

SYNTHESIS OF INORGANIC MATERIALS AND NANOMATERIALS

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Outline

IV - FORMATION OF SOLIDS FROM SOLUTIONS

1) Glass

-  a) The structural theory of glass formation
- b) Crystallization versus glass formation
- c) Glass melting
- d) Metallic glass
- e) Composition of glasses

2) Precipitation

3) Biomaterials

1) Glass a) The structural theory of glass formation

Difference between crystalline and amorphous silica

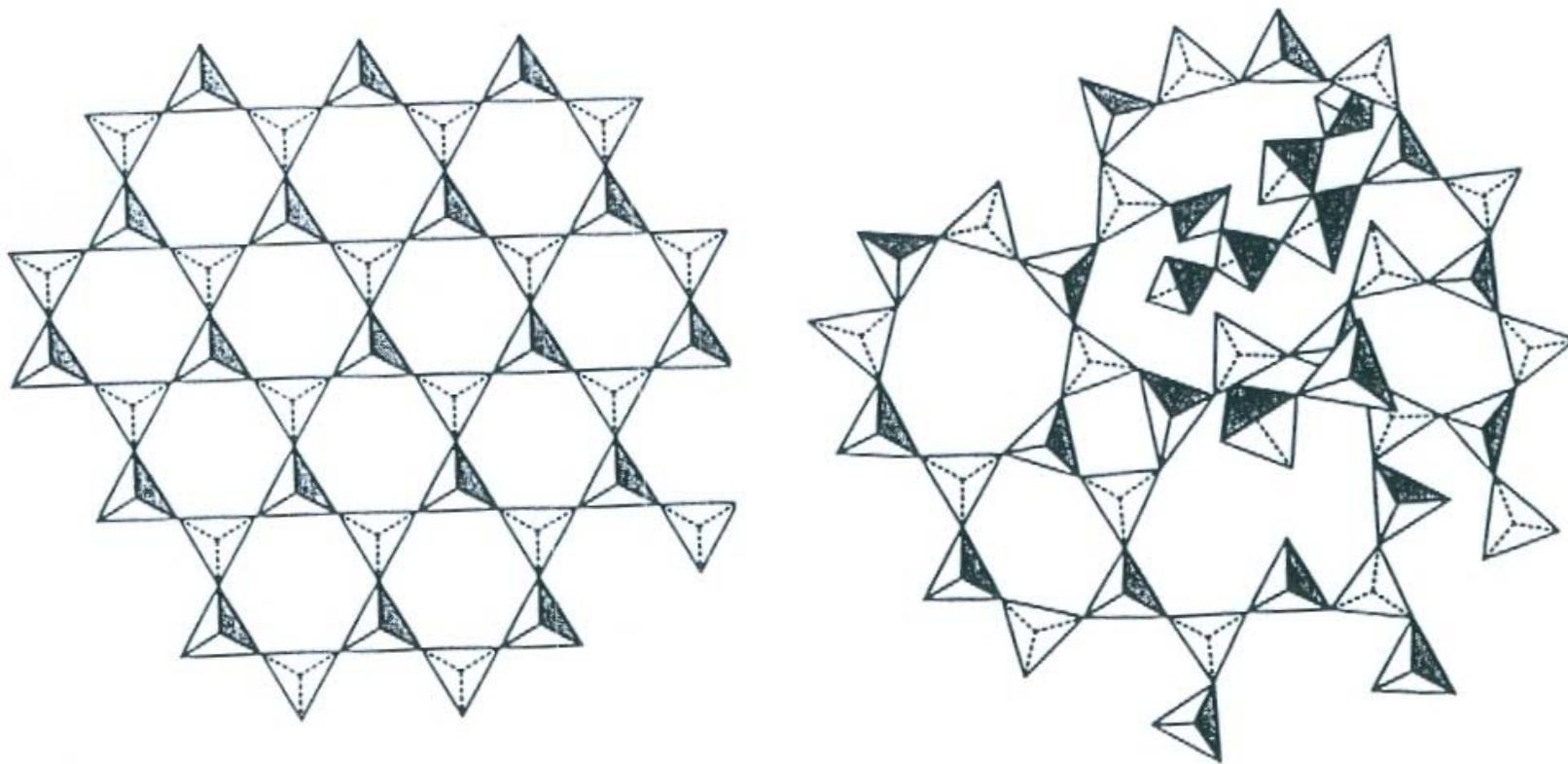


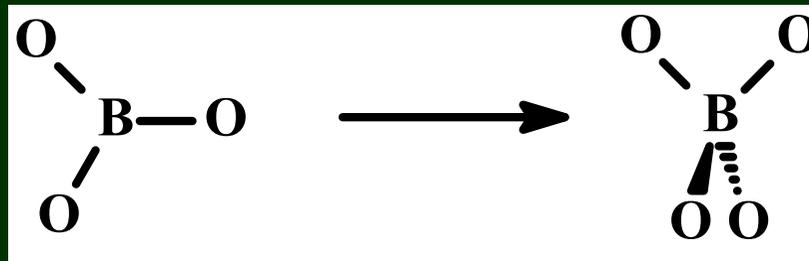
Figure 4-2. Schematic structure of crystalline (left) and amorphous silica (right). In the crystalline forms of silica the $[\text{SiO}_4]$ tetrahedra (the silicon atoms are located in the center of the tetrahedra, and the oxygen atoms at the vertices) are regularly arranged. There is no long-range order in the amorphous form.

