2010 Spring

“Amorphous Materials”

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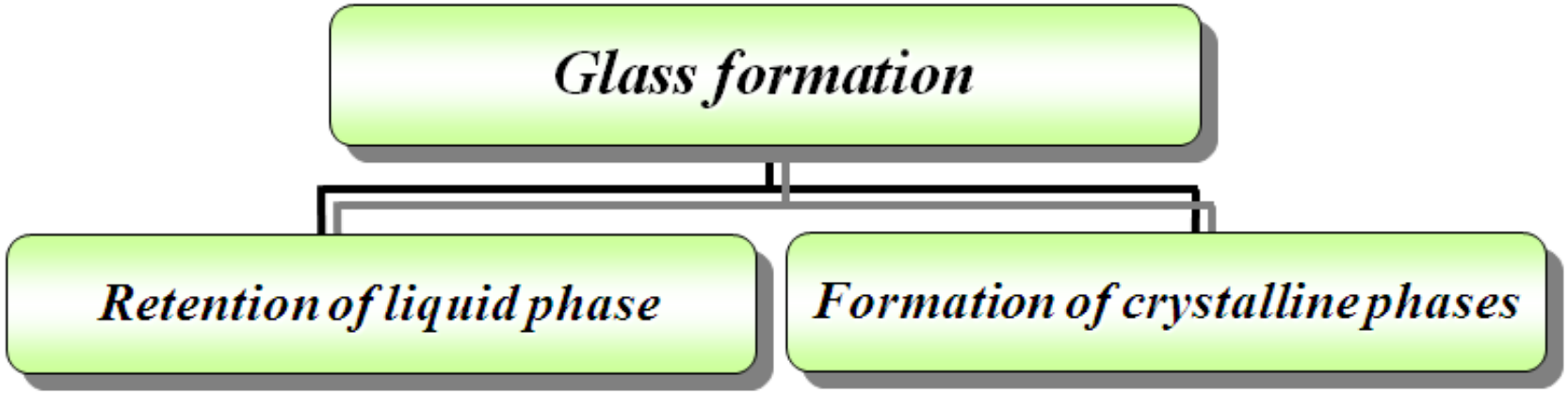
Eun Soo Park

Office: 33-316
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

Contents for previous class



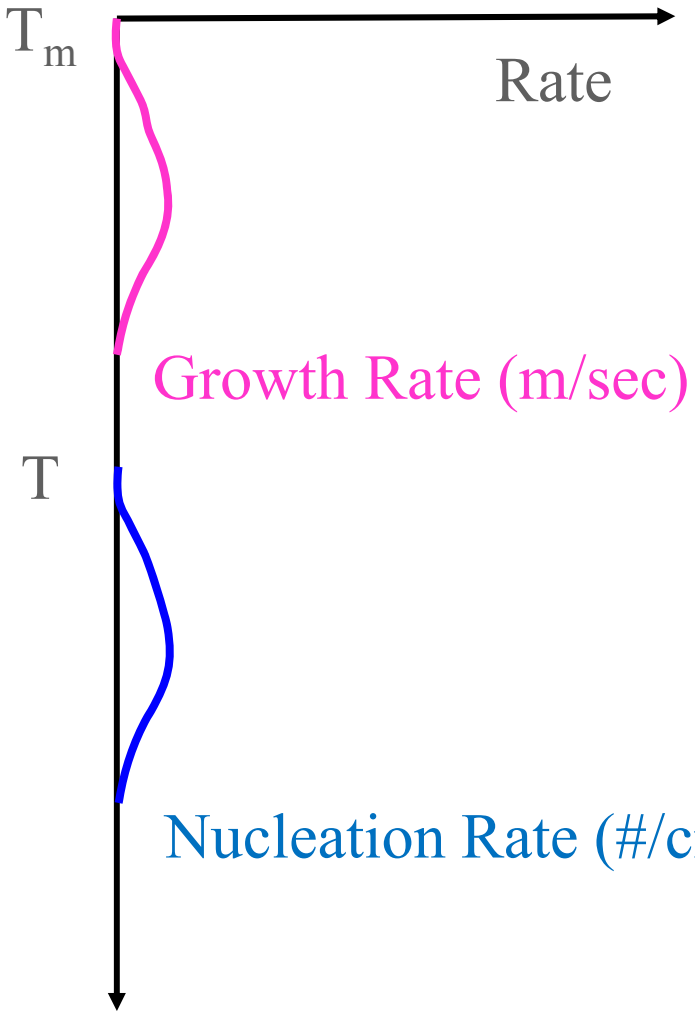
Glass Formation results when

Liquids are cooled to below T_m (T_L) sufficiently fast to avoid crystallization.

