid, however, form amorphous solid. Transformation of a liquid to a crystalline solid occurs by the formation of *nuclei* and their *subsequent growth*. Both these processes require time. If the rate of removal of the thermal energy is faster than the time needed for crystallization, glass will form.

ΔG_v at $T < T_m \approx \Delta H_{fusion}\left(\frac{T_m - T}{T_m}\right)$

Homogeneous nucleation

Solid → Liquid

$\Delta S_f = \Delta H_f / T_m$; ΔH_f is the heat of fusion; measure of enthalpy difference between the liquid and solid, the entropy difference is ΔS_f and T_m is the melting point (in K). At T_m the free – energy change per mole associated with the solid to liquid transformation, $\Delta G_f = 0$

For small undercooling

$\Delta G_v = \Delta H_f - (T.\Delta H_f)/T_m = \Delta H_f [(T_m - T)/T_m] = \Delta H_f[(\Delta T)/T_m]$

Driving force for crystallization increases linearly with increasing ΔT (undercooling)

So, you can understand the formation of the glass and differentiate from a normal crystalline solid that at the melting point suddenly the specific volume is dramatically reduced in case of crystalline material and in case of glass the specific volume is not that much prominently reduced.

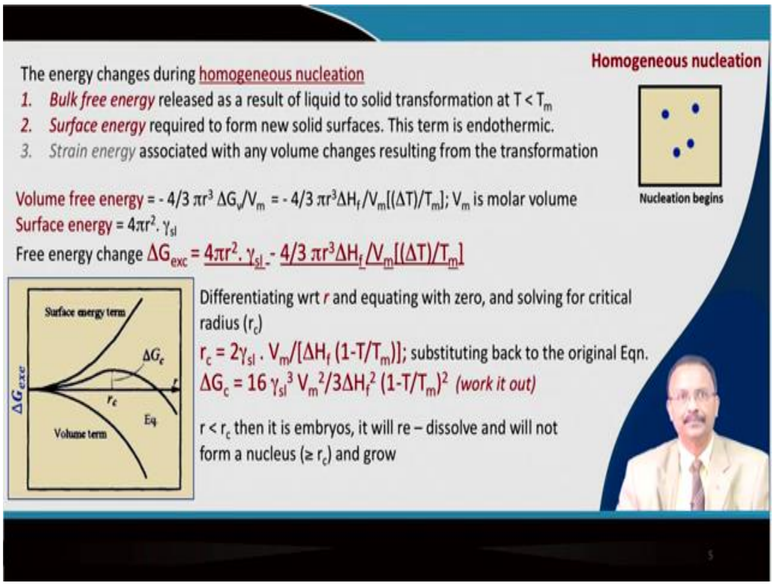
So, this is the particular relation of free energy versus temperature and you see that below this melting point you have the situation where the solid is having lower free energy than the liquid. So, this phase is stable and this phase is this liquid free energy is less than that the solid. So, liquid is more stable. So, you have the melting point here in this case then both the energy this value the formation free energy is 0.

So, that already I have described or solid to liquid transition. So, here the entropy part it can be defined as this enthalpy of formation divided by the melting point. So, this del H f is the heat of fusion I am sorry. The heat of fusion and this is actually the measurement of the enthalpy difference between liquid and solid phase and at melting point you can define this relation.

So, if you put the value in the volume volumetric free energy for a small under cooling from this melting point. Then, you write this relation H minus T S and, S is replaced by this this del S is replaced by this. So, your del G v the volumetric free energy that is given by this expression, which is heat of fusion if it is del H f.

So, that is there and degree of under cooling and the melting temperature. So, this is a standard driving force for the crystallization and this increases linearly with the under cooling. So, under cooling is the all important term falling to make the glass.

(Refer Slide Time: 06:08)



Homogeneous nucleation

The energy changes during homogeneous nucleation

1. *Bulk free energy* released as a result of liquid to solid transformation at $T < T_m$
2. *Surface energy* required to form new solid surfaces. This term is endothermic.
3. *Strain energy* associated with any volume changes resulting from the transformation

Volume free energy = $- 4/3\ \pi r^3\ \Delta G_v/V_m = - 4/3\ \pi r^3 \Delta H_f/V_m[(\Delta T)/T_m]$; V_m is molar volume

Surface energy = $4\pi r^2 .\ \gamma_{sl}$

Free energy change $\Delta G_{exc} = 4\pi r^2 .\ \gamma_{sl} - 4/3\ \pi r^3 \Delta H_f /V_m[(\Delta T)/T_m]$

Differentiating wrt *r* and equating with zero, and solving for critical radius (r_c)

$r_c = 2\gamma_{sl} .\ V_m/[\Delta H_f\ (1-T/T_m)]$; substituting back to the original Eqn.

$\Delta G_c = 16\ \gamma_{sl}^3\ V_m^2/3\Delta H_f^2\ (1-T/T_m)^2$ *(work it out)*

$r < r_c$ then it is embryos, it will re – dissolve and will not form a nucleus ($\geq r_c$) and grow

Now, in case of a homogenous nucleation. So, if I assume that there is a possibility for this glass melt to form a crystalline particle if this is possible and inside a melt you have the crystalline particle that is nucleated then and if I assume this is a spherical one. Then basically 3 different types of energy that is involved here.

The first one is a bulk free energy that is released because the liquid is transformed into solid below the melting point. Second one is a new surface is being created otherwise it was not there only it is nucleating.