1) Glass a) The structural theory of glass formation

Difference between crystalline and amorphous silica

Role of boron → borate glass

From planar geometry to tetrahedral geometry



higher degree of crosslinking

→ preserve the glass state

→ reduce dilatation effect → no breaking by heating

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1) Glass b) Crystallization versus glass formation

Crystallization → nucleation-growth process

Glass formation → no nucleation, activation energy E_a too high

Nucleation rate:

$$v = A \exp - \left(\frac{\Delta G_N + \Delta G_D}{kT} \right)$$

v = N(nuclei) $V^{-1} s^{-1}$

ΔG_N = free (or Gibbs) energy change when a nucleus is formed

ΔG_D = kinetic barrier for diffusion across the liquid-nucleus interface

1) How to estimate the term ΔG_N ?

Assumption: spherical nuclei of radius r

ΔG_N = volume term V + surface term S

V related to the change in free energy for liquid – crystal transition

→ negative because $G_{\text{crystal}} < G_{\text{liquid}}$ $\Delta_v G = G_{\text{liquid}} - G_{\text{crystal}}$ (J m^{-3})

$$V = - (4/3) \pi r^3 \Delta_v G$$

S related to the formation of a solid-liquid interface

→ positive because energy is needed to create an interface

$$S = 4 \pi r^2 \gamma_{SL} \quad \gamma_{SL} \text{ interfacial energy (J } m^{-2}\text{)}$$

$$\Delta G_N = - (4/3) \pi r^3 \Delta_v G + 4 \pi r^2 \gamma_{SL}$$

1) Glass

b) Crystallization versus glass formation

$$\Delta G_N = - (4/3) \pi r^3 \Delta_v G + 4 \pi r^2 \gamma_{SL}$$

→ see the plot

For low values of r → $\Delta G_N > 0$

→ the nuclei will melt or dissolve

If few nuclei survive (statistical events) they can growth

→ $\Delta G_N < 0$

formation of stable nuclei, r increase

How can we determine the critical radius r^*

At the maximum, we have

$$\partial \Delta G_N / \partial r = 0$$

$$0 = - 4 \pi r^2 \Delta_v G + 8 \pi r \gamma_{SL}$$

$$\rightarrow r^* = 2 \gamma_{SL} / \Delta_v G$$

Magnitude of r^* ?

When $\Delta T = T_m - T$ is low

→ $\Delta_v G$ is low → r^* is large

→ The probability for a nucleus to survive is very low

When $\Delta T = T_m - T$ is large

→ $\Delta_v G$ increases → r^* decreases → ΔG^* decreases

→ probability of formation of nuclei becomes significant → nucleation rate ↑

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$$\Delta G_N = - (4/3) \pi r^3 \Delta_v G + 4 \pi r^2 \gamma_{SL}$$

2) How to estimate the term ΔG_D ?

rate is limited by the diffusion → importance of viscosity

→ viscosity increases when $T \downarrow$

Total rate → max for nucleation rate vs T

→ max for growth rate versus temperature

(see figures)

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TTT plot → **Time – Temperature – Transformation**

t = time needed to obtain a given volumic fraction of crystal from liquid
 $V_x / V = f(t)$

When T is close to T_m → time increases as T ↑

When T is much lower than T_m → effect of viscosity → time increases as T ↓

See figure (nose plot)

Definition of the critical cooling rate $v_c = (dT / dt) = (T_m - T_c) / t_c$

→ minimum cooling rate to get a glass → slope of the tangent to the nose curve

For SiO_2 → rate to obtain a crystal

→ $v < 10^{-5} \text{ K s}^{-1}$

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1) Glass

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Definition of the critical cooling rate $v_c = (dT / dt) = (T_m - T_c) / t_c$

→ minimum cooling rate to get a glass

For metals → $v_c = 10^6$ to 10^{10} K s⁻¹

→ very fast cooling

→ formation of ribbon on cooled rotating drum

dimension of the ribbon: few mm wide, 10 to 50 μm thick

→ different mechanical properties

(see video)

Liquidmetal™ and stainless steel

Stainless steel spheres dropped on Liquidmetal® (left) and stainless steel (right) demonstrate loss of energy into grain boundaries. Liquidmetal is an amorphous alloy of titanium, zirconium, nickel, copper, and beryllium.

Maraging steel, Liquidmetal™, titanium

Stainless steel spheres dropped on maraging steel (left), Liquidmetal® (center) and titanium (right) Maraging steel contains Fe, Mo, Cr, and Ni.

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Window glass

SiO₂	Al₂O₃	MgO	CaO	Na₂O	
72	1.5	3.5	8.5	14.5	wt.-%

Laboratory glass

SiO₂	Al₂O₃	MgO	CaO	Na₂O	B₂O₃	
80	3	1	1	5	10	wt.-%

Fluoride fiber glass

ZrF₄	BaF₂	NaF	AlF₃	LaF₃	LnF₃	
53	20	20	3	2	2	wt.-%