- **Nucleation of crystalline seeds are avoided**
- **Growth of Nuclei into crystallites (crystals) is avoided**

Kinetic aspect for GF (Decrease of nucleation and growth rate)

➡ High glass-forming ability



Growth Rates μ(T)

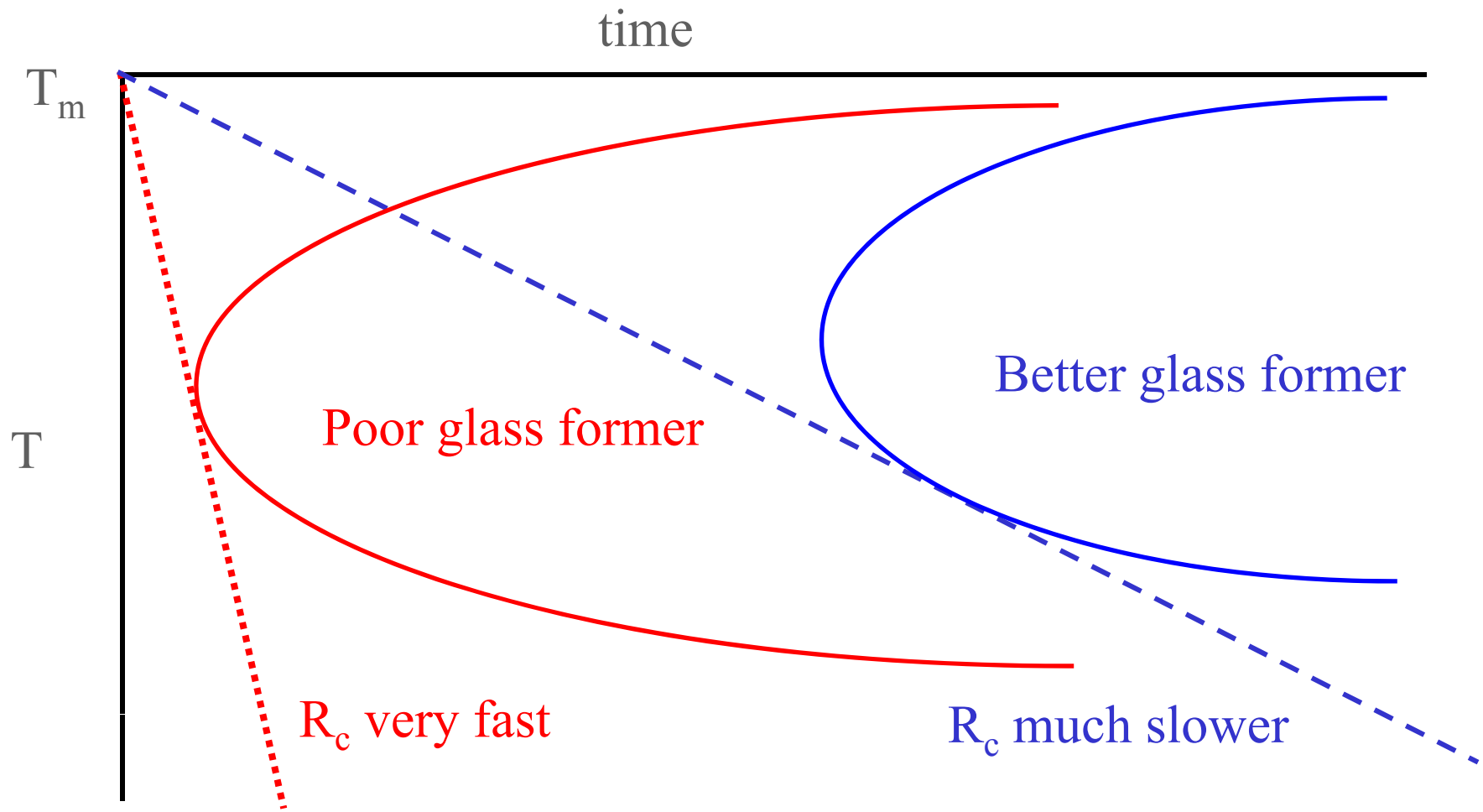
$$\mu(T) = \left(\frac{fRT}{3N\pi a^2 \eta(T)}\right)\left(1 - \exp\left[\left(\frac{\Delta H_m}{RT}\right)\left(\frac{\Delta T}{T_m}\right)\right]\right)$$