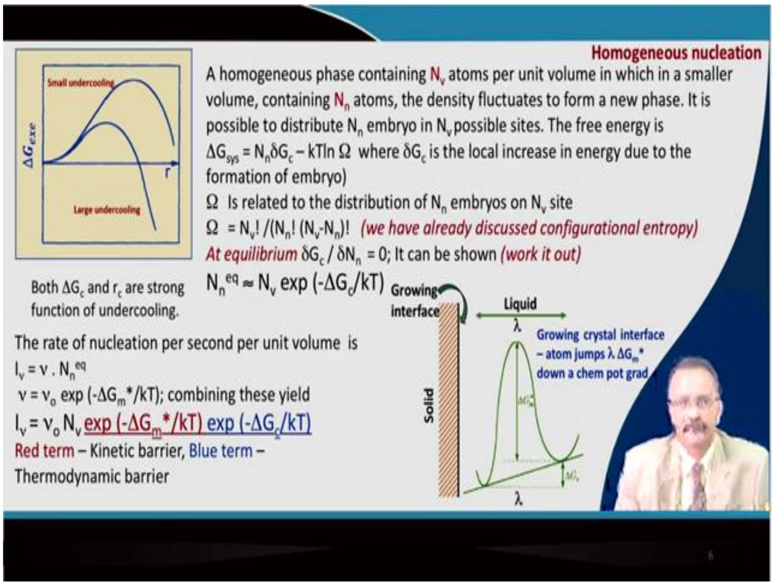
So, the surface energy required to form a solid surface and of course, this will be an exothermic term a positive term and also it has some kind of volume change if it is there then a strain energy is also involved. So, 3 different energy term is involved. So, the volume free energy that is you know I have considered a spherical thing. So, 4 by 3 pi r cube, r is the radius of this circle and per unit molar volume I have considered and this energy associated is del G v. So, I put this part which I derived for del G v.

So, then this expression is valid and additionally I have a surface energy. So, the total energy is the surface energy which is a positive term and this is a negative term, the volume free energy and I am neglecting the strain energy. So, this relation I am sorry. So, this relation one part is the negative part this volume term, another one is the positive part which is a surface term. So, it will give you also some kind of maxima and this maxima you can get if you differentiate this with respect to the radius of the nuclei.

So, this will give you a critical radius and critical radius will tell that what is the minimum size of this nucleus that is required for it to grow once it is form then it will start to grow.

So, what is that critical size and, this size you can put back into this original equation of the free energy change then you get the energy barrier which is defined as del G c. So, the critical radius if the nucleating particle is having a lower critical radius then it will dissolve back into the system, if it is higher than that it will start to grow.

(Refer Slide Time: 09:11)



Homogeneous nucleation

A homogeneous phase containing N_v atoms per unit volume in which in a smaller volume, containing N_n atoms, the density fluctuates to form a new phase. It is possible to distribute N_n embryo in N_v possible sites. The free energy is

$\Delta G_{sys} = N_n \delta G_c - kT\ln\Omega$ where δG_c is the local increase in energy due to the formation of embryo)

Ω Is related to the distribution of N_n embryos on N_v site

$\Omega = N_v! / (N_n! (N_v - N_n)!$ *(we have already discussed configurational entropy)*

At equilibrium $\delta G_c / \delta N_n = 0$; It can be shown *(work it out)*

$N_n^{eq} \approx N_v \exp(-\Delta G_c/kT)$

Both ΔG_c and r_c are strong function of undercooling.

The rate of nucleation per second per unit volume is

$I_v = \nu \,.\, N_n^{eq}$

$\nu = \nu_o \exp(-\Delta G_m^*/kT)$; combining these yield

$I_v = \nu_o N_v \underline{\exp(-\Delta G_m^*/kT)}\ \underline{\exp(-\Delta G_c/kT)}$

Red term – Kinetic barrier, Blue term – Thermodynamic barrier

Growing crystal interface – atom jumps λ ΔG_m^* down a chem pot grad

So, the homogeneous space if I consider that this n small n atoms that atoms per unit volume, which in a very smaller volume it is nucleating. So, it is having in n atom and there is always a density fluctuates inside that to form a new phase it is possible to introduce the entropy term into it. So, that is the idea.

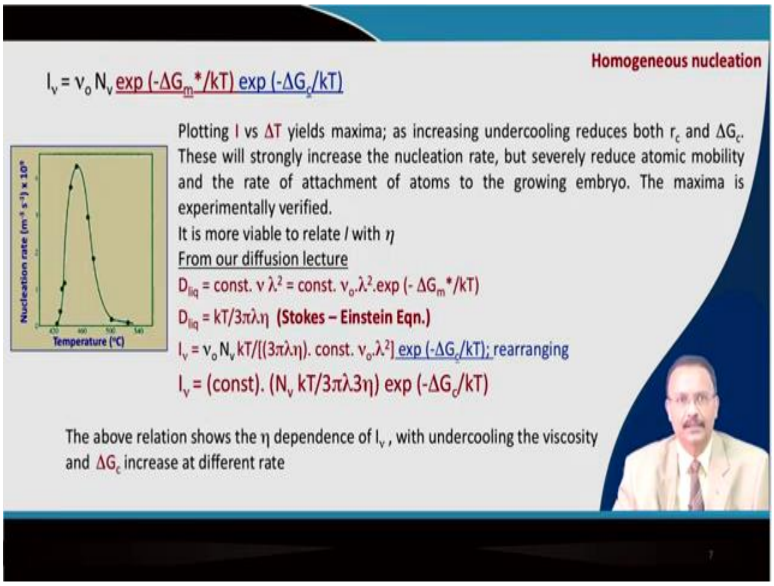
The free energy that will be this N_n number of atoms and there is a small change in this energy that is there and that, basically will be the formation term and then you have an entropy term. So, this is configurational entropy and configurational entropy will tell you that these many embryo how you can distribute in a total site, N site.