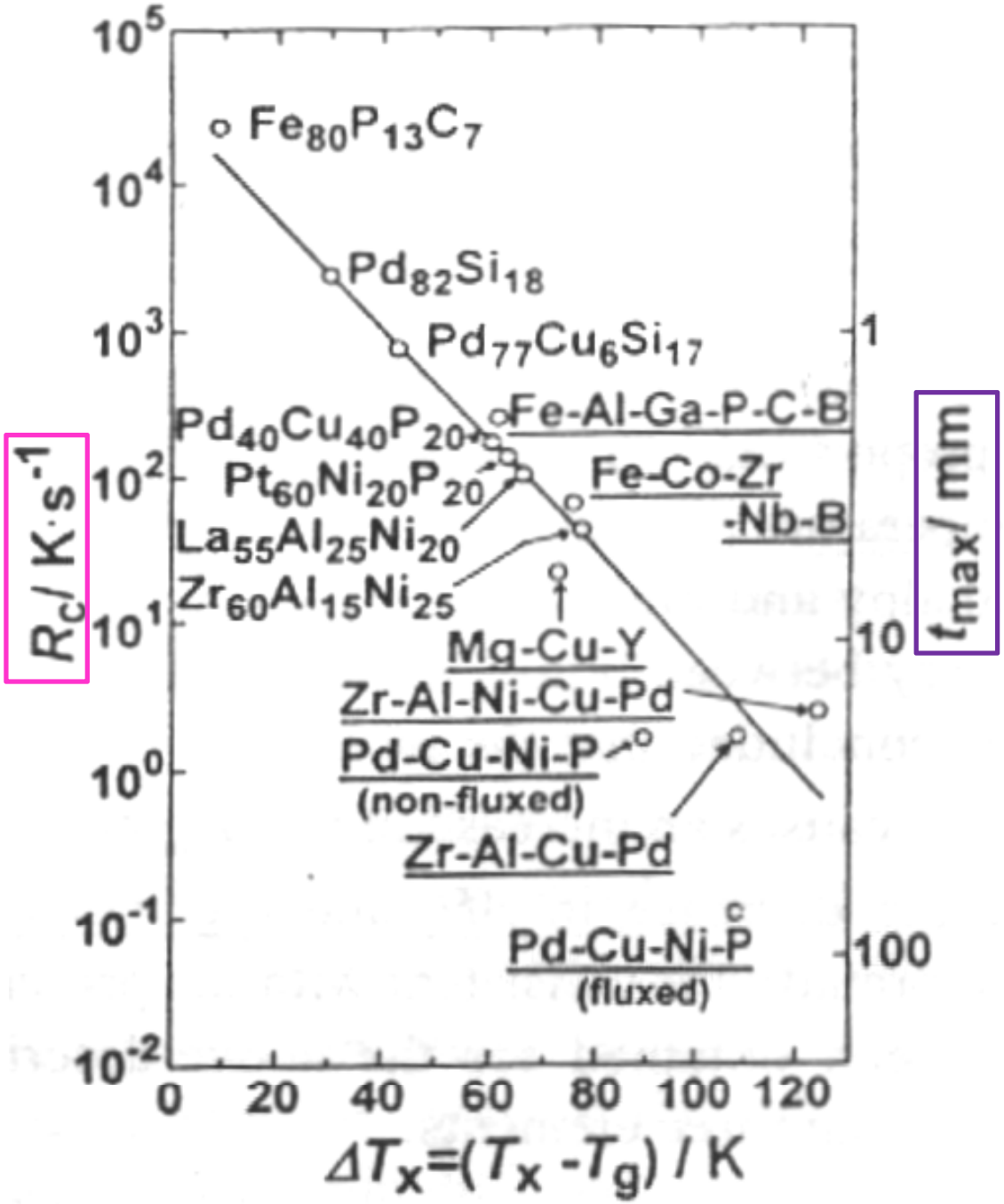
Nucleation Rate I(T)

$$I = n\nu \exp\left\{\left(\frac{16\pi\Delta H_{cryst}}{81RT}\right)\left(\frac{T_m}{\Delta T}\right)^2\right\}\exp\left\{\frac{-\Delta E_D}{RT}\right\}$$

TTT curves and the critical cooling rate, R_c

TTT diagram ➡ $X(t,T) \sim \pi I(T)\mu(T)^3 t^4/3$




R_c / K·s^{-1}
t_{max} / mm
$\Delta T_x = (T_x - T_g)$ / K
$Fe_{80}P_{13}C_7$
$Pd_{82}Si_{18}$
$Pd_{77}Cu_6Si_{17}$
$Pd_{40}Cu_{40}P_{20}$
$Pt_{60}Ni_{20}P_{20}$
$La_{55}Al_{25}Ni_{20}$
$Zr_{60}Al_{15}Ni_{25}$
Fe-Al-Ga-P-C-B
Fe-Co-Zr
-Nb-B
Mg-Cu-Y
Zr-Al-Ni-Cu-Pd
Pd-Cu-Ni-P
(non-fluxed)
Zr-Al-Cu-Pd
Pd-Cu-Ni-P
(fluxed)

Ease of glass formation

- How do glasses form? ➡ Glass transition
- Why do glasses form? ➡ High glass forming ability in some systems

  - Glass forming ability: basically depending on glass transition

    ➡ unsolved mystery

    ➡ no universal rule: empirical rules

    ➡ still alchemy stage: by trial & error considering various aspects

Empirical Rule

Based on their experiment work, Inoue have proposed empirical rules for exploring BMGs with high GFA and large supercooled liquid region.

1. The multi component system consisting of more than three elements

2. Significant difference in atomic size ratios above about 12% among the main constituent elements

3. Large negative heats of mixing among their elements

1. Structure & topology

Liquid is frustrated by internal structure that hinders nucleation and growth of crystals.

1932: Zachanasen 1st attempt

Why SiO_2 glass former? ➡ Internal energy

Na_2O non-glass former?

$2Na_2O \cdot SiO_2$ glass former?

- 1) Internal energy : decided by atomic arrangement

  : mainly considered in oxide glasses

➡ Internal energy of glass is slightly higher than that of crystal.

➡ Not too much difference

➡ If the gap is large, ⟶ crystallization tendency ↑

➡ If the gap is small, ⟶ crystallization tendency ↓

1. Structure & topology (atomic arrangement)

- Internal energy

➡ Depends on the bonding types and arrangements of constituent element

➡ similar types and arrangements of atomic bonding in crystal and amorphous (=similar atomic structure) ⟶ GFA ⬆

ex) SiO_2: Joined structure of SiO_4 tetrahedron at the corner

Oxide glass: periodic array of oxygen polyhedra (triangular, tetrahedral, octahedral) ➡ crystalline state

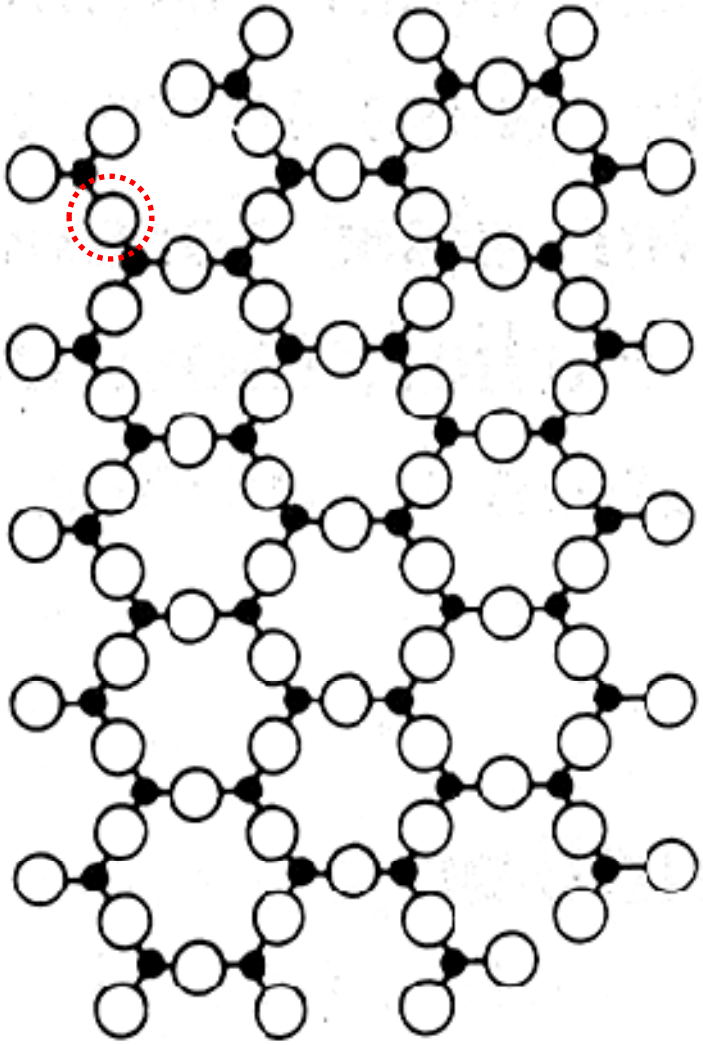
⟶ It's possible to be aperiodic structure by relative orientation difference of oxygen polyhedra.

⟶ **Continuous Random Network (CRN)** ➡ GFA ⬆

1. Structure & topology (atomic arrangement)

- A_2O_3 (B_2O_3)

  1) crystal: oxygen is shared by two AO_3 triangles.



(a)

1. Structure & topology (atomic arrangement)

- A_2O_3 (B_2O_3)

2) glass: oxygen is shared
by two AO_3 triangles.

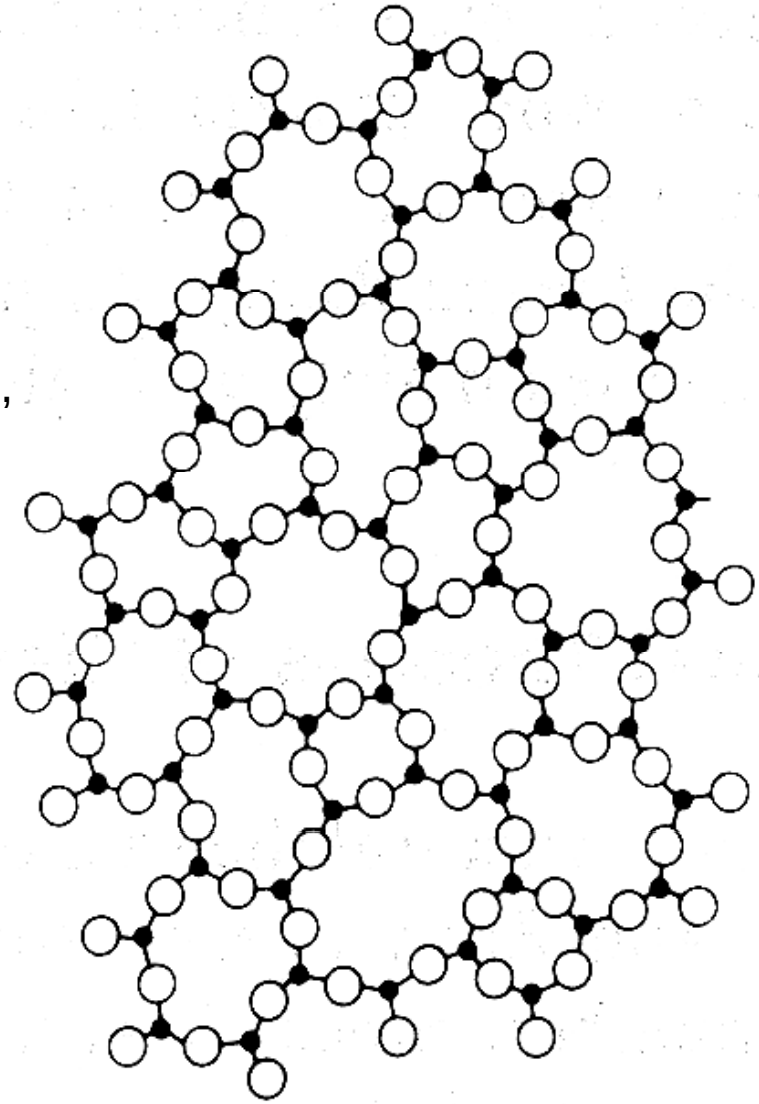
Although relative orientation is different,
relative orientation of bond is