So, this already I have derived that you can give by given by this relation factorial of N_n sorry factorial of N_v with factorial of N_n and the total number of atoms. So, already we have described the configurational entropy now again at equilibrium this part will be 0. So, you can come up with this equilibrium number of small embryo that is forming with N v and this potential gradient.

So, now, we will calculate the rate which is involved and this will be dependent on this number and the frequency term. So, frequency term here as I have worked it out earlier this potential barrier is involved. So, now, you can combine these 2 putting this value and this value together. So, you have a term which is a kinetic barrier and another term which is a thermodynamic barrier.

So, the physical parameter is something like this the solid surface is being formed and you have the atom, which are crossing this potential barrier and then it is incorporating into the solid phase and once it is incorporating the solid phase then, this front increases. So, the atom basically jumps this lambda and this is the energy that it cross down to the potential gradient and then this nucleation is extended.

(Refer Slide Time: 12:18)



Homogeneous nucleation

$I_v = \nu_o N_v \underline{\exp(-\Delta G_m^*/kT)}\ \underline{\exp(-\Delta G_c/kT)}$

Plotting I vs ΔT yields maxima; as increasing undercooling reduces both r_c and ΔG_c. These will strongly increase the nucleation rate, but severely reduce atomic mobility and the rate of attachment of atoms to the growing embryo. The maxima is experimentally verified.

It is more viable to relate *I* with η

From our diffusion lecture

D_{liq} = const. $\nu \lambda^2$ = const. $\nu_o . \lambda^2 . \exp(-\Delta G_m^*/kT)$

$D_{liq} = kT/3\pi\lambda\eta$ **(Stokes – Einstein Eqn.)**

$I_v = \nu_o N_v kT/[(3\pi\lambda\eta).\ \text{const.}\ \nu_o.\lambda^2]\ \underline{\exp(-\Delta G_c/kT)}$; rearranging

$I_v = (\text{const}).\ (N_v\ kT/3\pi\lambda 3\eta)\ \exp(-\Delta G_c/kT)$

The above relation shows the η dependence of I_v , with undercooling the viscosity and ΔG_c increase at different rate

So, we will calculate the nucleation rate and the nucleation rate is given by this relation and if you plot this you will see that there are 2 competing parameter is involved and therefore, you get always a bell shaped curve. So, this yields increasing under cooling that basically will reduce both the radius critical radius of the nucleus what is forming and also the potential gradient both will be dependent if you increase the under cooling then this will be expedite.

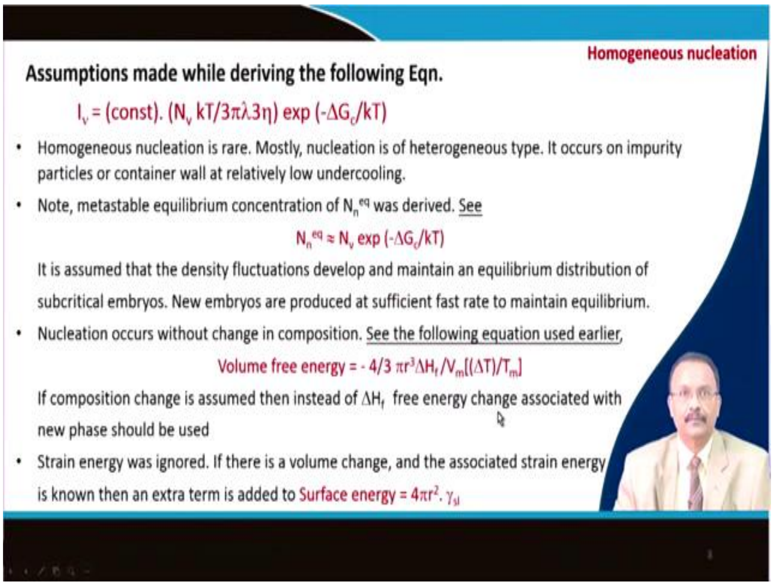
So, that eventually if this is happening the barrier is reducing and this is also having a tendency to grow then it will not go into the melt. So, it will strongly increase the nucleation rate.

Now the nucleation rate is increasing, but simultaneously when you are reducing the temperature under cooling is more than the viscosity is simultaneously increase. So, there is a tug of war come the thing. So, viscosity is increase so atomic mobility is less and your nucleation; nucleation try to increase. So, this competing force will give rise to this type of ah bell shaped curve.

So, in our diffusion lecture I already derive this relation and now, I can define a Stoke, Einstein equation which relate the diffusibility of the liquid phase with the viscosity of the salt, viscosity of the melt and then I put back it to the nucleation this nucleation rate equation.

So, I come up with after doing this algebra and rearranging I can get this relation and this relation shows the dependence of nucleation with the viscosity. So, with under cooling the viscosity and this barrier both increases, but it increase at a different rate.

(Refer Slide Time: 14:56)



Homogeneous nucleation

Assumptions made while deriving the following Eqn.

$I_v = (\text{const}).\ (N_v\ kT/3\pi\lambda 3\eta)\ \exp(-\Delta G_c/kT)$

- Homogeneous nucleation is rare. Mostly, nucleation is of heterogeneous type. It occurs on impurity particles or container wall at relatively low undercooling.
- Note, metastable equilibrium concentration of N_n^{eq} was derived. See

  $N_n^{eq} \approx N_v \exp(-\Delta G_c/kT)$

  It is assumed that the density fluctuations develop and maintain an equilibrium distribution of subcritical embryos. New embryos are produced at sufficient fast rate to maintain equilibrium.
- Nucleation occurs without change in composition. See the following equation used earlier,

  Volume free energy = $- 4/3\ \pi r^3 \Delta H_f / V_m [(\Delta T)/T_m]$

  If composition change is assumed then instead of ΔH_f free energy change associated with new phase should be used
- Strain energy was ignored. If there is a volume change, and the associated strain energy is known then an extra term is added to Surface energy = $4\pi r^2 . \gamma_{sl}$

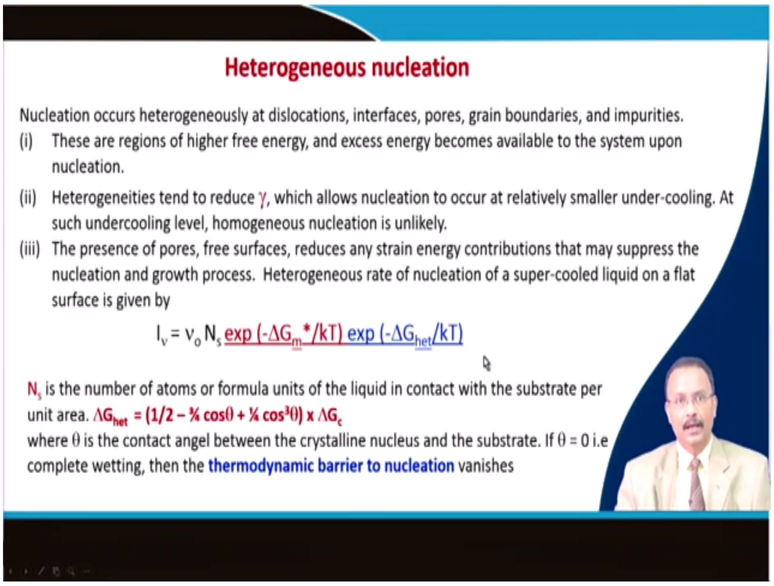
So, while we derive this relation this relation, what we derived we tacitly assumed the following assumption. The first one is a homogeneous nucleation. So, nucleation is happening throughout the glass melt and in practice it is not the case usually the nucleation is of heterogeneous type of different types of defect or the container wall it takes place, but it is not the case here.

Now, the concentration of this metastable equilibrium whatever was formed that was derived. So, this derivation we have done which relates with the energy barrier with the equilibrium kind of this nucleation that it formed.

So, the fluctuation of the composition that is happening we considered that it is maintained in a equilibrium state and the embryos are produced which is at a sufficient rate to maintain the equilibrium continuously the nucleation is happening and the volume free energy is given by the following relation.

So, if composition change is assumed then instead of this del H term the free energy change associated with the new phase that should be used and the strain energy was ignored and we only considered that the surface energy is the positive term, which is playing a major role. So, if strain energy you want to introduce because of the volume change that is happening then certainly you will have to use an additional term into it.

(Refer Slide Time: 17:05)



Heterogeneous nucleation

Nucleation occurs heterogeneously at dislocations, interfaces, pores, grain boundaries, and impurities.

(i) These are regions of higher free energy, and excess energy becomes available to the system upon nucleation.

(ii) Heterogeneities tend to reduce γ, which allows nucleation to occur at relatively smaller under-cooling. At such undercooling level, homogeneous nucleation is unlikely.

(iii) The presence of pores, free surfaces, reduces any strain energy contributions that may suppress the nucleation and growth process. Heterogeneous rate of nucleation of a super-cooled liquid on a flat surface is given by

$$I_v = \nu_o N_s \underline{\exp(-\Delta G_m^*/kT)}\ \underline{\exp(-\Delta G_{het}/kT)}$$

N_s is the number of atoms or formula units of the liquid in contact with the substrate per unit area. $\Delta G_{het} = (1/2 - 3/4\cos\theta + 1/4\cos^3\theta) \times \Delta G_c$

where θ is the contact angel between the crystalline nucleus and the substrate. If $\theta = 0$ i.e complete wetting, then the **thermodynamic barrier to nucleation** vanishes

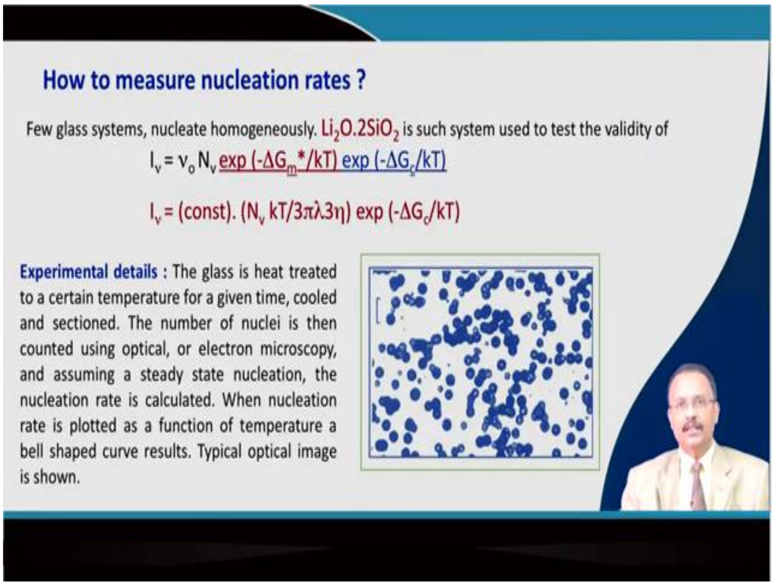
Now, in case of a heterogeneous nucleation this occurs heterogeneously on dislocation, or interface, or pore grain boundary. So, inside the material it takes place and these regions are usually having high energy, high excess energy and this becomes available when nucleation is taking place and heterogeneity that tries to reduce the surface energy term also.