→ easy and small change

→ easily can form CRN.

Small gap of internal energy
between crystal and glass

→ GFA ↑

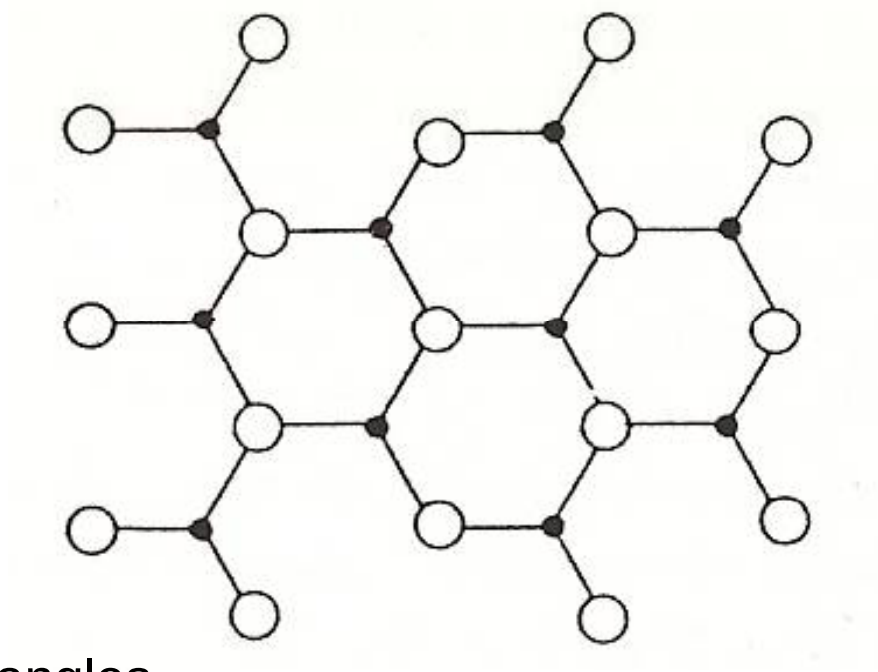


(b)

1. Structure & topology (atomic arrangement)

- crystal AO

- Basic unit is AO_3 triangle.



- Oxygen is shared by three AO_3 triangles.

Difficult change of orientation

→ GFA ⬇

→ **Energy for orientation change is relatively large.**

→ **Gap of internal energy between glass and crystalline is large.**

Zacharaisen's Rules for Glass Formation- not so important

- Oxygen atoms are linked (bonded) to no more than two atoms
- Oxygen coordination around glass-forming cations is small, 3, 4
- Cation polyhedra share corners and not edges or faces
- At least three corners are shared

William H. Zachariasen, Journal of the American Chemical Society ***54*** *(1932) 3841-3851*

→ AO & A_2O: do not form glass

→ A_2O_3 — triangular (3)

AO_2, A_2O_5 — tetrahedra (4)

→ form glass

So far, simple oxide network

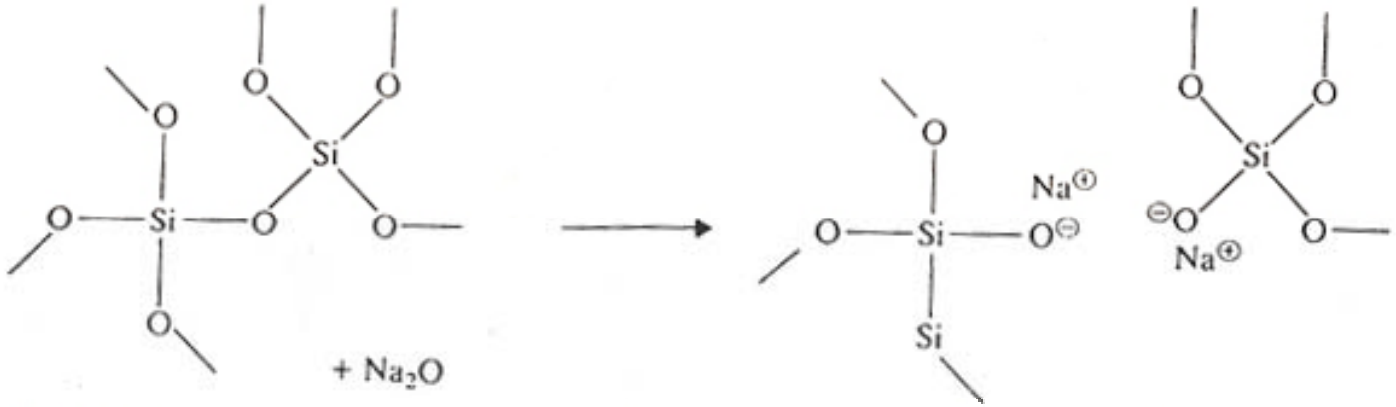
Modified Zacharaisen's Rules for Glass Formation