So, nucleation it allows to occur at relatively smaller degree of under cooling and that such under cooling level, homogeneous nucleation is unlikely. So, heterogeneous nucleation will be expedite because, homogenous nucleation with that kind of delta T is not possible. The presence of pore, surface that reduces the strain energy contribution and that can suppress the nucleation and growth process.

So, if you assume a flat surface then this relation is valid. So, here this number of atoms per formula unit that is your N s term and now this delta G volumetric energy term that is replaced by heterogeneous energy term and which is related to the wetting of the glass surface or the melt surface on the solid that is preparing.

So, it is dependent on the wetting angle theta and a relation can be walked out with this wetting angle and the actual value of del G c. So, when you have exactly a complete wetting theta if it is 0, then it is a complete wetting a thermodynamic barrier is gone for the heterogeneous nucleation.

(Refer Slide Time: 19:15)



How to measure nucleation rates ?

Few glass systems, nucleate homogeneously. $Li_2O.2SiO_2$ is such system used to test the validity of

$$I_v = \nu_o N_v \underline{\exp(-\Delta G_m^*/kT)}\ \underline{\exp(-\Delta G_c/kT)}$$

$$I_v = (\text{const}).\ (N_v\ kT/3\pi\lambda 3\eta)\ \exp(-\Delta G_c/kT)$$

Experimental details : The glass is heat treated to a certain temperature for a given time, cooled and sectioned. The number of nuclei is then counted using optical, or electron microscopy, and assuming a steady state nucleation, the nucleation rate is calculated. When nucleation rate is plotted as a function of temperature a bell shaped curve results. Typical optical image is shown.

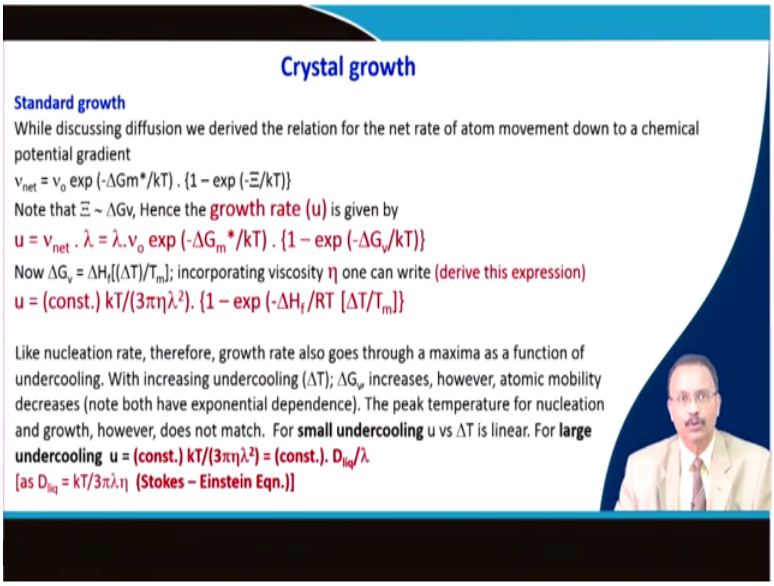
So, now the next question is that, how you can measure the nucleation rate? Now, in case of heterogeneous system it is difficult because it occurs at various types, various locations depending on the defects that is present.

But, fortunately there are some system like lithium oxide and silicon dioxide in this type of system it is more or less homogeneous nucleation. So, this volumetric term del G c is involved and we have derived both this relation one is the normal rate equation and another one is when the viscosity is involved here.

So, the in the experimentation the glass that is formed that is again heat treated at certain temperature for a given time and then it is cool down and once you cool down and section the glass then the nucleation you can see by an optical microscope or the electrical microscope if at all it happens homogenous nuclear.

The composition is such that nucleation will occur and you know the time and eventually if you consider it is a steady state nucleation then you can get the rate of this nucleation with time you can physically measure it for this kind of system.

(Refer Slide Time: 20:55)



Crystal growth

Standard growth

While discussing diffusion we derived the relation for the net rate of atom movement down to a chemical potential gradient

$\nu_{net} = \nu_o \exp(-\Delta Gm^*/kT) . \{1 - \exp(-\Xi/kT)\}$

Note that $\Xi \sim \Delta Gv$, Hence the growth rate (u) is given by

$u = \nu_{net} . \lambda = \lambda.\nu_o \exp(-\Delta G_m^*/kT) . \{1 - \exp(-\Delta G_v/kT)\}$

Now $\Delta G_v = \Delta H_f[(\Delta T)/T_m]$; incorporating viscosity η one can write (derive this expression)

$u = (\text{const.})\, kT/(3\pi\eta\lambda^2). \{1 - \exp(-\Delta H_f/RT\, [\Delta T/T_m]\}$

Like nucleation rate, therefore, growth rate also goes through a maxima as a function of undercooling. With increasing undercooling (ΔT); ΔG_v, increases, however, atomic mobility decreases (note both have exponential dependence). The peak temperature for nucleation and growth, however, does not match. For **small undercooling** u vs ΔT is linear. For **large undercooling** $u = (\text{const.})\, kT/(3\pi\eta\lambda^2) = (\text{const.}). D_{liq}/\lambda$

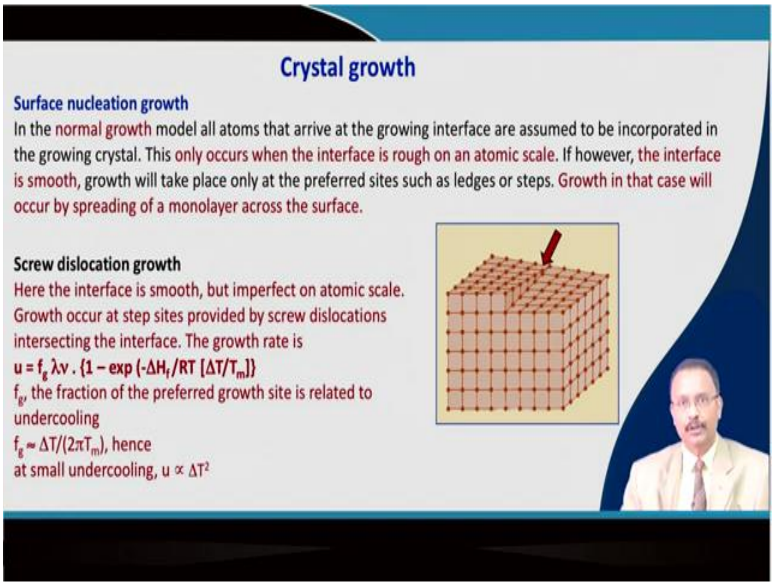
[as $D_{liq} = kT/3\pi\lambda\eta$ **(Stokes – Einstein Eqn.)**]

So, eventually it will start to growth. So, once the nucleation is stable then it will grow inside the matrix and we derive this relation of the net rate of atom movement down to a chemical potential gradient. So, this already we have derived. So, in this case the energy here is del G v. So, we can calculate the growth rate and this growth rate is this net frequency into the diffusion length lambda.

So, I just put this value this is here and now, I replace this volumetric free energy term with this enthalpy term which I derived in the first slide and this equation you can start to derive do the algebra and this will be the growth equation. So, like the nucleation rate also growth goes through a maxima although the peak temperature of nucleation and growth they differ because of the kinetic problem and it depends on the degree of under cooling and you can have 2 situation one is a small under cooling.

So, if you go for the small under cooling then it is a linear dependence with the growth and if it is a large under cooling then this value is very large. So, you have only this relation left, this expression left and this is nothing but the Stokes-Einstein relation that we talked about. So, two extreme you can think of when you are thinking the crystal growth process in a glass matrix.

(Refer Slide Time: 22:49)



Crystal growth

Surface nucleation growth

In the normal growth model all atoms that arrive at the growing interface are assumed to be incorporated in the growing crystal. This only occurs when the interface is rough on an atomic scale. If however, the interface is smooth, growth will take place only at the preferred sites such as ledges or steps. Growth in that case will occur by spreading of a monolayer across the surface.

Screw dislocation growth

Here the interface is smooth, but imperfect on atomic scale. Growth occur at step sites provided by screw dislocations intersecting the interface. The growth rate is

$u = f_g \lambda v . \{1 - \exp(-\Delta H_f/RT [\Delta T/T_m]\}$

f_g, the fraction of the preferred growth site is related to undercooling

$f_g \approx \Delta T/(2\pi T_m)$, hence

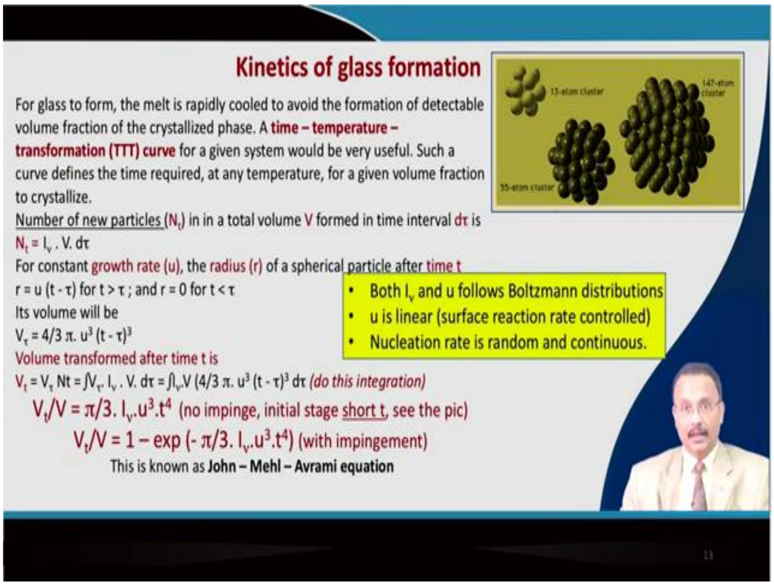
at small undercooling, $u \propto \Delta T^2$

So, there are 3 different types of growth model. The first one is the normal growth model where, the atoms are arriving at the interface and it is assumed to be incorporated into the growth and this only occurs when the interface is rough on the atomic scale, but if it is very smooth; the interface of the nucleating surface is very smooth then it will only take place in a preferred site.

So, this will be some kind of spreading of monolayer. So, you can identify the growth so this is the surface nucleation growth. It can also occur in the screw dislocation growth mode as well and if you have it is in a screw dislocation mode then the growth equation this part will remain same, but it is given by this factor of f g the fraction of the preferred growth site that will be there. So, and diffusion length and frequency term will also be there.

And this can be approximated it comes with the undercooling divided by some constant into the melting point. So, its small under cooling you can see that the growth is proportional to the square of this under cooling. So, these are the 3 different growth model that can happen that can take place.