- Oxide glass containing non-glass former

  SiO_2 (**glass former**) + Na_2O (**non-glass former**) ➡ $2Na_2O \cdot SiO_2$ (**glass former**)

  < General rule >

  1. **High portion of (network forming) cations are surrounded by oxygen tetrahedra or triangles.**
  2. **The oxygen polyhedra only share corners with each other.**
  3. **Some oxygen atoms are linked to only two cations, and do not form additional bonds with any other cations.**



Schematic illustration of the effect of the addition of alkali oxide (e.g. Na_2O) to silica. Each molecule of Na_2O added converts a bridging oxygen to two non-bridging oxygens (negatively charged). Diffusion in the melt would ensure that separation of the non-bridging oxygen atoms would occur.

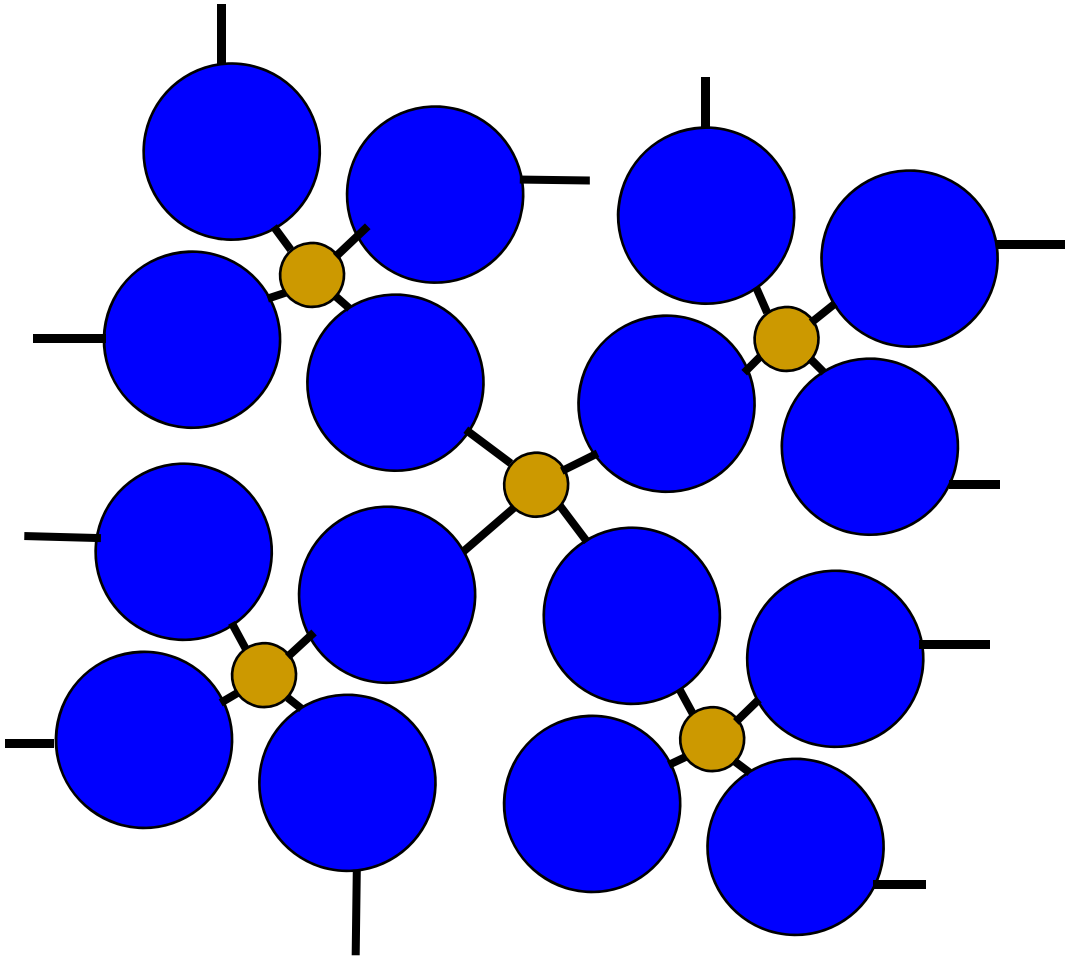
Zacharaisen's Rules for Glass Formation

- Apply these rules to the following:
  - $SiO_{4/2}$
  - B_2O_3 or $BO_{3/2}$