(Refer Slide Time: 24:32)



Kinetics of glass formation

For glass to form, the melt is rapidly cooled to avoid the formation of detectable volume fraction of the crystallized phase. A **time – temperature – transformation (TTT) curve** for a given system would be very useful. Such a curve defines the time required, at any temperature, for a given volume fraction to crystallize.

Number of new particles (N_t) in in a total volume V formed in time interval $d\tau$ is

$N_t = I_v . V. d\tau$

For constant growth rate (u), the radius (r) of a spherical particle after time t

$r = u (t - \tau)$ for $t > \tau$; and $r = 0$ for $t < \tau$

Its volume will be

$V_\tau = 4/3\, \pi .\, u^3 (t - \tau)^3$

Volume transformed after time t is

$V_t = V_\tau\, Nt = \int V_{\tau} . I_v . V.\, d\tau = \int I_v V\, (4/3\, \pi .\, u^3 (t - \tau)^3\, d\tau$ *(do this integration)*

$V_t/V = \pi/3.\, I_v . u^3 . t^4$ (no impinge, initial stage short t, see the pic)

$V_t/V = 1 - \exp(- \pi/3.\, I_v . u^3 . t^4)$ (with impingement)

This is known as **John – Mehl – Avrami equation**

- Both I_v and u follows Boltzmann distributions
- u is linear (surface reaction rate controlled)
- Nucleation rate is random and continuous.

Now, it is important for us to consider the kinetic of the glass formation. So, in order to glass if it wants to form, if the glassy phase is required then it should be rapidly cooled and then you should know the time and temperature involved along with the fraction of the liquid that is transforming into a solid phase. So, these 3 factors are simultaneously involved. So, eventually you will have to construct a time, temperature and transformation this kind of diagram.

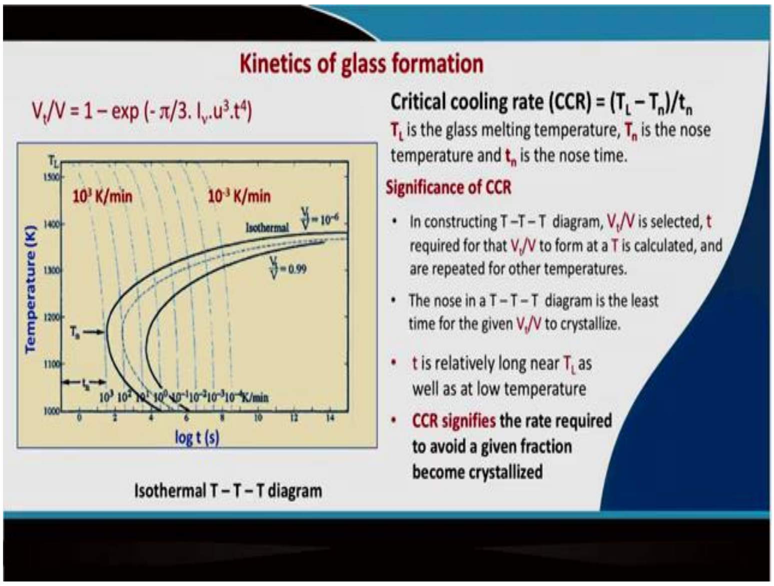
Now, this kind of diagram in order to make it you need to consider certain thing. So, first is the number of new particle that is forming in a volume which is V, in a time interval which is say small time interval d tau. So, you can write this relation this is the rate of nucleation into the total volume and this is the time interval for the constant growth, then you have 2 situation the first one is that when this tau is beyond a certain time limit t.

Then, you have it a linear relationship with the radius whatever is formed is growth rate into time and when it is less than tau then you can see that this will be 0 the radius will not be there so that means, the embryo will form embryo will form, but eventually it will get dissolve into the glass melt.

So, the volume transfer that is given by this relation and then eventually in the time limit you will have to integrate it. So, you have the relation final relation of the fraction of the volume that is crystallize with respect to the total volume this is given by this exponential relationship. So, this relation is valid when we consider that the atoms are forming inside the glass melt the nucleation is forming and there is no impingement. So, it is growing eventually, but even if it grows it is not touching the other cluster.

So, something similar to this is slowly it is forming and then it is growing, but there is no impingement then the relation of the volume fraction whatever is forming is given by this relation. So, both your nucleation rate and the growth that follow a Boltzmann statistics and growth rate is linear. So, it is controlled by the surface straight and nucleation rate is random, but it is continuous anywhere it can nucleate, but continuously it will grow once the embryo forms.

(Refer Slide Time: 27:46)



Kinetics of glass formation

$V_t/V = 1 - \exp(-\pi/3.\ I_v.u^3.t^4)$

Isothermal T – T – T diagram

Critical cooling rate (CCR) = $(T_L - T_n)/t_n$

T_L is the glass melting temperature, T_n is the nose temperature and t_n is the nose time.

Significance of CCR

- In constructing T –T – T diagram, V_t/V is selected, t required for that V_t/V to form at a T is calculated, and are repeated for other temperatures.
- The nose in a T – T – T diagram is the least time for the given V_t/V to crystallize.
- t is relatively long near T_L as well as at low temperature
- **CCR signifies the rate required to avoid a given fraction become crystallized**

Now, this relation the volume of the transform phase with respect to the original V. So, this is the volume fraction of the phase which is getting crystallize inside the glass melt and this relation you can always plot a isothermal T-T-T diagram. So, in a particular temperature in isothermal condition you have calculated the rate nucleation rate you have calculated the growth rate you know the time of cooling.

So, say for a particular volume fraction you get this kind of curve. So, here what I am doing I am progressively reducing the temperature the melting point is somewhere here. So, at higher temperature it is lower than the melting point, then I progressively reducing the temperature and keeping this volume fraction constant.