- Apply these rules to the following:
  - CaO
  - Na_2O

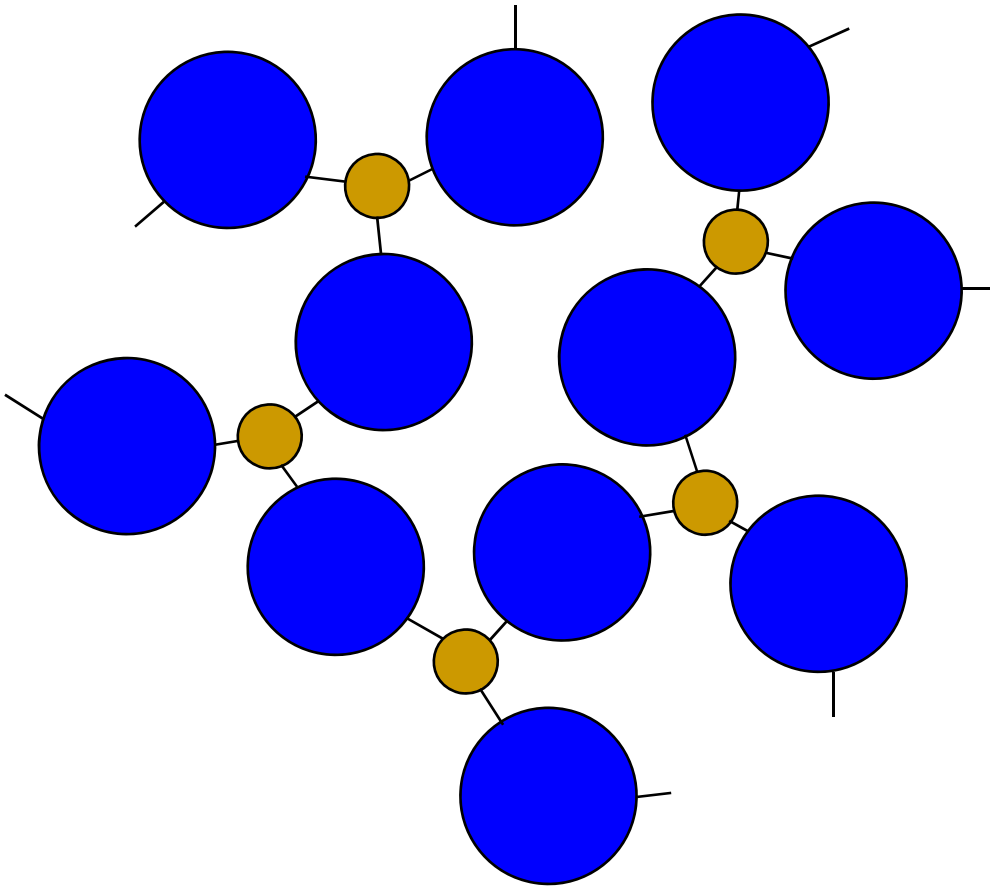
Zacharaisen's Rules for Glass Formation

- $SiO_{4/2}$



Zacharaisen's Rules for Glass Formation

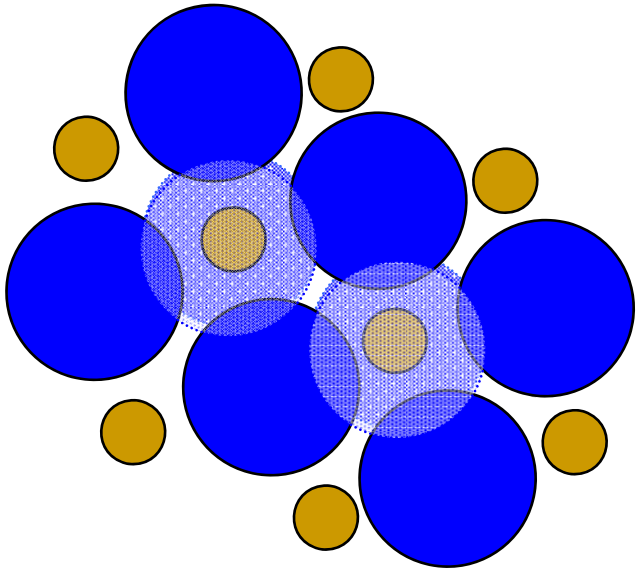
- B_2O_3 or $BO_{3/2}$



Zacharaisen's Rules for Modifiers

Ca_1O_1 (CaO) Closed-packed cubic

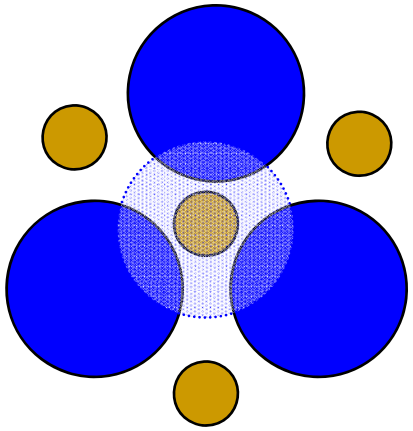
- Ca occupying all octahedral sites
- Octahedral sites = Ca = O



Zacharaisen's Rules for Modifiers – M_2O

Na_2O_1 (Na_2O) Closed-packed cubic

- Na occupying tetrahedral sites
- Tetrahedral sites = 2 x O = Na



→ A_mB_nO

→ A: network forming cations

B: network modifing cautions

→ Intermediate class of oxide

TeO_2, WO_3, MoO_3 • • •

: with modifier ⟶ GFA ⬆

2) Randomly dense packed structure → ex) metallic glasses

1) Atomic size difference: TM – metalloid (M, ex) Boron)

→ M is located at interstitial site of random packed structure of TM.

→ denser ⇨ by increasing resistivity of crystallization, GFA ⇧

→ Ex) Fe-B: tetrahedron with B on the center position

1) interstitial site, B= simple atomic topology

2) skeleton structure

3) bonding nature: close to covalent bonding

2) min. solute content, C_B*: empirical rule

By Egami & Waseda: in A-B binary system

$$C_B^{min}\left|\frac{(v_B - v_A)}{v_A}\right| = C_B^{min}\left|\left(\frac{r_B}{r_A}\right)^3 - 1\right| \approx 0.1$$

minimum concentration of B for glass formation

v: atomic volume

A: matrix, B: solute

→ Inversely proportional to atomic volume mismatch

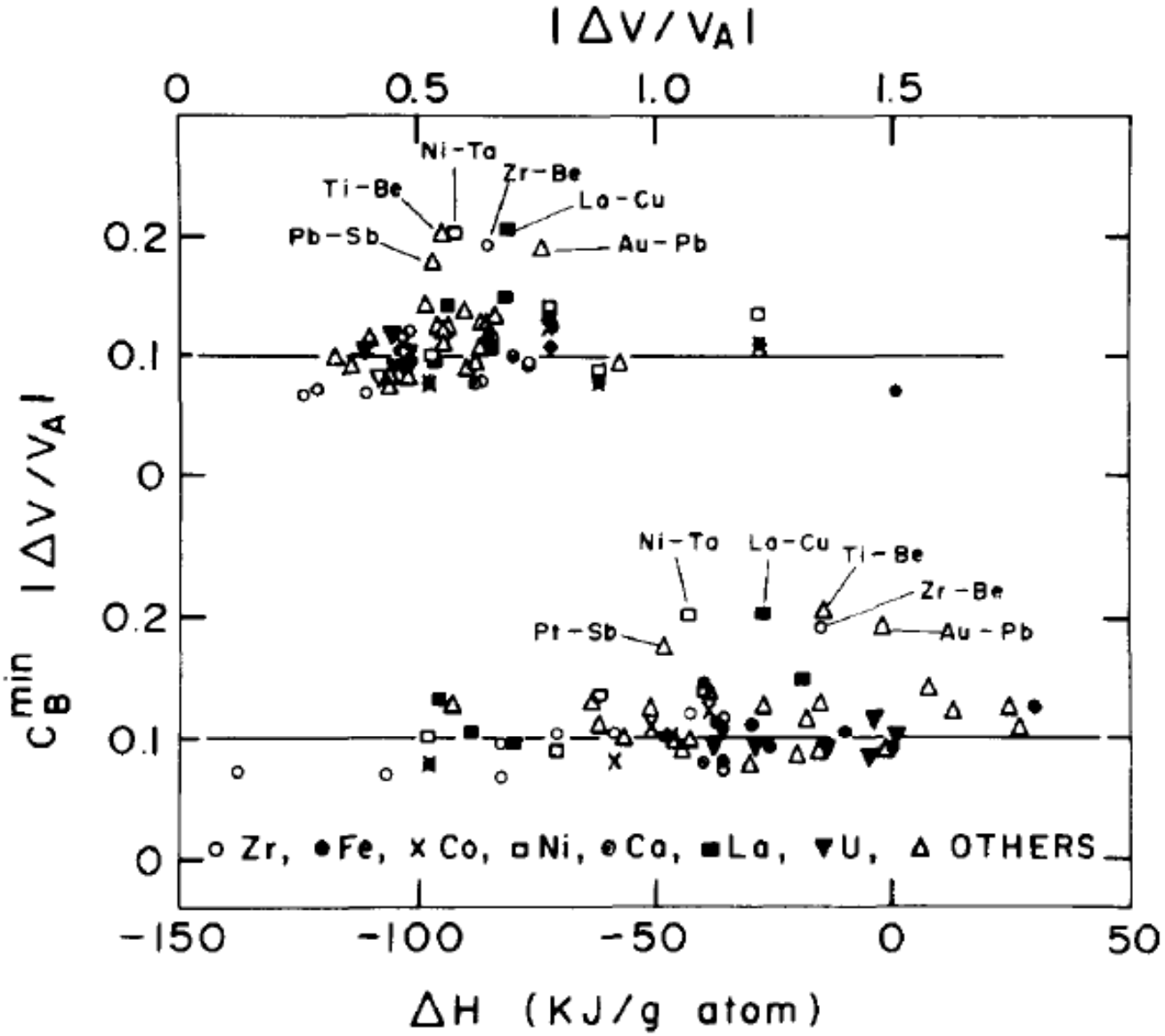


Fig. 1. Relation between $|\lambda_0| = C_B^{min}\,|\Delta v/v_A|$, and $|\Delta v/v_A|$ and ΔH, for 66 binary systems which can be vitrified by liquid quenching.