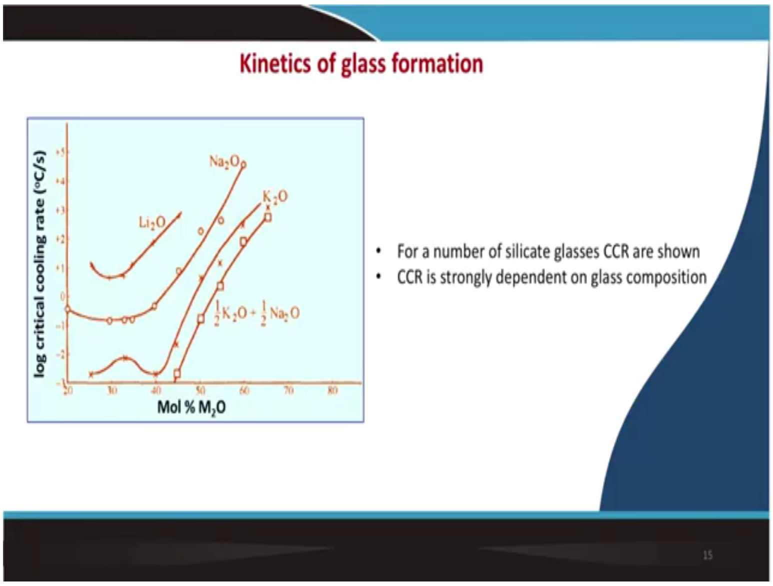
So, I always will end up this kind of curve. So, this is called a time temperature transformation diagram and you can see that there is a nose part here. So, that denotes the temperature and you have the time corresponding to that temperature corresponding to this nose.

So, you can calculate a critical cooling rate which is given by the melting point which is steel then the nose temperature divided by the time corresponding to this nose temperature. So, this is a critical cooling rate that you can calculate corresponding to any volume fraction in a isothermal condition.

So, lot of experimentation you will have to do. So, this is done for another volume fraction where almost all of it is crystalline and then you come up with a particular cooling rate and this is critical cooling rate. So, it is very very significant. So, this I have described that how to construct this.

So, stepwise I have defined that first step volume fraction is selected and then, you have a T-T-T diagram which is drawn and these are all the cooling rate this corresponding this lines are the cooling rate. So, this signifies that the rate is required to avoid a given fraction become crystallized. So, that is all that is important that if you; if you get this critical cooling rate then you know that if you maintain this critical cooling rate then a crystallization is not possible.

(Refer Slide Time: 30:47)



Kinetics of glass formation

- For a number of silicate glasses CCR are shown
- CCR is strongly dependent on glass composition

So, here I have shown that for silicate glass of different composition what is the critical cooling rate and as you can see it strongly depend on the oxide content in a silicate system. So, I will define that what is the role of these oxides in the silica this is called a modifier.

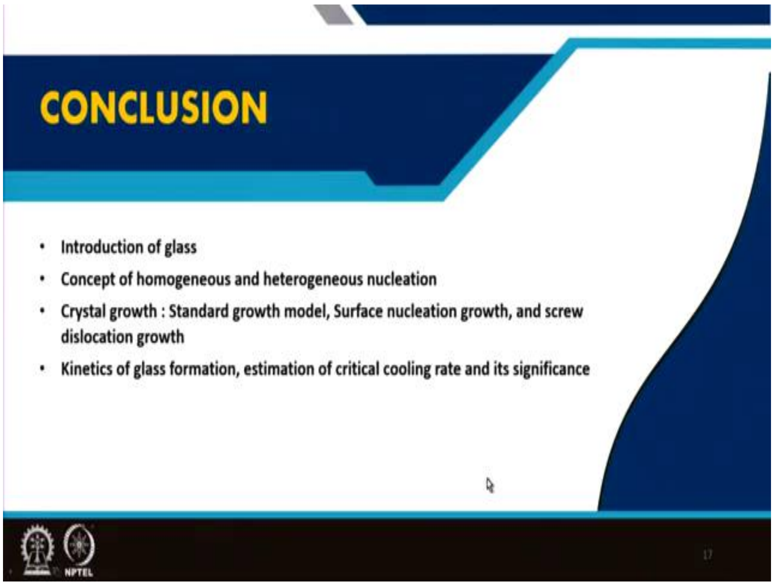
(Refer Slide Time: 31:09)

REFERENCES

- **Michael W Barsoum,** Fundamental of Ceramics, Chapter – 9 page 279 – 292; 2nd Edition, CRC Press, New York (Study material)
- **H. Rawson,** Properties and applications of glass, vol 3, Glass Science and Technology, Elsevier, Amsterdam, 1980
- **R. Doremus,** Glass Science, Wiley, New York, 1973
- **G.W. Morey,** The Properties of Glass, Reinhold, New York, 1954

So, this is the reference that you should consider mostly from the book by Barsoum and there are other good books on glass material.

(Refer Slide Time: 31:21)



CONCLUSION

- Introduction of glass
- Concept of homogeneous and heterogeneous nucleation
- Crystal growth : Standard growth model, Surface nucleation growth, and screw dislocation growth
- Kinetics of glass formation, estimation of critical cooling rate and its significance

And here I derive the concept of homogeneous and heterogeneous nucleation then, crystal growth it is having 3 different model standard growth, surface nucleation and screw dislocation then more importantly we talked about the kinetics of the glass formation and estimation of this critical cooling rate and what is their significance in order to understand the maintain of the glassy nature of a melt.

Thank you for your attention.